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Drought effects on volatile organic compound emissions from Scots pine stems

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Abstract

Tree stems have been identified as sources of volatile organic compounds (VOCs) that play important roles in tree defence and atmospheric chemistry. Yet, we lack understanding on the magnitude and environmental drivers of stem VOC emissions in various forest ecosystems. Due to the increasing importance of extreme drought, we studied drought effects on the VOC emissions from mature Scots pine (*Pinus sylvestris* L.) stems. We measured monoterpenes, acetone, acetaldehyde and methanol emissions with custom-made stem chambers, online PTR-MS and adsorbent sampling in a drought-prone forest over the hot-dry summer of 2018 and compared the emission rates and dynamics between trees in naturally dry conditions and under long-term irrigation (drought release). The pine stems were significant monoterpene sources. The stem monoterpene emissions potentially originated from resin, based on their similar monoterpene spectra. The emission dynamics of all VOCs followed temperature at a daily scale, but monoterpene and acetaldehyde emission rates decreased nonlinearly with drought over the summer. Despite the dry conditions, large peaks of monoterpene, acetaldehyde and acetone emissions occurred in late summer potentially due to abiotic or biotic stressors. Our results highlight the potential importance of stem emissions in the ecosystem VOC budget, encouraging further studies in diverse environments.

KEYWORDS

acetaldehyde, acetone, methanol, monoterpene, stem VOCs, volatile organic compounds

1 | INTRODUCTION

Plants produce and emit diverse volatile organic compounds (VOCs) that play central roles both in plant defence against stressors and in atmospheric chemistry (Niinemets & Monson, 2013). VOCs are products of fundamental plant processes, such as photosynthesis and growth, and they are also synthesized to protect plants against biotic and abiotic stressors. For example, isoprene helps leaves mitigate heat stress (Velikova et al., 2012), and monoterpenes, such as limonene, Δ^3 -carene and α - and β -pinene, are harmful to herbivores

(Phillips & Croteau, 1999; Reid et al., 2017; Seybold et al., 2006; Smith, 1965). In addition, many VOCs are used as cues in communication within the plant, among plants, and between plants and insects (for a review, see Bouwmeester et al., 2019).

Once emitted to ambient air, VOCs play important roles in atmospheric chemistry. They contribute to the growth of secondary organic aerosols (Ziemann & Atkinson, 2012) that can serve as seeds for cloud formation, leading to a cooling net effect on the climate (Kulmala et al., 2013, 2014; Paasonen et al., 2013). By reacting with OH, that is the most important oxidant of methane, VOCs may

increase methane lifetime in the atmosphere (Kaplan et al., 2006), and by reacting with nitrogen oxides, VOCs produce tropospheric ozone and affect local air quality (Atkinson, 2000). To understand the effects of VOCs in the current and changing climate, VOC emission patterns need to be quantified and modelled accurately. This requires, among others, an improved mechanistic understanding regarding the behaviour of the diverse VOC sources in various ecosystems.

The availability of water and incidence of drought are important factors shaping VOC emission patterns both temporally and spatially within and between ecosystems. In forest ecosystems, soil water availability has been found to affect VOC emissions from the canopy: a mild drought can either reduce or trigger emissions of isoprene and monoterpenes, or have no effect (Blanch et al., 2007; Ormeño et al., 2007), but a long-lasting or severe drought usually reduces their emissions (Bertin & Staudt, 1996; Llusà & Peñuelas, 1998; Lüpke et al., 2016, 2017; Ormeño et al., 2007; Staudt et al., 2002). The increasing emissions have been explained, for example, by decreasing transpiration that leads to warmer leaf temperatures and higher vapour pressures of the VOCs, increasing their release (Wu et al., 2015) and potentially by reduced substomatal CO₂ concentrations that may enhance isoprenoid synthesis (Staudt et al., 2008). Moderate drought may also increase carbon allocation to VOC production due to limitations in growth and other carbon sinks (Herms & Mattson, 1992; Lerdau et al., 1994; Llusà & Peñuelas, 1998). A decrease in VOC emissions during a long-term or severe drought has been associated with restrained photosynthesis and a reduced supply of energy and carbon to VOC production (Bertin & Staudt, 1996; Staudt et al., 2002). Other drought-related effects that have been suggested to be responsible for decreased VOC emissions are reduced permeability of the leaf cuticula (Bertin & Staudt, 1996; Llusà & Peñuelas, 1998; D. T. Tingey et al., 1991) or the reduced effect of xylem water potentials on VOC storage structures, for example resin ducts (Lüpke et al., 2017). In addition, tree water status may regulate the emissions of short-chained oxygenated VOCs (OVOCs), such as methanol, acetone and acetaldehyde, because they are water-soluble and their emissions thus respond to stomatal conductance and transpiration rates (Bourtsoukidis et al., 2014; Niinemets et al., 2004; Rissanen et al., 2018).

In comparison to the canopy, tree stems are less intensively investigated but a known source of VOC emissions (Amin et al., 2012, 2013; Gara et al., 1993; Ghimire et al., 2016; Hejjari et al., 2011; Kovalchuk et al., 2015; Lusebrink et al., 2013, 2016; Rhoades, 1990; Rissanen et al., 2016; Staudt et al., 2019; Vanhatalo et al., 2015, 2020). Particularly, the responses of stem VOC emissions to drought and variations in soil water availability remain poorly understood. Thus far, most stem VOC studies have concentrated on trees with adequate water availability (Hejjari et al., 2011; Kovalchuk et al., 2015; Rissanen et al., 2016, 2020; Vanhatalo et al., 2015, 2020), or the effects of water availability have not been included in analyses (Amin et al., 2012, 2013; Gara et al., 1993; Ghimire et al., 2016; Rhoades, 1990). However, Lusebrink et al. (2013) reported increased monoterpene emissions from the stems of

lodgepole × jack pine hybrid seedlings in a dry treatment compared with the control. Water deficiency had no effect on the total monoterpene emissions from stems of mature lodgepole (*Pinus contorta* Douglas ex Loudon) or jack pines (*Pinus banksiana* Lamb.) in a Canadian boreal forest (Lusebrink et al., 2016). In contrast, Staudt et al. (2019) found that high pinene emissions from mature maritime pine (*Pinus pinaster* Aiton) stems coincided with rainy days in south-west France. Rissanen et al. (2020) found positive correlations between soil water potential (SWP) and monoterpene and acetaldehyde emission potentials from mature Scots pine (*Pinus sylvestris* L.) stems in a humid boreal forest. Droughts can also affect VOC emissions indirectly by weakening the tree against secondary stressors, such as insect pests, and these stressors may strongly alter both the quantity and composition of VOC emissions from tree stems (Amin et al., 2012, 2013; Gara et al., 1993; Ghimire et al., 2016; Lusebrink et al., 2013) and from the whole ecosystem (Berg et al., 2013).

As droughts are predicted to become more frequent and intense, affecting forests especially in already dry regions (Jia et al., 2019), understanding the effects of soil water availability on the whole ecosystem VOC emissions—including tree stems—is increasingly important. We studied VOC emission dynamics from the stems of six mature Scots pine trees in a naturally drought-prone forest, where a long-term irrigation experiment enabled the comparison of different levels of soil water availability and potential effects of long-term acclimation to drought and to drought release. The objectives of the study were to describe Scots pine stems as potential VOC sources and to explore the following questions: (1) How do temporal variations in SWP and temperature affect monoterpene, methanol, acetaldehyde and acetone emissions from the stem? (2) Do these effects, or the level or composition of VOC emissions differ between drought-exposed and drought-released (i.e., long-term irrigated) trees that are acclimated to differing conditions?

2 | METHODS

2.1 | Site

Measurements were conducted over the dry and hot summer of 2018 at the long-term experimental irrigation site in the naturally drought prone Pfywald forest, which is part of the Swiss Long-term Forest Ecosystem Research Program LWF (www.lwf.ch). Pfywald (46°18'N, 7°36'E, at elevation 615 m a.s.l.), is located on an alluvial fan and debris cone on a sandy soil in an interalpine valley in Canton Valais, Switzerland. The forest is dominated by approximately 100- to 120-year-old naturally regenerated Scots pines reaching a dominant height of approximately 12 m (Schaub et al., 2016). The undergrowth is composed of sessile and pubescent oak (*Quercus petraea* (Matt.) Liebl. and *Q. pubescens* Willd.), downy birch (*Betula pubescens* Ehrh.) and whitebeam (*Sorbus aria* (L.) Crantz). The approximate stand density is 730 trees per ha (Dobbertin et al., 2010), and no logging has taken place at or near

the experimental site. The annual precipitation is approximately 600 mm and annual mean temperature 10.1°C. The precipitation is generally distributed evenly through the year, with approximately 350 mm of precipitation over the growing season (April–October). In 2018, the precipitation over April–October was approximately 258 mm (Federal Office of Meteorology and Climatology MeteoSwiss). The monthly mean temperature ranges from 20.1°C (July) to −0.1°C (January) at the nearby long-term weather station (Sion, 20 km from the experimental site, MeteoSwiss, period 1981–2010). In 2018, the July mean temperature was 23.3°C (Federal Office of Meteorology and Climatology MeteoSwiss). The soil is a shallow Pararendzina (Brunner et al., 2009).

Four plots of 1000 m² in the forest have been irrigated with sprinklers during night-time with additional 600 mm of water over the growing season (April–October) since 2003, and four similar plots serve as dry control plots. For details about the experimental set-up, see Dobbertin et al. (2010) and Bose et al. (2021, in press). The irrigation effects on the soil nutrient status have been minor (Herzog et al., 2014). The measurements of this study were performed on two adjacent plots: one irrigated and one control plot, after 15 consecutive summers with irrigation.

2.2 | PTR-MS stem emission measurements

We measured stem VOC emissions from three dry control trees and three irrigated trees on two adjacent plots over June, July and August ('measurement period' from hereon). Tree diameters at breast height were from 20 to 31 cm (Table 1). We measured the stem VOC emissions with chambers consisting of six to eight supporting aluminium brackets and fluorinated ethylene propylene (FEP) foil that were adjusted around the stem (Figure S1). Elastic cable ties secured the foil around the stem above and below the supporting frames. To ensure proper chamber fit, we gently smoothed the outer bark under the elastic cable ties, taking care not to wound the inner bark. The chambers were at a height of approximately 4 m, and their inner volume varied from 0.9–1.3 L. Two of the aluminium frames on the opposite sides of the stems had inlet and outlet connectors for tubing, along with opening and closing caps and small fans that helped to flush the chamber with ambient air between measurements and to circulate air through the chamber during the measurement.

