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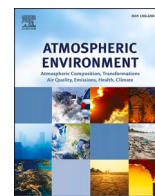
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Decline of soil volatile organic compounds from a Mediterranean deciduous forest under a future drier climate

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HIGHLIGHTS

- BVOC forest soil emission rate decreased by 43% under long term amplified drought (after 10 years of summer rain exclusion).
- Forest soil respiration was a strong driver of soil BVOC emissions.
- Temperature was positively correlated to forest soil BVOC emissions following Tingey's model.
- Forest soil BVOC followed a diurnal pattern with maximum emissions during central hours of the day.
- Forest soil was mainly a source of BVOC but it was a sink of isoprene.

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ABSTRACT

Biogenic volatile organic compounds (BVOCs) are crucial for ecosystem functioning, atmospheric chemistry and climate. While modulation of BVOC emissions from living vegetation with biotic and abiotic factors is well documented, how these factors drive soil BVOC emissions remain less understood, particularly in Mediterranean forests. To fill this gap, this pioneer study investigates whether BVOC fluxes from natural soil covered by litter (referred to as forest soil) vary under natural and amplified long-term water stress (35% annual rain exclusion over the past 10 years) in a deciduous oak Mediterranean forest (*Quercus pubescens* Willd.) compared to natural climate conditions. This aim has only been tackled in a single evergreen Mediterranean forest so far. Using proton transfer reaction time of flight mass spectrometer (PTR-ToF-MS) we also provide, for the first time, a detailed diurnal cycle of soil BVOCs in relation to air temperature, air humidity, and biotic factors including soil respiration and litter content in lignin, cellulose and hemicellulose. The main results revealed that forest soil represents a source of most BVOCs (e.g., acetaldehyde, acetone, acrolein, hexanol, monoterpenes) with maximum values at mid-day ($42 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) in response to higher temperatures while it acts as a clear sink of isoprene. Total soil BVOC emission rates, together with soil respiration, decreased by 43% after a decade of partial rain restriction. These results will contribute to enhance further modeling of soil BVOC emissions under various climate scenarios both at regional and global scales.

1. Introduction

Terrestrial ecosystems are a significant source of biogenic volatile organic compounds (BVOCs) (Guenther et al., 1995; Sindelarova et al., 2014), which play important roles in the ecosystem functioning, tropospheric processes and climate (Harrison et al., 2013). Key BVOCs,

such as benzenoids and isoprenoids, are essential plant defenses against biotic and abiotic stresses own to their antioxidant role (Laoué et al., 2022; Ormeño et al., 2020; Peñuelas and Staudt, 2010; Sharkey and Monson, 2017). Additionally, BVOCs are closely linked to litter decomposition and play a key role in mediating trophic interactions among plants and other organisms, both above and below ground

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(Chomel et al., 2016; Peñuelas et al., 2014; Santonja et al., 2019) and influence wildfire behavior by increasing vegetation flammability (Ormeño et al., 2009). Once BVOCs are readily oxidized in the atmosphere through reactions with tropospheric oxidants, primarily hydroxyl radicals (OH[•]), they participate in recycling the nitric oxide (NO) into nitrogen dioxide (NO₂), which is then photolyzed into NO and oxygen singlet (O) to form ozone (O₃) with di-oxygen, as reviewed by Atkinson and Arey (2003). Oxidized VOCs are also a source of secondary organic aerosols (SOA) (Atkinson, 2000; Yu, 2000). Both O₃ and SOA pose significant environmental concerns in the Mediterranean area (Ochoa-Hueso et al., 2017) since the former is related to human and crop health and accounts for a greenhouse gas, while SOA is implicated in cloud formation, both contributing indirectly to climate modulation (Gong et al., 2019; Kern, 2021).

BVOCs encompass a wide variety of molecules, with isoprene accounting for 70% of total flux at the global scale, followed by monoterpenes (11%), methanol (6%), acetone (3%) and sesquiterpenes (2.5%) (Sindelarova et al., 2014). To date, BVOC emissions are estimated to account for 90% of total VOCs representing an annual total emission ranging from 760 to 1000 Tg(C). y⁻¹ (Acosta Navarro et al., 2014; Guenther et al., 1995; Laothawornkitkul et al., 2009; Sindelarova et al., 2014). Since these BVOC estimates typically include emissions from living plant foliage (regarded as the major source) and exclude soil BVOCs, such estimations are likely underestimated. Yet, recent literature indicates that leaf litter from numerous species is a significantly source of BVOC emission rates (Bourtsoukidis et al., 2018; Hellén et al., 2006; Viros et al., 2021), although how abiotic and biotic factors influence their release requires further research.

Litter releases a diverse array of BVOCs, including aliphatic hydrocarbons, aromatic hydrocarbons, monoterpenoids, carbonyl compounds, alcohols, esters, sulfur- and chlorine-containing compounds. Indeed, litter can account for a reservoir and thus a source of soil BVOCs (Isidorov and Zaitsev, 2022; Ormeño et al., 2009), and trophic relationships between soil decomposers imply oxidation-reduction processes that result in released BVOCs (Das and Varma, 2011; Li et al., 2019; Mamlouk and Gullo, 2013). Root and soil microorganisms also biosynthesize BVOCs (Peñuelas et al., 2014; Tang et al., 2019) together with organic acids and enzymes (Adeleke et al., 2017; Brzostek et al., 2013) which facilitate litter decomposition. BVOCs stored in litter, such as simple phenolic compounds and terpenes, continue to be emitted until their storage structures degrade (Chomel et al., 2014; Viros et al., 2021). During litter decomposition, cellulosic and lignin carbon chains become sources of short-chain oxygenated compounds once oxidized (Warneke et al., 1999). Understanding how soil microorganisms drive BVOC emissions remains however complex since they release but also consume a wide range of BVOCs (e.g., acetone, aldehydes, isoprenoids; Gray et al., 2015; Kramshøj et al., 2018; Rinnan and Albers, 2020) depending on microbial community composition and litter species (Abis et al., 2018; Misztal et al., 2018; Viros et al., 2020). Soil BVOC fluxes are also clearly influenced by abiotic factors such as temperature and humidity (Aaltonen et al., 2013; Greenberg et al., 2012), through modulation of BVOC volatility, thermochemical oxidation (Warneke et al., 1999), adsorption – diffusion (Petersen et al., 1994), and decomposing activity of microorganisms (Quer et al., 2022; Tang et al., 2017). BVOC deposition, adsorption and leaching during water runoff depend on intermolecular van der Waals interactions and hydrogen bonds (Delle Site, 2001; Rinnan and Albers, 2020; van Hees et al., 2005). Although laboratory studies indicate that total BVOC emission rates from litter of some species (*Quercus* spp., *Salix* spp., *Acer* spp., *Erica* spp., *Ulex* spp.) are very low (<0.1 μgC.g_{DM}⁻¹. h⁻¹, Viros et al., 2020) compared to their respective emissions from green leaves. However, litter emissions can be significantly enhanced during decomposition, after rain events, and with rising temperatures (Greenberg et al., 2012; Isidorov et al., 2005, 2010; Rossabi et al., 2018; Svendsen et al., 2018; Viros et al., 2021).

In Mediterranean ecosystems, litter of several typical species (e.g., *Rosmarinus officinalis* L., *Thymus vulgaris* L. and *Pinus halepensis* Mill.)

feature significant BVOC emission rates (Viros et al., 2020). Their leaves (living and litter) contain specialized storage structures where BVOCs including monoterpenes, sesquiterpenes, and simple phenolics accumulate in high concentrations. As a result, litter BVOC emissions approach those of the corresponding living green leaves (up to 4.0 μgC.g_{DM}⁻¹. h⁻¹, Viros et al., 2020). Moreover, the slow litter decomposition due to long and dry Mediterranean summer favors litter accumulation on soil (Quer et al., 2022; Sardans et al., 2008).

