Is ~~L~~litter biomass ~~as ~~a driver of soil VOC fluxes in ~~a ~~Mediterranean forest?

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Abstract. Soil biogenic volatile organic compound (BVOC) emissions have been studied in different biomes, showing that their emissions are ~~not negligible~~considerable. 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. To fill these gaps, the present work aimed to study BVOC fluxes in a Mediterranean deciduous forest, with a particular attention to the relationships between litter biomass accumulation on soil~~soil BVOC fluxes~~, microbial abundance and soil BVOC fluxes~~litter biomass accumulation on soils~~. 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). We investigated in-situ daily BVOC fluxes from bare soil ~~alone ~~and different litter biomasses mimicking ~~low, ~~current, lower, or ~~high, and very ~~higher litter production, ~~respectively, ~~as both decreases and increases ~~of ~~in litter accumulation are expected in the Mediterranean region under the current context of climate change and greening management policies. The results showed a high BVOC diversity with more than 135 emitted compounds. For a large majority of the measured compounds, fluxes were negative, suggesting that soil (bare soil covered by litter) is taking up ~~uptakes~~ compounds through biochemical and/or physical processes. Some compounds, such as acetone, methanol or sesquiterpenes, increased with increasing litter biomass, suggesting the importance of considering litter accumulation when assessing soil BVOC emissions from Mediterranean deciduous forests. Microbial abundance was highlighted as a potential driver of this relation between litter biomass and VOC fluxes.

1- Introduction

Biogenic volatile organic compounds (BVOCs) are key components of the atmosphere's oxidative capacity through their influence on the OH radical, O_3 and NOx budgets, among others. They also play a critical role in the formation of the secondary organic aerosol (SOA) (Hallquist et al., 2009; Kulmala et al., 2004; Mahilang et al., 2021; Seinfeld and Pandis, 2016), contributing to health and climate impacts (Seinfeld and Pandis, 2016; Thornhill et al., 2021). 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 ~~se estimates are likely to be underestimated as they neglect the contribution ~~of soil (bare soil covered by litter) VOC exchanges (emission and immission) processes are still unclear due to the scarcity of studies. The recent interest on soil BVOCs shows bi-directional VOC fluxes (i.e. positive and negative) with net emissions from soils covered by litter (Bourtsoukidis et al., 2018; Legros et al., 2025; Peñuelas et al., 2014; Viros et al., 2020; Yang et al., 2024b). Soil could thus be a significant source of BVOCs affecting atmospheric chemistry and related climate~~f~~ impacts (Kramshøj et al., 2019; Yang et al., 2024a).

Soil-atmosphere exchanges have been measured in different regions of the world, such as tropical (Artaxo et al., 2022; Bourtsoukidis et al., 2018; Jardine et al., 2015, 2017), boreal (Aaltonen et al., 2013; Artaxo et al., 2022; Mäki, 2019), temperate (Isidorov et al., 2024; Isidorov and Zaitsev, 2022; Leff and Fierer, 2008; Mäki, 2019; Svendsen et al., 2018), and Mediterranean forests (Asensio et al., 2008; Rezaie et al., 2023; Viros et al., 2020; Yang et al., 2024b). Recent studies have reviewed most VOCs emitted from soil compartments (roots, bare soil, soil covered by litter or litter alone) (Tang et al., 2019; Yang et al., 2024a). Most frequently reported VOCs are isoprene, monoterpenes, sesquiterpenes, and oxygenated VOCs such as methanol (Gray et al., 2010). Methanol is both emitted and consumed by soil bacteria and rhizosphere microorganisms (Asensio et al., 2007a). Other studies have reported important VOC deposition fluxes of hexanal or acetone (Peñuelas et al., (2014), and references therein).

Abiotic (soil moisture and temperature) and biotic (e.g. microbial community composition and biomass, soil and litter nutrient availability) parameters can drive VOC degradation (Cleveland and Yavitt, 1998; Rinnan and Albers, 2020; Trowbridge et al., 2020). Processes and sources related to soil VOC emissions are reviewed in Isidorov and Zaitsev (2022) and Tang et al. (2019) and highlight the importance of both biotic and abiotic parameters, as evaluated in several studies (Abis et al., 2020; Asensio et al., 2007a; Jiao et al., 2023; Leff and Fierer, 2008; Mackie and Wheatley, 1999; Wilkins, 1996). BVOC emissions are known to increase with microbial activity, through microbial decomposition of litter or soil organic carbon, and evaporation of litter-stored VOCs (Aaltonen et al., 2013; Insam and Seewald, 2010; Leff and Fierer, 2008; Stahl and Parkin, 1996). Plant roots are also known to be a source of VOCs, acting as mediators of belowground interactions between plants and soil microorganisms (Asensio et al., 2007a; Wenke et al., 2010; Yang et al., 2024a).

Soil also acts as a sink for BVOCs, 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). BVOCs can also diffuse through soil pores, where they can be adsorbed onto soil particles or dissolved in soil water until equilibrium is reached (Ahn et al., 2020; Ruiz et al., 1998). Although these uptake processes are less well understood, VOC uptake is considered to be a widespread process in soil (Jiao et al., 2023; Rinnan and Albers, 2020) as well as in the canopy (Niinemets et al., 2014). Among the different drivers of soil VOC fluxes, temperature and drought are important abiotic factors (Asensio et al., 2007a; Legros et al., 2025; Rezaie et al., 2023; Trowbridge et al., 2020), suggesting that these fluxes will be affected by climate change.

Indeed, Mediterranean ~~forests~~ 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, ~~microbial activity~~, (Quer et al., 2022; Santonja et al., 2017, 2022) and thus affects BVOC exchanges between soil and atmosphere (Peñuelas et al., 2017; Yang et al., 2024b). While bare soil appears to be a sink for VOCs in Mediterranean ecosystems and other biomes (Asensio et al., 2007b), the soil surface covered by litter and litter alone have been highlighted as a source of BVOCs, with negligible to moderate fluxes compared to leaf emissions (Legros et al., 2025; Peñuelas et al., 2014; Viros et al., 2020). However, the influence of the amount of litter biomass on soil VOC fluxes in Mediterranean forests has never been investigated. On the one hand, increasing litter accumulation is expected in this region, as intensive drought reduces litter mixture interactions and decomposition, leading to litter accumulation on the soil (Santonja et al., 2015, 2017). Moreover, greening policies and gradual abandonment (in the years around 1855-1870) of wood in shipbuilding have contributed to an increase in forest area, which has doubled since the mid-19th century. On the other hand, chronic limited precipitation expected in the coming decades in the Mediterranean region will lead to lower leaf production and thus a lower litter fall in these ecosystems.

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 ~~major~~ 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.~~We focussed on the relationships between litter BVOC fluxes and litter biomass accumulation on the soil surface and associated microbial communities.~~

2- Material and methods

2-1 Experimental site and sampling strategy

Measurement of litter BVOC emissions were performed at the O$_3$HP experimental site, an AnaEE (Analysis and Experimentation on Ecosystems, https://www.anaee.eu) *in situ* platform located in the research center Observatoire de Haute Provence (5°42 E, 43°55 N, 650 m a.s.l., Saint-Michel l'Observatoire, France). AnaEE is a European network providing ecosystem data, research tools, and experimental facilities to study real ecosystems under environmental stress. 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). The O$_3$HP site was created in 2009 in order to study the *Q. pubescens* forest ecosystem (≈ 90 % of the biomass and ≈ 75 % of the trees) at different compartments (~~the~~ soil, leaves and canopy~~tree~~ scales). A rainfall exclusion set up (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.

~~, under both natural and accentuated water stress conditions induced by a rainfall exclusion device (an automated monitored roof deployed during rain events) set up over a part of the O$_3$HP canopy.~~ Litter production of *Q. pubescens* within the site ranges between 1.4 and 1.6 t ha^{-1} yr^{-1}, that is 166 g~~.~~ m^{-2} yr^{-1} (Genard-Zielinski et al., 2015; Viros et al., 2020)~~(Genard-Zielinski et al., 2015; Viros et al., 2020)~~. A dense network of sensors in the soil, under and above the canopy, continuously recorded the climatic and edaphic parameters (air and soil temperatures and relative humidity, photosynthetically active radiation or PAR). More details can be found in ~~(~~Garnier et al.~~,~~ (2021).