Figure S2 in Supporting Information illustrates the measurement set-up. When the chamber was in measurement mode, the caps closed and incoming ambient air was drawn through a 10-L buffer

TABLE 1 Diameter at breast height (DBH), crown transparency (CT) and mean stem emission rates of monoterpenes, methanol, acetaldehyde and acetone from online (PTR-MS) measurements, and monoterpenes and sesquiterpenes from adsorbent tube samplings (GC-MS) in June and August (stem emissions from sampling normalized to 24°C to correspond to the shoot measurement temperature)

	Irrigated				Dry control			
	Tree 1	Tree 2	Tree 3	Mean	Tree 4	Tree 5	Tree 6	Mean
Tree metrics								
DBH (cm)	23	26	24		31	28	20	
CT (%)	25	20	25		70	35	40	
VOC emissions								
Stem online PTR-QMS (ng m ⁻² s ⁻¹)								
Monoterpenes	28.4 (44.0)	147.2 (203.8)	29.4 (51.5)	58.4 (121.0)	205.7 (296.9)	6.1 (8.98)	181.5 (310.1)	149.3 (272.3)
Methanol	15.8 (9.68)	16.7 (8.65)	8.8 (516)	14.3 (9.1)	18.9 (12.6)	19.6 (9.25)	13.2 (8.76)	17.8 (11.3)
Acetone	1.25 (1.33)	2.14 (0.97)	0.98 (0.59)	1.42 (1.18)	1.38 (0.95)	0.48 (0.23)	3.65 (2.94)	1.66 (1.92)
Acetaldehyde	1.12 (0.87)	1.16 (0.74)	0.52 (0.31)	0.98 (0.78)	1.05 (0.84)	0.88 (0.61)	0.85 (0.55)	0.96 (0.73)
Stem sampling GC-MS (ng m ⁻² s ⁻¹)								
Monoterpenes								
June	313	759	777	616 (214)	2	22	2.269	906 (1.247)
August	5.6	7.5	0.38	4.50 (3.0)	692	0.54	143	279 (298)
Sesquiterpenes								
June	0.43	0.81	0.60	0.61 (0.15)	0.013	0.011	0.99	0.339 (0.462)
August	0.006	0.052	0.000	0.019 (0.023)	0.22	0	0.14	0.123 (0.093)

Note: Measured from mature Scots pine (*Pinus sylvestris*) on irrigated and dry control plots in Pfywald, Switzerland over June, July and August in 2018. Mean values, standard deviation in parentheses.

Abbreviations: GC-MS, measured with gas chromatograph-mass spectrometer; PTR-QMS, measured with proton transfer reaction-mass spectrometer; VOC, volatile organic compound.

cylinder from top of a scaffold tower, 1.5 m above the canopy, using a laboratory pump (Model N816.3KT.45.18, KNF Neuberger GmbH). The pump had polytetrafluoroethylene-coated (PTFE) diaphragms and perfluoroelastomer (FFPM) valves and sealings to avoid any effect on VOC concentrations. The incoming airflow was approximately 1.5 L min^{-1} and a part of the flow dispatched as overflow before entering the chamber. Sample air was drawn from the chamber to the analyser with a flow rate of approximately 1 L min^{-1} . We continuously recorded the temperature within the chamber using T-type thermocouples installed preferentially in shade and on the northside of the stem, and sample airflow using a flow metre (PFMV530-1, SMC). PTFE tubes (inner diameter 4 mm, approximately 25 m long) led the sample air into a proton transfer reaction quadrupole mass spectrometer (PTR-QMS, IONICON). A cable heater warmed the tubes to approximately 1°C above the ambient temperature to reduce the risk of water condensation. The inlet flow to the PTR-QMS was 0.115 L min^{-1} , and the rest of the sample airflow was released outside as overflow. We set the PTR-QMS to measure methanol (m/z 33), acetaldehyde (m/z 45), acetone (m/z 59) and monoterpenes (m/z 137), along with the primary ion signal and control signals (m/z 21, 18, 25, 30, 31, 32 and 37). Reaction chamber pressure stayed at 2.19–2.21 mbar and E/N at approximately 135 Td, except for a few instrument malfunctions that were removed from the final data. We performed calibration with a standard gas containing known concentrations of the measured compounds every four weeks, following the protocol in Taipale et al. (2008).

Four out of the six chambers were simultaneously lined up in the measurement rotation as follows: (1) we measured one tree on the irrigated plot (Tree 1) and one tree on the control plot (Tree 4) throughout the measurement period from June to August; (2) we measured two trees on the irrigated plot (Trees 2 and 3) and two trees on the control plot (Trees 5 and 6) in 2-week intervals so that we measured Trees 2 and 5 for 2 weeks first and then switched to Trees 3 and 6, and so forward (Figure 1a–h). During the measurement rotation, one chamber closed for measurement for 7 min, after which we measured the ambient air for 20 min before the measurements began in the next chamber. Thus, each of the four chambers was closed and measured 13 times per day. The long ambient air measurement after each chamber measurement and the constant flushing of the chambers allowed a thorough clean-up of the chambers, tubing and PTR-QMS even when the sample air VOC concentrations were very high.

We calculated the VOC concentrations in the sample air from the PTR-QMS counts per second according to the protocol in Taipale et al. (2008). Then, we calculated the stem VOC emission rates per surface area of stem covered by the chamber (Equation 1).

$$E = \frac{F(c_{\text{chamber}} - c_{\text{ambient}})}{A}, \quad (1)$$

where E is VOC emissions rate ($\text{ng m}^{-2} \text{ s}^{-1}$), c_{chamber} is concentration in chamber air (ng m^{-3}) as the mean of the last 40 s (equals 10 measurement points) of the chamber closure, that is, during the

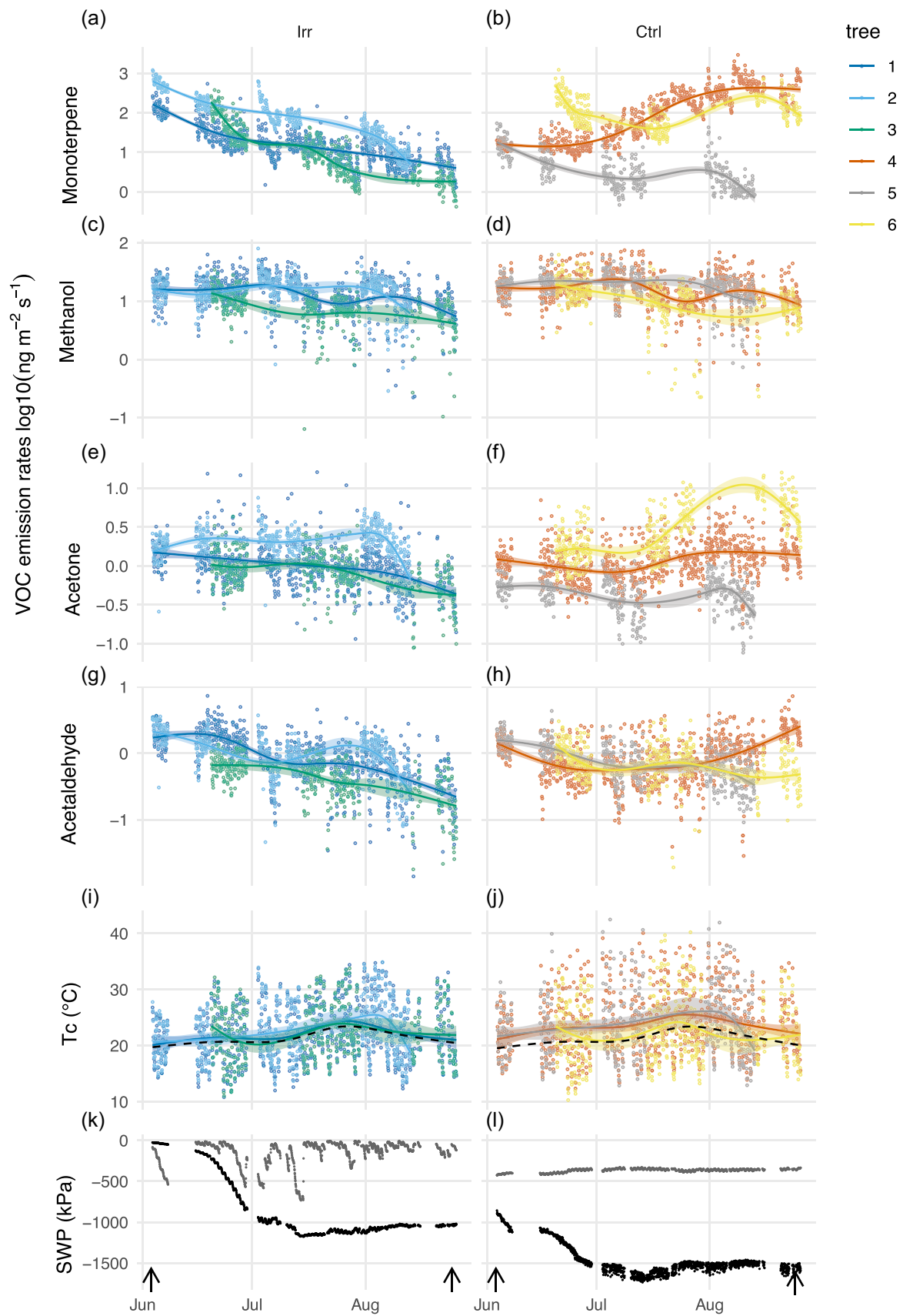
steady state. c_{ambient} is the concentration in ambient air (ng m^{-3}) used as replacement air, interpolated from the ambient air measurements before the chamber closure and before the following chamber closure to temporally correspond to the last 40 s of the chamber closure. F is the sample airflow ($\text{m}^3 \text{ s}^{-1}$) and A the surface area of the stem covered by the chamber (m^2).

