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. However, previous studies have so far neglected the role of litter accumulation 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 relationship between soil BVOC fluxes and 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 PTR-ToF-MS. We investigated in-situ daily BVOC fluxes from soil alone and different litter biomasses mimicking low, current, high, and very high litter production, respectively, as both decreases and increases of 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, the BVOC fluxes were negative, suggesting that soil (bare soil covered by litter) 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

25 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) (Kulmala et al., 2004; Hallquist et al., 2009; Seinfeld and Pandis, 2016; Mahilang et al., 2021), 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, these estimates are likely to be underestimated as they neglect the contribution of soil (bare soil covered by litter) due to the scarcity of studies. The recent interest on soil BVOCs shows bi-directional VOC fluxes with positive net fluxes from soils covered by litter (Peñuelas et al., 2014; Bourtsoukidis et al., 2018; Viros et al., 2020; Yang et al., 2024a; Legros et al., 2025). Soil could thus be a significant source of BVOCs affecting atmospheric chemistry and related climate impacts (Kramshøj et al., 2019; Yang et al., 2024b).

Soil-atmosphere exchanges have been measured in different regions of the world, such as tropical (Jardine et al., 2015, 2017; Bourtsoukidis et al., 2018; Artaxo et al., 2022), boreal (Aaltonen et al., 2013; Mäki et al., 2019; Artaxo et al., 2022), temperate (Leff and Fierer, 2008; Svendsen et al., 2018; Mäki, 2019; Isidorov and Zaitsev, 2022; Isidorov et al., 2024), and Mediterranean forests (Asensio et al., 2008; Viros et al., 2020; Rezaie et al., 2023; Yang et al., 2024a). 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., 2024b). Most 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) processes can contribute to 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 (Tang et al., 2019; Isidorov and Zaitsev, 2022) and highlight the importance of both biotic and abiotic parameters, as

evaluated in several studies (Wilkins, 1996; Mackie and Wheatley, 1999; Asensio et al., 2007a; Leff and Fierer, 2008; Abis et al., 2020; Jiao et al., 2023a). BVOC emissions are known to increase with microbial activity, through microbial decomposition of litter or soil organic carbon, and evaporation of litter-stored VOCs (Stahl and Parkin, 1996; Leff and Fierer, 2008; Insam and Seewald, 2010; Aaltonen et al., 2013). 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., 2024b).

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 (Shennan, 2006; Kramshøj et al., 2018; McGenity et al., 2018; Zhang et al., 2020; Jiao et al., 2023b). BVOCs can also diffuse through soil pores, where they can be adsorbed onto soil particles or dissolved in soil water until equilibrium is reached (Ruiz et al., 1998; Ahn et al., 2020). Although these uptake processes are less well understood, VOC uptake is considered to be a widespread process in soil (Rinnan and Albers, 2020; Jiao et al., 2023b) 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; Trowbridge et al., 2020; Rezaie et al., 2023; Legros et al., 2025), suggesting that these fluxes will be affected by climate change.

Indeed, Mediterranean forests are strongly affected by increasing warming and aridity (Peñuelas, 2008), which limit soil functioning (e.g. litter decomposition, microbial activity, Santonja et al., 2017; Quer et al., 2022) and thus BVOC exchanges between soil and atmosphere (Peñuelas et al., 2017; Yang et al., 2024a). While bare soil appears to be a sink for VOCs in Mediterranean ecosystems and other biomes (Asensio et al 2007), 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 (Peñuelas et al., 2014, Viros et al., 2020, Legros et al., 2025). However, the influence 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 (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.

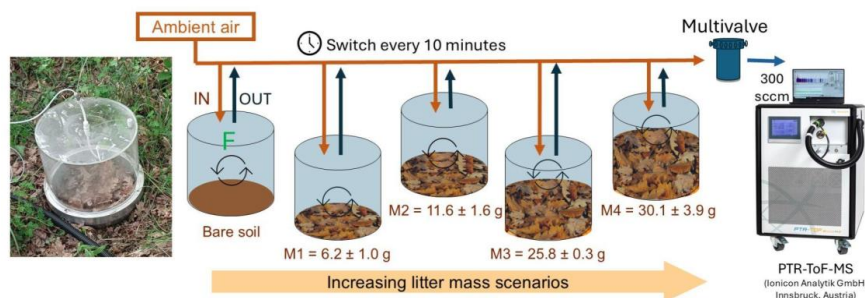
In this context, the present study aimed to investigate *in situ* BVOC emissions from soils in a Mediterranean deciduous forest dominated by the downy oak (*Quercus pubescens* Willd.), the major deciduous forest in the Southern Mediterranean part of France. We focussed on the relationships between litter 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

Litter BVOC measurements were performed at the O_3HP experimental site, an AnaEE *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). The climate is typical of the Mediterranean region, characterized by a dry and hot summer. The O_3HP 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, 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_3HP 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). 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. Chamber 1 covered bare soil, while chambers 2 to 5 circled bare soil fully covered by 8 g, 16 g, 32 g and 48 g of fresh mass of *Q. pubescens* litter, respectively, corresponding to litter dry mass ranging from 6.2 to 30.01 g (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 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. Emissions from each chamber were monitored over a 24 h period and repeated three times using renewed fresh litter each day while the bare soil remained unchanged.

105   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 Life – Mass Spectrometer 600X2, Ionicon Analytik GmbH, Innsbruck, Austria). Each chamber and the ambient inlet were connected to a flow through multivalve (VICI VALCO) placed inside the PTR-ToF-MS through ~20 m long ⅛" teflon lines, with a

110   flow around 0.3 L min-1 in each line. Parameters of PTR-ToF-MS were set up as the reaction chamber pressure was fixed at 2.6 ± 0.001 mbar, drift tube voltage at 450 V and temperature at 120 °C, corresponding to an E/N ratio (electric field strength over buffer gas number density) of $\approx$125 Td (1 Td = 10−17 V cm-2). Each sample (bare soil, LM1 to LM4 and ambient air) was sequentially monitored every 10 min during 24 h, leading to a one-hour cycle. Measurements were repeated for three days using a new pool of litter each day within each chamber

115   (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.

PTR-ToF-MS data were post-processed with IDA software (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

120   ($C_6H_4I.H^+$, 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 (Yáñez-Serrano et al., 2021). BVOC mixing ratios were finally calculated using the proton transfer theory where the rate constant k (cm^3 s^{-1}) was determined for each molecular formula based on the method proposed by

125   Cappellin et al. (2012). The relative ion transmission efficiency was calculated using a standard gas calibration mixture containing 14 different VOCs at 100 ± 10 ppb in nitrogen (TO-14A Aromatic Mix, Restek Corporation, Bellefonte, USA).

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

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

130   Where $C_{chamber}$ and $C_{ambient}$ are BVOC concentrations in ng/L at the chamber outlet and inlet respectively, Q is the flow rate inside the chamber (= 0.3 L min-1) and A the soil surface (0.0616 m2) circled by the chamber.

2-3 Phospholipid fatty acid analysis (PLFA) measurements

After the end of BVOC measurements, the soil and 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

135   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

140   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 Gram-positive bacteria, Gram-negative bacteria, Actinobacteria, saprotrophic fungi and
        arbuscular mycorrhizal (AM) fungi (Frostegård and Bååth 1996; Biryol et al. 2024). Microbial biomasses were
145   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
150   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 i-buttons (Whitewater, WI 53190
USA). Litter humidity was estimated from measurement of fresh and dry litter using 3 aliquots of 8 g each day
155   (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).