The experiment was conducted in spring, from 23rd to 26th May 2023. Five dynamic soil chambers (14 L volume) consisting of polycarbonate cylinders with a stainless-steel basement were used (for a full description see Legros et al., 2025). Each chamber covered 0.067 m² of soil surface. Fresh litters were removed from the soil, weighted and installed for the experiment~~s~~. Aliquots were ~~performed~~made to calculate equivalent dry masses of the 12 litter biomass pools used in this experiment (Table S~~.~~1). Chamber 1 covered bare soil (i.e. 0 g m^{-2} of litter), while chambers 2 to 5 circled bare soil ~~circled bare soil~~ fully covered by ~~8~~ 119 g m^{-2}~~, 16~~ 238 g m^{-2}~~g, 32~~ 477 g m^{-2}~~g and 48~~ 716 g m^{-2}~~g of fresh mass of *Q. pubescens* litter, respectively, corresponding to~~ litter dry mass of *Q. pubescens* ranging from ~~6.2~~92.5 to ~~30.01~~449.7 g m^{-2} ~~g~~ over the 3 days of experiment (Table S1, Figure 1)~~.~~. ~~These added litter masses are hereafter referred to as LM1, LM2, LM3 and LM4 in the text.~~ All chambers were flushed using ambient air at 0.~~6~~3 L min^{-1}, and an inlet to measure ambient air was placed at 50 cm above ground level, at a central position from the 5 chambers. 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. Most abundant ambient VOC concentrations are reported in Table S.2. Emissions from each chamber were monitored over a 24 h period. ~~and repeated three times using renewed fresh litter each day w~~A~~hile the bare soil remained unchanged~~ new litter pool was added each day in chambers 2 to 5, resulting in a total of 15 samples over the 3 days of experiment, i.e. 3 bare soils and 12 different litter biomasses representing the gradient of increasing litter biomass accumulation.~~.~~

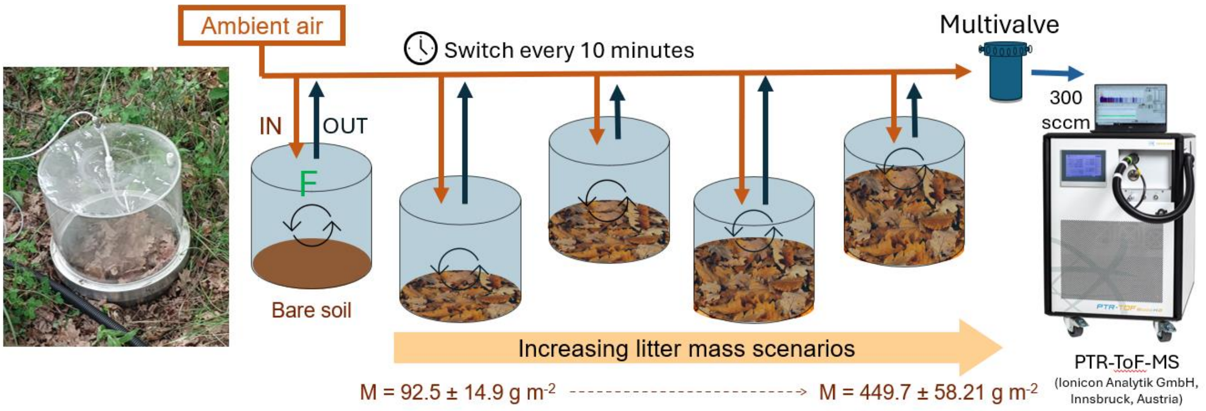


Figure 1. Experimental setup for bare soil and soil covered by different litter accumulations.

2-2 PTR-ToF-MS parameters, data treatment and flux calculation

BVOCs were monitored by a PTR-ToF-MS (Proton Transfer Reaction – Time of Flight – Mass Spectrometer 6000X2, Ionicon Analytik GmbH, Innsbruck, Austria). Each chamber and the ambient inlet were connected to a flow through multivalve (Valco Instruments Co. Inc, VICI VALCO, Huston, USA) placed inside the PTR-ToF-MS through ~20 m long ⅛” Teflon lines, with a flow around 0.3 L min^{-1} in each line. Parameters of PTR-ToF-MS were set ~~up as the~~to a reaction chamber pressure ~~was fixed at~~of 2.6 ± 0.001 mbar, a drift tube voltage and temperature ~~at~~ of 450 V and ~~temperature at~~ 120 °C, respectively corresponding to an E/N ratio (electric field strength over buffer gas number density) of ≈125 Td (1 Td = 10^{-17} V cm^{-2}). Each of the 15 samples (bare soil or soil covered by litter~~, LM1 to LM4~~) and ambient air~~)~~ w~~as~~ 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. Measurements were ~~repeated~~ performed during 3 days~~for three days~~ using a new pool of litter each day within each chamber~~ (i.e. day 1, 2 and 3, chamber one encircled a soil surface containing each day a different litter pool of 8 g of fresh litter biomass)~~. ~~BVOC concentrations on a large range of mass to charge (m/z) up to m/z 500.~~

A large range of BVOCs has been identified with mass to charge (m/z) up to m/z 500. PTR-ToF-MS data were post-processed with IDA software (Ionicon Data Analyzer, Ionicon Analytik GmbH, Innsbruck, Austria). First, mass calibration was performed based on H_3O^+ isotope ($H_2{}^{18}O.H^+$, m/z 21.022), $H_3O^+.H_2O$ isotope ($H_2O.H_2{}^{18}O.H^+$, m/z 39.033), diiodobenzene (an internal calibrant) parent ion ($C_6H_4I_2.H^+$, m/z 330.848) and its main ~~main~~ fragment ($C_6H_4I.H^+$, m/z 203.943). Then peak fitting and high-resolution integration were performed. Peak identification was done based on peak position and the most probable combination of C, H, N, and O atoms. When possible, molecular formulas were assigned to organic compounds based on previous references on BVOC emissions (Inomata et al., 2014; Meischner et al., 2022; Yáñez-Serrano et al., 2021). BVOC mixing ratios were finally calculated using the proton transfer theory where the rate constant k (in $cm^3\ s^{-1}$) was determined for each molecular formula based on the method proposed by Cappellin et al. (2012). The relative ion transmission efficiency was calculated using a standard gas calibration mixture containing 14 different VOCs (summarized in Table S.3) at 100 ± 10 ppb in nitrogen (TO-14A Aromatic Mix, Restek Corporation, Bellefonte, USA).

~~BVOC concentrations on a large range of mass to charge (m/z) up to m/z 500.~~

BVOC fluxes (F) from ~~dynamic chamber~~soil were calculated as described in ~~(~~Yang et al.~~,~~ (2024a):

$$F = \frac{(C_{chamber} - C_{ambient}) \times Q}{A} \quad [\mu g\ m^{-2}\ h^{-1}] \qquad (1)$$

Where $C_{chamber}$ and $C_{ambient}$ are BVOC concentrations in ng/L at the chamber outlet and in ambient air respectively, Q is the flow rate inside the chamber (= 0.3 L min^{-1}) and A the soil surface (0.0616 m^2) ~~circled by the chamber~~.

2-3 Phospholipid fatty acid analysis (PLFA) measurements

After the end of BVOC measurements, the 15 soil and 12 litter samples were collected, frozen, lyophilized during 72 h and then ground into powder prior to microbial analyses. The phospholipid fatty acids (PLFAs) are essential components of all living cells and are used as biomarkers of soil microbial communities (Frostegård and Bååth, 1996). The PLFA extraction, identification and quantification followed the protocol described by Aupic-Samain et al. (2021) and Biryol et al. (2024). Litter lipid contents were extracted with Bligh-Dyer solution containing a quantification standard (C19:0; MIDI, Inc., Newark, DE, USA). The lipids were then separated using a 96-well solid-phase extraction (SPE) plate (SilactSPE Silica Affinisep®). To identify and quantify the lipids present, a gas chromatography mass spectrometer (a GC-MS Agilent 7890 system with a MSD5977A Network mass detector, an ALS7693 automatic injector, and HP5-MS apolar column) was employed with Mass-Hunter and Sherlock software (MIDI, Inc., Newark, DE, USA). Among the PLFAs identified in the samples, 10 were analyzed because they are markers for Gram-positive bacteria, Gram-negative bacteria, *Actinobacteria*, saprotrophic fungi and arbuscular mycorrhizal (AM) fungi (Biryol et al., 2024; Frostegård and Bååth, 1996). Microbial biomasses were obtained by converting the peak areas into µg/g of litter or soil.

2-4 Measurements of environmental variables

Ambient meteorological parameters (temperature, relative humidity and precipitation, wind speed and direction, rain, solar radiation) were recorded using a Sentinel weather station. Temperature and precipitation within the plot during one year prior to this study are shown in the ombrothermic diagram in Figure 2 (for more details on climate at O_3HP, referring to Garnier et al., 2021). It illustrates that 2022 was very dry, with 5 months of drought (January, March, June, July and October 2022), while May 2023 (measurement period for this study) was rainy with an accumulated precipitation of 120 mm.

Temperature and humidity inside the chambers were continuously monitored by sensors (~~–~~i-buttonsLink, ~~(~~Whitewater, WI 53190 USA). Litter humidity was estimated from measurement of fresh and dry litter using 3 aliquots of 8 g each day (Table S.1). Litter aliquots were dried using oven-drying at 65 °C for 3 days. Litter humidity calculated as $\frac{dry\ mass\ (g) \times 100}{fresh\ mass\ (g)}$, ranged from 14 % to 41 % (Table S.1).

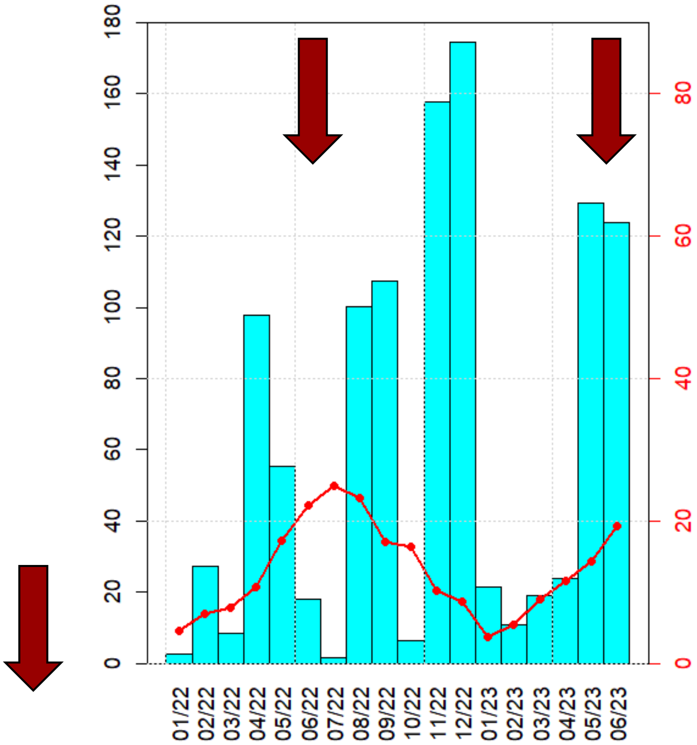


Figure 2. Ombrothermic diagram from January 2022 to June 2023 (mm/yy). Red arrows refer to the field campaign in June 2022 (Legros et al., 2025) performed within the natural and accentuated water stress conditions plots and May 2023 (this study).