Studies focusing on BVOC emission rates from forest soils and their variability in response to biotic and abiotic factors remain limited under natural conditions, regardless of the climate compared to those centered on canopy BVOC fluxes (Gray et al., 2010; Isidorov and Zaitsev, 2022; Peñuelas et al., 2014; Tang et al., 2019; Viros et al., 2020). At the Mediterranean scale, *in situ* measurements of soil BVOCs have only been carried out in an evergreen forests of *Quercus ilex* L. (Asensio et al., 2007; Mu et al., 2022; Yang et al., 2024a) and *Pinus pinaster* Ait. (Staudt et al., 2019). Moreover, the studies of Asensio et al. (2007) (based on bare soil) and Yang et al. (2024a) (using bare soil and soil covered by litter), examined the impact of a long-term drought stress in the Mediterranean region, with an exclusion experiment starting in 1999. They concluded that an amplified long-term drought decreased total BVOC emissions. They discussed that the soil acts either as a sink or a relatively low source of BVOCs, a result attributed to root responses and microbial activity. Additionally, several authors (Asensio et al., 2007; Mu et al., 2022; Yang et al., 2024a) reported significant seasonal variations of soil BVOC fluxes, with higher emissions in early spring. It is worth noting that these studies focused on terpene measured using off-line techniques.

Additional studies in various ecosystems are thus required to assess forest soil BVOC fluxes and related contribution to secondary air pollutant formation at regional and global scales (using for example MEGAN and ORCHIDEE; Guenther et al., 2006; Lathière et al., 2006; Messina et al., 2016). Based on the SSP5 8.5 scenario from the IPCC, climate change projections in the Mediterranean basin by 2100 indicate a 3.1 °C increase in annual mean surface temperature and a 20–30% decrease in annual precipitation (Essa et al., 2023; Seker and Gumus, 2022) compared to the end of the 1979 to 2015 period. This severe long-term drought intensification will alter ecosystem carbon emission rates (Cai et al., 2021; Peñuelas et al., 2017). Yet, the effect of future Mediterranean drought on soil BVOC emissions has only been explored in a single evergreen Mediterranean forest as previously described (Asensio et al., 2007; Yang et al., 2024a) and has never been investigated in deciduous forests.

In this context, the present study aims to assess, for the first time, how abiotic factors (amplified long-term drought, air temperature and humidity), and biotic factors (soil respiration, litter chemical composition) modulate soil BVOC emissions within a deciduous Downy oak forest, which is largely widespread in the Mediterranean region. To achieve this goal, we compared the response of soil BVOC emission rates under long-term amplified drought (simulating the effect of a future drought scenario in the Mediterranean region) to natural drought. We examined BVOC emissions diurnal cycles and the associated variability with air temperature and humidity using *on-line* PTR-ToF-MS. Since understanding the variability of soil BVOC fluxes with temperature is crucial for future modeling exercises, the relationship between BVOCs and air temperature was also tested as well as the fit between experimental and calculated emission rates using the temperature-dependent algorithm of Tingey et al. (1980), typically used for green foliage BVOCs.

Since the abiotic factors considered (drought, air temperature, and air humidity) strongly influence litter chemical composition (lignin, cellulose, hemicellulose) and soil respiration (Pereira et al., 2019; Quer et al., 2022) which in turn, could affect soil BVOC emission rates (Isidorov and Zaitsev, 2022; Peñuelas et al., 2014; Tang et al., 2017; Yang et al., 2024b), we tested the relationship between these biotic variables and soil BVOCs. We hypothesized that BVOC emission rates from forest soils would be modulated by i) air temperature reaching the highest values during the central hours of the day in relation with BVOC

volatility, and ii) amplified drought conditions, as previous studies have shown fluctuations in BVOC fluxes (both decrease and increase depending on compounds and seasons) from bare soil and litter own to lower soil moisture and reduced soil activity (Schade and Goldstein,

2001; Asensio et al., 2007; Greenberg et al., 2012; Rossabi et al., 2018; Yang et al., 2024a). All experiments were performed on soil covered by litter, referred to as forest soil hereafter.

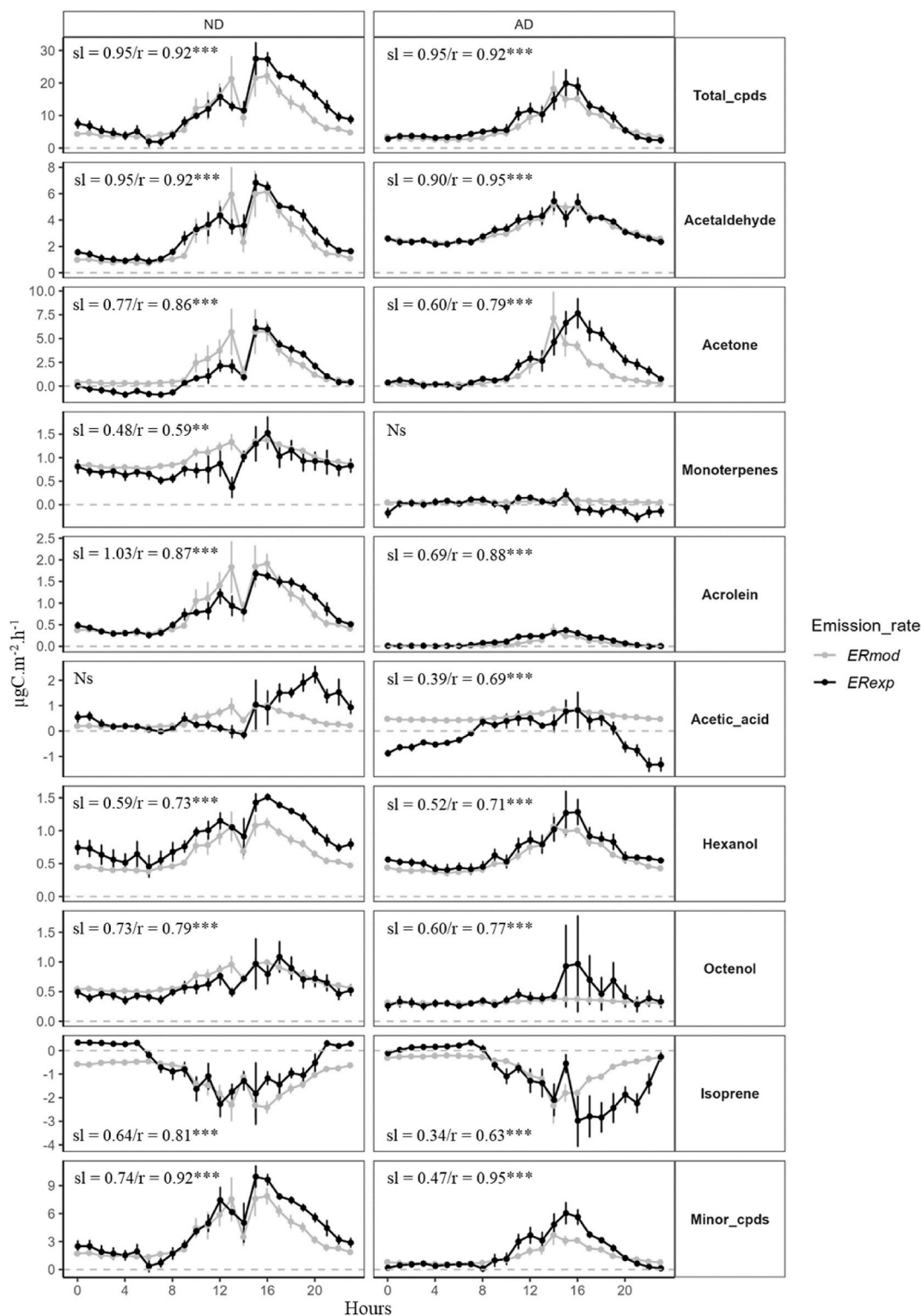


Fig. 1. Measured (ER_{exp} , brown line) and modeled (ER_{mod} , grey line) BVOC emission rates ($\mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) over the diurnal cycle (24 h). Points represent the hourly mean ($\pm\text{SE}$) emission rates averaged over the five soil replicates per drought condition (ND: natural drought; AD: amplified drought). Modeled emissions are calculated using the temperature dependent model of Tingey et al. (1980), Pearson correlation coefficient (r), slope (sl) between measured (x axis) and modeled (y axis). All presented correlations were significant (**: $0.001 < P < 0.01$ and *** $P < 0.001$). “Total_cpds” and “Minors_cpds” are the respective abbreviations for “Total_compounds” and “Minor_compounds”.