Emission rate calculation is sensitive to unstable concentrations, especially concentrations measured from ambient air before and after closure. To ensure that only the most reliable emission rate recordings were used in data analysis, we filtered the emission rates based on the difference of ambient measurements before and after chamber closure (ambient air representativeness), the variance in the ambient air concentration before chamber closure (ambient air stability) and the variation in sample air concentration during the steady state (sample air stability). We also removed any data points with below-zero emission rate, because most of the below zero values occurred when ambient concentrations were abnormally high (Figure S3). The filtering procedure and the limits per each compound are detailed in Supporting Information: Data Filtering. This filtering removed approximately 8%–11% of the data. In late June, exposed resin on the bark surface inside the chamber of Tree 6 (control) caused large monoterpene emissions that saturated the PTR-QMS detector. Thus, we detached this chamber from the measurement cycle for 2 days. As a precaution for potential lingering monoterpene accumulation in the chamber or tube walls, we did not use the monoterpene emissions data from this chamber until the next 2-week period. The detector saturation affected emission measurements of other compounds and chambers, too, and these effects were removed by the above-mentioned filtering procedures.

We also removed from methanol, acetaldehyde and acetone data any points when relative humidity (RH) was above 75%. High humidity in the measurement chamber may lead to water condensation on the surfaces, and these water films adsorb and rerelease water-soluble compounds, potentially causing an error in the emission measurements (Altimir et al., 2006). These points represented approximately 40% of the methanol, acetone and acetaldehyde data, and were more representative of night-time than of daytime.

2.3 | Monoterpene and sesquiterpene sampling from stem and shoots

To assess the monoterpene composition of the stem emissions, we took additional adsorbent tube samples (Tenax TA and Carbopack B) from all six stem chambers during the beginning (2–3 June) and the end (27–28 August) of the PTR-QMS measurements. Because this method allowed for sesquiterpene sampling, we also analysed them. Before sampling, we flushed the stem chambers for 10 min with ambient air at a flow rate of $0.9\text{--}1.1 \text{ L min}^{-1}$. We next maintained the inflow and sampled incoming ambient air and outgoing sample air with the adsorbent tubes at a flow rate of $0.04\text{--}0.05 \text{ L min}^{-1}$ for 40 min. During the flushing and sampling, we continued to record the chamber temperature with the T-type thermocouples.

**FIGURE 1** (See caption on next page)

To estimate the monoterpene and sesquiterpene emission composition in the canopy, we cut one shoot from the sun-exposed mid-canopy of each measurement tree after the stem chamber sampling. To reduce the stress effect caused by wounding on the measured emissions and to measure the shoots under standard conditions, we followed Bäck et al. (2012) and enclosed the cut shoots in plastic bags and stored them in complete darkness at 8°C until the next day. Before monoterpene and sesquiterpene sampling, we let the shoot acclimate to light and to room temperature (24°C) for 30 min, and then carefully placed it into a FEP bag with inlet and outlet tubes. The cut surface of the shoot twig was left outside the bag to exclude emissions coming directly from the exposed resin. We flushed the bag with a 0.07–0.12 L min⁻¹ flow rate of ambient air for 15 min to ensure the steady state. Then, we sampled both incoming ambient air and outgoing sample air using the adsorbent tubes (Tenax TA and Carbopack B) with a flow rate of 0.04–0.05 L min⁻¹ for 30 min. The temperature and light conditions remained constant in the room during the sampling.

We stored the adsorbent tubes at 8°C and analysed them within 2 weeks using a TD-GC-MS: thermal desorption unit (PerkinElmer, TurboMatrix 650) that led the sample to a gas chromatograph (PerkinElmer, Clarus 600) connected with a quadrupole mass spectrometer (PerkinElmer, Clarus 600T). The sample analysis and calculation procedures followed Aaltonen et al. (2011) and Mäki et al. (2017). We calculated the emission rates from the measured concentrations with Equation (1), scaling the stem measurements to the stem area covered by the chamber and the shoot measurements to the needle dry weight of the measured shoot. Thus, we assumed that the shoot emissions were only or mainly produced by the needles, although the woody part of the shoot may also affect the emissions.

2.4 | Resin sampling and analysis

To gain a tentative understanding of the potential sources of stem monoterpene and sesquiterpene emissions, we wanted to compare the monoterpene and sesquiterpene emission composition to the resin composition in the stem of the six measurement trees. We took resin samples from the stems of the six measurement trees at breast height on 3–4 June and 22–23 August. To collect the stem resin samples, we punched a 6-mm hole onto the surface of the xylem and waited for a few drops of resin to appear. Then, we scooped these drops of approximately 3–5 mg into a 10-ml glass vial with a spatula. To compare with the shoot emissions, we also collected resin samples from the woody twigs of the shoots used for the adsorbent tube

sampling of the emissions (2–3 June and 27–28 August). The drops of resin that appeared after cutting the shoot we scooped into a 10-ml glass vial. In both cases, we closed the glass vial and stored it under cool and dark conditions (8°C) immediately after each sample collection. At the end of the sample collection day, we moved the vials to approximately –5°C until analysis.

We analysed the spectra of most abundant monoterpenes and sesquiterpenes in the resin by taking adsorbent tube (Tenax TA and Carbopack B) samples from the vial headspace. We choose to use the headspace measurements rather than analysing the resin dissolved in a solvent, because we wanted to mimic the conditions in which the monoterpenes and sesquiterpenes would evaporate from the stem resin and contribute to the stem VOC emissions. In this scenario, the relative contribution of each compound is determined not only by their abundance in the resin, but also by their volatility. We first heated the glass vial in a water bath at approximately 40°C for 10 min to enhance the release of volatile compounds. We next pushed two injection needles through the septum of the vial cap. We let purified air (generated with HPZA 3500 220, Parker Balston) into the vial headspace through one needle and drew the sample air out through the other needle, maintaining a flow of 0.25–0.91 L min⁻¹ through the vial headspace. Before sampling, we flushed the vial headspace for 2 min. Then, we sampled both incoming and outgoing air into adsorbent tubes for another 2 min. The sampling flow rate through each adsorbent tube was 0.04–0.05 L min⁻¹. The adsorbent tubes stayed in 4°C before the analysis in TD-GC-MS, which was conducted as described above (see Section 2.3; Aaltonen et al., 2011; Mäki et al., 2017). We calculated the vial headspace concentrations as the difference between incoming and outgoing sample air. Because measuring headspace concentrations did not allow us to quantify the precise monoterpene or sesquiterpene concentrations in resin, we only used their relative abundances in the comparisons.

2.5 | Auxiliary measurements

We used auxiliary measurements of SWP to study the drought effects on VOC stem emission rates and ambient air RH to analyse the potential effects of dry air. RH was measured continuously over the dry control plot canopy (Sensirion, Stäfa, Switzerland) and SWP was measured continuously at two locations and two soil depths on each plot (10 and 80 cm, MPS-2, Decagon Devices). We used the SWP data closest to the sample trees on each plot. The distance from the SWP measurement location to the measured trees was approximately 13 m on the dry control plot and 8 m on the irrigated plot.

FIGURE 1 Volatile organic compound emission rates from Scots pine (*Pinus sylvestris*) tree stems over June, July and August 2018. Emissions rates of monoterpenes (a, b), methanol (c, d), acetone (e, f) and acetaldehyde (g, h) and chamber air temperatures (T_c) (i, j) on irrigated (blue-green shades, Trees 1–3) and dry control plots (grey-yellow shades, Trees 4–6). The coloured lines represent the trend over time with a gam fit ($k = 6$), the dashed black line in (i) and (j) represent the ambient air temperature measured at the top of forest canopy. Soil water potentials (SWP) at depths of 10 cm (grey) and 80 cm (black) (k, l) in Pfywald, Switzerland. The arrows at the bottom indicate times of adsorbent tube sampling [Color figure can be viewed at wileyonlinelibrary.com]

In a parallel study, we also measured resin pressure dynamics on the dry control and irrigated plots, including the trees equipped with the stem chambers (Rissanen et al., 2021). The aim of the parallel study was to understand how drought affects carbon allocation to resin defences at short and long timescales, but we were able to use a part of the resin pressure dynamics data to explain the trends in stem monoterpene emission rates. In addition to the resin pressure measurements, we monitored mid-day water potential in twigs of five trees both on dry and on irrigated plot (twig water potential, TWP) two times per week using pressure chambers (Rissanen et al., 2021). Here, we used the mean mid-day value over the five trees per plot to compare with the daily mean stem VOC emissions.

To explain tree-to-tree variation in VOC emission rates and emission spectra, we used crown transparency as an indicator of tree vitality and the state of crown defoliation. Crown transparency is regularly estimated in Pfywald by trained observers as part of the Long-term Forest Ecosystem Research Programme (LWF) and following the guidelines of ICP Forests. The protocol is described by Dobbertin et al. (2004) and can be downloaded at <http://icp-forests.net/page/icp-forests-manual> (see Part IV Visual assessment of crown condition and damaging agents).

2.6 | Data analysis

Firstly, to understand how much the emission rates of each compound from each tree could be explained by chamber air temperature (T_c), we analysed the bivariate relations between the VOC emissions and T_c . We calculated these regressions using exponential fit, because the VOC volatility is exponentially related to air temperature (e.g., Guenther et al., 1993). Then, we also tested a linear fit because methanol, acetone and acetaldehyde emissions may also be related to transpiration rate and thus VPD (Bourtsoukidis et al., 2014; Niinemets et al., 2004; Rissanen et al., 2018), potentially changing the shape of the temperature relation. To generalize these regressions over the treatment (irrigated or dry control), we calculated the same regressions using mixed-effect models ('lme' function of R package nlme v3.1-149, Pinheiro et al., 2021) with the tree number as a random effect.