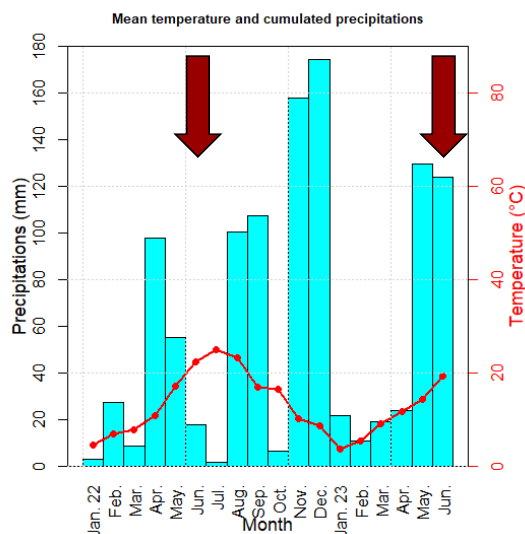



Figure 2. Ombrothermic diagram from January 2022 to June 2023. Red arrows refer to the field campaign in June
2022 (Legros et al., 2025) performed within the natural and accentuated water stress conditions plots and May
160   2023 (this study).

2-5 Statistical analysis

Data were analyzed, statistically computed and plotted using RStudio. A holistic approach was used to investigate
emissions, meaning that all VOCs detected by PTR-ToF-MS were considered in the data analysis steps described
as follows. First, a *Welsh* t-test was used to select only ions showing significant differences between ambient and
165   chamber measurements. 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 these 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

170   clusters of VOC fluxes, environmental and biological parameters. The optimal number of clusters was estimated using a k-means clustering method technique (Steinley, 2006).

3- Results and discussion

3-1 Diversity of VOC fluxes

Considering all treatments, more than 135 compounds were identified, which is much more than in previous studies
175   focusing VOC fluxes from litter soil (Asensio et al., 2007b; Viros et al., 2020; Yang et al., 2024a; Legros et al., 2025), 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 immision) of - 0.85 µg m^{-2} h^{-1}. Considering the most abundant VOC fluxes (compounds with absolute value of average fluxes
180   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 3, Table S.2).

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., 2024a) 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
185   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 (Yang et al., 2024a; Legros et al., 2025). 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
190   assimilation 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
195   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).

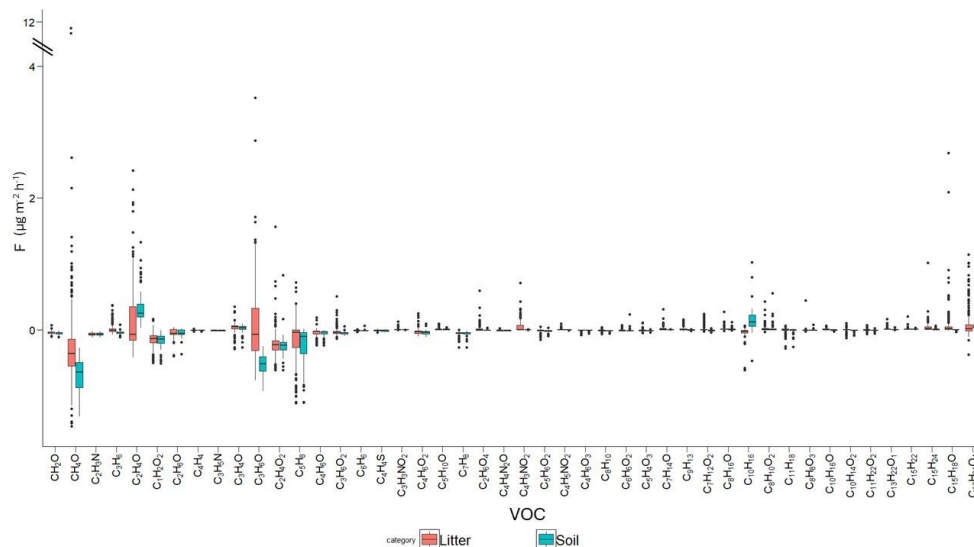



Figure 3. Most abundant compounds and their measured VOC fluxes (in µg m^{-2} h^{-1}) during the field campaign. The line that divides the box represents the median of measured fluxes, ends of the box indicate the upper (Q3) and lower (Q1) quartiles, up and down whiskers represent max and min values and outliers are represented by dots. VOC fluxes for this figure were obtained from the 24-h measurements of all replicates for both soil and the four LM in the case of litter.

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 occurred with a high variability, 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 (Warneke et al., 1999; Schade and Goldstein, 2001) 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$_3$HP (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.

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 chlorophylls (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 (Lee et al., 2005; Atagana et al., 2006). 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., 2024a). 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$_3$HP (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 (Weikl et al., 2016; Mäki et al., 2017). 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.

250 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$_3$HP 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 class such as Micrococcaceae).

255 ***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).

260 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 ± 0.035 and -0.027 ± 0.040 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., 2024b), 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
265 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
270 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} for LM 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} for LM 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} for LM and -0.017 ± 0.22 µg m^{-2} h^{-1} for bare soil). Previous studies showed contrasted features: while in agreement with our results
275 some studies observed deposition in Mediterranean forests (Asensio et al., 2007a, 2007b), 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 (Wheatley et al., 1996; Leff and Fierer, 2008), while acetic or formic acids are reported to be produced by bacteria and fungi (Wheatley et al., 1996; Mielnik et al., 2018). Indeed, considering
280 the environmental conditions (i.e. humid) we hypothesize that carboxylic acid deposition processes linked to the soil moisture are dominating, leading to 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 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, 1997; Gray et al., 2014, 2015; McGenity et al., 2018; Legros et al., 2025). Higher negative fluxes were estimated by Legros et
285 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$_3$HP.

290 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.

295 As 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). 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},
300 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 one year, (Gouw et al., 2003; Andersen et al., 2018)), and deposition of this compound occurred in our forest soil.

VOCs both emitted and immitted

305   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
310 contrast a 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 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-
315 dione, cyclohexanecarboxylic acid (CHC acid) has not yet been reported in other studies using either bare soil or 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
320 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 (White, 1994; Marmulla and Harder, 2014). Bacteria also consume
325 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 of 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
330 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

335 Correlations of VOC fluxes with the litter masses inside the chambers were performed (Figure 4). Surprisingly, only a few compounds showed significant relationships between 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 that are more important drivers of emission/deposition.

340 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 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 compounds, the net flux is increasing with litter mass, from a negative flux in bare soil to a positive flux at high
345 LM. As a result, it suggests that the soil alone acts as a sink for these 4 compounds, while litter mostly emits them, the resulting net fluxes depending on the amount of LM and maybe environmental conditions. However, a deeper study dedicated to separate the respective contribution of soil and litter will be necessary to fully elucidate this point.

Negative response has only been observed between acetaldehyde fluxes 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 compounds, emissions are observed for bare soil while the net fluxes turned negative with increasing LM, 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 (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 (Weikl et al., 2016; Mäki et al., 2017) should depend on LM.