2. Material and methods

2.1. Site description

This study was performed at the O₃HP (Oak Observatory at the Observatoire de Haute Provence), located in Southern France, from May 30th to June 10th 2022. The site is part of AnaEE-France, AnaEE-ERIC (Analysis and Experimentation on Ecosystems - European Research Infrastructure Consortium) and Long-term monitoring in Ecology and Evolution (SEE-Life) sites of CNRS. The site exhibits a supra-Mediterranean sub-humid bioclimate with an average annual precipitation of 784 mm and an annual mean temperature of 13.1 °C according to the climate series from 1993 to 2022 (Laoué et al., 2024b). It is represented by a deciduous forest mainly composed of *Q. pubescens* (90% of the biomass and 75% of the trees), whose living foliage represents a remarkable source of isoprene (Genard-Zielinski et al., 2015). Since April 2012, this *in natura* site is equipped with a rainfall exclusion device over the amplified drought (AD) plot, consisting of an automated roof covering 300 m² above the canopy which is deployed mostly in summer during specific rain events, in order to exclude ~ 35% precipitation simulating a drier precipitation climate (see Garnier et al., 2021 for details). This AD plot is compared to an adjacent plot under natural drought (ND) of 550 m² surface which receives natural rainfall (Supplementary data Fig. 1). Such rain exclusion resulted in 375 mm and 610 mm precipitation in AD and ND plots respectively the year prior to the measurements (from June 2021 to June 2022) and involves lower soil water content in the amplified drought plot as documented in previous studies in 2012 (Genard-Zielinski et al., 2018), 2019 and 2020 (Garnier et al., 2021). Comparison of both plots thereby allows to study how changes in precipitation affect the functioning of the *Q. pubescens* ecosystem.

2.2. Collection and analysis of BVOC emissions from forest soil (covered by litter)

Soil BVOCs were collected using dynamic soil chambers positioned over a soil surface of 616 cm² fully covered by fresh litter of *Q. pubescens* (15.73 ± 0.52 g). Each chamber consisted in an aluminum strapping (6 L, 14.0 cm radius and 10.0 cm height) surmounted by a polycarbonate cylinder (14 L volume, 14.0 cm radius and 20.5 cm height). BVOC emissions were collected during 24 h (from 3 p.m. from day *n* to 3 p.m. of day *n*+1) and these measurements were replicated using five different leaf litter samples within each soil surface under both ND and AD plots. Air temperature and humidity were monitored at the soil surface both, inside and outside the chambers using IButtons® (Datalogger). BVOC emissions were measured *on-line* using a proton transfer reaction - time of flight - mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik GmbH, Innsbruck, Austria). Each dynamic chamber was connected to the instrument *via* its own 20 m-long 1/8" O.D. PTFE tubing. As described by Saunier et al. (2017) for branch-scale BVOC measurements, a multi-position common outlet flow path selector valve system (Vici) and a vacuum pump were used to routinely analyze air from the sequences: ambient air, AD, ND. This valve set-up was designed to minimize VOC losses on the tubing surface, as all sampling lines were continuously flushed. Each sequence was analyzed during 15 min every 45 min. Mass spectra in the range 0–500 amu were recorded with 2 min integration time. The reaction chamber pressure was fixed at 2.1 mbar, the drift tube voltage at 550 V and the drift tube temperature at 313 K, corresponding to an electric field strength applied to the drift tube (*E*) to a buffer gas density (*N*) ratio of 125 Td (1 Td = 10–17 V cm²). High resolution peak fitting and ion elemental composition analysis were executed using Tofware software (version 2.5.10, TOFWERK AG, Thun, Switzerland), running in the Igor Pro 6.3 environment (version 6.37, Wavemetrics Inc.). Mass calibration was performed based on the H₃O⁺ isotope (*m/z* 21.022 Da) and protonated acetone (*m/z* 59.0497 Da) and primary ion intensity was calculated based on H₃O⁺ and ¹⁸O isotope

intensity, corrected for natural isotope abundance (ratio of 488). BVOC mixing ratios were calculated using the following equation:

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

Where *RH*⁺ and *H*₃*O*⁺ are the signal intensities in count per seconds (cps) of the individual protonated ion and the reagent ion corrected by their relative transmission (*Tr*) respectively, *U*_{drift}, *T*_{drift} and *p*_{drift} are the voltage (V), temperature (K), and pressure (mbar) in the drift tube respectively and *k* the reaction rate (cm³ s⁻¹) between the reagent ion and VOCs. A calibration gas standard, consisting of a mixture of 14 aromatic organic compounds (TO-14 A Aromatic Mix, Restek Corporation, Bellefonte, USA, 100 ± 10 ppb in nitrogen), was used to experimentally determine the relative ion transmission. For formaldehyde, an additional correction was applied to account for its sensitivity to humidity, as described by (Vlasenko et al., 2010). The identified peaks were assigned to specific VOC on the basis of previous relevant studies (Supplementary data Table 1). BVOCs considered in this study and their corresponding ions include those with emission rates of at least 0.1 μgC.m_{soil}⁻². h⁻¹ in absolute value at some point during the analysis.

2.3. Calculation of experimental soil BVOC emission rates

In order to compare our results to soil and litter BVOC emissions but also to green leaf BVOC emission rates reported in past *in situ* and laboratory studies, BVOC emissions were expressed *i*) on a soil surface basis (μgC.m⁻². h⁻¹, Supplementary data Table 2), which is the typical unit used in field studies (Peñuelas et al., 2014) *ii*) on a dry litter mass basis (ngC.g_{DM}⁻¹. h⁻¹, Supplementary data Table 3), commonly used for expressing green leaf BVOC emissions both in laboratory and field studies (Peñuelas et al., 2014; Saunier et al., 2017; Viros et al., 2020). The experimental emission rate (*ER*_{exp}) was calculated as follows:

$$ER_{exp} = Q \times (C_{out} - C_{in}) / \alpha$$

Where, *ER*_{exp} (μg.m⁻². h⁻¹ or μg.g_{DM}.h⁻¹) represents BVOC emission rates from soil covered by litter, *Q* (m⁻³. s⁻¹) is the inflow to the soil chamber (0.4 L min⁻¹), *C*_{in} (μg.m⁻³) is the amount of BVOCs in the chamber headspace, *C*_{out} (μg.m⁻³) is the amount of atmospheric BVOC 0.5 m above the forest soil, and *α* is either the soil surface covered by the chamber (0.062 m²) or the dry leaf litter mass which ranged between 14.4 and 15.2 (g_{DM}).

2.4. Modeled soil BVOC emission rates with a temperature-based algorithm

The temperature-dependent algorithm (*T*-algorithm) of Tingey et al. (1980) was used to *i*) calculate BVOC emission factors (emission rates at 30 °C) and *ii*) evaluate its accuracy to assess soil BVOC emission rates by fitting calculated (*ER*_{mod}) and experimental emission rates (*ER*_{exp}). This algorithm uses an empirical temperature parameter *β* which defines the temperature dependency of BVOC emissions for green foliage (Guenther et al., 1993) and whose standard value is 0.09 (K⁻¹) although it changes between 0.04 and 0.21 K⁻¹ according to VOCs and species as documented in numerous studies (Fares et al., 2011; Helmig et al., 2013). By contrast, available *β* factors related to litter BVOC emission rates rely on a single value of *β* (0.06 K⁻¹ on average) documented by Greenberg et al. (2012) using litter of several coniferous species. Since the value of the *β* coefficient for broadleaf deciduous litter remains unknown, we first calculated it using our experimental dataset and then used this value for modeling the emission rates. Modeled and experimental emission rates were plotted to analyze their linear correlation. Modeled emissions were calculated using the temperature-dependent algorithm as follows:

$$ER_{mod} = EF_{mod} \times C_T \quad (1)$$

$$ER_{mod} = EF_{mod} \times \exp^{\beta(T-T_s)} \quad (2)$$

Where, ER_{mod} ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) is the modeled BVOC emission expressed on a soil surface basis, EF_{mod} ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) is the emission factor calculated as the mean of the slopes from correlations between ER_{exp} and the C_T algorithm ($\exp^{\beta(T-T_s)}$), β (K^{-1}) is the mean of the slopes of the correlations between $\ln ER_{exp}$ and $\ln EF_{exp}$ (EF_{exp} , $\mu\text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, measured at 30 ± 2 °C) and the difference between experimental temperatures and standard temperature (30 °C), T is the experimental soil surface temperature (K) and T_s is the standard temperature (303 K). Note that these calculations were only carried out on emissions calculated on a soil surface basis alone.