Secondly, to distinguish potential treatment effects from the tree-to-tree variation in the emission rates of monoterpenes, methanol, acetaldehyde and acetone, and to study the effects of T_c , RH, SWP and the phase of the growing season (month) on the VOC emission rates, we used generalized additive models (GAM). We conducted these analyses using the 'bam' function in the R package mgcv (version 1.8-31, Wood, 2017), separately for each compound. The treatment as factor, interaction between treatment and month, T_c and RH, and their interactions with treatment were the effects in the parametric part of the model. To allow for different temperature sensitivities between trees and months, we also added a three-way interaction between the tree, month and T_c . Because of nonlinearity in the relation between SWP and VOC emission rates that we observed in the preliminary data exploration, we added a smooth term

with $k = 15$ to the effect of SWP and allowed the smoother to be different between the two treatments. We tested the effect of SWP both at a depth of 10 and 80 cm and chose to use 80 cm because it provided better fit and smaller AIC (Akaike Information Criterion) in the models. To account for the repeated measurements on one tree, we added the individual tree as a random effect by giving the tree number a random smoother.

To acquire a normal distribution of the GAM residuals, we had to transform the VOC emission data before modelling. We tested both log and square-root transformations separately for each compound and evaluated the residual normality visually by QQ plots and plotting residuals against fitted values. Finally, we added autocorrelation terms due to residual autocorrelation in the models; 0.82, 0.66, 0.50 and 0.43 in the monoterpene, methanol, acetaldehyde and acetone models, respectively. To do this, we used function 'start_value_rho' of itsadug R-package, with lag = 2 (van Rij et al., 2020). With this form of the models, we tested the importance of each model effect with ANOVA (Wald test) and removed the least significant effects ($p > .05$) from the final models.

Thirdly, we tested the relations between mid-day TWP (as a mean over the five trees measured per plot) and daily daytime (11–14 h) mean emission rate of each compound. We could not add TWP in the GAM models due to the small frequency of the TWP measurements. To test the relation, we used linear mixed-effect models ('lme' function of R package nlme v3.1-149, Pinheiro et al., 2021) with the tree number as random effect, and treatment and interaction between the TWP and treatment as explanatory variables. We also tested the relations between 3-day means of resin pressure after a pressure transducer installation measured in a parallel study (Rissanen et al., 2021) and mean stem monoterpene emission rates over the corresponding 3 days to find out if increases in resin pressure corresponded with elevated emission rates.

3 | RESULTS

The stems of both, the irrigated and dry control Scots pines emitted monoterpenes and smaller amounts of methanol, acetaldehyde and acetone (Table 1). α -pinene and β -pinene were the main monoterpenes emitted from all tree stems, accompanied by smaller amounts of limonene, myrcene, camphene, Δ^3 -carene, p-cymene and terpinolene. The mean monoterpene emission rates per tree varied largely, from 6 to 214 $\text{ng m}^{-2} \text{s}^{-1}$ (Figure 1a,b, Table 1). The tree-to-tree variations in methanol, acetone and acetaldehyde emission rates were smaller (Figure 1c–h, Table 1). In the adsorbent tube samples, we also detected sesquiterpenes (Table 1), mainly longicyclene, α -gurjenene, β -farnesene and β -caryophyllene.

3.1 | VOC emission dynamics

The diurnal patterns of the emission rates of all compounds followed T_c and ambient air temperatures, with highest emissions at 16:00 to

18:00 CET and the lowest emissions at dawn (Figure 2). The timing of peak emissions differed between trees, but we did not observe consistent differences in the diurnal emission rate patterns between irrigated and dry control trees (Figure 2a–h).

Because of this diurnal pattern, the emission rates of all compounds were positively related to T_c (Table 2, Figure 3). For monoterpene emissions, the temperature relation was better captured by exponential fit, whereas for methanol a linear fit was more representative (Table 2). For acetone and acetaldehyde, the fit varied between trees, but the exponential fit seemed to represent the relation slightly better over all trees (Table 2). However, a large part of the temporal variation in the emission rates over the measurement period was not explained by T_c , particularly regarding the monoterpene emission rates (Table 2, Figure 3a,b). At a shorter timescale of 12–15 days, the temperature relations were stronger (see Table S2 for examples).

Monoterpene emission rates from the irrigated trees decreased with decreasing SWP in June and continued to decrease towards the end of August (Figure 1a). In June and July, dry control Trees 5 and 6 followed a similar pattern, but Tree 4 deviated from the pattern with increasing emissions in June (Figure 1b). Contrary to the irrigated trees, the control trees showed large monoterpene emission peaks in August (Figure 1b). The largest monoterpene emission peak, from Tree 4 in early August, corresponded to a precipitation event that was the first major one in approximately 2 months (Figure 4, see also Figure S5). Emission rates of other compounds also momentarily increased during the precipitation, but the peaks did not surpass the range of normal daily variation (not shown), and we did not observe any notable increase in ambient monoterpene concentrations following the rain event (Figure S5). The other monoterpene emission peaks were not clearly connected to such exceptional weather events.

The temporal variation in methanol, acetone and acetaldehyde emission rates was less pronounced than in monoterpene emission rates over the course of the measurement period (Figure 1c–h). Their emission rates over the whole measurement period were also better explained by T_c (Table 2, Figure 3). In contrast to monoterpene emissions, methanol and acetone emission rates did not appear to be affected by decreasing SWP in June (Figure 1c–f). Both the irrigated and dry control trees seemed to have two periods of increased methanol emissions rates (Figure 1c,d): in early July and early August, potentially corresponding to the phases of rapid radial stem growth (Zweifel et al., 2020), root growth (Iivonen et al., 2001) and to the warm daytime temperatures in early August (Figure 1i,j). Acetaldehyde emissions resembled the monoterpene emissions: emission rates in both the dry control and irrigated trees decreased slightly from June to July, seemingly following the course of reduced SWP (Figure 1g,h). We also detected emission peaks of acetone (Tree 6, Figure 1f) and acetaldehyde (Tree 4, Figure 1h) on the dry control plot in late August, slightly after the largest monoterpene peaks (Figure 1b).

The GAM models revealed no clear differences in the emission rates of monoterpenes, methanol, acetone and acetaldehyde

between the two treatments over the measurement period, suggesting that the differences in SWP may have explained any treatment-level differences (Table 3, see also Figure 5). Yet, the treatment \times month interaction in all the models indicated that for all compounds, the emission dynamics over the measurement period were different between the dry control and irrigated trees, and that a part of the temporal variation was not explained by the SWP or the other model effects (Table 3).

Similarly to the bivariate relations (Table 2), the models showed positive effects of T_c on the emission rates of all the compounds (Tables 3 and S3–S6). In the monoterpene model, T_c effect differed between the treatments (Table 3). The coefficient of T_c —related to the β -parameter of the Guenther temperature model (Guenther et al., 1993) but at a monthly timescale—was on average larger in the irrigated trees than in the dry control trees (0.11 and 0.08, respectively) (Table S3). In all the models, the T_c effect also varied between trees and within each tree between the months, indicated by the $T_c \times$ tree \times month interaction (Table 3). Among the irrigated trees, T_c tended to have smaller effect on emission rates of all compounds in July than in June, but the effect was larger again in August (Tables S3–S6). In the methanol model, the tendency was similar among the dry control trees (Table S4). The RH effect was positive in all the models (Tables 3 and S3–S6). In the methanol and acetaldehyde models, this effect was larger in the dry control trees than in the irrigated trees (Tables 3, S4 and S6). In the other models, there was no clear interaction between RH and treatment (Table 3).

The models also revealed nonlinear effects of SWP on the emission rates of all the compounds, and these effects differed between the irrigated and dry control trees (Table 3, Figure 5). The smoothed fits of SWP for emissions from the irrigated trees showed a common tipping point approximately between -800 and -900 kPa for all the compounds (Figure 5, blue-green shades). When SWP decreased further, the VOC emissions of irrigated trees dropped (Figure 5, blue-green shades). For emissions from the dry control trees, monoterpene, acetaldehyde and acetone models showed similar tipping points, but the points occurred at even lower SWPs and at different points for the different compounds; at around -1400 kPa in the monoterpene model (Figure 5a, yellow-grey shades), at around -1100 and -1500 kPa in the acetone model (Figure 5c, yellow-grey) and at around -1000 and -1300 kPa in the acetaldehyde model (Figure 5d, yellow-grey). Interestingly, methanol emission rates from the dry control trees seemed to increase when the SWP dropped below -1500 kPa (Figure 5b, yellow grey). We note that the smoothed trends in the high and low extremes of SWP of each treatment derive from smaller number of data points and should thus be interpreted with caution.

Overall, the models captured well the variation in emission rates of monoterpenes, with explained deviance of 87% (Table 3). The acetone and acetaldehyde models explained 84% and 76% of the deviances (Table 3). The methanol emission rates were less well described, with an explained deviance of 62% (Table 3). The residuals of the methanol, acetone and acetaldehyde models did not show strong patterns, but the monoterpene model residuals of the dry control trees reflected the unexplained late summer emission peaks (Figure S6).