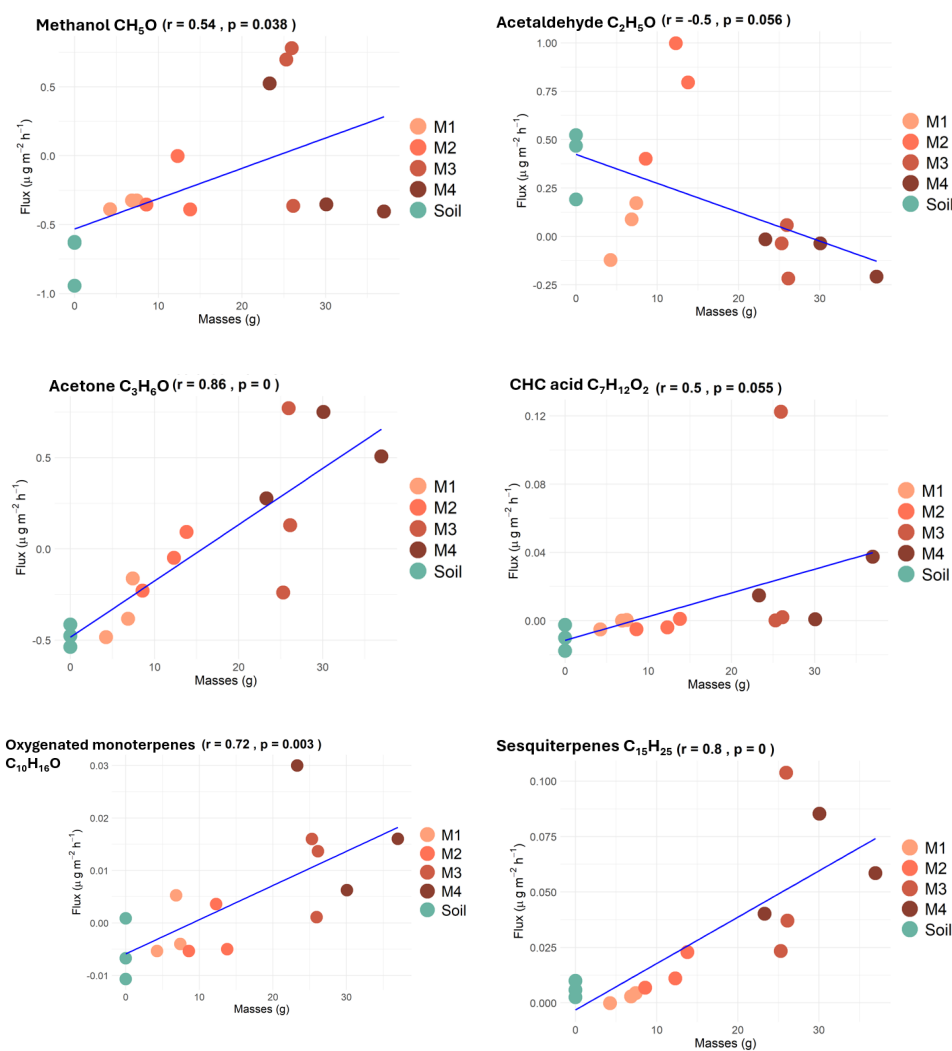



Figure 4. Correlation plots of methanol, acetaldehyde, acetone, oxygenated monoterpenes, CHC acid and sesquiterpenes fluxes (µg m^{-2} h^{-1}) with litter masses (0 in bare soil).

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.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. 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. Indeed, similar patterns can be highlighted for 1H-pyrrole, CHC acid, lindestrene and sesquiterpenes with higher emissions 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 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 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 (Monson et al., 1992; Kesselmeier et al., 1998; Owen et al., 2002). Around midnight, isoprene fluxes were stable in all LM 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. 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.

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 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 LM 3, the environmental conditions showed few differences with higher temperature and then lower humidity during the measurements, 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 (Cleveland and Yavitt, 1998; Schade and Goldstein, 2001; Asensio et al., 2007b; Gray et al., 2015; Jiao et al., 2023b).

Positive fluxes were observed during the day for acetaldehyde (0.184 ± 0.245 µg m^{-2} h^{-1}), except for LM4 and negative acetaldehyde fluxes were observed during nighttime for 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; Peñuelas et al., 2014; Jiao et al., 2023b). 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,

410   environmental conditions were completely different and the soil was not submitted to the same constraints explaining the differences observed between our fluxes and this previous study.

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})

415   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}).

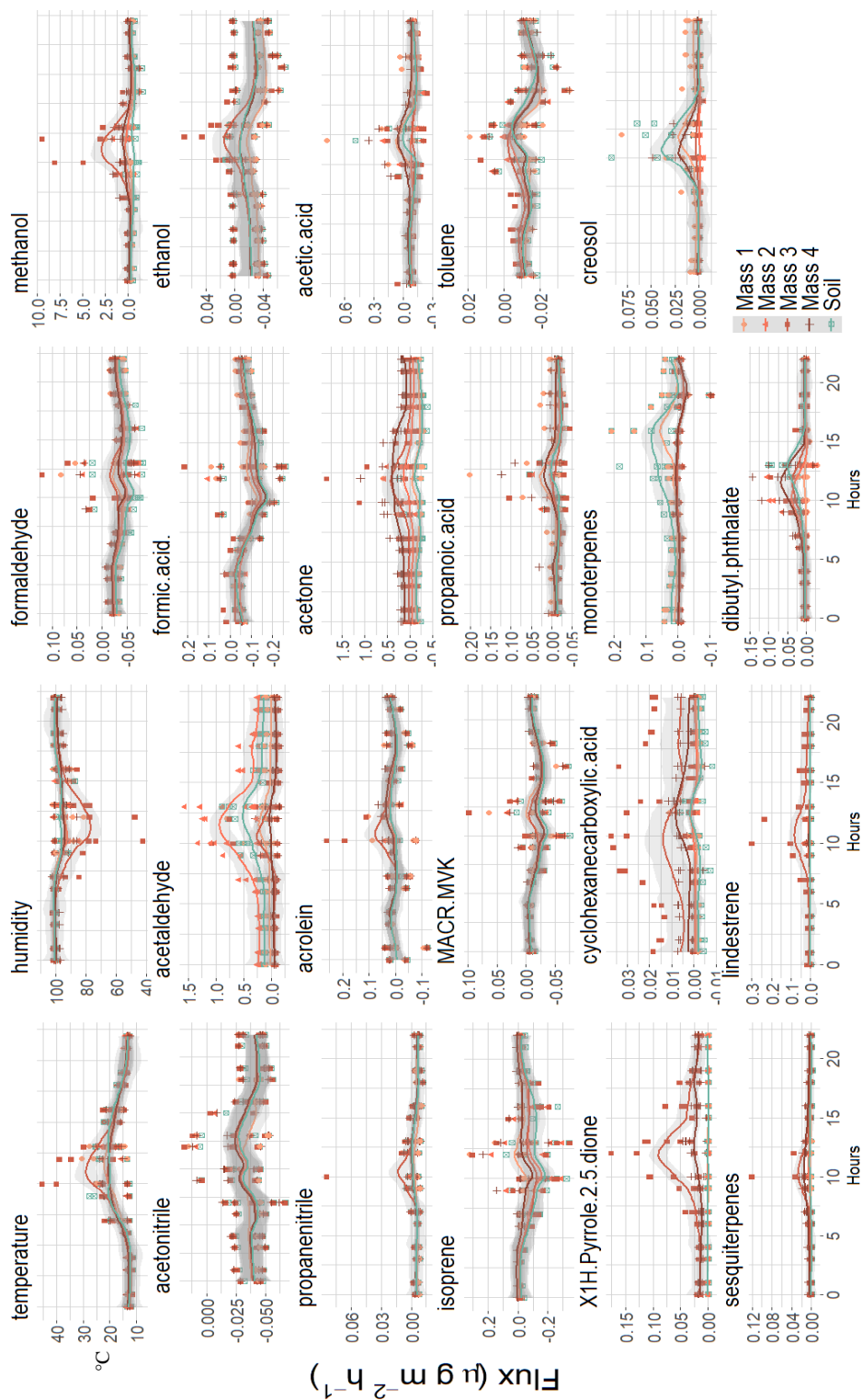



Figure 5. Temperature and humidity diurnal cycles (24h) and measured BVOC fluxes (µg m⁻² h⁻¹) for bare soil and soil covered by increasing litter mass (LM 1, 2, 3, 4).