2.5. Litter decomposition assessment

Litter decomposition was assessed using three indicators: litter decomposition rate, litter content in recalcitrant polymers (lignin, hemicellulose and cellulose) and soil respiration.

Litter decomposition rate was measured using a litterbag approach as described in Viros et al. (2021). Five litterbags (20×20 cm, 6 mm mesh size) filled with 9.50 ± 0.02 g_{DM} of senescent leaves were placed on the soil of each plot within the O₃HP site in February 2022. Just after the campaign in June 2022 (i.e., after 4 months of decomposition), litterbags were collected from each plot and immediately sealed in plastic bags and transported to the laboratory. Leaf litter was freeze-dried (Lyovac GT2®) and the resulting dry mass was used to measure the decomposition rate (%) (Santonja et al., 2015).

Lignin, hemicellulose and cellulose were extracted and quantified according to the van Soest extraction protocol using a fiber analyzer (Fibersac 24; Ankom, Macedon, NJ, USA, Soest and Wine, 1967) as described in Santonja et al. (2017). Their concentration was studied using litters previously analyzed in terms of BVOC emission rates ($n = 5$ by plot).

Soil respiration represents CO₂ released by the whole soil system (bare soil, litter covering this soil surface, plant roots below the soil surface, soil organisms) and was used herein as an indicator of litter degradation through soil microorganisms. It was recorded under AD and ND plots mainly using a portable gas analyzer (IRGA, EGM-5, PP Systems) connected to a closed soil respiration chamber (SRC-1, PP Systems, Massachusetts). Prior to measurements, the chamber was fitted to a PVC tube (10 cm diameter) buried 5 cm deep into the soil to prevent CO₂ leakage. Concomitantly, soil temperature and humidity were recorded at 7 cm depth using a soil temperature probe (STP-1, PP Systems) and a portable time-domain reflectometry (TDR) device (Delta-T Devices, ML2 Theta Probes) connected to the respirometer, respectively. Soil respiration was measured on five different soil surfaces fully covered by *Q. pubescens* litter (1.77 ± 0.04 g fresh litter) from the corresponding plot (AD or ND) at three different times every day (8 a.m., 1 p.m. and 5 p.m.). This low frequency soil respiration measurements were correlated to BVOC measurements and used to test differences between ND and AD plots (cf. Statistical analysis).

Additionally, soil respiration was monitored at high frequency (every 15 min) through *on-line* measurements using two fixed and automated soil gas flux system (LiCor 8100 A): one flux system was placed under the AD plot and the other under the ND plot. Since there was no soil surface replication, values were averaged over 5 days within each plot.

2.6. Statistical analysis

To test whether BVOC emission rates differed according to the drought scenario and understand biotic-mediated modification of BVOC emission rates, two statistical approaches were employed. First, a principal component analysis (PCA) followed by a PERMANOVA test were used gathering data from BVOC emissions, soil respiration and litter chemical composition under AD and ND. Second, Student tests were applied (after checking for data homoscedasticity and normality) to assess significant differences between BVOCs under both drought

conditions (ND and AD). These analyses were performed using soil BVOC emission rates averaged over 24 h, during central hours (11 a.m.–4 p.m.) of the day and during night and early morning hours (9 p.m.–7 a.m.) separately. This classification was meant to distinguish between daytime periods.

A *t*-test was also used to evaluate whether abiotic (air temperature and air humidity) and biotic variables (soil respiration, litter decomposition rate and litter chemical composition) differed between ND and AD. Note that Student tests on low frequency respiration (measured with EGM5) were applied using five different replicates ($n = 5$) by drought condition, that is five different litters (cf. 2.5 Litter decomposition assessment), while Student test on high frequency soil respiration (LICOR 8100 A) was applied using five different pseudo replicates by drought conditions (the same litter was studied all through the campaign within each drought condition, so each pseudoreplicate represents the average value of a diurnal cycle).

To explain BVOC fluctuations over the diurnal cycle (24 h), drought condition and the associated-litter degradation level, Pearson correlations were performed between BVOCs and air temperature, air humidity (within the soil chambers), soil respiration and litter lignin concentration but also between BVOCs.

Statistical analyses were performed on major BVOC compounds or groups of compounds (>5% each, see section 2.2) and on the total minor compounds (<5% each). All statistical analyses were performed with the R software (version 4.2.2, R Development Core Team, 2022).

3. Results

3.1. BVOC diversity

Eighty-two different protonated fragments were measured during the campaign. Compounds such as ethanol and formaldehyde whose emission rates were always <0.1 $\mu\text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (in absolute value, see material and methods section 2.2) were excluded from the analysis. Consequently, a total of 27 fragments were considered, representing 21 compounds or groups of compounds from different chemical families: aldehydes, ketones, alkanes, alcohols, isoprenoids and acids (Supplementary data Fig.2).

Acetaldehyde and acetone were the two major BVOCs released. Acetaldehyde accounted for 24% and 46% and acetone accounted for 10% and 29% of total BVOC emission rates over 24 h under ND and AD conditions, respectively (Supplementary data Fig.2). Other compounds present in smaller proportions (5–10% of total emissions) included monoterpenes, acrolein, acetic acid, hexanol and octenol under ND conditions, whereas under AD, only hexanol and octenol were emitted in this proportion. Thirteen minor compounds (<5 % of total emissions) were also emitted including methanol, butanone, acetoin, hexanal, octenal, octanal, OVOC₁, MVK/MACR/ISOPOOH, OVOC₂, nonanal, sesquiterpenoids, OVOC₃, OVOC₄ (Supplementary data Table 1). These minor compounds accounted for 37% and 24% of total emissions over 24 h under both, ND and AD conditions respectively. Regarding immissions, several compounds exhibited negative emission rates under AD conditions, including isoprene (-13.2% of the total emissions), acetic acid (-2.4%) and monoterpenes (-0.2%). By contrast, under ND, soil only accounted for a sink for isoprene (-5%) over the diurnal cycle (24 h).

3.2. BVOC experimental emission rates over the diurnal cycle

The ER_{exp} of total BVOCs was 9.1 ± 0.6 $\mu\text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (Supplementary data Table 2) averaged over the two drought conditions and the whole diurnal cycle (24 h). Emission rates of total BVOCs, most compounds or groups of compounds exhibited a similar diurnal pattern, with maximum ER_{exp} from 11 a.m. to 4 p.m. and minimum ER_{exp} during the night and early morning (from 9 p.m. to 7 a.m.) (Supplementary data Table 2, Fig. 1). The highest total BVOC emission rate was 42.1 $\mu\text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 3 p.m. and the lowest -2.6 $\mu\text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 7 a.m. under ND.