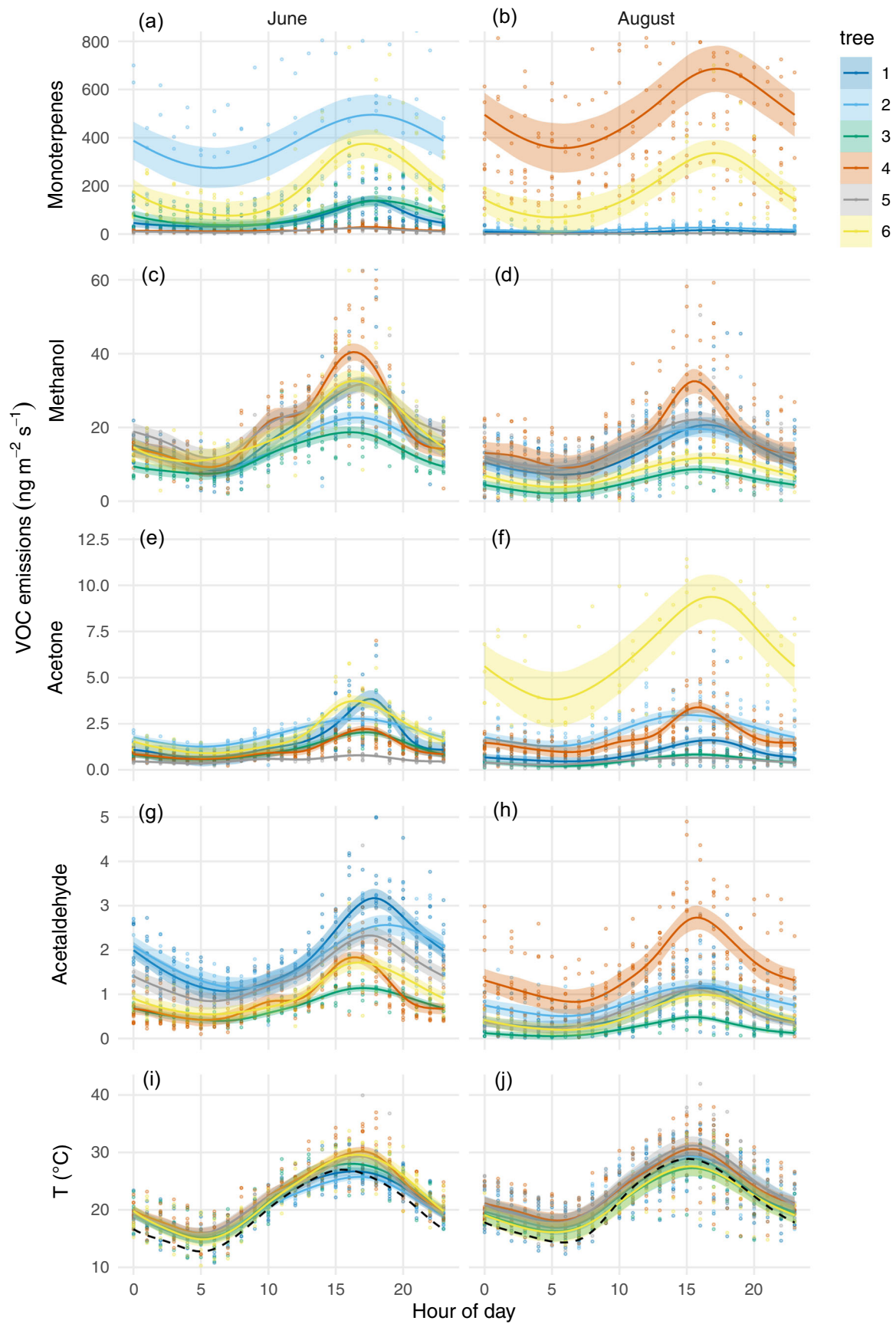
**FIGURE 2** (See caption on next page)

TABLE 2 R^2 for exponential and linear regressions between stem VOC emission rates and chamber air temperature (T_c), both separately for each tree and combined for the treatment using linear mixed-effect models (lme)

	Irrigated			All trees (lme)	Dry control			All trees (lme)
	Tree 1 <i>n</i> = 673–745	Tree 2 <i>n</i> = 372–396	Tree 3 <i>n</i> = 309–370		Tree 4 <i>n</i> = 740–767	Tree 5 <i>n</i> = 350–372	Tree 6 <i>n</i> = 281–327	
Monoterpenes								
Exp	0.13	0.01	0.07	0.04 (0.07 [0.006])	0.08	0.18	0.20	0.03 (0.07 [0.006])
Linear	0.04	(0.00)	0.05	0.00 (1.65 [0.56])	0.03	0.10	0.05	0.02 (7.4 [1.20])
Methanol								
Exp	0.30	0.41	0.19	0.23 (0.08 [0.003])	0.41	0.44	0.14	0.29 (0.07 [0.003])
Linear	0.36	0.50	0.27	0.29 (1.03 [0.04])	0.50	0.62	0.26	0.43 (1.29 [0.04])
Acetone								
Exp	0.44	0.56	0.54	0.32 (0.09 [0.002])	0.62	0.35	0.37	0.14 (0.07 [0.002])
Linear	0.21	0.68	0.51	0.24 (0.12 [0.005])	0.55	0.37	0.28	0.11 (0.13 [0.006])
Acetaldehyde								
Exp	0.23	0.23	0.34	0.20 (0.09 [0.004])	0.44	0.38	0.55	0.44 (0.09 [0.002])
Linear	0.18	0.18	0.38	0.14 (0.06 [0.003])	0.38	0.33	0.63	0.39 (0.08 [0.003])

Note: The temperature-sensitivity (for exponential fit β , for linear fit the slope) is given in parentheses for the treatment-level relations with their standard errors in brackets. For all effects $p < .05$, n is the number of observations per tree that varies among the compounds.

Abbreviation: VOC, volatile organic compound.

When comparing mean mid-day TWP with daily mean VOC emissions, we observed a potential positive relation between TWP and acetaldehyde emissions both among the dry control and the irrigated trees (Table S7 and Figure S7). The other compounds did not show important relations with the TWP (Table S7 and Figure S7). Among irrigated trees and the dry control Tree 5, high resin pressures tended to correspond to higher stem monoterpene emission rates (Figure S8), but these relations were generally not significant and could not explain the high emission peaks from dry control trees in August.

3.2 | Monoterpene and sesquiterpene spectra in the emissions and resin of the stem and shoots

Comparing the resin samples and the adsorbent tube samples of monoterpene and sesquiterpene emissions revealed certain potential differences between stems and shoots. In stems of our six study trees, the terpene spectrum in resin and emissions was dominated by α -pinene and β -pinene, with very small contributions of other compounds and relatively little variation between the trees or treatments (Figure 6a,c). Stem resin samples and stem emissions showed similar

monoterpene and sesquiterpene spectrums and corresponding tree-to-tree variation among the most abundant compounds, hinting that the monoterpene and sesquiterpene emissions from the stem may originate mainly from resin (Figure 6a,c, see also Figure S9).

In comparison to stems, shoots of our six study trees had larger shares of myrcene, camphene and limonene, both in their emissions and in their resin (Figure 6b,d). In the shoots, the terpene spectrum of resin and emissions also diverged more from each other and varied more between the trees and treatments with, for example, a relatively larger presence of myrcene and limonene in the dry control tree samples (Figures 6b,d and S10). No consistent differences in the terpene spectra were evident between June and August sampling (Figure 6).

4 | DISCUSSION

We found that in a naturally dry environment, Scots pine stems were considerable monoterpene sources. They also emitted methanol, acetone and acetaldehyde. The stem emission rates of these compounds followed temperature at a daily scale, corresponding to earlier findings (Rissanen et al., 2016; Staudt et al., 2019; Vanhatalo et al., 2020). Over

FIGURE 2 Average daily dynamics of (a, b) monoterpene, (c, d) methanol, (e, f) acetone and (g, h) acetaldehyde stem emission rates of three irrigated (blue-green shades, Trees 1–3) and three dry control (grey-yellow shades, Trees 4–6) Scots pine (*Pinus sylvestris*) trees in Pfywald, Switzerland with (i, j) the daily dynamics of the air temperature in the respective stem chambers over June (a, c, e and g) and August (b, d, f and h) 2018. In (i) and (j), the dashed black line represents ambient air temperature measured at the top of canopy. The y-axis is scaled for visibility, omitting the largest emission peaks, but all available data per month and chamber is included for plotting the mean hourly emission rate ($n_{\text{chamber} \times \text{month}} = 72\text{--}236$). The shaded areas represent the 95% confidence interval [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

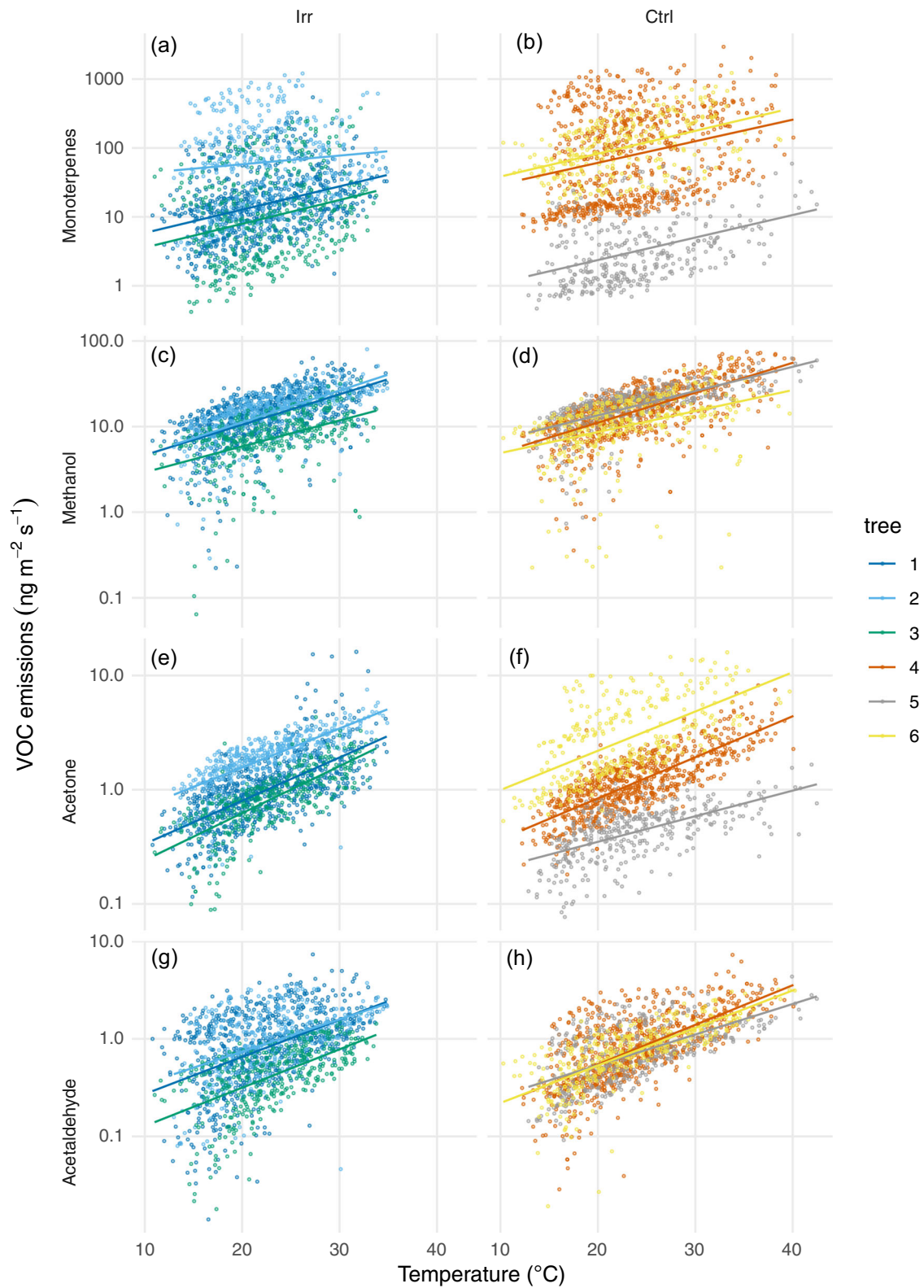


FIGURE 3 Relations between air temperature in the chamber (T_c) and (a, b) monoterpene, (c, d) methanol, (e, f) acetone and (g, h) acetaldehyde emissions from mature Scots pine (*Pinus sylvestris*) stems on irrigated (blue-green shades, Trees 1–3) and dry control plots (yellow-grey shades, Trees 4–6) in Pfynwald, Switzerland over June, July and August 2018. Lines represent least-square fits. Note log₁₀ scale on y-axis [Color figure can be viewed at wileyonlinelibrary.com]