3-4 VOC fluxes linked to environmental and biological parameters

420   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 and presented in Figure 6.

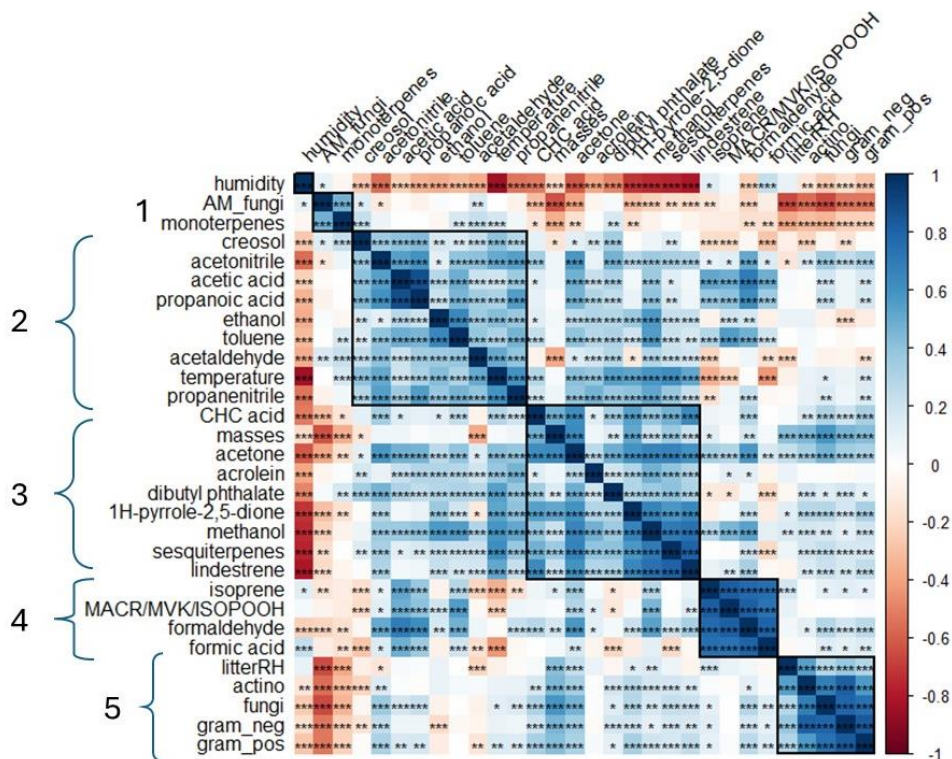
First, a strong positive correlation can be observed between monoterpenes and arbuscular mycorrhizal (AM) fungi, forming the first cluster (r = 0.48, p_{value} < 0.001, Figure 6). We suggested earlier that soil fungi are the main source
425   of monoterpenes, as negative monoterpene fluxes were observed when LM increased. The concentration of AM fungi is observed to be higher in the bare soil compared to LM, 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 of monoterpene 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
430   negatively related to relative humidity. 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 * ($r_{acetonitrile/temp}$ = 0.50, $r_{propanenitrile/temp}$ = 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
435   (Heiden et al., 1999; Nyalala et al., 2011, 2013; Misztal et al., 2015). 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 ($r_{acetonitrile/propanenitrile}$ = 0.55, $r_{acetonitrile/propanoic acid}$ = 0.60, $r_{acetonitrile/acetic acid}$ = 0.55 and $r_{acetonitrile/acetone}$ = 0.58, respectively). As a few positive fluxes
440   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_{value} < 0.001), confirming that there is no strong photochemistry inside the chambers. However, strong
445   relationships were observed with toluene and methanol with ethanol ($r_{ethanol/toluene}$ = 0.64, $r_{ethanol/methanol}$ = 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. $r_{acetone/LM}$ = 0.63, $r_{CHC acid/LM}$ = 0.58). In addition, we showed previously (Figure 4) that these compounds present the same pattern with higher
450   emissions during daytime and in LM3 and LM4. This means that the emissions of these compounds are either directly related to the litter (emission from the dead leaves) 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,
455   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.

460   Temperature was negatively related to compounds in cluster 4. Surprisingly, isoprene fluxes were negatively correlated with temperature (r = -0.35, p_{value} < 0.001), and so does for their oxidation products MACR/MVK/ISOPOOH (r = -0.24, p_{value} < 0.001) and formic acid (r = -0.43, p_{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 higher with high
465   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
470   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
475 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
480 but moderate relationships of monoterpenes fluxes with fungi have been observed ($r_{monop/fungi} = -0.33$, $p_{value} < 0.001$). Monoterpene and acetaldehyde 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.

485 **Figure 6.** Correlation matrix between BVOC fluxes and abiotic (air temperature and humidity) and biotic (litter mass, litter humidity content, PLFA) factors. Positive correlations (r > 0) were highlighted in blue and negative (r < 0) in red. Stars represent p_{values} and their confidence: * ≧ 0.05, 0.01 < ** < 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.

490 **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. 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 most uptaken compounds were ethanol, formaldehyde, isoprene,
495 acetonitrile, toluene, formic and acetic acids. Thanks to holistic methodology of measurement, 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 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 LM 3 that we correlated to higher fluxes for some compounds such as lindestrene, CHC acid or 1H-pyrrole-2,5-dione. We performed correlations between VOC fluxes, environmental parameters 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. 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 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. It is not sufficient to conclude that litter mass has no effect on VOC emissions. 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 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.

Acknowledgements

The authors gratefully acknowledge the MASSALYA instrumental platform (Aix Marseille Université, lce.univ-amu.fr) for the provision of analysis and measurements. We are grateful to O₃HP site managed by IMBE, and ECCOREV as well as OSU Pytheas and especially OHP for accommodation, facilities and technical support through engineering work. We thank AnaEE-ERIC and AnaEE-France networks and specifically the PIA ("Plan d'Investissements d'Avenir") from ANR (ANR-11-INBS-0001 AnaEE France) for providing long term funding for the site functioning and SEE-life network from CNRS for funding long-term studies in Ecology and Evolution at O3HP. We thank Ilja Reiter for providing climatic data. This work received support from the French government under the France 2030 investment plan, as part of the Initiative d'Excellence d'Aix Marseille Université - A*MIDEX - (AMX-21-RID-009, LITOSMED).