2-5 Statistical analysis

Data were analyzed, statistically computed and plotted using RStudio (version 2024.12.0). A holistic approach was used to investigate emissions, meaning that all VOCs detected by PTR-ToF-MS (710 compounds) were considered in the data analysis steps described as follows. F~~-~~irst,~~First,~~ a ~~*Welsh*~~ *Welch* t-test was used to only select ions showing an average concentration significantly different when comparing ambient and chamber measurements. 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).~~Dataset was filtered to keep ions with p_{value}> 0.001. BVOC targeted in this study are summarized in Table S.2. Statistics were carried out using filtered VOC data, that is, the most abundant VOC fluxes in each chamber with fluxes > 0.002 µg m^{-2} h^{-1} (in absolute value).~~

To investigate the link between environmental parameters with main measured VOC fluxes, a correlation matrix has been built based on Pearson correlations by merging all chamber data. A heatmap correlation plot was classified into 5 clusters of VOC fluxes, environmental and biological parameters. The optimal number of clusters was estimated using a k-means clustering method technique (Steinley, 2006)~~(Steinley, 2006)~~.

3- Results and discussion

3-1 Diversity of VOC fluxes

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 VOCs 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)~~, reflecting highly diverse VOC fluxes from *Q. pubescens* litter~~. This finding might be the consequence of contrasting conditions compared to other studies. Furthermore, the holistic approach used in this study tends to include a higher diversity of ions. Altogether, these compounds represent a total negative flux (or immission) of -0.85 µg m^{-2} h^{-1}. Considering the most abundant VOC fluxes (compounds with absolute value of average fluxes above 0.01 µg m^{-2} h^{-1}, a total of 46 compounds) in each chamber, the average total flux of VOC reached -0.72 µg m^{-2} h^{-1}, representing 90 % of the total flux (Figure S.1~~3~~, Table S.~~2~~4).

In comparison, Legros et al. (2025) reported emissions of 9.11 ± 0.64 µg m^{-2} h^{-1} when considering total VOC fluxes. ~~(~~Yang et al.~~,~~ (2024b) showed that fluxes are dependent on seasonality. Indeed, they found negative fluxes in summer and winter (-25.9 ± 9.36 and -2.77 ± 3.84 µg m^{-2} h^{-1}, respectively) and positive fluxes in autumn and spring (4.54 ± 7.18 and 3.86 ± 2.59 µg m^{-2} h^{-1}, respectively).

Regarding individual compounds, positive and negative fluxes occurred from bare soil and soil covered by litter, as often reported earlier (Legros et al., 2025; Yang et al., 2024b). Figure 3 presents the~~-~~ positive and negative net fluxes for major compounds, while results for all VOCs are reported in Supplementary data. Almost 48 % of the compounds showed negative fluxes, meaning they were immitted by the soil and soil covered by litter through ~~assimilation~~ degradation or adsorption processes, 37 % were both emitted and immitted and 15 % were only emitted (Supplementary data).

Soil covered by litter and bare soil mainly differed in terms of methanol (CH_4O), acetone (C_3H_6O) and isoprene (C_5H_8) fluxes, which were bidirectional (emitted and immitted) in presence of litter, whereas they were only emitted or immitted by bare soil (Figure 3). For monoterpenes ($C_{10}H_{16}$) and acetaldehyde (C_2H_4O) fluxes, higher net positive emissions were observed for bare soil than soil covered by litter. This suggests that soil can be a source of monoterpenes and acetaldehyde to the atmosphere. The presence of litter on the soil physically reduces the transfer to the atmosphere, or favours the presence of microorganisms that consumes these two VOCs (Marmulla and Harder, 2014; McBride et al., 2023).

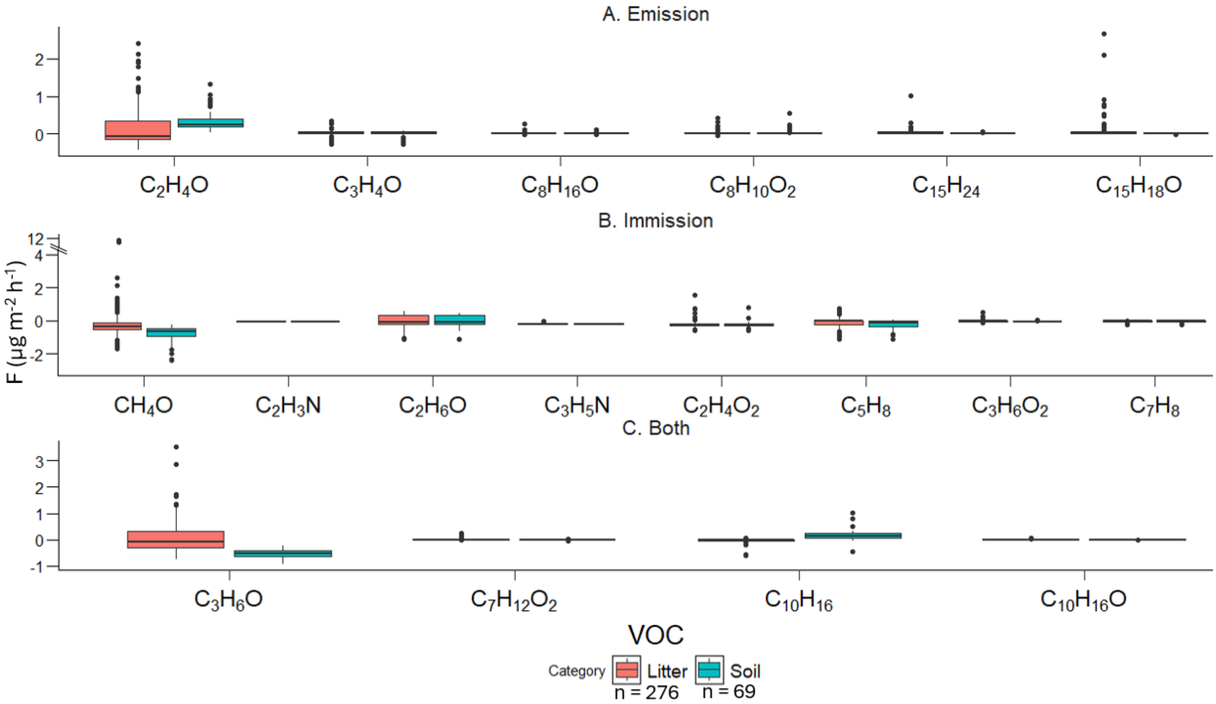


Figure 3. ~~Most abundant compounds and their m~~Measured VOC fluxes (in µg m^{-2} h^{-1}) during the field campaign for A. Major emitted compounds, B. Major immitted compounds and C. Both emitted and immitted compounds for litter chambers ~~(n = 276)~~ and bare soil chambers. ~~(n = 69).~~ The line that divides the box represents the median of measured fluxes, ends of the box indicate the upper (Q3) and lower (Q1) quartiles, up and down whiskers represent max and min values and outliers are represented by dots. VOC fluxes for this figure were obtained from the ~~24~~24~~3~~-h measurements of 12 soil covered by litter samples (~~23h x 12 samples =~~ 276 VOC flux measurements) ~~all replicates for both~~and 3 bare soil samples (~~ soil and the four LM in the case of litter~~~~23h x 3 samples =~~ 69 flux measurements).

VOC emissions

VOCs are only considered as emitted in this section, when they have positive average VOC fluxes for each modality (bare soil and soil covered by litter), and conversely for immission (next section). The compounds with the highest emissions were acetaldehyde (C_2H_4O), acrolein (C_3H_4O), 1H-pyrrole-2,5-dione ($C_4H_4NO_2$), lindestrene ($C_{15}H_{18}O$), creosol ($C_8H_{10}O_2$), sesquiterpenes ($C_{15}H_{24}$), octanal ($C_8H_{16}O$) and dibutyl phthalate ($C_{16}H_{20}O_4$).

On average, we measured positive acetaldehyde fluxes of 0.056 ± 0.192 and 0.186 ± 0.226 µg m^{-2} h^{-1} from soil covered by litter and bare soil, respectively. In both cases, the fluxes were highly variable, resulting in positive and negative fluxes with respect to the diurnal cycle (sections 3.3 and 3.4).. Emissions of acetaldehyde have been previously measured during litter emissions experiments (Asensio et al., 2007a; Gray et al., 2010, 2014). The origin of acetaldehyde can be attributed to root and leaf litter emissions (Schade and Goldstein, 2001; Warneke et al., 1999) formed by the oxidation of VOCs, but this second source is expected to be minor considering the residence time in dynamic chambers.

Although acrolein is mostly considered as an anthropogenic compound originating from combustion sources (Koss et al., 2018; Schieweck et al., 2021), positive acrolein fluxes were observed in all chambers with an average flux of 0.009 ± 0.033 µg m^{-2} h^{-1}. Acrolein has previously been associated with the decomposition of litter biomass in a mixed broadleaf and coniferous forest (Ehrlich and Cahill, 2018). Indeed, higher concentrations were measured from fresh leaves compared to senescent or decomposing leaves. Acrolein was also previously detected in litter of *Pinus halepensis* Mill. by Viros et al. (2021) and in litter of *Q. pubescens* litter in a previous study performed at O_3HP (Legros et al., 2025), which reported an average flux 100 times higher than in the present study (0.79 ± 0.04 µg m^{-2} h^{-1}). Drier conditions during Legros et al. (2025) study compared to our experiment (Figure 2) could explain the differences observed between the two studies.