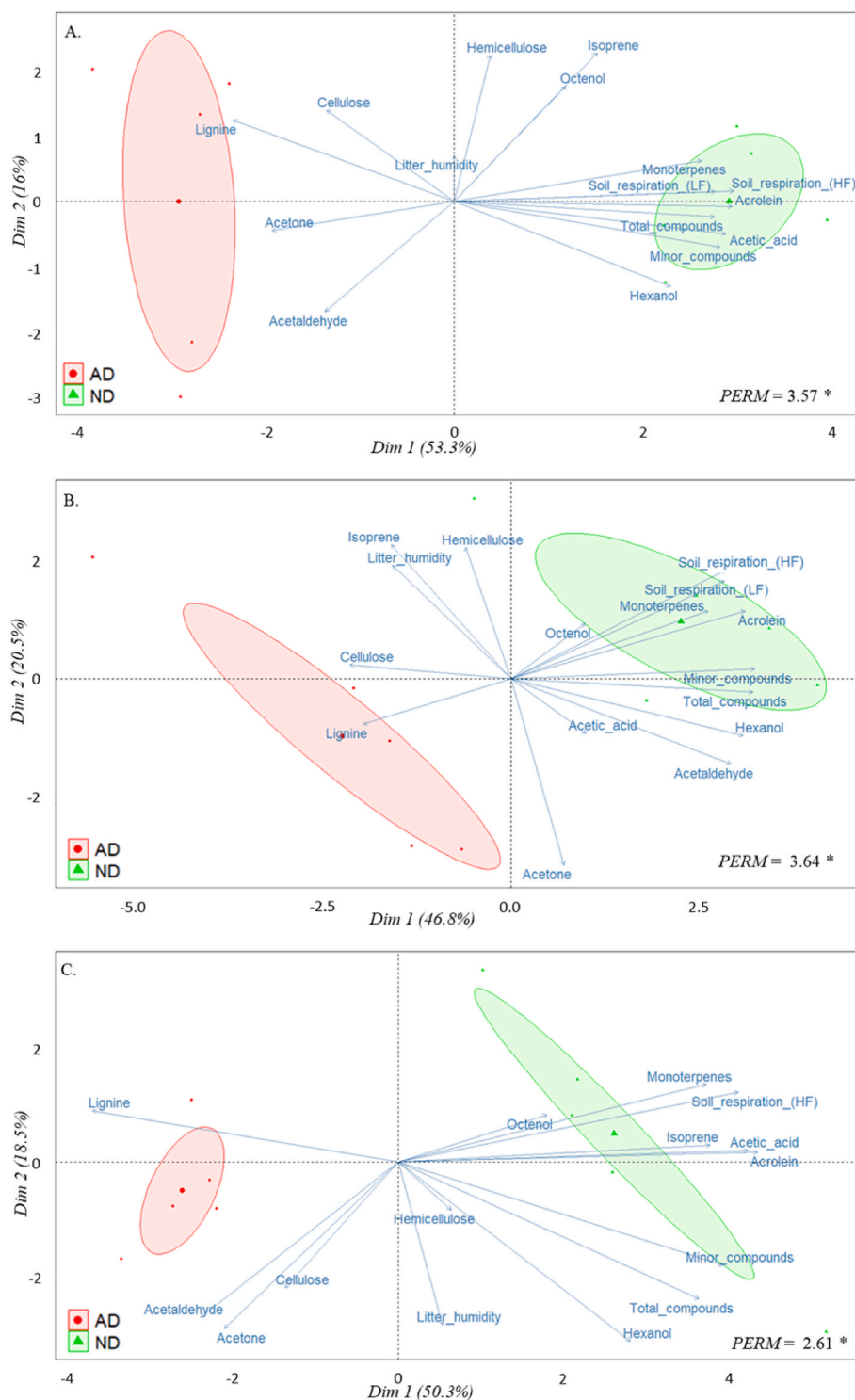


Fig. 2. Principal component analyses representing differences between natural (ND) and long-term amplified drought (AD) in terms of BVOC emission rates and litter degradation indicators (litter content in lignin, cellulose and hemicellulose, soil respiration). A, B and C refer to BVOC ER_{exp} under the entire diurnal cycle (24 h), central hours of the day and night and early morning respectively. Analyses were followed by PERMANOVA (PERM, *, $0.01 < P < 0.05$) to test the differences in soil BVOC emissions between the two drought conditions ($n = 5$ by plot). Soil_respiration_(HF) and Soil_respiration_(LF) refer to high and low frequency soil respiration respectively (see section 2.5).

Negative minimum emission rates were measured for several compounds or groups of compounds, including acetone under ND, monoterpenes, acetic acid, and the sum of all minor compounds under AD (Fig. 1). The diurnal cycle of both acetic acid and isoprene differed compared to the other compounds. Acetic acid emissions peaked in the later afternoon (at 8 p.m.), but only under ND. Isoprene mostly exhibited

negative emission rates under both drought conditions with a maximum immission at noon under ND and 4 p.m. under AD. Slight positive isoprene emission rates were recorded only between midnight and 6 a.m.

3.3. BVOC experimental emission rates under natural and amplified drought

A clear dichotomy was observed between the ER_{exp} released by soil under the different precipitation conditions (Fig. 2, PERMANOVA, $P < 0.05$). Total ER_{exp} were significantly higher under ND compared to AD, both throughout the entire diurnal cycle (ND: $11.2 \pm 0.8 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$; AD: $7.0 \pm 0.5 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$) and during the central hours of the day (ND: $18.5 \pm 1.4 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$ and AD: $12.3 \pm 1.3 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$) (t -test, $P < 0.05$, Supplementary data Table 2). Monoterpenes, acrolein, acetic acid and minor compounds all contributed to this pattern since their emission rates were consistently higher under ND (Fig. 2 A, B, C, Supplementary data Table 2). Monoterpene ER_{exp} (considering the average over the entire diurnal cycle) reached $0.8 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$ under ND and were close to zero under AD. They were even negative between 4 p.m. and 1 a.m. under AD, while values were always positive under ND (Fig. 1). Acrolein ER_{exp} under ND were 5 and 8 times as high as under AD over the whole diurnal cycle and at mid-day respectively and were not emitted at night and early morning within the AD plot unlike ND (t -test, $P < 0.05$). Acetic acid ER_{exp} clearly contrasted between the two treatments. Diurnal emissions (over 24 h), night and early morning emissions exhibited positive emission rates under ND and negative emission rates under AD, resulting in significant higher ER_{exp} from soil under ND (t -test, $P < 0.05$). Significant differences in hexanol emissions between treatments occurred at mid-day when ER_{exp} reached $1.2 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$ under ND and $0.9 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$ under AD. Only octenol emission rates remained similar between treatments regardless of the timing (t -test, $P > 0.05$).

By contrast, the two major compounds (acetaldehyde and acetone) were released in significantly higher amounts under AD conditions. This pattern occurred for acetone emissions independently of the time of the day, while acetaldehyde emission under AD outstripped those from ND from 7 a.m. to 9 p.m. alone (Supplementary data Table 2, Fig. 1). Under ND, soil acted as a sink of acetone between 1 a.m. and 8 a.m. ($-0.6 \pm 0.3 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$), while emission rates were close to zero under AD ($0.3 \pm 0.3 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$) during the same period.

3.4. Abiotic variables as drivers of BVOC emission rates

Throughout the sampling campaign, all measurements were conducted within an air temperature range comprised between 13 and 31 °C and an air humidity ranging between 51 and 96%, with no significant differences between AD and ND. Temperature appeared as the major driver of ER_{exp} for most BVOCs regardless of the drought conditions. Temperature exhibited a strong correlation with ER_{exp} of numerous compounds including acetaldehyde, acetone, acrolein, hexanol, octenol, minor compounds and total BVOCs, under both treatments (Pearson, $0.60 < r < 0.90$, $P < 0.05$, Table 1). There were however two notable exceptions: isoprene increased as temperature decreased, and monoterpenes showed no correlation (Table 1). Logically, air humidity - which negatively correlated with air temperature due to the exponential variation in water vapor saturation pressure in the classical Clausius-Clapeyron equation - was inversely related to most BVOC species (Pearson, $-0.90 < r < -0.53$, $P < 0.05$). Accordingly, isoprene ER_{exp} significantly decreased with lower humidity, and monoterpenes were not associated to air humidity variability. Averaged litter moisture content was $6.3 \pm 1.2\%$ in both treatments, with low variability between replicates, as no water exclusion was applied during the months preceding the experiment. Consequently, litter moisture content did not correlate to any BVOC ER_{exp} .

3.5. Fitting modeled and experimental emission rates and calculation of emission factors under different drought conditions

Since most BVOC compounds were tightly correlated with temperature, the T -algorithm was used to calculate ER_{mod} which was then fitted

Table 1

Pearson correlations between experimental emission rates ($\mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$) (y) and air temperature, air humidity and soil respiration ($\text{gC.m}^{-2} \cdot \text{h}^{-1}$) and lignin litter concentration. Compounds are shown in the increasing emission rate order. Values shown refer to Pearson coefficient correlation (r).

Emission rates of compounds/ Group of compounds	Air temperature ^a	Air humidity ^a	Low frequency soil respiration ^b	Lignin concentration ^b
Acetaldehyde	0.90 ***	-0.90 ***	-0.54 ns	0.02 ns
Acetone	0.89 ***	-0.95 ***	-0.83 **	0.15 ns
Monoterpenes	0.22 ns	-0.18 ns	0.95 ***	-0.44 ns
Acrolein	0.60 ***	-0.56 ***	0.90 ***	-0.74 *
Acetic acid	0.46 ***	-0.45 ***	0.78 **	-0.89 ***
Hexanol	0.48 ***	-0.53 ***	0.61 (*)	-0.62 (*)
Octenol	0.75 ***	-0.77 ***	0.32 ns	-0.11 ns
Isoprene	-0.77 ***	0.73 ***	0.37 ns	-0.22 ns
Minor compounds	0.85 ***	-0.83 ***	0.78 **	-0.91 ***
Total compounds	0.86 ***	-0.88 ***	0.70 *	-0.87 ***

(*): $0.05 < P < 0.10$; *: $0.01 < P < 0.05$; **: $0.001 < P < 0.01$ and *** $P < 0.001$; ns: not significant.