References

Aupic-Samain, A., Santonja, M., Chomel, M., Pereira, S., Quer, E., Lecareux, C., ... & Baldy, V. (2021). Soil biota response to experimental rainfall reduction depends on the dominant tree species in mature northern Mediterranean forests. Soil biology and biochemistry, 154, 108122. https://doi.org/10.1016/j.soilbio.2020.108122

Biryol, C., Aupic-Samain, A., Lecareux, C., Gauquelin, T., Baldy, V., & Santonja, M. (2024). Interactive effects of soil moisture, air temperature and litter nutrient diversity on soil microbial communities and *Folsomia candida* population. Oikos, 2024(7), e10345. https://doi.org/10.1111/oik.10345

Frostegård, A., & Bååth, E. (1996). The use of phospholipid fatty acid analysis to estimate bacterial and fungal biomass in soil. Biology and Fertility of Soils, 22(1), 59–65. https://doi.org/10.1007/BF00384433

Aaltonen, H., Aalto, J., Kolari, P., Pihlatie, M., Pumpanen, J., Kulmala, M., et al. (2013). Continuous VOC flux measurements on boreal forest floor. *Plant Soil* 369, 241–256. doi: 10.1007/s11104-012-1553-4

545   Abis, L., Loubet, B., Ciuraru, R., Lafouge, F., Houot, S., Nowak, V., et al. (2020). Reduced microbial diversity induces larger volatile organic compound emissions from soils. *Sci. Rep.* 10, 6104. doi: 10.1038/s41598-020-63091-8

Ahn, J., Rao, G., Mamun, M., and Vejerano, E. P. (2020). Soil–air partitioning of volatile organic compounds into soils with high water content. *Environ. Chem.* 17, 545–557. doi: 10.1071/EN20032

550   Andersen, S. T., Kyte, M., Andersen, L. L., Nielsen, O. J., and Sulbaek Andersen, M. P. (2018). Atmospheric chemistry of n-CH3(CH2)CN (x = 0–3): Kinetics and mechanisms. *Int. J. Chem. Kinet.* 50, 813–826. doi: 10.1002/kin.21215

Artaxo, P., Hansson, H.-C., Andreae, M. O., Bäck, J., Alves, E. G., Barbosa, H. M. J., et al. (2022). Tropical and Boreal Forest – Atmosphere Interactions: A Review. *Tellus B Chem. Phys. Meteorol.* 74, 24. doi:
555   10.16993/tellusb.34

Asensio, D., Peñuelas, J., Filella, I., and Llusià, J. (2007a). On-line screening of soil VOCs exchange responses to moisture, temperature and root presence. *Plant Soil* 291, 249–261. doi: 10.1007/s11104-006-9190-4

Asensio, D., Peñuelas, J., Ogaya, R., and Llusià, J. (2007b). Seasonal soil VOC exchange rates in a Mediterranean holm oak forest and their responses to drought conditions. *Atmos. Environ.* 41, 2456–2466. doi:
560   10.1016/j.atmosenv.2006.05.007

Asensio, D., Peñuelas, J., Prieto, P., Estiarte, M., Filella, I., and Llusià, J. (2008). Interannual and seasonal changes in the soil exchange rates of monoterpenes and other VOCs in a Mediterranean shrubland. *Eur. J. Soil Sci.* 59, 878–891. doi: 10.1111/j.1365-2389.2008.01057.x

Atagana, H. I. (2004). Biodegradation of phenol, o-cresol, m-cresol and p-cresol by indigenous soil fungi in soil
565   contaminated with creosote. *World J. Microbiol. Biotechnol.* 20, 851–858. doi: 10.1007/s11274-004-9010-z

Atagana, H. I., Haynes, R. J., and Wallis, F. M. (2006). Fungal Bioremediation of Creosote-Contaminated Soil: A Laboratory Scale Bioremediation Study Using Indigenous Soil Fungi. *Water. Air. Soil Pollut.* 172, 201–219. doi: 10.1007/s11270-005-9074-x

Borowik, A., and Wyszkowska, J. (2016). Soil moisture as a factor affecting the microbiological and biochemical
570   activity of soil. *Plant Soil Environ.* 62, 250–255. doi: 10.17221/158/2016-PSE

Bourtsoukidis, E., Behrendt, T., Yañez-Serrano, A. M., Hellén, H., Diamantopoulos, E., Catão, E., et al. (2018). Strong sesquiterpene emissions from Amazonian soils. *Nat. Commun.* 9, 2226. doi: 10.1038/s41467-018-04658-y

Cleveland, C. C., and Yavitt, J. B. (1997). Consumption of atmospheric isoprene in soil. Available at: https://agupubs-onlinelibrary-wiley-com.lama.univ-amu.fr/doi/abs/10.1029/97GL02451 (Accessed December 10,
575   2024).

Cleveland, C. C., and Yavitt, J. B. (1998). Microbial Consumption of Atmospheric Isoprene in a Temperate Forest Soil. *Appl. Environ. Microbiol.* 64, 172–177. doi: 10.1128/AEM.64.1.172-177.1998

Ehrlich, J., and Cahill, T. M. (2018). Identification of broadleaf and coniferous trees as a primary source of acrolein. *Atmos. Environ.* 191, 414–419. doi: 10.1016/j.atmosenv.2018.08.033

580   Farooq, A., Atta-ur-Rahman, and Choudhary, M. I. (2004). Fungal Transformation of Monoterpenes. *Curr. Org. Chem.* 8, 353–366. doi: 10.2174/1385272043485945

Garnier, S., Giordanengo, E., Saatkamp, A., Santonja, M., Reiter, I. M., Orts, J.-P., et al. (2021). Amplified drought induced by climate change reduces seedling emergence and increases seedling mortality for two Mediterranean perennial herbs. *Ecol. Evol.* 11, 16143–16152. doi: 10.1002/ece3.8295

585   Genard-Zielinski, A.-C., Boissard, C., Fernandez, C., Kalogridis, C., Lathière, J., Gros, V., et al. (2015). Variability of BVOC emissions from a Mediterranean mixed forest in southern France with a focus on *Quercus pubescens*. *Atmospheric Chem. Phys.* 15, 431–446. doi: 10.5194/acp-15-431-2015

Gouw, J. A. de, Warneke, C., Parrish, D. D., Holloway, J. S., Trainer, M., and Fehsenfeld, F. C. (2003). Emission sources and ocean uptake of acetonitrile (CH3CN) in the atmosphere. *J. Geophys. Res. Atmospheres* 108, 1–8. doi:
590   10.1029/2002JD002897

Gray, C. M., Helmig, D., and Fierer, N. (2015). Bacteria and fungi associated with isoprene consumption in soil. *Elem. Sci. Anthr.* 3, 000053. doi: 10.12952/journal.elementa.000053

Gray, C. M., Monson, R. K., and Fierer, N. (2010). Emissions of volatile organic compounds during the decomposition of plant litter. *J. Geophys. Res. Biogeosciences* 115. doi: 10.1029/2010JG001291

595   Gray, C. M., Monson, R. K., and Fierer, N. (2014). Biotic and abiotic controls on biogenic volatile organic compound fluxes from a subalpine forest floor: Controls on BVOC fluxes from forest soil. *J. Geophys. Res. Biogeosciences* 119, 547–556. doi: 10.1002/2013jg002575

Gros, V., Lathière, J., Boissard, C., Jambert, C., Delon, C., Staudt, M., et al. (2022). "Emissions from the Mediterranean Vegetation," in *Atmospheric Chemistry in the Mediterranean Region: Volume 2 - From Air*
600   *Pollutant Sources to Impacts*, eds. F. Dulac, S. Sauvage, and E. Hamonou (Cham: Springer International Publishing), 25–49. doi: 10.1007/978-3-030-82385-6_3

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., et al. (2012). The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev.* 5, 1471–1492. doi: 10.5194/gmd-5-1471-2012

605   Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., et al. (2009). The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chem. Phys.* 9, 5155–5236. doi: 10.5194/acp-9-5155-2009

Hanif, N. M., Hawari, N. S. S. L., Othman, M., Hamid, H. H. A., Ahamad, F., Uning, R., et al. (2021). Ambient volatile organic compounds in tropical environments: Potential sources, composition and impacts – A review.
610   *Chemosphere* 285, 131355. doi: 10.1016/j.chemosphere.2021.131355

Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., Shao, M., and Wildt, J. (1999). Toluene emissions from plants. *Geophys. Res. Lett.* 26, 1283–1286. doi: 10.1029/1999GL900220

Holzinger, R., Warneke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., et al. (1999). Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide. *Geophys. Res.*
615   *Lett.* 26, 1161–1164. doi: 10.1029/1999GL900156