$C_4H_3NO_2$ was tentatively assigned as 1H-pyrrole-2,5-dione is observed for the first time in litter VOC fluxes. This ~~1H-pyrrole-2,5-dione ($C_4H_3NO_2$) was identified here for the first time in litter VOC fluxes. This~~ compound is a monopyrrolic derivative of the maleimide class/family corresponding to a transformation product of chlorophyll (Naeher et al., 2016). Maleimides are commonly studied in paleoecological and human-based studies and possess various biological activities such as antibacterial, and antifungal properties (Ma et al., 2022).

Two other compounds not previously measured were identified in this study as $C_{15}H_{18}O$, proposed to be lindestrene (average flux of 0.006 ± 0.014 µg m^{-2} h^{-1}), and creosol ($C_8H_{10}O_2$, 0.003 ± 0.006 µg m^{-2} h^{-1}). To our knowledge, no previous study documented lindestrene emissions (or immission) from soil, but it has been reported in emissions from tree resins (Taiti et al., 2018). Regarding creosol, it is a natural organic compound degradation in creosote, which can be further degraded by several fungal species (Atagana et al., 2006; Lee et al., 2005). This degradation process highlights the role of fungi in the decomposition of complex organic compounds, potentially contributing to soil and ecosystem health by removing phenols from contaminated soils (Atagana, 2004; Atagana et al., 2006).

Sesquiterpenes were also detected with average fluxes of 0.003 ± 0.006 µg m^{-2} h^{-1} and are frequently reported in litter of terpene storing species (Asensio et al., 2008; Viros et al., 2021; Yang et al., 2024b). Viros et al. (2020) reported VOC fluxes from *Q. pubescens* litter, but they did not observe sesquiterpenes, and it was only reported as minor emissions in a previous field study at O_3HP (Legros et al., 2025). Since no storage organs are present in *Q. pubescens* leaves, the observed emission can be related to fungi, known to release high amounts of sesquiterpenes (Mäki et al., 2017; Weikl et al., 2016). However, no studies in the Mediterranean region report a relationship between fungi and sesquiterpenes fluxes.

Octanal ($C_8H_{16}O$, detected at m/z 129.132) fluxes reached on average 0.002 ± 0.004 µg m^{-2} h^{-1} for litter. Octanal has been previously found in Mediterranean litters for *Q. pubescens, Quercus suber* L. and *Ulex parviflorus* Pourr.

(Viros et al., 2020; Legros et al., 2025), and more specifically in tundra soils where it accounts for about 75 % of the total VOC emissions (Kramshøj et al., 2016). The processes responsible for octanal emissions remain unexplored.

Dibutyl phthalate ($C_{16}H_{20}O_4$) fluxes were similar for both bare soil and soil with litter (on average: 0.007 ± 0.019 µg m^{-2} h^{-1}). The occurrence of this compound in a rural environment such as O_3HP seems surprising as it is known as plasticizer compound, but emission can be related to microbial taxa, as shown by Sillo et al. (2024), who reported a significant correlation between dibutyl phthalate fluxes and the abundance of *Paenarthrobacter* genus (~~actinomycete~~ Actinomycota class such as Micrococcaceae).

VOC immission

Immission was frequently observed for oxygenated compounds, such as alcohols (methanol, CH_4O, ethanol, C_2H_6O), carboxylic acids (acetic, $C_2H_4O_2$, propanoic, $C_3H_6O_2$ and formic CH_2O_2 acids) and also for alkenes (isoprene, C_5H_8 and toluene, C_7H_8) and two nitrogenous compounds (acetonitrile, C_2H_3N and propanenitrile, C_3H_5N).

Average fluxes for both bare soil and soil covered by litter were negative for methanol (-0.033 ± 0.038 and -0.044 ± 0.047 µg m^{-2} h^{-1}, respectively) and ethanol (-0.~~024~~ 383 ± 0.~~035~~ 468 and -0.~~027~~346 ± 0.447~~040~~ µg m^{-2} h^{-1}, respectively). In contrast, most of previous studies suggest that soil is a source of alcohols (Asensio et al., 2008; Gray et al., 2010; Yang et al., 2024a), except for Asensio et al. (2007a) who reported both methanol and ethanol deposition in a Mediterranean *Quercus ilex* L. forest of northern Spain (from -95.04 µg m^{-2} h^{-1} to -71.28 ng m^{-2} h^{-1}). Thus, whether these compounds are primarily emitted from soils or deposited is strongly dependent on both biotic (microbial activity) and abiotic (meteorological parameters) factors. For example, Asensio et al. (2007a) showed that VOC immission of alcohol is related to soil moisture. More generally, lignocellulose, which is the most widespread and abundant source of carbon in nature for microorganisms (Abdeshahian et al., 2020), reached concentrations of about 187.6 ± 1.5 mg g$^{-1}_{DW}$ in *Q. pubescens* litter (Santonja et al., 2015), is considered the preferred consumed biomass by bacteria for the production of ethanol (Du et al., 2015).

Carboxylic acids showed negative fluxes, with acetic acid having the highest deposition rate (-0.088 ± 0.115 µg m^{-2} h^{-1} on average for ~~LM~~ litters and -0.096 ± 0.117 µg m^{-2} h^{-1} for bare soil), followed by formic acid (-0.082 ± 0.099 µg m^{-2} h^{-1} on average for ~~LM~~ litters and -0.089 ± 0.105 µg m^{-2} h^{-1} for bare soil) and propanoic acid (-0.011 ± 0.022 µg m^{-2} h^{-1} on average for ~~LM~~ litter and -0.017 ± 0.22 µg m^{-2} h^{-1} for bare soil). Previous studies showed contrasted features: while in agreement with our results some studies observed deposition in Mediterranean forests (Asensio et al., 2007b, a). Legros et al. (2025) observed emissions of acetic and formic acids. These compounds are sensitive to soil moisture, which favors microbial uptake and deposition of VOC on wet surfaces (Asensio et al., 2007a). Propanoic acid is known to be released during microbial fermentation (Leff and Fierer, 2008; Wheatley et al., 1996), while acetic or formic acids are reported to be produced by bacteria and fungi (Mielnik et al., 2018; Wheatley et al., 1996). ~~Indeed, considering~~Given the environmental conditions (i.e. humid) inside the chambers, we hypothesize that carboxylic acid deposition processes linked to the soil moisture ~~are dominating~~dominate, ~~leading to~~resulting in net deposition (further discussed in section 3.4).

Isoprene showed an average immission rate of -0.048 ± 0.106 µg m^{-2} h^{-1} for litters~~LM~~ and -0.082 ± 0.128 µg m^{-2} h^{-1} for bare soil. Accordingly, most studies have shown negative fluxes for isoprene (Cleveland and Yavitt, 1998; Gray et al., 2014, 2015; Legros et al., 2025; McGenity et al., 2018). Higher negative fluxes were estimated by Legros et al., (2025), with - 0.92 ± 0.20 µg m^{-2} h^{-1}, and Gray et al. (2014) with values up to -138.04 ± 89.76 µg m^{-2} h^{-1}. The isoprene fluxes are driven by the microbial activity, as this compound is consumed by bacterial and fungal taxa (Gray et al., 2015), and it can be also released by root exudates (Asensio et al., 2007a). In addition isoprene is well known to be emitted by the canopy of *Q. pubescens* (Genard-Zielinski et al., 2015), and it is possible that specific bacteria or fungi that can use isoprene as carbon source developed in soil and litter at O_3HP.

Toluene (C_7H_8) immission occurred in both bare soil and soil covered by litter (-0.013 ± 0.014 µg m^{-2} h^{-1} on average), indicating that litter and soil are a sink for this compound. This VOC is well known to be of anthropogenic origin, associated with fossil fuel and biomass burning (Hanif et al., 2021) and, to a lesser extent, of plant stress (Heiden et al., 1999; Misztal et al., 2015). This compound may thus have been transported in the air masses affected by anthropogenic emissions and deposited on this rural ecosystem.

~~As t~~oluene, 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).

However, acetonitrile emission has been reported in some plant species such as *Gynandropsis gynandra* L. (Briq.), where it is a repellent against spider mites (Nyalala et al., 2011, 2013). In our study, the averaged fluxes of acetonitrile and propanenitrile were negative with -0.038 ± 0.040 µg m^{-2} h^{-1} and -0.005 ± 0.006 µg m^{-2} h^{-1}, respectively. Acetonitrile deposition has been already measured in Mediterranean forest soils, ranging from -75.6 to -15 ng m^{-2} h^{-1} (Asensio et al., 2008). In the present study, the origin of the acetonitrile and propanenitrile is probably regional rather than local, since these compounds are well known to have a long lifetime (more than a year, Andersen et al., 2018; Gouw et al., 2003), and deposition of this compound occurred in the forest soil of this study.

VOCs both emitted and immitted

Many oxygenated compounds showed bidirectional fluxes, or fluxes of opposite magnitude when comparing bare soil average fluxes to soil covered by litter, such as acetone (C_3H_6O), cyclohexanecarboxylic acid (CHC acid, $C_7H_{12}O_2$), monoterpenes ($C_{10}H_{16}$) and oxygenated monoterpenes ($C_{10}H_{16}O$).

Among these compounds, acetone is one of the most commonly detected volatiles released from soils (Asensio et al., 2008; Gray et al., 2010), with an average immission of -0.217 ± 0.220 µg m^{-2} h^{-1} from bare soil, while by contrast a positive flux of 0.019 ± 0.195 µg m^{-2} h^{-1} from soil covered by litter. The positive flux is lower than Legros et al. (2025) who reported an average acetone flux of 1.15 ± 0.30 µg m^{-2} h^{-1}. This can be attributed to the different environmental conditions encountered during measurements.