^a Correlations were performed using data over the diurnal cycle (24 h) for each replicate ($n = 24$ by drought stress condition).

^b Correlations were performed using mean per litter replicate ($n = 5$ by plot).

Table 2

Abiotic and biotic variables under natural drought (ND) and amplified drought (AD) conditions. Differences are tested using a student test. Values are mean \pm SE.

Abiotic and biotic factors	ND	AD	t -test	P
Air temperature (°C) ^a	20.21 \pm 0.82	19.73 \pm 0.65	-0.46	ns
Air humidity (%) ^a	87.11 \pm 1.17	87.15 \pm 0.98	0.02	ns
Litter moisture content (%) ^a	6.37 \pm 1.14	6.32 \pm 1.20	-0.03	ns
Soil temperature (°C) ^b	24.30 \pm 0.90	24.56 \pm 0.95	0.21	ns
Soil moisture content (%) ^b	5.36 \pm 0.34	5.23 \pm 0.32	-0.28	ns
Respiration (LF, $\text{gC.m}^{-2} \cdot \text{h}^{-1}$) ^b	0.13 \pm 0.00	0.09 \pm 0.00	-6.88	***
Respiration (HF, $\text{gC.m}^{-2} \cdot \text{h}^{-1}$) ^c	0.10 \pm 0.00	0.06 \pm 0.00	-24.10	***
Litter decomposition rate (%) ^d	14.50 \pm 1.12	11.84 \pm 0.80	-1.92	(*)
Lignin (%) ^d	16.82 \pm 0.59	20.39 \pm 0.69	3.91	***
Cellulose (%) ^d	19.52 \pm 0.71	23.67 \pm 1.00	3.37	***
Hemicellulose (%) ^d	23.65 \pm 1.04	24.71 \pm 1.00	-0.74	ns

(*): $0.05 < P < 0.10$; *: $0.01 < P < 0.05$; **: $0.001 < P < 0.01$ and *** $P < 0.001$; ns: not significant.

^a Inside the dynamic chamber ($n = 5$ by plot).

^b Respiration low frequency (LF) values refer to the average of 5 replicates by plot ($n = 5$), where each replicate refers to a different forest soil surface. The value of each replicate was calculated as the average of three soil respiration measurements (from 8 to 9 a.m., 1–2 p.m. and 6–7 p.m., see material and methods).

^c Respiration high frequency (HF) values refer to the average of 5 replicates over the entire diurnal cycle (24 h, $n = 5$ days per drought condition).

^d Values refer to the mean percentage calculated using 5 litter replicates by plot ($n = 5$) (the same litter was used for soil BVOC analyses).

to ER_{exp} . Volatiles with the highest correlation with temperature (acetaldehyde, acetone, acrolein, and total BVOC emission rates) exhibited the best correlation between ER_{mod} and ER_{exp} ($r > 0.79$) (Fig. 1). The EF_{mod} were always higher than EF_{exp} ($P < 0.05$, Supplementary data Table 4). For example, calculated EF_{mod} of total compounds was 32.6 ± 9.0 and $24.4 \pm 4.6 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$ under ND and AD, respectively, whereas the experimental EF_{exp} was 22.1 ± 9.0 and $14.6 \pm 5.2 \mu\text{gC.m}^{-2} \cdot \text{h}^{-1}$ under ND and AD respectively. Nevertheless, results indicate that, excepting acrolein, the T -algorithm underestimates soil BVOC emissions since the slope of ER_{exp} and ER_{mod} correlations were consistently below 1 for all compounds or groups of compounds ($0.35 \leq \text{sl} \leq 0.95$).

To calculate ER_{mod} and EF_{mod} , we used the average β value from our data set which was 0.16 ± 0.2 for both ND or AD conditions. Significant

differences were observed in EF_{exp} between ND and AD for several BVOCs including monoterpenes, acrolein, octenol, minor compounds and total BVOCs. For instance, the EF_{exp} of acrolein was 1.5 ± 0.3 under ND and $0.4 \pm 0.1 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ under AD ($P < 0.05$, Supplementary data Table 4). By contrast, the EF_{mod} did not differ significantly between treatments for most compounds, except for monoterpenes and acrolein, which had higher values under ND, like their experimental emissions.

3.6. Biotic variables as drivers of BVOC emission rates

Soil respiration, measured both at high and low frequency, was positively correlated with ER_{exp} of monoterpenes, acrolein, acetic acid, minor compounds and total BVOCs (Pearson, $0.95 < r < 0.61$, $P < 0.05$). By contrast, lignin concentrations showed a negative correlation with acrolein, acetic acid, minor compounds and ER_{exp} of total BVOCs (Pearson, $-0.91 < r < -0.74$, $P < 0.05$, Table 1). Clear differences were observed in biotic parameters between ND and AD conditions throughout the day (Fig. 2, A, B, C). Specifically, soil respiration rates (both high and low frequencies) and litter decomposition rates were higher under ND (Student t -test, $P < 0.05$ and $0.1 < P < 0.05$, respectively, Table 2). Additionally, cellulose and lignin concentrations reached higher concentrations in litter from the AD condition (Student t -test, $P < 0.05$, Table 2).

3.7. Relationship between compound emission rates

Independently of the drought condition, acetaldehyde, acetone, acrolein and hexanol featured significant positive correlations with the other volatile compounds (Pearson, $r > 0.7$, $P < 0.05$). However, notable differences were observed between the two treatments. Under ND, increases in acetaldehyde ER_{exp} occurred as monoterpene emissions increased (Pearson, $r > 0.7$, $P < 0.05$), while acetone and isoprene ER_{exp} positively correlated with acrolein. On the one hand, these correlations were not observed under AD. On the other hand, strong correlations ($r > 0.7$, $P < 0.05$) between acetaldehyde and acetic acid, as well between acetone and isoprene were only pointed out under AD. These correlations will be further explored when discussing ER_{exp} correlations between compounds or groups of compounds under ND and AD in the next section (see section 4.3).

4. Discussion

Research on emissions from forest soils is relatively recent and remains less developed compared to emissions from living foliage. When considering *in situ* BVOC fluxes in forest soils, only a dozen studies present fluxes from different plant functional type stands (deciduous broadleaf, evergreen broadleaf and coniferous trees) and climates (e.g., Mediterranean, boreal, oceanic or continental, Supplementary data Table 5). Among these studies, four have been conducted in the Mediterranean region, three focusing on the same *Q. ilex* forest (Asensio et al., 2007; Mu et al., 2022; Yang et al., 2024a) and one on *P. pinaster* forest (Staudt et al., 2019). Two of these studies investigated the impact of predicted limited precipitation through offline analyses of terpene species (Asensio et al., 2007; Yang et al., 2024a). Consequently, our study is the first to provide daily cycle fluxes of terpenic and non-terpenic compounds (non-targeted analysis) under contrasting drought conditions in a deciduous oak forest soil.

4.1. BVOC emission rates from soil in a mediterranean downy oak forest

The mean ER_{exp} of total BVOCs over the 24 h period was $9.1 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (Supplementary data Table 2). This is consistent with the findings of Yang et al. (2024b), who reported similar ER_{exp} in spring of total terpenes from soil covered by litter, and Asensio et al. (2007), who measured total terpenes from bare soil. In contrast, the ER_{exp} values obtained on different soil horizons using on-line PTR-MS measurements,

were ten times lower than those in our study (Mu et al., 2022). These differences highlight the significant role of bare soil as a sink of BVOCs. Additionally, ER_{exp} from coniferous forest soils in Boreal ecosystems were up to 10 times higher than those reported in our study (Isidorov et al., 2005, 2010; Svendsen et al., 2018). Coniferous litter both stores and then releases large amounts of terpenes (Ormeño et al., 2009; Viros et al., 2020). These results underscore the importance of litter in influencing both diversity and quantity of BVOCs.