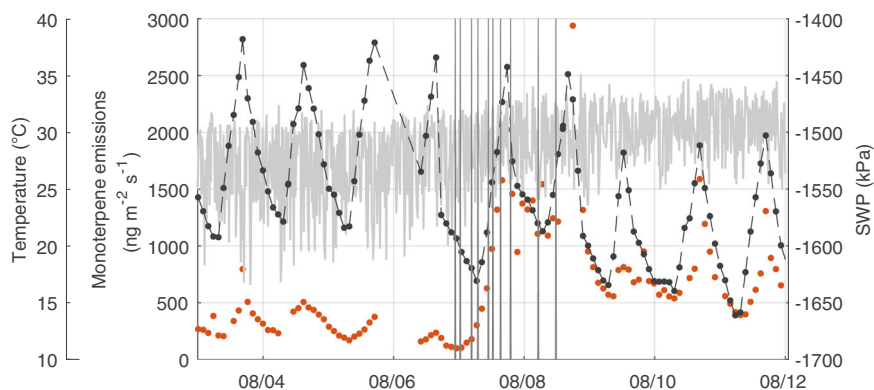


FIGURE 4 Increase in monoterpene emissions (orange dots) from a mature Scots pine (*Pinus sylvestris*) stem (Tree 4) on the dry control plot during rainy days (precipitation events marked with grey vertical lines) in August 2018. Rain did not instantly affect air temperature in the chamber (Tc, black dots and line) or soil water potential at 80 cm (SWP, light grey line) [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

Model variables	Monoterpenes, Dev. expl. 87%, n = 2906	Methanol, Dev. expl. 62%, n = 1868	Acetone, Dev. expl. 84%, n = 1838	Acetaldehyde, Dev. expl. 76%, n = 1886
Treatment	(0.591)	(0.742)	(0.461)	(0.124)
Tc (°C)	<0.001	<0.001	<0.001	<0.001
RH (%)	0.002	(0.513)	<0.001	<0.001
Month × treatment	<0.001	<0.001	<0.001	<0.001
Tc × treatment	0.005	(0.706)	(0.780)	(0.343)
RH × treatment	(0.603)	<0.001	(0.379)	0.002
Tc × tree × month	<0.001	<0.001	<0.001	<0.001
s(tree, as random effect)	<0.001	<0.001	<0.001	<0.001
s(SWP × treatment)				
Ctrl	<0.001	<0.001	<0.001	<0.001
Irr	<0.001	<0.001	<0.001	<0.001

TABLE 3 ANOVA Wald test *p*-values of the model effects, interactions, and smoothers in a generalized additive model (GAM) explaining log-transformed monoterpene and acetaldehyde, and square-root transformed methanol and acetone emissions from mature Scots pine stems in the drought-prone Pfywald forest

Note: The values in parentheses indicate effects or interaction that were removed from the final model due to low significance. See the effect sizes of the final model parameters in Tables S2–S5. Dev. Expl.: deviance explained by the model, Month: June, July or August, *n*: number of observations used in model, RH: ambient relative humidity, *s*: smoother term for nonlinear relations, Tc: air temperature in the chamber, Treatment: irrigation (Irr) or control (Ctrl).

the measurement period from June to August, emission rates generally decreased with decreasing SWP with the exception of late-summer emission peaks of dry control trees. On the contrary, methanol emission rates were not strongly affected by the dry conditions. There were no distinct differences between the emission rates from the dry control and the irrigated tree stems when the effect of the differing SWPs on the emission rates was taken into account.

4.1 | Scots pine stem as a VOC source

The monoterpene emission rates from stems, dominated by α - and β -pinene emissions, ranged from 0.5 to 59 ng m⁻² s⁻¹ in the tree with the lowest emissions and from 6.2 to 2900 ng m⁻² s⁻¹ in the tree with

the highest emissions, when the chamber air temperatures ranged between 10 and 42°C. In comparison, α - and β -pinene emission rates ranged between -2 and 99 ng m⁻² s⁻¹ from maritime pine stems in France, in a temperature range of 15 to 34°C (Staudt et al., 2019). In moist and cool boreal conditions, the summertime monoterpene emission rates of the lower stem were generally smaller, 0–25 ng m⁻² s⁻¹ (Vanhatalo et al., 2020).

The high monoterpene stem emission rates suggest that the contribution of the stem emissions to the tree- or ecosystem-scale emissions may be more important in the drought-prone Pfywald forest than previously estimated in other forests. For example, in a boreal Scots pine forest the estimated contribution of the stems to total ecosystem monoterpene emissions was estimated to be approximately 2% (Vanhatalo et al., 2020), but the maximum stem

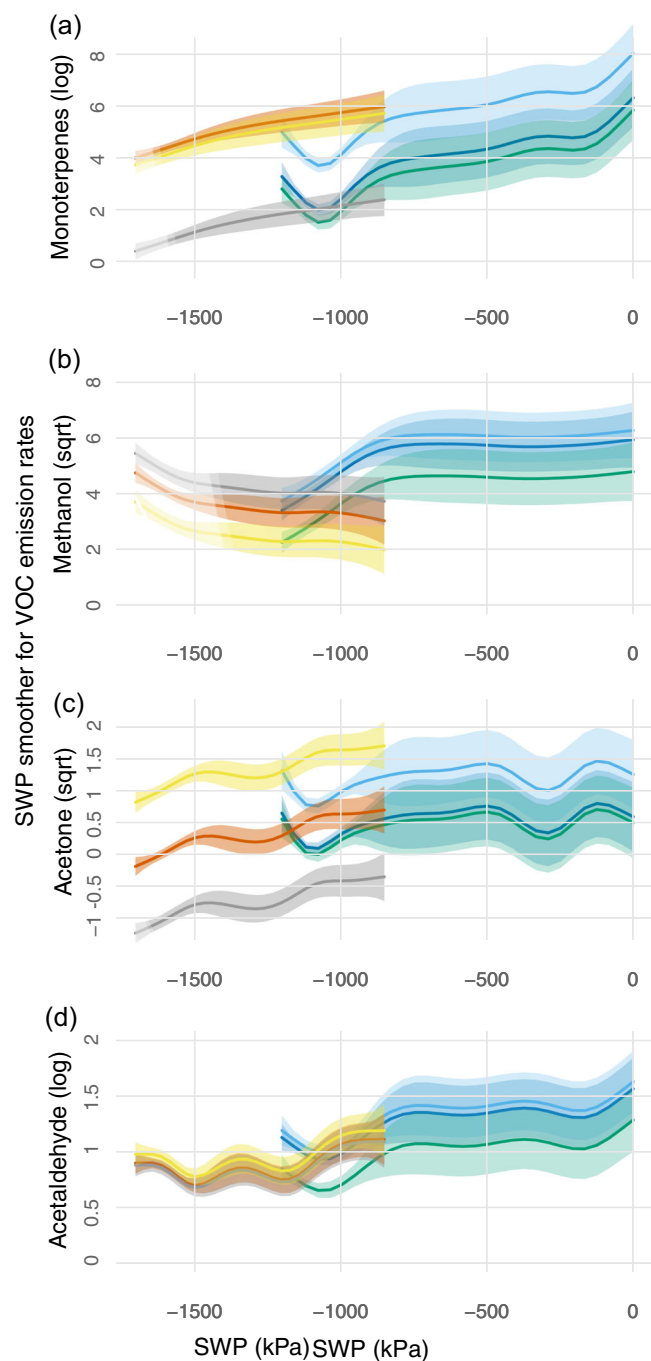


FIGURE 5 Generalized linear model smoothers for nonlinear relation between soil water potential (SWP) and log or square-root transformed (a) monoterpene, (b) methanol, (c) acetone and (d) acetaldehyde emissions from mature Scots pine (*Pinus sylvestris*) stems on irrigated (blue-green shades, Trees 1–3) and dry control plot (yellow-grey shades, Trees 4–6) in Pfywald, Switzerland in June 2018. The shaded area represents standard error with 95% confidence interval. The smoothed trends in the high and low extremes of SWP derive from smaller number of data points and should thus be interpreted with caution [Color figure can be viewed at wileyonlinelibrary.com]

emissions measured under these conditions were 2–100 times smaller than in Pfywald. Thus, our results highlight that the stems should be considered as potentially important monoterpene sources, particularly under extremely dry conditions. To avoid underestimations and biases in ecosystem-scale emission estimation, it would be important to further explore the monoterpene emission patterns in various forest ecosystems and environmental conditions.

In addition to the monoterpene emission rates, the methanol emission rates measured in our study, ranging from 0 to $80 \text{ ng m}^{-2} \text{ s}^{-1}$ were larger and more varied than methanol emission rates measured from boreal Scots pine: $0\text{--}20 \text{ ng m}^{-2} \text{ s}^{-1}$ (Rissanen et al., 2020; Vanhatalo et al., 2020). The acetaldehyde emission rates, ranging from 0 to $7.4 \text{ ng m}^{-2} \text{ s}^{-1}$, were of the same magnitude as measured in boreal Scots pine: $0\text{--}12 \text{ ng m}^{-2} \text{ s}^{-1}$ (Rissanen et al., 2020).