Cyclohexanecarboxylic acid (CHC acid, $C_7H_{12}O_2$) was found to have average positive flux in litter~~LM~~ chambers (0.003 ± 0.006 µg m^{-2} h^{-1}) and negative for bare soil (-0.002 ± 0.003 µg m^{-2} h^{-1}). Like lindestrene and 1H-pyrrole-2,5-dione, cyclohexanecarboxylic acid (CHC acid) has not been reported yet in other studies about bare soil, litter alone or bare soil covered by litter. CHC acid is produced naturally as part of the shikimate pathway, a major metabolic pathway for the biosynthesis of aromatic compounds in bacteria (*Alicylobacillus acidocaldarius* and *Streptomyces collinus)*, plants, and fungi (Shende et al., 2024). This pathway is key to the formation of phenolic compounds (Laoué et al., 2022). Thus, this novel finding highlights the potential for further exploration of its sources and ecological role.

Monoterpene fluxes were negative when the soil was covered by litter (-0.007 ± 0.015 µg m^{-2} h^{-1} on average). By contrast to soil covered by litter, bare soil showed positive fluxes of monoterpenes (0.026 ± 0.043 µg m^{-2} h^{-1} on average), as a previous study already observed (Leff and Fierer, 2008). The negative fluxes when the soil was covered by litter suggest that microorganisms consume monoterpenes, as these compounds have been reported as a carbon and energy source for microorganisms (Marmulla and Harder, 2014; White, 1994). Bacteria also consume monoterpenes in order to protect themselves from the monoterpene-related toxic effects (Marmulla and Harder, 2014), and fungi are known to transform monoterpenes during growth (Farooq et al., 2004).

Fluxes of oxygenated monoterpenes were measured at 0.001 ± 0.002 µg m^{-2} h^{-1} for litters emissions and -0.001 ± 0.002 µg m^{-2} h^{-1} for bare soil, on average. While it has not been reported for *Q. pubescens* forests, previous study has shown concentrations of camphor from *Rosmarinus officinalis* in the Mediterranean region (3.18 ± 0.42 mg g^{-1}_{DW} by Ormeño et al. (2008) and 9.9 ± 3.4 mg g^{-1}_{DW} by Staudt et al. (2017). Oxygenated monoterpenes ($C_{10}H_{16}O$, such as camphor, fenchone or carveol) may originate from litter decomposed by fungi, as proposed by Isidorov and Jdanova (2002).

3-2 VOC variation with different litter masses

Correlations of VOC fluxes with the litter masses inside the chambers were performed (Figure 4). Surprisingly, only a few compounds showed significant relationships between increasing litter masses and fluxes. Correlations were positive only for methanol, acetone, oxygenated monoterpenes, CHC acid and sesquiterpenes. 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~~ which are more important drivers of emission/deposition.

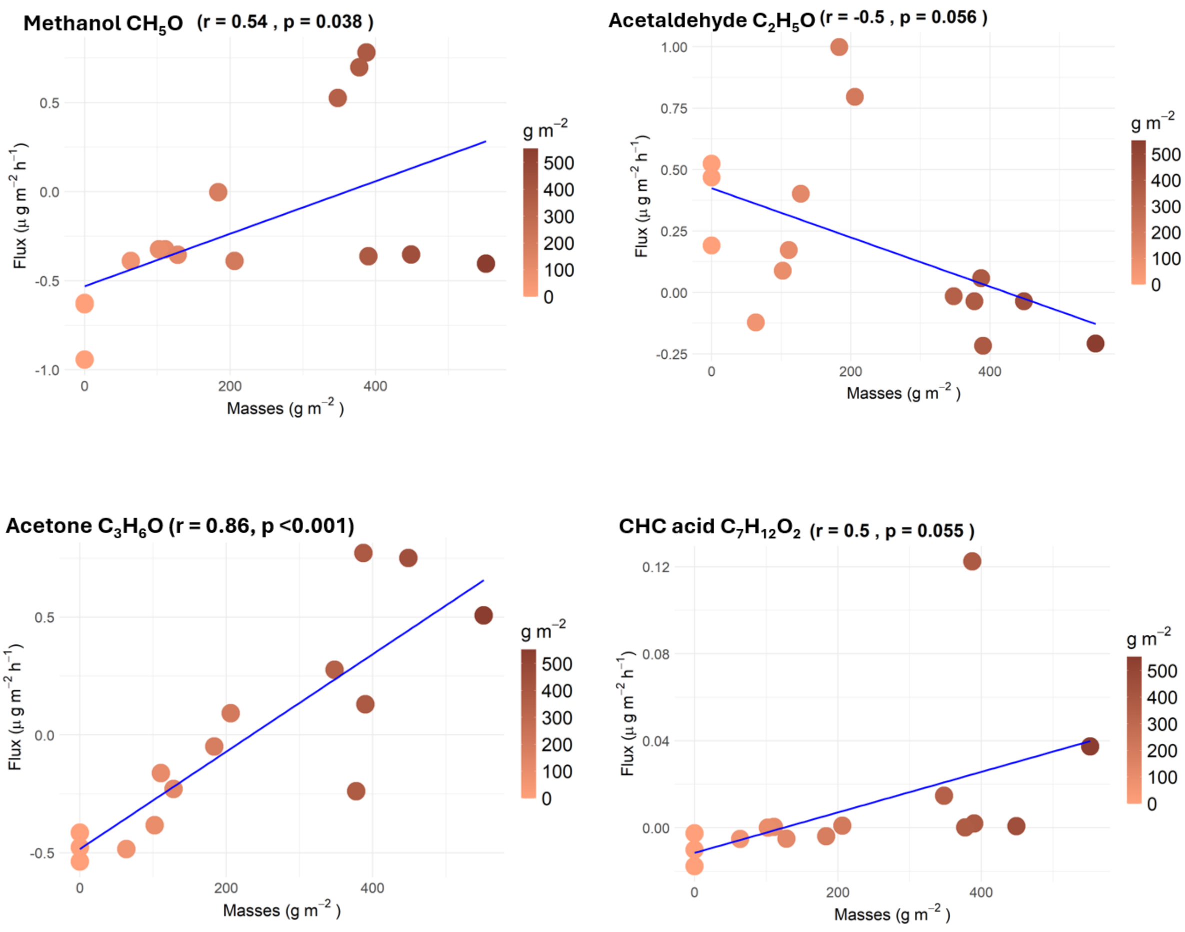
Methanol, acetone, oxygenated monoterpenes and CHC acid fluxes showed a positive correlation with litter masses (Figure 4), but average bare soil fluxes were negative. For methanol and CHC acid, the correlation with ~~LM~~ litter mass is weaker (r = 0.54, p_{value} = 0.038 for methanol, r = 0.50, p_{value} = 0.055 for CHC acid) than acetone and oxygenated monoterpenes (r = 0.63, p_{value} < 0.001 for acetone, r = 0.86, p_{value} < 0.001 for oxygenated monoterpenes). For these ~~4~~ four compounds, the net flux is increasing with litter mass, from a negative flux in bare soil to a positive flux at high ~~LM~~litter mass. As a result, it suggests that the soil alone acts as a sink for these

~~4 ~~four compounds, while litter mostly emits them, the resulting net fluxes depending on the litter mass amount~~ of LM ~~ and maybe environmental conditions. 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.

Negative response has only been observed between acetaldehyde flux and litter mass ~~es and LM ~~($r = -0.50$, $p_{value} = 0.056$)~~, although average positive fluxes were reported for LM 2 (0.343 ± 0.379 µg m^{-2} h^{-1}, Figure 4)~~. Opposite to the previous ~~4 ~~four compounds, emissions are observed for bare soil while the net fluxes turned negative with increasing ~~LM~~litter mass, suggesting that the soil is a source of acetaldehyde, further deposited on litter. It may be due to the presence of microorganisms on leaf litter uptaken acetaldehyde~~, or different environmental conditions~~.

Finally, sesquiterpenes were the most significant VOC linked to the ~~LM ~~litter mass ($r = 0.80$, $p_{value} < 0.001$), with positive fluxes for all modalities increasing together with litter mass. If no storage organs are present in *Q. pubescens* leaves, the abundance of potential fungi associated with sesquiterpene emissions, as suggested by ~~(~~Mäki et al. (~~,~~2017) and~~;~~ Weikl et al.~~,~~ (2016) should depend on litter mass~~LM~~.

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.



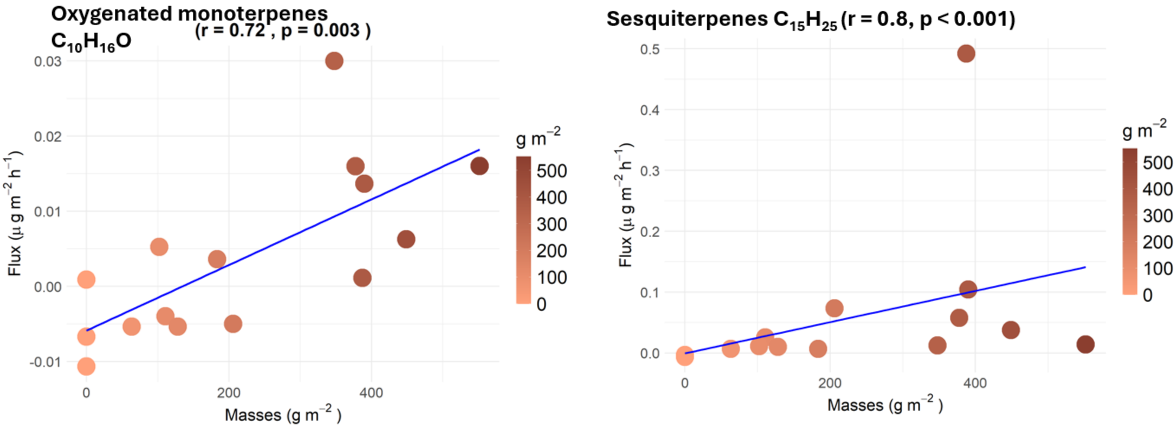


Figure 4. Correlation plots of methanol, acetaldehyde, acetone, oxygenated monoterpenes, CHC acid and sesquiterpenes fluxes (µg m^{-2} h^{-1}) with litter masses per area (0 in bare soil in g m^{-2}).