In general, the canopy is considered a more substantial source of BVOC emissions compared to litter alone, bare soil, or soil covered by litter (Peñuelas et al., 2014). This is also supported by our study since total averaged experimental soil emission rates during mid-day (11 a.m.–4 p.m.) reported herein were $18.5 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ under ND conditions. These emissions were 200-fold lower than branch emissions of *Q. pubescens* at the same study site (O₃HP) and under the same ND plot. Indeed, Saunier et al. (2017) reported an average branch emission rate of $22.8 \mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ (88% isoprene, 4% acetaldehyde, 2% acetone, 4% methanol, 0.8% formaldehyde and 0.4% MVK-MACR-ISOPROOH) between noon and 15 p.m. during the growing season, which represents $3741.9 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ after converting leaf dry mass emission to soil surface equivalents, considering an LAI of $2.2 \text{m}^2 \text{green leaf surface}\cdot\text{m}_{\text{soil}}^{-2}$ (Genard-Zielinski et al., 2018) and an LMA of $74.6 \text{g}_{\text{DM}}\cdot\text{m}^{-2}$ (Saunier et al., 2017) in the study site. Although BVOC emissions from Downy oak forest soils are thus lower compared to those from the canopy during the same period, it is important to note that Downy oak litter can provide a continuous BVOC source all year long whereas green leaves are a source of BVOCs from May to November alone (Genard-Zielinski et al., 2018). Furthermore, experimental emissions of acetaldehyde and acetone from our forest soils reached respectively 5.2 and $3.5 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ on average at mid-day (11 a.m.–4 p.m.). These values account for 3 % and 6% of the acetaldehyde and acetone emissions respectively released by Downy oak at the branch scale in the same forest site under ND conditions, which reached 164.1 and $82.1 \mu\text{gC}\cdot\text{m}_{\text{soil}}^{-2}\cdot\text{h}^{-1}$ respectively (Genard-Zielinski et al., 2018; Saunier et al., 2017). These later emission rates were obtained again by transforming emissions from $\mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$ given by Saunier et al. (2017) to $\mu\text{gC}\cdot\text{m}_{\text{soil}}^{-2}\cdot\text{h}^{-1}$ using the previously cited LAI and LMA. When expressing soil emission rates on a dry mass basis, those compounds account for 0.3% of their respective branch emissions (Supplementary data Table 3).

BVOCs can also be adsorbed or deposited on forest soils (bare soil and litter) and subsequently re-emitted to the atmosphere, especially during heat waves and rain events (Greenberg et al., 2012; Schade and Goldstein, 2001; Warneke et al., 1999). In coniferous species, litter has been documented to release the highest terpene emission rates ranging from 1.5 to $8.0 \mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$, after 2–3 months of decomposition (Scot pine and Norway spruce, Isidorov et al., 2010; Aleppo pine, Viros et al., 2021), which are comparable to those from their respective green foliage (Ormeño et al., 2007; Pikkarainen et al., 2022).

All identified compounds in the present investigation (Supplementary data Table 1) have been previously documented in studies on BVOCs from bare soils and decomposing litter both *in natura* or laboratory (Aaltonen et al., 2013; Asensio et al., 2007; Ehrlich and Cahill, 2018; Gray et al., 2014; Greenberg et al., 2012; Mu et al., 2022; Trowbridge et al., 2020; Viros et al., 2020). Although their origins remain poorly understood, it is well established that they can be both emitted (Abis et al., 2020, 2021; Leff and Fierer, 2008; Stahl and Parkin, 1996) and consumed (Estrada et al., 2013; Kramshøj et al., 2018; Ramirez et al., 2010; Rinnan and Albers, 2020) by microorganisms. The observed abundance of oxygenated compounds in our study can be attributed to the soil oxidation of other BVOCs, with or without the involvement of microorganisms (Das and Varma, 2011; Mamlouk and Gullo, 2013), as well as to the physicochemical degradation of organic matter (e.g., Maillard reaction; Evershed et al., 1997; Warneke et al., 1999; Tang et al., 2019). These processes (emission, consumption, and transformation of BVOCs in soils) are highly dependant to environmental conditions (Das and Varma, 2011; Tang et al., 2019). Further

laboratory studies will be crucial for distinguishing their specific influences.

4.2. Diurnal soil BVOC emission rates: dependency on air temperature and humidity

Total BVOC emission rates exhibited a clear diurnal cycle, peaking at mid-day (reaching $42.1 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ under ND) and reaching the lowest values in the early morning ($-2.6 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). This pattern can be attributed to the positive dependence of BVOC emissions to temperature coupled with the negative correlation with air humidity (Table 1), in agreement with Greenberg et al. (2012) and Aaltonen et al. (2013). Moreover, as temperatures rise in the early morning, compounds that were adsorbed or deposited in the soil, or dissolved in soil water and dew during the night, are likely to return back to the gas phase (Li et al., 2019; Rinnan and Albers, 2020), according to Henry's law.

Correlations between acetaldehyde, acetone and acrolein with temperature were particularly remarkable (Table 1). Warneke et al. (1999) showed that acetaldehyde and acetone emissions are closely related to the oxidation of decomposing litter. Our findings further demonstrate that the increase in litter BVOC emissions with temperature can be effectively modeled using the *T*-algorithm, traditionally applied to green leaf BVOC emissions (Fares et al., 2011; Guenther et al., 1995). Specifically, temperature strongly influenced emissions of acetaldehyde, acetone and acrolein in this study, suggesting that the *T*-algorithm could be integrated in future forest ecosystems BVOC modeling exercises. The values of EF_{mod} using this algorithm ($32.6 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $24.4 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ under ND and AD conditions) provided in this study will also be highly valuable for future modeling exercises. Overall, the temperature-dependence coefficient (β) of 0.16 and ranging between 0.05 and 0.26, aligns with the values reported in the literature for green leaf emission (Fares et al., 2011; Guenther et al., 1995; Saunier et al., 2017). Many of the released compounds, such as acetaldehyde, acrolein, and monoterpenes, are recognized as ozone precursors (Supplementary data Table 4; Carter, 2010). This underscores the critical importance of characterizing their soil emissions and understanding the factors that influence their variability.

This study also highlights that soil acts as a sink for isoprene as already documented in various ecosystems (Cleveland and Yavitt, 1998; Gray et al., 2015; Tang et al., 2019; Singh and Dubey, 2023; Yang et al., 2024a). It implies that a fraction of the isoprene emitted from the canopy is transferred to soil where it undergoes physical, chemical and biological transformations (Tang et al., 2019). Consequently, while isoprene is the most emitted BVOC at the global scale ($\sim 500 \text{TgC}\cdot\text{y}^{-1}$, Arneeth et al., 2008) and is strongly involved in ozone formation (Supplementary data Table 4; Carter, 2010), this value may be overestimated since isoprene immission by soils is not considered in current models. Our results indicate that isoprene immissions and emissions from forest soil are almost 1000-fold lower compared to daytime emissions from *Q. pubescens* leaves, known to be a remarkable isoprene emitter (Guenther et al., 1995; Saunier et al., 2017). Negative isoprene soil fluxes (relying on adsorption/deposition/consumption processes) appear negligible when focusing solely on isoprene fluxes at the ecosystem scale. However, regional and global modeling exercises should be conducted to determine the importance of soil in the removal of atmospheric isoprene at larger scales.

Isoprene differed markedly from the other compounds, exhibiting predominantly negative ER_{exp} , with the lowest values occurring around 4 p.m. ($-6.8 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). This was reflected in a negative calculated emission factor ($\sim -3.4 \mu\text{gC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and a strong negative correlation of ER_{exp} with temperature ($r = -0.80$) consistent with findings by Gray et al. (2014), Trowbridge et al. (2020) and Mu et al. (2022). These results can likely be attributed to the deposition of isoprene on soil matrices or waxy leaf layers or its oxidation to short chain oxygenated compounds (e.g., acetaldehyde, acetone, acrolein), coupled with its consumption by soil microorganisms (see section 4.3), both of which are

facilitated by increasing temperatures.