4.2 | What may cause the large stem monoterpene emissions?

One reason for the unexpectedly large stem monoterpene emission rates may be the heatwaves that occurred in large parts of Europe in the summer of 2018, also in Switzerland (OFEV, 2019). The vapour pressures and thus the emission rates of VOCs increase with temperature (e.g., M. D. T. Tingey, 1980). However, as the monoterpene emission trends over the measurement period were not clearly connected to temperature trends, a direct temperature effect cannot be used as the only explanation.

Because monoterpenes are a part of the conifer defence system, biotic and abiotic stressors are important causes for their large emission rates (Amin et al., 2012, 2013; Gara et al., 1993; Ghimire et al., 2016; Lusebrink et al., 2013). Stress-related emissions could be one reason for the elevated emission rates we observed, too. On one hand, we observed a tendency of two of the dry control trees to maintain higher monoterpene emission rates than irrigated trees if they were compared under equally dry conditions (see Figure 5, SWP approximately -1000 kPa), which may be related to the higher level of stress (either abiotic or biotic) or to long-term drought acclimation. On the other hand, at the late phase of a prolonged drought when the dry control trees were probably most vulnerable to pest insects and pathogens (Rissanen et al., 2021), the high levels of monoterpene emissions were partly constituted by the large emission peaks. These peaks resembled emissions from exposed resin, and although we could pinpoint exposed resin as a cause of the emission peak only at one instance, smaller resin leaks within the bark remain possible. In addition, a part of the large tree-to-tree variation in emission rates and composition may be related to the varying levels of stress previously observed at the site (Schönbeck et al., 2020, 2021). For example, the tree that averaged the largest monoterpene emission rates was also the most defoliated (i.e., highest crown transparency) (Table 1, see Tree 4). An effect of biotic stressors is also suggested by

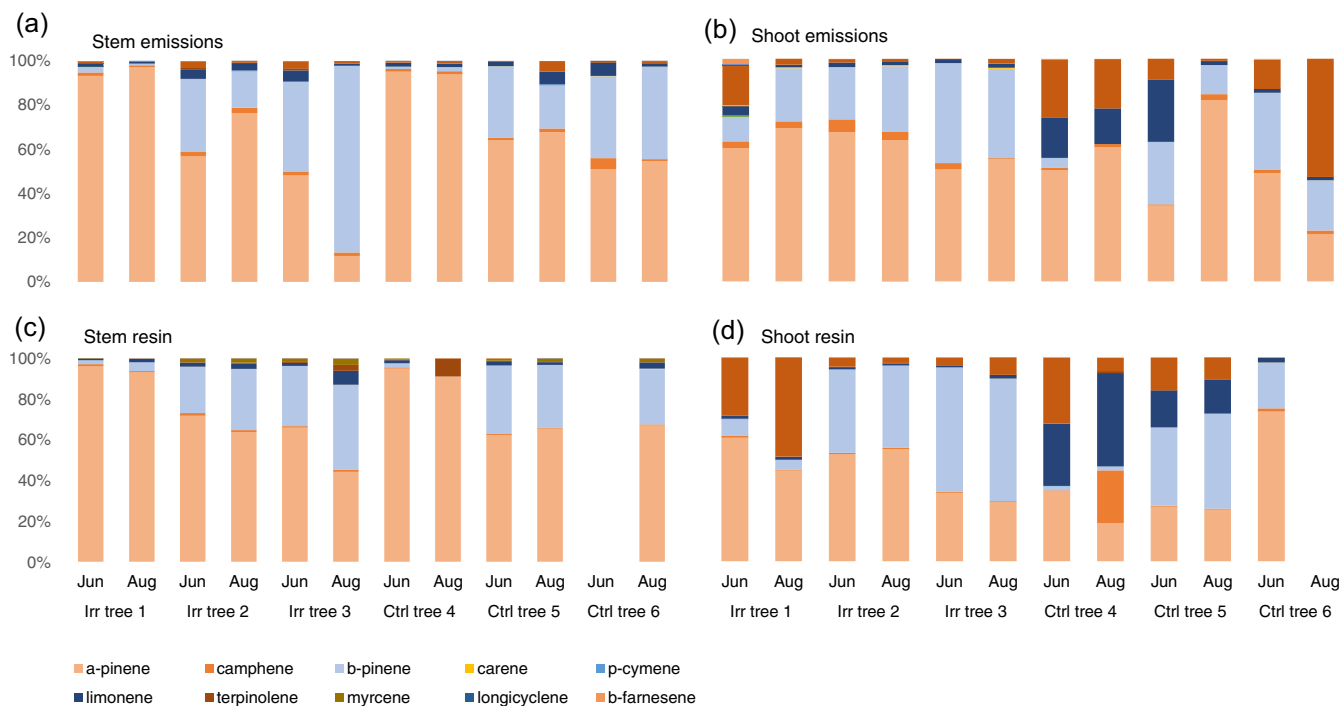


FIGURE 6 Relative abundances of monoterpenes and sesquiterpenes detected from (a) stem emissions, (b) shoot emissions, (c) stem resin and (d) shoot resin of six mature Scots pines (*Pinus sylvestris*) on irrigated and dry control plot in Pfywald, June and August 2018. For clarity, only the 10 most abundant compounds are included in the figure [Color figure can be viewed at wileyonlinelibrary.com]

the large shares of limonene and myrcene—monoterpenes that are related to abiotic or biotic stresses (Smith, 1965; Sturgeon, 1979; Thoss & Byers, 2006)—in the shoot resin and shoot emissions of the dry control trees.

Finally, it is possible that the wood and resin duct anatomy of pines in dry conditions favours the emissions of monoterpenes from storages. For example, Rigling et al. (2003) showed that resin duct production was strong in dry conditions and decreased with irrigation in Scots pine in the Valais. Overall, further studies on the mechanisms of monoterpene stem emissions in the contexts of drought and biotic stresses seem necessary and while difficult to predict and model, the peak emissions can be an important part of the ecosystem VOC fluxes in high-stress environment and should not be lightly discarded as noise.

4.3 | Tree-to-tree variation in terpene emission spectra

Despite the large tree-to-tree variation in the total monoterpene emission rates from the stem, the tree-to-tree and temporal variation in the terpene spectra of stem emissions and resin were small in our sample of six trees. Furthermore, the terpene spectra of stem emissions and resin corresponded within one tree, suggesting that the monoterpenes stored in resin could be a major source for stem monoterpene emissions. The effects of other sources (e.g., bacteria or lichen on the bark) would thus be minor. In the shoots, the tree-to-tree variation, and the differences in the terpene spectra between

emissions and resin were larger. Qualitative differences between shoot resin and emissions are expected because of the emissions of *de novo* synthesized monoterpenes that are independent from the stored compounds (Ghirardo et al., 2010; Lüpke et al., 2017; Vanhatalo et al., 2018). In addition, shoot emissions were measured from the whole shoot, including the needles and the woody twig, but resin samples were collected from the woody twig without a direct contribution of the needle resin. The larger tree-to-tree variation in resin composition and monoterpene emissions among shoots than among stems can be related to the small size of the resin pool within needles, which allows for faster changes in the observed monoterpene composition in case of stress or another effect that alters the monoterpene production patterns. The slightly diverging terpene spectra between the stems and shoots correspond to the results of Staudt et al. (2019), who found diverging molecular structures of pinenes between stem and shoot emissions and suggested that their sources may differ. However, we note that as our results base on only two measurement points on six trees, dedicated studies on the origin of stem monoterpene emissions and terpene profiles in the tree parts (stem vs. shoots) would be required to explore these relations further.

4.4 | Effects of temporal variation in soil humidity on VOC emission rates

Over the measurement period, decreasing SWP reduced the emission rates of monoterpene, acetone and acetaldehyde in a nonlinear way. Moreover, the different SWPs between the irrigated and dry control

treatments seemed to explain any differences in the emission rates between the treatment according to the GAMs. An effect of soil water content on Scots pine stem monoterpene emission rates has also been reported in humid boreal conditions (Rissanen et al., 2020). Drought has been hypothesized to reduce monoterpene and isoprene emission rates from shoots by decreasing photosynthesis and by reducing substrate and energy availability for VOC production (Bertin & Staudt, 1996; Staudt et al., 2002). The same effect, intensified by decreasing phloem sap flow and slow substrate supply (Salmon et al., 2019; Sevanto, 2018), may affect VOC emission rates from the stem.

Monoterpene release from the storages have been suggested to relate to the pressures within and around the monoterpene storages, such as resin ducts (Lüpke et al., 2017, Rissanen et al., 2016). Thus, decrease in xylem water potential and turgor pressures in stem, which may reduce resin pressures (Rissanen et al., 2021), might also reduce the emissions of monoterpenes from stem storages. However, we did not see clear relation between resin pressure dynamics and monoterpene emission rates. A rapid increase in water availability and humidity may have nevertheless contributed to one of the large monoterpene peaks that we observed after the rare rain event. After a drought period, rehydration and swelling of the bark and stem tissues observed at the site (Zweifel et al., 2020) may release monoterpenes accumulated in the stem air spaces or other temporary storages (Loreto & Schnitzler, 2010; Staudt et al., 2019). The peak we detected was clear in the tree (Tree 4) with overall the highest monoterpene emissions rates, which potentially contributed to its substantial rewetting reaction. Such rain-related peaks have previously been observed for shoots (Helmig et al., 1998; Schade et al., 1999).