3-3 VOC diurnal variations

The diurnal variations of the main VOC fluxes (F > 0.005 µg m^{-2} h^{-1}, 13 % of the total compounds = 21 compounds, ~75 % of the total fluxes) and temperature and relative humidity are shown in Figure 5 and Figure S.2~~1~~. The temperature was highest between 8 h and 15 h (local time), ranging from 15 °C to 20 °C, and exceptionally up to 30 °C in ~~LM 3~~some litter samples. By contrast, the humidity decreased during the same hours up to 75 %, ~~for LM 3~~ and reached 100 % during nighttime.

Most of the compounds showed an increase of their fluxes between 10 h and 15 h local time. Strong diurnal variations were measured with high fluxes during daytime ~~in LM 3~~ for methanol (0.797 ± 2.355 µg m^{-2} h^{-1}), 1H-pyrrole-2,5-dione (0.050 ± 0.040 µg m^{-2} h^{-1}), CHC acid (0.009 ± 0.014 µg m^{-2} h^{-1}) and acetone (0.165 ± 0.402 µg m^{-2} h^{-1}).

Patterns can vary between compounds within the ~~LM~~litter mass gradient. Indeed, similar patterns can be highlighted for 1H-pyrrole, CHC acid, lindestrene and sesquiterpenes with higher emissions associated with high litter masses (> ~~XXX~~400 g m^{-2} ~~per chamber~~) ~~in LM 3 and 4~~ during the day and very low during nighttime. The 1H-pyrrole-2,5-dione, lindestrene and CHC acid fluxes were only significant in the two highest litter mass~~LM~~ scenarii (Supplementary Information, averaged fluxes). These fluxes are dependent on the litter mass but not linearly, and include a threshold effect, explaining why they were not discussed in the previous section.

Monoterpenes were released from bare soil and ~~LM 1~~ low litter masses between 12 h and 17 h, and then uptaken from 18 h to midnight (Figure 5). A specific pattern was shown for isoprene, formaldehyde (HCHO) and formic acid. Indeed, these fluxes decreased between 5 h and 10 h and increased around 12 h~~-~~, when isoprene emissions from trees were maximal, as they are linked to temperature and solar radiation (Kesselmeier et al., 1998; Monson et al., 1992; Owen et al., 2002). Around midnight, isoprene fluxes were stable in all ~~LM~~ litter masses and no exchange occurred between the soil and the atmosphere (i.e. concentrations inside the chamber were identical to ambient concentrations). As expected, isoprene oxidation products (methacrolein, MACR; methyl vinyl ketone, MVK and Isoprene Hydroxy Hydroperoxide, ISOPOOH) showed the same pattern as isoprene, with an uptake of this compound in bare soil and all ~~LM~~litter masses. Their fluxes increased between 10 h and 12 h with averaged fluxes up to -0.021 ± 0.022 µg m^{-2} h^{-1} during daytime.

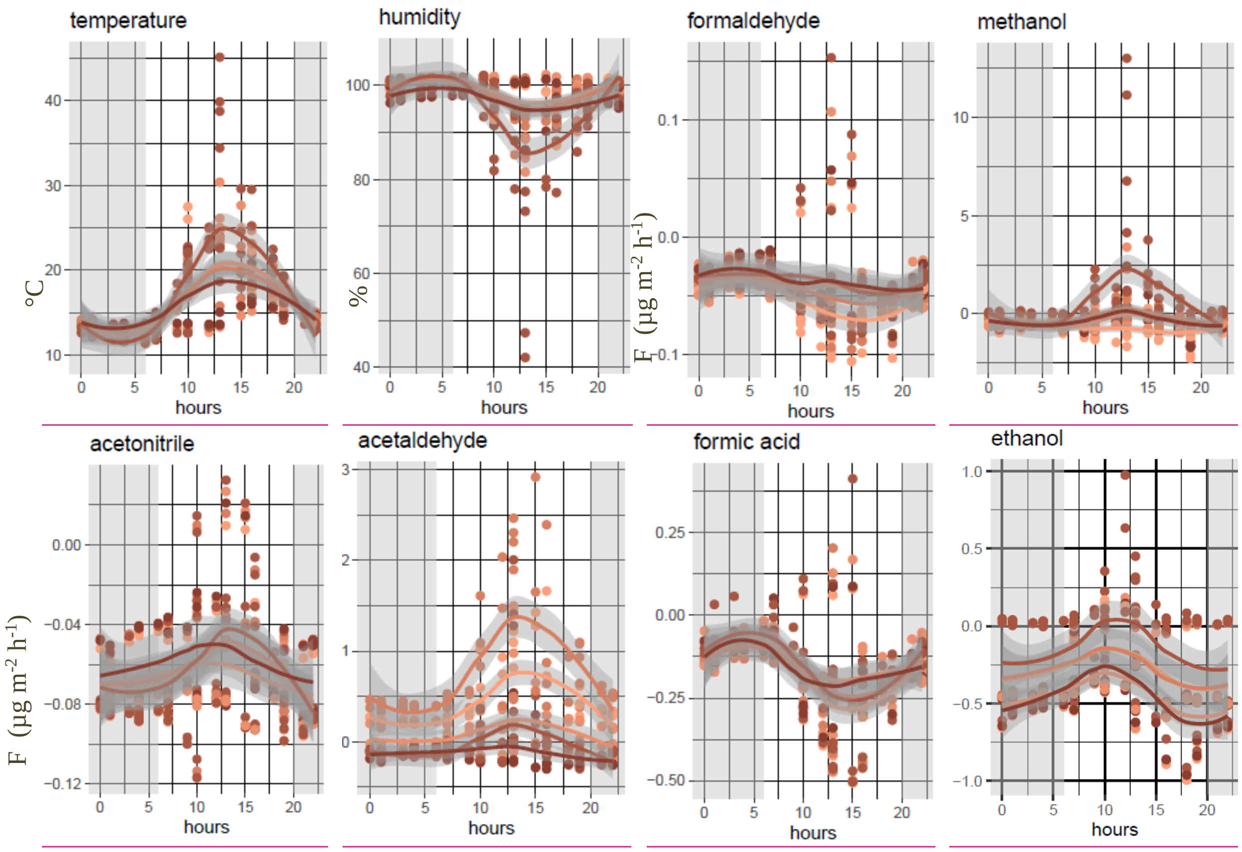
The uptake of formic acid, acetone and formaldehyde by the soil was particularly high at night ~~Formic acid, acetone and formaldehyde were especially sinked by the soil during nighttime~~ when the humidity increased and reached 100 % (-0.052 ± 0.023 µg m^{-2} h^{-1}, -0.059 ± 0.073 µg m^{-2} h^{-1} and -0.027 ± 0.008 µg m^{-2} h^{-1}, respectively). Propanoic and acetic acids also showed negative fluxes (-0.008 ± 0.027 µg m^{-2} h^{-1} and -0.077 ± 0.114 µg m^{-2} h^{-1}) during daytime. These differences can be attributed to the fact that fluxes of these oxygenated compounds are influenced by abiotic factors, particularly soil moisture and temperature. ~~(~~Jacob et al.~~,~~ (2002) have demonstrated that both acetone fluxes and concentrations increase with rising temperatures. Furthermore, the physicochemical degradation of VOCs can act as a sink for VOCs at the soil level (Peñuelas et al., 2014). Our results are in line with Legros et al., (2025) for daytime acetone and isoprene fluxes where they measured positive and negative fluxes for acetone and isoprene (3.52 ± 0.40 and -1.45 ± 0.41 µg m^{-2} h^{-1} in Legros et al., 2025, respectively).

Negative methanol fluxes were recorded for all chambers and essentially during nighttime (Figure 5) and slightly positive during daytime except for litter masses between 120 g m^{-2} and 300 g m^{-2} ~~LM 2 and LM 3~~ where the flux is higher than the other days (up to 0.797 ± 2.354 µg m^{-2} h^{-1}). For litters masses ~350 g m^{-2}~~LM 3~~, the environmental conditions showed few differences with higher temperature and then lower humidity during the measurements (temperature and ~~humidit~~humidity inside the chambers in Figure 5), which can explain differences in observed fluxes. The role of environmental parameters in the processes of consumption or emission of methanol by microorganisms have been already studied (Asensio et al., 2007b; Cleveland and Yavitt, 1998; Gray et al., 2015; Jiao et al., 2023; Schade and Goldstein, 2001).

Positive fluxes were observed during the day for acetaldehyde (0.184 ± 0.245 µg m^{-2} h^{-1}), except for ~~LM4~~ litter masses > 400 g m^{-2} and negative acetaldehyde fluxes were observed during nighttime for litter masses at medium-high scenario (300 g m^{-2} < M < 400 g m^{-2}~~LM 3 and LM 4, (~~-0.076 ± 0.029 µg m^{-2} h^{-1} and -0.066 ± 0.033 µg m^{-2} h^{-1}, respectively). This result is in line with previous studies that showed that acetaldehyde can be both emitted and uptaken by soil (Asensio et al., 2008; Jiao et al., 2023; Peñuelas et al., 2014). Ethanol fluxes showed the same pattern as acetaldehyde with higher fluxes between 10h and 12h (-0.017 ± 0.022 µg m^{-2} h^{-1} on average daytime).