Inomata, S., Fujitani, Y., Fushimi, A., Tanimoto, H., Sekimoto, K., and Yamada, H. (2014). Field measurement of nitromethane from automotive emissions at a busy intersection using proton-transfer-reaction mass spectrometry. *Atmos. Environ.* 96, 301–309. doi: 10.1016/j.atmosenv.2014.07.058

Insam, H., and Seewald, M. S. A. (2010). Volatile organic compounds (VOCs) in soils. *Biol. Fertil. Soils* 46, 199–
620   213. doi: 10.1007/s00374-010-0442-3

Isidorov, V. A., and Zaitsev, A. A. (2022). Reviews and syntheses: VOC emissions from soil cover in boreal and temperate natural ecosystems of the Northern Hemisphere. *Biogeosciences* 19, 4715–4746. doi: 10.5194/bg-19-4715-2022

Isidorov, V., and Jdanova, M. (2002). Volatile organic compounds from leaves litter. *Chemosphere* 48, 975–979.
625   doi: 10.1016/S0045-6535(02)00074-7

Isidorov, V., Maslowiecka, J., and Sarapultseva, P. (2024). Bidirectional emission of organic compounds by decaying leaf litter of a number of forest-forming tree species in the northern hemisphere. *Geoderma* 443, 116812. doi: 10.1016/j.geoderma.2024.116812

Jacob, D. J., Field, B. D., Jin, E. M., Bey, I., Li, Q., Logan, J. A., et al. (2002). Atmospheric budget of acetone. *J.*
630   *Geophys. Res. Atmospheres* 107, ACH 5-1. doi: 10.1029/2001jd000694

Jardine, K. J., Jardine, A. B., Holm, J. A., Lombardozzi, D. L., Negron-Juarez, R. I., Martin, S. T., et al. (2017). Monoterpene 'thermometer' of tropical forest-atmosphere response to climate warming. *Plant Cell Environ.* 40, 441–452. doi: 10.1111/pce.12879

Jardine, K., Yañez-Serrano, A. M., Williams, J., Kunert, N., Jardine, A., Taylor, T., et al. (2015). Dimethyl sulfide in the Amazon rain forest. *Glob. Biogeochem. Cycles* 29, 19–32. doi: 10.1002/2014GB004969

Jiao, Y., Davie-Martin, C. L., Kramshøj, M., Christiansen, C. T., Lee, H., Althuizen, I. H. J., et al. (2023a). Volatile organic compound release across a permafrost-affected peatland. *Geoderma* 430, 116355. doi: 10.1016/j.geoderma.2023.116355

Jiao, Y., Kramshøj, M., Davie-Martin, C. L., Albers, C. N., and Rinnan, R. (2023b). Soil uptake of VOCs exceeds production when VOCs are readily available. *Soil Biol. Biochem.* 185, 109153. doi: 10.1016/j.soilbio.2023.109153

Kesselmeier, J., Bode, K., Schäfer, L., Schebeske, G., Wolf, A., Brancaleoni, E., et al. (1998). Simultaneous field measurements of terpene and isoprene emissions from two dominant mediterranean oak species in relation to a North American species. *Atmos. Environ.* 32, 1947–1953. doi: 10.1016/S1352-2310(97)00500-1

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., et al. (2018). Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment. *Atmospheric Chem. Phys.* 18, 3299–3319. doi: 10.5194/acp-18-3299-2018

Kovacs, E. D., Kovacs, M. H., Kovacs, E. D., and Kovacs, M. H. (2023). "Global Change Drivers Impact on Soil Microbiota: Challenges for Maintaining Soil Ecosystem Services," in *Vegetation Dynamics, Changing Ecosystems and Human Responsibility*, (IntechOpen). doi: 10.5772/intechopen.111585

Kramshøj, M., Albers, C. N., Holst, T., Holzinger, R., Elberling, B., and Rinnan, R. (2018). Biogenic volatile release from permafrost thaw is determined by the soil microbial sink. *Nat. Commun.* 9, 1–9. doi: 10.1038/s41467-018-05824-y

Kramshøj, M., Albers, C. N., Svendsen, S. H., Björkman, M. P., Lindwall, F., Björk, R. G., et al. (2019). Volatile emissions from thawing permafrost soils are influenced by meltwater drainage conditions. *Glob. Change Biol.* 25, 1704–1716. doi: 10.1111/gcb.14582

Kramshøj, M., Vedel-Petersen, I., Schollert, M., Rinnan, Å., Nymand, J., Ro-Poulsen, H., et al. (2016). Large increases in Arctic biogenic volatile emissions are a direct effect of warming. *Nat. Geosci.* 9, 349–352. doi: 10.1038/ngeo2692

Kulmala, M., Vehkamäki, H., Petäjä, T., Maso, M. D., Lauri, A., Kerminen, V. M., et al. (2004). Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.* 35, 143–176. doi: 10.1016/J.JAEROSCI.2003.10.003

Laoué, J., Fernandez, C., and Ormeño, E. (2022). Plant Flavonoids in Mediterranean Species: A Focus on Flavonols as Protective Metabolites under Climate Stress. *Plants* 11, 172. doi: 10.3390/plants11020172

Lee, K., Lee, S., Takeoka, G. R., Kim, J., and Park, B. (2005). Antioxidant activity and characterization of volatile constituents of beechwood creosote. *J. Sci. Food Agric.* 85, 1580–1586. doi: 10.1002/jsfa.2156

Leff, J. W., and Fierer, N. (2008). Volatile organic compound (VOC) emissions from soil and litter samples. *Soil Biol. Biochem.* 40, 1629–1636. doi: 10.1016/j.soilbio.2008.01.018

Legros, T., Temime-Roussel, B., Kammer, J., Quivet, E., Wortham, H., Reiter, I. M., et al. (2025). Decline of soil volatile organic compounds from a Mediterranean deciduous forest under a future drier climate. *Atmos. Environ.* 340, 120909. doi: 10.1016/j.atmosenv.2024.120909

Ma, Z., Qiu, S., Chen, H.-C., Zhang, D., Lu, Y.-L., and Chen, X.-L. (2022). Maleimide structure: a promising scaffold for the development of antimicrobial agents. *J. Asian Nat. Prod. Res.* 24, 1–14. doi: 10.1080/10286020.2021.1877675

675 Mackie, A. E., and Wheatley, R. E. (1999). Effects and incidence of volatile organic compound interactions between soil bacterial and fungal isolates. *Soil Biol. Biochem.* 31, 375–385. doi: 10.1016/S0038-0717(98)00140-0

Mahilang, M., Deb, M. K., and Pervez, S. (2021). Biogenic secondary organic aerosols: A review on formation mechanism, analytical challenges and environmental impacts. *Chemosphere* 262, 127771. doi: 680 10.1016/j.chemosphere.2020.127771

Mäki, M. (2019). Volatile organic compound fluxes from northern forest soils. *Diss. For.* 2019. doi: 10.14214/df.275

Mäki, M., Aaltonen, H., Heinonsalo, J., Hellén, H., Pumpanen, J., and Bäck, J. (2019). Boreal forest soil is a significant and diverse source of volatile organic compounds. *Plant Soil* 441, 89–110. doi: 10.1007/s11104-019-685 04092-z

Mäki, M., Heinonsalo, J., Hellén, H., and Bäck, J. (2017). Contribution of understorey vegetation and soil processes to boreal forest isoprenoid exchange. *Biogeosciences* 14, 1055–1073. doi: 10.5194/bg-14-1055-2017