4.3. Soil BVOC emissions: dependence on drought stress and biotic factors

This study focused on the impact of long-term drought (10 years) using an *in natura* experiment initiated in 2012, excluding around 35% of precipitation mainly during summer (from June to September, see section 2.1, Supplementary data Fig. 1). The aim is to simulate a drier summer drought (in duration and intensity) as predicted by IPCC models. Since our campaign took place by late May, litter and soil humidity did not show significant differences between the two drought conditions (AD, ND), as no water exclusion had been applied during the months preceding our investigation (Table 2, Supplementary data Fig. 1). This finding is crucial, as it highlights that the observed differences in BVOC emissions under the two drought conditions stem from a prolonged decade of amplified summer drought, which also affects the activity and diversity of litter decomposers at our study site (Pereira et al., 2019; Santonja et al., 2017). The consistent abiotic conditions during the campaign period also provide a clear advantage for discriminating the response of BVOCs to biotic factors due reduced precipitation. Amplified summer drought stress in the Mediterranean region is known to affect the activity of plants and soil organisms responsible for litter degradation, significantly hindering the processes of litter composition and decomposition (Ogaya and Peñuelas, 2021; Quer et al., 2022). Accordingly, BVOC emissions exhibited two distinct patterns between the two plots. On the one hand, total BVOC emission rates decreased with increasing water stress, largely due to reduced ER_{exp} of monoterpenes, acrolein, acetic acid, hexanol, and the sum of the thirteen minority compounds, and, to a lesser extent, isoprene (whose immission tended to be less important under ND). On the other hand, the ER_{exp} of acetone (all through the day) and acetaldehyde (at night) increased under drier conditions. These two contrasting responses are explored in further detail below.

The ER_{exp} of total BVOC and numerous single BVOCs decreased with lower soil microorganism activity under long-term rain exclusion, as indicated by the reduction in soil respiration and the positive correlation between BVOC emissions and soil respiration (Table 1, Table 2, Supplementary data Table 2). Understanding how soil microorganism activity and soil respiration drive soil BVOC emissions remains particularly complex *in natura*. For example, bacteria and fungi both release (Leff and Fierer, 2008; mVOC, Lemfack et al., 2018; Misztal et al., 2018; Abis et al., 2018) and consume BVOCs (Kramshøj et al., 2018; Rinnan and Albers, 2020), the balance between microbial synthesis and consumption determining their overall impact on soil BVOC emission rates. A previous study at the same forest site (Pereira et al., 2019) shed light on the possible role of microbiota on soil BVOC emissions, since it revealed that respiration, and soil microbial biomass were severely diminished under AD (Pereira et al., 2019). This is due to low soil humidity, a key driver of microbial activity in Mediterranean climates (Ogaya and Peñuelas, 2021; Yang et al., 2024a). Consequently, the higher emissions under ND conditions suggest that microorganisms contributed more to releasing these volatiles under ND compared to AD. Besides soil and litter humidity, the reduced activity and biomass of microorganisms under AD must be influenced by variation in chemical litter composition. Specifically, litter under AD was found to be more concentrated in lignin (Table 2) and a previous study in the same field site showed that litter under AD also contains higher concentrations of phenolic compounds (Quer et al., 2022). Both lignin and phenolic compounds are known to inhibit decomposition of litter (Chomel et al., 2016). Therefore, slower litter decomposition is likely linked to reduced BVOC emissions. Given this, it is plausible that the average ER_{exp} measured in this study during late spring represents the peak values for the year. However, further research is needed to fully explore the seasonal dynamic of soil BVOCs at our study site.

Acrolein, acetic acid, hexanol, octenol and various minor compounds are probably products of the oxidation of fatty acid derivatives (Ehrlich

and Cahill, 2018; Kreuzwieser et al., 1999; Matsui, 2006). The higher emission of acrolein, acetic acid, hexanol and minor compounds under ND suggests a stronger biological activity and a more efficient litter degradation compared to AD. The reduction in monoterpene emission rates under AD (50 times lower than ND) is likely to be due to lower concentrations of monoterpenes within litter under AD conditions (Santonja et al., 2015). This reduction may be attributed to the decreased density of leaf glandular trichomes (terpene storage structures) under AD as recently shown in green leaves of Downy oak (Laoué et al., 2024a). As detailed in section 4.2, isoprene diurnal fluxes show clear negative fluxes during the day, and minimal emissions at night. Although isoprene is both emitted (Kuzma et al., 1995) and consumed by soil microorganisms (Dawson et al., 2020; Larke-Mejía et al., 2019; Murrell et al., 2020), significant differences in nocturnal isoprene emissions were observed (from 9 p.m. to 7 a.m., Supplementary data Table 2). This can be imputed to higher isoprene emissions from soil/litter microorganisms, which exhibit increased activity (soil respiration) under ND conditions. The low positive emissions of isoprene at night can also be explained by the lower atmospheric concentration of isoprene compared to daytime, reducing the concentration differential between the soil and the atmosphere and leading to desorption processes (Li et al., 2019). Additionally, isoprene showed negative correlations with several oxygenated compounds (acetaldehyde, acetone and acrolein, $-0.81 < r < -0.57$, Supplementary data Fig. 3). Some of these transformations, such as isoprene oxidation leading to MVK/MACR/ISO-POOH and acetaldehyde suggest that isoprene oxidation is another process driving soil isoprene fluxes (Li et al., 2019; Tang et al., 2019).

In contrast to the other volatiles, acetaldehyde (one of the two major compounds) showed no significant differences between ND and AD over the 24 h analysis period, although its nocturnal emissions were lower under ND. This could be attributed to two factors. First, there may be a significant consumption of acetaldehyde by microorganisms especially under ND due to higher microorganism biomass in this plot. Soil microorganisms can utilize acetaldehyde to produce acetyl-CoA, essential for their metabolism (Qian et al., 2023). Second, the reduced emissions under ND could be explained by the lower concentration of lignin in litter under ND (Table 2), as acetaldehyde is produced during lignin decomposition (Kögel, 1986; Talbot et al., 2012).

Acetone (the second most abundant compound after acetaldehyde) consistently exhibited higher ER_{exp} under AD conditions, regardless of the time of day. This volatile compound is associated to both abiotic (Warneke et al., 1999) and biotic processes such as litter decomposition (Abis et al., 2018; Gray et al., 2010; Isidorov et al., 2016). The negative ER_{exp} found at night and early morning under ND conditions suggests a significant acetone consumption by soil microorganisms, as demonstrated by Taylor et al. (1980) in a laboratory experiment. More broadly, acetone is consistently consumed by soil microorganisms throughout the day, which could explain the reduced emissions under ND conditions. While it could be argued that acetone and acetaldehyde, as polar compounds, may have been more soluble in the soil water phase under ND conditions, this explanation is not substantiated by our results, as there was no difference in humidity and temperature between the two conditions. This indicates that the observed emission differences are likely related to biotic factors.

5. Conclusions

Mediterranean *Q. pubescens* forest soil was identified as a source of BVOCs during late spring, using on-line BVOC emission monitoring over 24 h. The majority of BVOC emissions exhibited a strong correlation with air temperature, with maximum values during central hours of the day. In agreement with this result, the experimental emissions significantly fitted with calculated emission rates using the temperature-based algorithm proposed by Tingey et al. (1980) and used for BVOC modeling exercises (Guenther et al., 2006, 2012).

Soil acetaldehyde and acetone experimental emission rates represent

3 % and 6 % of their respective branch emission rates at mid-day at the same forest site. However, while the canopy of Downy oak releases remarkable isoprene emissions ($3610 \mu\text{g}\cdot\text{m}_{\text{soil}}^{-2}\cdot\text{h}^{-1}$ at mid-day during the growing season, Saunier et al., 2017), soil of Downy oak forest rather acts as an isoprene sink according to the present study. Future modeling studies should account for this sink to assess its importance at larger scales. Additionally, under conditions of long-term amplified drought, this study revealed a substantial reduction of total BVOC emissions (−43%) and soil respiration (−30%) of soil covered by litter. This decrease can be attributed to chronic drought-induced modifications in the biotic factors driving soil carbon-fluxes. Future research should include real-time measurements of soil BVOCs under contrasting drought scenarios in needle-leaf Mediterranean forests, known to account for important terpene reservoirs, and soil BVOC measurements over the seasonal cycle. Such studies would enhance our understanding of forest soil BVOC drivers and their implication on both tropospheric secondary pollution and soil organism interactions.

CRedit authorship contribution statement

T. Legros: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **B. Temime-Roussel:** Writing – review & editing, Investigation, Formal analysis. **J. Kammer:** Writing – review & editing, Investigation, Funding acquisition, Data curation. **E. Quivet:** Investigation, Funding acquisition. **H. Wortham:** Writing – review & editing, Methodology, Data curation. **I.M. Reiter:** Writing – review & editing, Resources, Investigation. **M. Santonja:** Writing – review & editing, Methodology, Investigation, Formal analysis. **C. Fernandez:** Writing – review & editing, Supervision, Funding acquisition. **E. Ormeño:** Writing – original draft, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2024.120909>.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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