In Legros et al. (2025), acrolein has been shown to have high flux variations during day and night (diurnal cycle). Our measurements were made almost one year after the Legros et al. (2025) study at the same site. However, ~~environmental conditions~~temperature and humidity were ~~completely~~ strongly different and the soil was not submitted to the same constraints explaining the differences observed.

Toluene, creosol, propanenitrile and acetonitrile are compounds with long life time (> 1 year). Increases of the magnitude of fluxes during daytime have been reported. However, the fluxes remained negative for toluene (-0.012 ± 0.009 µg m^{-2} h^{-1}), propanenitrile (-0.004 ± 0.007 µg m^{-2} h^{-1}) and acetonitrile (-0.034 ± 0.018 µg m^{-2} h^{-1}) and turned positive for creosol (0.006 ± 0.011 µg m^{-2} h^{-1}). Dibutyl phthalate fluxes were positive and higher during daytime (0.016 ± 0.025 µg m^{-2} h^{-1}) than nighttime (0.003 ± 0.003 µg m^{-2} h^{-1}).



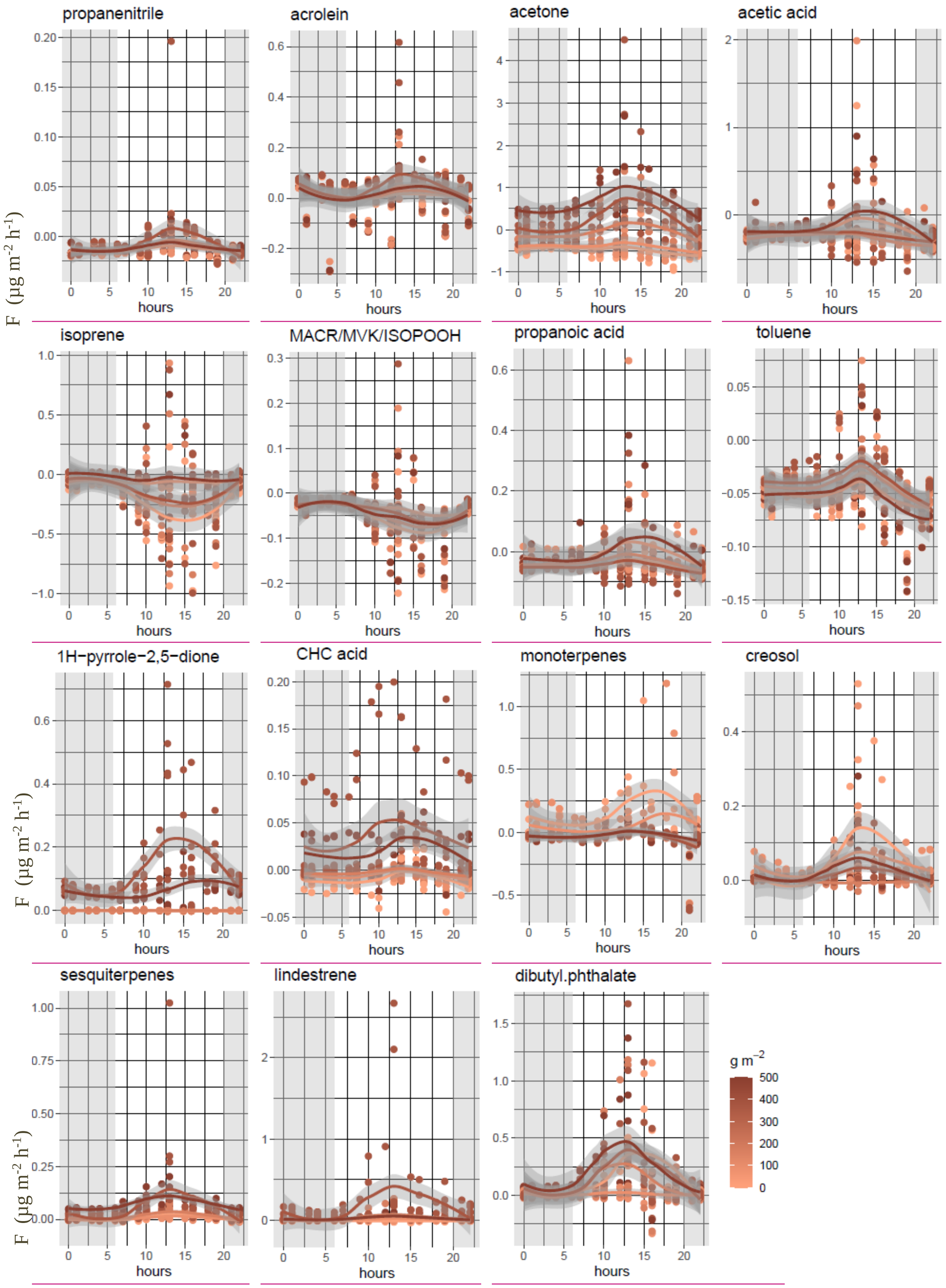


Figure 5. Temperature and humidity diurnal cycles (24 h) and measured BVOC fluxes (µg m^{-2} h^{-1}) for bare soil and soil covered by increasing the amount of litter.

3-4 VOC fluxes linked to environmental and biological parameters

As the previous section illustrates the strong variability during the hours of the day, but also between the different ~~LM~~ scenarii, we investigated the relation between BVOC fluxes and biotic/abiotic factors to better understand the main drivers of these fluxes. For this purpose, a correlation analysis was performed based on hourly fluxes merging the data of the 15 chambers ~~and all days of experiments~~ (n=345) and presented in Figure 6.

First, a strong positive correlation can be observed between monoterpenes and arbuscular mycorrhizal (AM) fungi, forming the first cluster ($r = 0.48$, $p_{\text{value}} < 0.001$, Figure 6). We suggested earlier that soil fungi are the main source of monoterpenes, as negative monoterpene fluxes were observed when ~~LM~~ litter mass increased. The concentration of AM fungi is observed to be higher in the bare soil compared to ~~LM~~soil covered by litter masses, which confirms that AM fungi can be the source of monoterpenes from the soil~~e~~. This confirms the results of previous studies, showing that fungi are ~~at the origin~~producers of monoterpenes~~ emissions~~ (Farooq et al., 2004; Marmulla and Harder, 2014).

Compounds observed in cluster 2 were positively related to the temperature inside the chambers, and logically negatively related to relative humidity ($r_{\text{(humidity/temperature)}} = -0.85$). Most of the compounds are deposited (except acetaldehyde and creosol), and their correlation with temperature indicates that deposition is higher when temperature is lower, or humidity is higher. Acetonitrile and propanenitrile were among the compounds with the strongest response to temperature ($r_{\text{acetonitrile/temp}} = 0.50$, $r_{\text{propanenitrile/temp}} = 0.59$). As mentioned previously, acetonitrile and propanenitrile main atmospheric sources are considered to be combustion processes, even if a few studies showed biogenic origins (Heiden et al., 1999; Misztal et al., 2015; Nyalala et al., 2011, 2013). This result may indicate that deposition is favoured by lower temperatures or higher humidity, with lower temperatures reducing the volatility of these species, and humidity favouring adsorption and dissolution in water (especially for hydrophilic compounds). Acetonitrile fluxes were linked to propanenitrile, propanoic and acetic acids and acetone ($r_{\text{acetonitrile/propanenitrile}} = 0.55$, $r_{\text{acetonitrile/propanoic acid}} = 0.60$, $r_{\text{acetonitrile/acetic acid}} = 0.55$ and $r_{\text{acetonitrile/acetone}} = 0.58$, respectively). As a few positive fluxes were observed for these nitrogen-containing VOCs, it suggests that their potential emissions can be biogenic, as acetone and acids have a microbial fermentation origin. Acetaldehyde and creosol are also included in this second cluster but are mainly emitted compounds (see section 3.1). Acetaldehyde has been described as an oxidation product of ethanol. However, only moderate correlations were measured between these two compounds ($r = 0.36$, $p_{\text{value}} < 0.001$), confirming that there is no strong photochemistry inside the chambers. However, strong relationships were observed with toluene and methanol with ethanol ($r_{\text{ethanol/toluene}} = 0.64$, $r_{\text{ethanol/methanol}} = 0.56$), indicating that these three compounds are likely to share a common origin.

Cluster 3 gathers compounds positively correlated with the litter masses highlighted in section 3.2, and some other compounds (CHC acid, acrolein, dibutyl phthalates and 1H-pyrrole-2,5-dione, e.g. $r_{\text{acetone/masses}\cancel{\text{LM}}} = 0.63$, $r_{\text{CHC acid/masses}\cancel{\text{LM}}} = 0.58$). In addition, we showed previously (Figure 4) that these compounds present the same pattern with higher emissions during daytime ~~and in LM3 and LM4~~for medium high and high amount of litter (> 300 g m^{-2}). This means that the emissions of these compounds are either directly related to the litter (emission from ~~the dead leaves~~ tissues) or indirectly through the presence of microorganisms. However, our study did not show a link between dibutyl phthalate fluxes and actinomycetes, as suggested by Sillo et al. (2024). This difference may be explained by the type of soil, since their study focused on urban soils that can be more polluted. Studies have demonstrated that both wet and dry conditions may influence microbial biomass, by creating environments unfavorable for aerobic g+ and gram-negative (g-) bacteria, as well as mycorrhizal fungi (Borowik and Wyszkowska, 2016). Most particularly, actinomycete abundance has been shown to increase with decomposing organic matter. However, actinomycetes are highly pH-sensitive organisms, and their abundance decreases significantly at pH levels below 5 (Kovacs et al., 2023). This parameter was not measured in our experiments, so we cannot establish a link with actinomycete abundance.