Mancuso, S., Taiti, C., Bazihizina, N., Costa, C., Menesatti, P., Giagnoni, L., et al. (2015). Soil volatile analysis by proton transfer reaction-time of flight mass spectrometry (PTR-TOF-MS). *Appl. Soil Ecol.* 86, 182–191. doi: 690 10.1016/j.apsoil.2014.10.018

Marmulla, R., and Harder, J. (2014). Microbial monoterpene transformations—a review. *Front. Microbiol.* 5. doi: 10.3389/fmicb.2014.00346

McGenity, T. J., Crombie, A. T., and Murrell, J. C. (2018). Microbial cycling of isoprene, the most abundantly produced biological volatile organic compound on Earth. *ISME J.* 12, 931–941. doi: 10.1038/s41396-018-0072-6

695 Meischner, M., Haberstroh, S., Daber, L. E., Kreuzwieser, J., Caldeira, M. C., Schnitzler, J.-P., et al. (2022). Soil VOC emissions of a Mediterranean woodland are sensitive to shrub invasion. *Plant Biol.* 24, 967–978. doi: 10.1111/plb.13445

Mielnik, A., Link, M., Mattila, J., Fulgham, S. R., and Farmer, D. K. (2018). Emission of formic and acetic acids from two Colorado soils. *Environ. Sci. Process. Impacts* 20, 1537–1545. doi: 10.1039/C8EM00356D

700 Misztal, P. K., Hewitt, C. N., Wildt, J., Blande, J. D., Eller, A. S. D., Fares, S., et al. (2015). Atmospheric benzenoid emissions from plants rival those from fossil fuels. *Sci. Rep.* 5, 1–10. doi: 10.1038/srep12064

Monson, R. K., Jaeger, C. H., Adams, W. W., Driggers, E. M., Silver, G. M., and Fall, R. (1992). Relationships among isoprene emission rate, photosynthesis, and isoprene synthase activity as influenced by temperature. *Plant Physiol.* 98, 1175–1180. doi: 10.1104/pp.98.3.1175

705 Mu, Z., Llusià, J., Zeng, J., Zhang, Y., Asensio, D., Yang, K., et al. (2022). An Overview of the Isoprenoid Emissions From Tropical Plant Species. *Front. Plant Sci.* 13. Available at: https://www.frontiersin.org/articles/10.3389/fpls.2022.833030 (Accessed November 21, 2023).

Naeher, S., Lengger, S. K., and Grice, K. (2016). A new method for the rapid analysis of 1H-Pyrrole-2,5-diones (maleimides) in environmental samples by two-dimensional gas chromatography time-of-flight mass 710 spectrometry. *J. Chromatogr. A* 1435, 125–135. doi: 10.1016/j.chroma.2016.01.026

Niinemets, Ü., Fares, S., Harley, P., and Jardine, K. J. (2014). Bidirectional exchange of biogenic volatiles with vegetation: emission sources, reactions, breakdown and deposition. *Plant Cell Environ.* 37, 1790–1809. doi: 10.1111/pce.12322

Nyalala, S. O., Petersen, M. A., and Grout, B. W. W. (2011). Acetonitrile (methyl cyanide) emitted by the African 715 spider plant (Gynandropsis gynandra L. (Briq)): Bioactivity against spider mite (Tetranychus urticae Koch) on roses. *Sci. Hortic.* 128, 352–356. doi: 10.1016/j.scienta.2011.01.036

Nyalala, S. o., Petersen, M. a., and Grout, B. w. w. (2013). Volatile compounds from leaves of the African spider plant (Gynandropsis gynandra) with bioactivity against spider mite (Tetranychus urticae). *Ann. Appl. Biol.* 162, 290–298. doi: 10.1111/aab.12021

720   Ormeño, E., Baldy, V., Ballini, C., and Fernandez, C. (2008). Production and Diversity of Volatile Terpenes from Plants on Calcareous and Siliceous Soils: Effect of Soil Nutrients. *J. Chem. Ecol.* 34, 1219–1229. doi: 10.1007/s10886-008-9515-2

Owen, S. M., Harley, P., Guenther, A., and Hewitt, C. N. (2002). Light dependency of VOC emissions from selected Mediterranean plant species. *Atmos. Environ.* 36, 3147–3159. doi: 10.1016/S1352-2310(02)00235-2

725   Peñuelas, J. (2008). An increasingly scented world. *New Phytol.* 180, 735–738. doi: 10.1111/j.1469-8137.2008.02658.x

Peñuelas, J., Asensio, D., Tholl, D., Wenke, K., Rosenkranz, M., Piechulla, B., et al. (2014). Biogenic volatile emissions from the soil. *Plant Cell Environ.* 37, 1866–1891. doi: 10.1111/pce.12340

Peñuelas, J., Sardans, J., Filella, I., Estiarte, M., Llusià, J., Ogaya, R., et al. (2017). Impacts of Global Change on 730   Mediterranean Forests and Their Services. *Forests* 8, 463. doi: 10.3390/f8120463

Quer, E., Pereira, S., Michel, T., Santonja, M., Gauquelin, T., Simioni, G., et al. (2022). Amplified Drought Alters Leaf Litter Metabolome, Slows Down Litter Decomposition, and Modifies Home Field (Dis)Advantage in Three Mediterranean Forests. *Plants* 11, 2582. doi: 10.3390/plants11192582

Rezaie, N., Pallozzi, E., Ciccioli, P., Calfapietra, C., and Fares, S. (2023). Temperature dependence of emission 735   of volatile organic compounds (VOC) from litters collected in two Mediterranean ecosystems determined before the flaming phase of biomass burning. *Environ. Pollut.* 338, 122703. doi: 10.1016/j.envpol.2023.122703

Rinnan, R. (2024). Volatile Organic Compound Emissions in the Changing Arctic. doi: 10.1146/annurev-ecolsys-102722-125156

Rinnan, R., and Albers, C. N. (2020). Soil Uptake of Volatile Organic Compounds: Ubiquitous and 740   Underestimated? *J. Geophys. Res. Biogeosciences* 125, e2020JG005773. doi: 10.1029/2020JG005773

Ruiz, J., Bilbao, R., and Murillo, M. B. (1998). Adsorption of Different VOC onto Soil Minerals from Gas Phase: Influence of Mineral, Type of VOC, and Air Humidity. *Environ. Sci. Technol.* 32, 1079–1084. doi: 10.1021/es9704996

Santonja, M., Fernandez, C., Gauquelin, T., and Baldy, V. (2015). Climate change effects on litter decomposition: 745   intensive drought leads to a strong decrease of litter mixture interactions. *Plant Soil* 393, 69–82. doi: 10.1007/s11104-015-2471-z

Santonja, M., Fernandez, C., Proffit, M., Gers, C., Gauquelin, T., Reiter, I. M., et al. (2017). Plant litter mixture partly mitigates the negative effects of extended drought on soil biota and litter decomposition in a Mediterranean oak forest. *J. Ecol.* 105, 801–815. doi: 10.1111/1365-2745.12711

750   Sarkar, C., Sinha, V., Kumar, V., Rupakheti, M., Panday, A., Mahata, K. S., et al. (2016). Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-ABC campaign: high acetaldehyde, isoprene and isocyanic acid in wintertime air of the Kathmandu Valley. *Atmospheric Chem. Phys.* 16, 3979–4003. doi: 10.5194/acp-16-3979-2016

Schade, G. W., and Goldstein, A. H. (2001). Fluxes of oxygenated volatile organic compounds from a ponderosa 755   pine plantation. *J. Geophys. Res. Atmospheres* 106, 3111–3123. doi: 10.1029/2000JD900592

Schieweck, A., Uhde, E., and Salthammer, T. (2021). Determination of acrolein in ambient air and in the atmosphere of environmental test chambers. *Environ. Sci. Process. Impacts* 23, 1729–1746. doi: 10.1039/D1EM00221J

Seinfeld, J. H., and Pandis, S. N. (2016). *Atmospheric Chemistry and Physics: From Air Pollution to Climate* 760   *Change*. John Wiley & Sons.