Temperature was negatively related to compounds in cluster 4. Surprisingly, isoprene fluxes were negatively correlated with temperature ($r = -0.35$, $p_{\text{value}} < 0.001$), and so ~~does~~ were for their oxidation products MACR/MVK/ISOPOOH ($r = -0.24$, $p_{\text{value}} < 0.001$) and formic acid ($r = -0.43$, $p_{\text{value}} < 0.001$). In other words, as these compounds are mostly deposited, the magnitude of deposition is increasing with temperature. Indeed, *Q. pubescens* is well documented as a strong isoprene emitter, emissions being well known to be positively influenced by temperatures (Genard-Zielinski et al., 2015). The temperature dependance of the deposition can thus be explained by the increasing production of isoprene by the green parts of *Q. pubescens*, which makes it more available for deposition. All compounds in this cluster are strongly correlated~~ between themselves~~. MACR/MVK/ISOPOOH, formaldehyde and formic acid are mostly associated as secondary products formed by the oxidation of isoprene. Isoprene fluxes have been found significantly correlated with MACR/MVK/ISOPOOH, formaldehyde and formic acid ($r_{isop/MACR} = 0.83$, $r_{isop/HCHO} = 0.78$ and $r_{isop/formic\ acid} = 0.75$ with $p_{value} < 0.001$). These compounds can be attributed to secondary origin from the degradation of isoprene. In addition, regarding the daily fluxes, isoprene, MACR/MVK/ISOPOOH, formaldehyde and formic acid fluxes presented the same pattern supporting the stronger relationship between these compounds. We can hypothesize here that the production of these compounds is following isoprene emissions, and the deposition rate simply increased accordingly. This hypothesis is further supported by the absence of a relationship between these cluster's compounds fluxes and PLFA (g+, g-, actinomycetes and fungi).

Finally, soil moisture (litterRH in Figure 6) showed positive correlations with gram-positive and gram-negative bacteria (g+ and g-), actinomycete and fungi ($r_{litterRH/g+} = 0.29$, $r_{litterRH/g-} = 0.37$, $r_{litterRH/actino} = 0.55$, $r_{litterRH/fungi} = 0.29$, with $p_{value} < 0.001$, values are reported in Supplementary file), all forming cluster 5. Negatively significant but moderate relationships of monoterpenes fluxes with fungi have been observed ($r_{monop/fungi} = -0.33$, $p_{value} < 0.001$). Monoterpenes fluxes were likely driven by the abundance of actinomycetes and gram-negative bacteria, and were consumed by these microorganisms. This explains why we observed a predominance of negative fluxes for these compounds when litter accumulation increased inside the chambers.

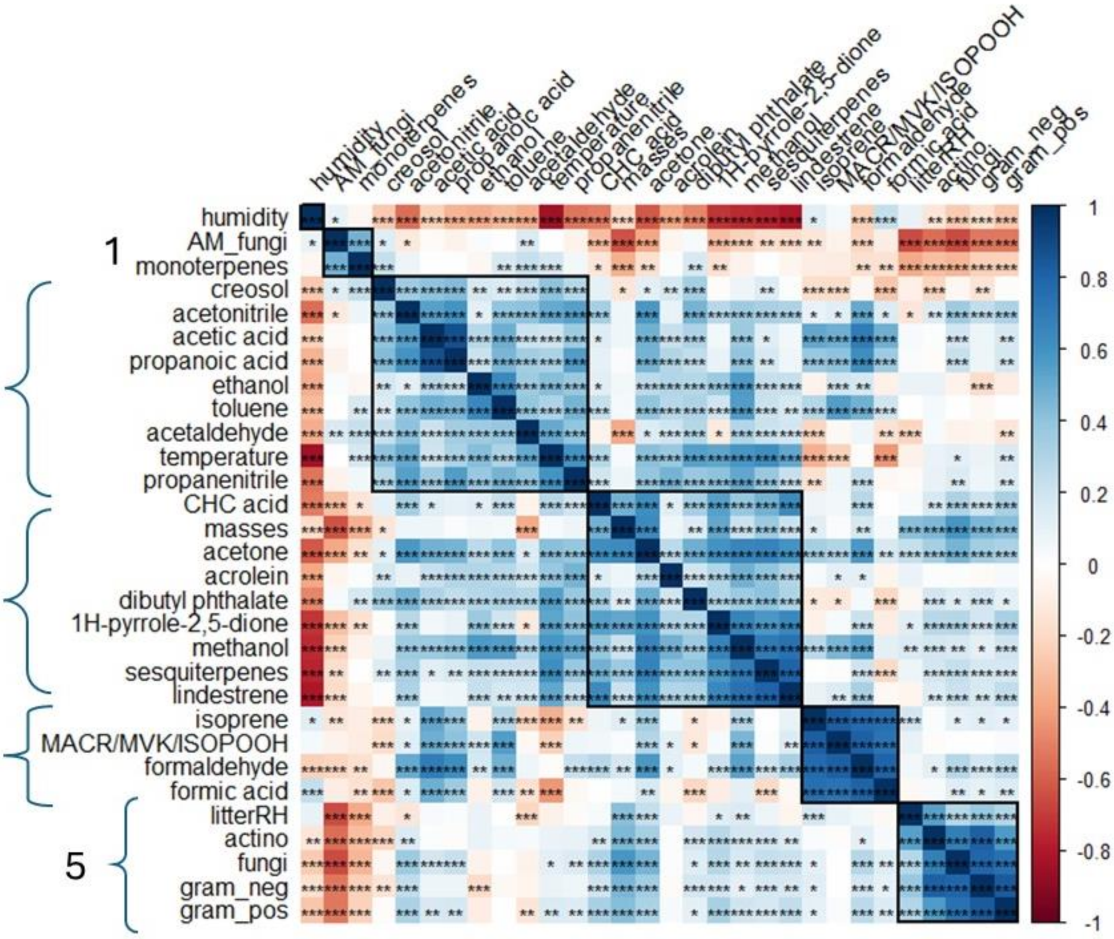


Figure 6. Correlation matrix between BVOC fluxes and abiotic (air temperature and humidity, litter humidity) and biotic (litter mass~~, litter humidity content, PLFA~~ and microbial biomass) factors ~~for all experimental days and~~ merging ~~all~~the data of the 15 chambers (n = 345). Positive correlations (r > 0) were highlighted in blue and negative (r < 0) in red. Stars represent p_{values} and their confidence: ~~*~~ p ≧ 0.05 (*), p < 0.01 ~~<~~ (**), p < ~~< 0.05 and~~ 0.001 ~~<~~ (***) ~~< 0.01~~. ~~CHC acid = cyclohexanecarboxylic acid.~~ Cluster's number is at the left of the correlation plot. AM_fungi = arbuscular mycorrhiza fungi;~~.~~ CHC acid = cyclohexanecarboxylic acid; litterRH = litter humidity.

4- Conclusion

A wide range of VOCs were measured from bare soil and litter, with over 135 compounds identified. Positive and negative fluxes were observed, with some fluxes appearing to be independent of litter mass such as toluene or formaldehyde. About 48% of the compounds showed negative fluxes, indicating uptake by the soil and soil covered by litter, 37% showed both emission and uptake, and 15% were emitted. The compounds with highest uptake rates were ~~The most uptaken compounds were~~ ethanol, formaldehyde, isoprene, acetonitrile, toluene, formic and acetic acids. ~~Thanks to~~ the holistic analysis of detected compounds, some VOCs such as lindestrene, cyclohexanecarboxylic acid (CHC acid) and 1H-pyrrole-2,5-dione, were identified from the litter for the first time. The origin of these compounds can be attributed to biological sources, particularly microbial activity.

The diurnal variation of the main VOC fluxes and environmental parameters showed an increase of their fluxes between 10h and 15h local time. Following the studied VOC, we observed positive or negative fluxes representing respectively emission or immission over bare soil and soil covered by litter. Indeed, temperature and humidity conditions were different in medium and high scenario of amount of litter (masses comprise between 120 g m^{-2} and 300 g m^{-2}) that we correlated to higher fluxes for some compounds such as tentatively assigned as lindestrene, CHC acid or 1H-pyrrole-2,5-dione. We performed correlations between VOC fluxes, environmental parameters (temperature and humidity) and microbial biomasses. Monoterpenes fluxes were negatively correlated with actinomycete and gram-negative bacteria biomasses and are therefore likely to be consumed by these organisms. However, monoterpenes fluxes were strongly positively correlated with AM fungi that were more observed in bare soil where fluxes of monoterpenes were positive. We also observed higher fluxes of acetonitrile, propanenitrile and acetaldehyde with increasing temperature, showing that these compounds can be biogenically emitted, but we cannot rigorously explain their origins at this time.

Based on the results of this study, we can conclude that, on a short term, no clear relationship between litter accumulation and VOC fluxes could be established, except for a few compounds such as acetone, sesquiterpenes, CHC acid or methanol. This study represents only a first step toward understanding the relationship between litter and VOC fluxes. ~~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 effect of the amount of litter accumulated on VOC fluxes~~We recommend that further experiments are carried out under varying environmental conditions and in different locations to gain a deeper understanding of the role and impact of litter accumulation on VOC fluxes~~.

Data availability:

All raw data can be provided by the corresponding authors upon request and most of ~~data~~the data are provided by the supplementary material.

Author contribution:

MR and JK analyzed the data. MR, JK, wrote the manuscript draft. EO, BTR, MS reviewed and edited the manuscript. EO, MS, BTR and EO planned the campaign and performed the measurements. CS and CL analyzed PLFA and provided PLFA raw data. EQ and HW reviewed the manuscript and served as the principal investigators responsible for securing funding for this project.

Competing interests:

The authors declare that they have no conflict of interest.

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