Shende, V. V., Bauman, K. D., and Moore, B. S. (2024). The shikimate pathway: gateway to metabolic diversity. *Nat. Prod. Rep.* 41, 604–648. doi: 10.1039/D3NP00037K

Shennan, J. L. (2006). Utilisation of C2–C4 gaseous hydrocarbons and isoprene by microorganisms. *J. Chem. Technol. Biotechnol.* 81, 237–256. doi: 10.1002/jctb.1388

765   Sillo, F., Neri, L., Calvo, A., Zampieri, E., Petruzzelli, G., Ferraris, I., et al. (2024). Correlation between microbial communities and volatile organic compounds in an urban soil provides clues on soil quality towards sustainability of city flowerbeds. *Heliyon* 10. doi: 10.1016/j.heliyon.2023.e23594

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., et al. (2014). Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. *Atmospheric Chem. Phys.* 14,
770   9317–9341. doi: 10.5194/acp-14-9317-2014

Stahl, P. D., and Parkin, T. B. (1996). Microbial Production of Volatile Organic Compounds in Soil Microcosms. *Soil Sci. Soc. Am. J.* 60, 821–828. doi: 10.2136/sssaj1996.03615995006000030020x

Staudt, M., Bourgeois, I., Al Halabi, R., Song, W., and Williams, J. (2017). New insights into the parametrization of temperature and light responses of mono - and sesquiterpene emissions from Aleppo pine and rosemary. *Atmos.*
775   *Environ.* 152, 212–221. doi: 10.1016/j.atmosenv.2016.12.033

Steinley, Douglas. (2006). K-means clustering: A half-century synthesis. *Br. J. Math. Stat. Psychol.* 59, 1–34. doi: 10.1348/000711005X48266

Svendsen, S. H., Priemé, A., Voriskova, J., Kramshøj, M., Schostag, M., Jacobsen, C. S., et al. (2018). Emissions of biogenic volatile organic compounds from arctic shrub litter are coupled with changes in the bacterial
780   community composition. *Soil Biol. Biochem.* 120, 80–90. doi: 10.1016/j.soilbio.2018.02.001

Taiti, C., Costa, C., Figorilli, S., Billi, M., Caparrotta, S., Comparini, D., et al. (2018). Volatome analysis approach for the taxonomic classification of tree exudate collection using Proton Transfer Reaction Time of Flight Mass Spectrometry. *Flavour Fragr. J.* 33, 245–262. doi: 10.1002/ffj.3439

Tang, J., Schurgers, G., and Rinnan, R. (2019). Process Understanding of Soil BVOC Fluxes in Natural
785   Ecosystems: A Review. *Rev. Geophys.* 57, 966–986. doi: 10.1029/2018RG000634

Thornhill, G., Collins, W., Olivié, D., Skeie, R. B., Archibald, A., Bauer, S., et al. (2021). Climate-driven chemistry and aerosol feedbacks in CMIP6 Earth system models. *Atmospheric Chem. Phys.* 21, 1105–1126. doi: 10.5194/acp-21-1105-2021

Trowbridge, A. M., Stoy, P. C., and Phillips, R. P. (2020). Soil Biogenic Volatile Organic Compound Flux in a
790   Mixed Hardwood Forest: Net Uptake at Warmer Temperatures and the Importance of Mycorrhizal Associations. *J. Geophys. Res. Biogeosciences* 125, e2019JG005479. doi: 10.1029/2019JG005479

Viros, J, C, F., H, W., J, G., C, L., and E, O. (2020). Litter of mediterranean species as a source of volatile organic compounds. *Atmos. Environ.* 242, 117815. doi: 10.1016/j.atmosenv.2020.117815

Viros, J., Santonja, M., Temime-Roussel, B., Wortham, H., Fernandez, C., and Ormeño, E. (2021). Volatilome of
795   Aleppo Pine litter over decomposition process. *Ecol. Evol.* 11, 6862–6880. doi: 10.1002/ece3.7533

Wang, H., Liu, X., Wu, C., and Lin, G. (2024). Regional to global distributions, trends, and drivers of biogenic volatile organic compound emission from 2001 to 2020. *Atmospheric Chem. Phys.* 24, 3309–3328. doi: 10.5194/acp-24-3309-2024

Warneke, C., Karl, T., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W., et al. (1999). Acetone, methanol, and
800   other partially oxidized volatile organic emissions from dead plant matter by abiological processes: Significance for atmospheric HOx chemistry. *Glob. Biogeochem. Cycles* 13, 9–17. doi: 10.1029/98GB02428

Weikl, F., Ghirardo, A., Schnitzler, J.-P., and Pritsch, K. (2016). Sesquiterpene emissions from Alternaria alternata and Fusarium oxysporum: Effects of age, nutrient availability and co-cultivation. *Sci. Rep.* 6, 22152. doi: 10.1038/srep22152

805   Wenke, K., Kai, M., and Piechulla, B. (2010). Belowground volatiles facilitate interactions between plant roots and soil organisms. *Planta* 231, 499–506. doi: 10.1007/s00425-009-1076-2

Wheatley, R. E., Millar, S. E., and Griffiths, D. W. (1996). The production of volatile organic compounds during nitrogen transformations in soils. *Plant Soil* 181, 163–167. doi: 10.1007/BF00011303

White, C. S. (1994). Monoterpenes: Their effects on ecosystem nutrient cycling. *J. Chem. Ecol.* 20, 1381–1406. doi: 10.1007/BF02059813

Wilkins, K. (1996). Volatile metabolites from actinomycetes. *Chemosphere* 32, 1427–1434. doi: 10.1016/0045-6535(96)00051-3

Yáñez-Serrano, A. M., Filella, I., LLusià, J., Gargallo-Garriga, A., Granda, V., Bourtsoukidis, E., et al. (2021). GLOVOCS - Master compound assignment guide for proton transfer reaction mass spectrometry users. *Atmos. Environ.* 244, 117929. doi: 10.1016/j.atmosenv.2020.117929

Yang, B., Zhang, H., Wang, Y., Zhang, P., Shu, J., Sun, W., et al. (2016). Experimental and theoretical studies on gas-phase reactions of NO3 radicals with three methoxyphenols: Guaiacol, creosol, and syringol. *Atmos. Environ.* 125, 243–251. doi: 10.1016/j.atmosenv.2015.11.028

Yang, K., Llusià, J., Preece, C., Ogaya, R., Márquez Tur, L., Mu, Z., et al. (2024a). Impacts of seasonality, drought, nitrogen fertilization, and litter on soil fluxes of biogenic volatile organic compounds in a Mediterranean forest. *Sci. Total Environ.* 906, 167354. doi: 10.1016/j.scitotenv.2023.167354

Yang, K., Llusià, J., Preece, C., Tan, Y., and Peñuelas, J. (2024b). Exchange of volatile organic compounds between the atmosphere and the soil. *Plant Soil* 501, 509–535. doi: 10.1007/s11104-024-06524-x

Zhang, Y., Zou, J., Meng, D., Dang, S., Zhou, J., Osborne, B., et al. (2020). Effect of soil microorganisms and labile C availability on soil respiration in response to litter inputs in forest ecosystems: A meta-analysis. *Ecol. Evol.* 10, 13602–13612. doi: 10.1002/ece3.6965