In contrast to monoterpenes, acetaldehyde and acetone are not stored in large quantities in the stem, but they are water-soluble, which potentially affected their responses to SWP changes. Acetone and acetaldehyde may be transported in the xylem sap in the stem, thus drought and decreased sap flow rates may limit their emission rates (Kreuzwieser et al., 2000; Rissanen et al., 2018). Like monoterpene emissions, acetaldehyde emission rates from Scots pine stems have been found to respond to changes in soil humidity in boreal conditions (Rissanen et al., 2020). Both acetone and acetaldehyde are released in organic matter decomposition in soil (Warneke et al., 1999), and acetone can be produced by soil fungi (Bäck et al., 2010). These processes decelerate in dry conditions, reducing the amounts of acetone and acetaldehyde in soil water. If these compounds are taken up by roots with soil water, dry conditions would therefore also reduce their uptake and later release from the stem. Acetaldehyde sensitivity to SWP may also be related to increased ethanol and subsequent acetaldehyde production when the soil is wetted (Fall, 2003; Filella et al., 2009; Kreuzwieser et al., 1999, 2000, 2001; Schade & Goldstein, 2001), but the relation between TWP and acetaldehyde emission rates suggests that the emissions may be linked to tree water status even more directly.

Despite the generally decreasing trends of the acetone and acetaldehyde emission rates, large emission peaks occurred from two

dry control trees in late summer. Although probably not directly connected to exposed resin, the fact that these peaks co-occurred with the monoterpene peaks suggest that they may have been caused by the same events—for example activity of biotic stressors or rewetting after rain.

Although methanol is also water-soluble and may be transported in the xylem sap (Folkers et al., 2008; Rissanen et al., 2018), its emission rates from the dry control trees seemed little affected by the decreasing water availability. This is somewhat surprising because the most important known sources of methanol in plants are growth processes (Galbally & Kirstine, 2002; Hüve et al., 2007), which are strongly limited in drought (McDowell, 2011; Weber et al., 2007). Slower growth rates on dry control in comparison to irrigated plots have been measured also in Pfynwald (Schaub et al., 2016; Zweifel et al., 2020). However, the methanol emissions rates from irrigated trees did eventually decrease with drying conditions, suggesting limitations in the methanol production or transport. Among the dry control trees that probably have low transpiration and sap flow rates, a larger share of the methanol produced in the stem is potentially directly emitted rather than captured and transported upwards in the xylem sap, increasing the local emission rates in the lower parts of stem. Overall, these results show that the dynamics of methanol sources in trees are still not well understood.

5 | CONCLUSIONS

Measuring VOC emissions from Scots pine stems in a drought-prone forest showed that stems may be large monoterpene sources. This highlights the importance of considering stem emissions in stand-level emission budgets and studying the role of stem emissions and stem emission dynamics in various environments. Drought seemed to reduce the emissions of monoterpenes, acetone and acetaldehyde, but integrating the impacts of potential secondary biotic stressors would be an important next step for better understanding drought effects on tree-level emissions.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

DATA AVAILABILITY STATEMENT

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

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REFERENCES

- Aaltonen, H., Pumpanen, J., Pihlatie, M., Hakola, H., Hellén, H., Kulmala, L. et al. (2011) Boreal pine forest floor biogenic volatile organic compound emissions peak in early summer and autumn. *Agricultural and Forest Meteorology*, 151, 682–691.
- Altimir, N., Kolari, P., Tuovinen, J.-P., Vesala, T., Bäck, J., Suni, T. et al. (2006) Foliage surface ozone deposition: a role for surface moisture? *Biogeosciences*, 3, 209–228.
- Amin, H., Atkins, P.T., Russo, R.S., Brown, A.W., Sive, B., Hallar, A.G. et al. (2012) Effect of bark beetle infestation on secondary organic aerosol precursor emissions. *Environmental Science & Technology*, 46, 5696–5703.
- Amin, H., Russo, R.S., Sive, B., Richard Hoebeke, E., Dodson, C., McCubbin, I.B. et al. (2013) Monoterpene emissions from bark beetle infested Engelmann spruce trees. *Atmospheric Environment*, 72, 130–133.
- Atkinson, R. (2000) Atmospheric chemistry of VOCs and NO(x). *Atmospheric Environment*, 34, 2063–2101.
- Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q. & Boy, M. (2012) Chemodiversity of a Scots pine stand and implications for terpene air concentrations. *Biogeosciences*, 9, 689–702.
- Bäck, J., Aaltonen, H., Hellén, H., Kajos, M.K., Patokoski, J., Taipale, R. et al. (2010) Variable emissions of microbial volatile organic compounds (MVOCs) from root-associated fungi isolated from Scots pine. *Atmospheric Environment*, 44, 3651–3659.
- Berg, A.R., Heald, C.L., Huff Hartz, K.E., Hallar, A.G., Meddens, A.J.H., Hicke, J.A. et al. (2013) The impact of bark beetle infestations on monoterpene emissions and secondary organic aerosol formation in western North America. *Atmospheric Chemistry and Physics*, 13, 3149–3161.
- Bertin, N. & Staudt, M. (1996) Effect of water stress on monoterpene emissions from young potted holm oak (*Quercus ilex* L.) trees. *Oecologia*, 107, 456–462.
- Blanch, J.S., Peñuelas, J. & Llusà, J. (2007) Sensitivity of terpene emissions to drought and fertilization in terpene-storing *Pinus halepensis* and non-storing *Quercus ilex*. *Physiologia Plantarum*, 131, 211–225.
- Bose, A.K., Rigling, A., Gessler, A., Hagedorn, F., Brunner, I. & Feichtinger, L. (2021, in press) Lessons learned from a long-term irrigation experiment in a dry Scots pine forest: impacts on traits and functioning. *Ecological Monographs*.
- Bourtsoukidis, E., Kawaletz, H., Radacki, D., Schütz, S., Hakola, H., Hellén, H. et al. (2014) Impact of flooding and drought conditions on the emission of volatile organic compounds of *Quercus robur* and *Prunus serotina*. *Trees*, 28, 193–204.
- Bouwmeester, H., Schuurink, R.C., Bleeker, P.M. & Schiestl, F. (2019) The role of volatiles in plant communication. *The Plant Journal*, 100, 892–907.
- Brunner, I., Pannatier, E.G., Frey, B., Rigling, A., Landolt, W., Zimmermann, S. et al. (2009) Morphological and physiological responses of Scots pine fine roots to water supply in a dry climatic region in Switzerland. *Tree Physiology*, 29, 541–550.
- Dobbertin, M., Eilmann, B., Bleuler, P., Giuggiola, A., Graf Pannatier, E., Landolt, W. et al. (2010) Effect of irrigation on needle morphology, shoot and stem growth in a drought-exposed *Pinus sylvestris* forest. *Tree Physiology*, 30, 346–360.
- Dobbertin, M., Hug, C. & Mizoue, N. (2004) Using slides to test for changes in crown defoliation assessment methods. Part I: visual assessment of slides. *Environmental Monitoring and Assessment*, 98, 295–306.
- Fall, R. (2003) Abundant oxygenates in the atmosphere: a biochemical perspective. *Chemical Reviews*, 103, 4941–4951.
- Filella, I., Peñuelas, J. & Seco, R. (2009) Short-chained oxygenated VOC emissions in *Pinus halepensis* in response to changes in water availability. *Acta Physiologiae Plantarum*, 31, 311–318.
- Folkers, A., Hüve, K., Ammann, C., Dindorf, T., Kesselmeier, J., Kleist, E. et al. (2008) Methanol emissions from deciduous tree species: dependence on temperature and light intensity. *Plant Biology*, 10, 65–75.
- Galbally, I.E. & Kirstine, W. (2002) The production of methanol by flowering plants and the global cycle of methanol. *Journal of Atmospheric Chemistry*, 43, 195–229.
- Gara, R.I., Littke, W.R. & Rhoades, D.F. (1993) Emission of ethanol and monoterpenes by fungal infected lodgepole pine trees. *Phytochemistry*, 34, 987–990.
- Ghimire, R.P., Kivimäenpää, M., Blomqvist, M., Holopainen, T., Lyytikäinen-Saarenmaa, P. & Holopainen, J.K. (2016) Effect of bark beetle (*Ips typographus* L.) attack on bark VOC emissions of Norway spruce (*Picea abies* Karst.) trees. *Atmospheric Environment*, 126, 145–152.
- Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J.P. & Rinne, J. (2010) Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by ¹³C₂ labelling and PTR-MS analysis. *Plant, Cell and Environment*, 33, 781–792.
- Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K. & Fall, R. (1993) Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. *Journal of Geophysical Research*, 98, 12609–12617.
- Heijari, J., Blande, J.D. & Holopainen, J.K. (2011) Feeding of large pine weevil on Scots pine stem triggers localised bark and systemic shoot emission of volatile organic compounds. *Environmental and Experimental Botany*, 71, 390–398.
- Helmig, D., Greenberg, J., Guenther, A., Zimmerman, P. & Geron, C. (1998) Volatile organic compounds and isoprene oxidation products at a temperate deciduous forest site. *Journal of Geophysical Research: Atmospheres*, 103, 22397–22414.
- Herms, D.A. & Mattson, W.J. (1992) The dilemma of plants: to grow or defend. *Quarterly Review of Biology*, 67, 283–335.
- Herzog, C., Steffen, J., Graf Pannatier, E., Hajdas, I. & Brunner, I. (2014) Nine years of irrigation cause vegetation and fine root shifts in a water-limited pine forest. *PLoS One*, 9, e116642.
- Hüve, K., Christ, M.M., Kleist, E., Uerlings, R., Niinemets, Ü., Walter, A. et al. (2007) Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata. *Journal of Experimental Botany*, 58, 1783–1793.

- Iivonen, S., Rikala, R. & Vapaavuori, E. (2001) Seasonal root growth of Scots pine seedlings in relation to shoot phenology, carbohydrate status, and nutrient supply. *Canadian Journal of Forest Research*, 31, 1569–1578.
- Jia, G., Shevliakova, E., Artaxo, P., De Noblet-Ducoudré, N., Houghton, R., House, J. et al. (2019) Land–climate interactions. In: Shukla, P.R., Skea, J., Calvo Buendia, E., Masson-Delmotte, V., Pörtner, H.-O., Roberts, D.C., Zhai, P., Slade, R., Connors, S., van Diemen, R., Ferrat, M., Haughey, E., Luz, S., Neogi, S., Pathak, M., Petzold, J., Portugal Pereira, J., Vyas, P., Huntley, E., Kissick, K., Belkacemi, M. & Malley, J. (Eds.) *Climate Change and Land: An IPCC special report on climate change, desertification, land degradation, sustainable land management, food security, and greenhouse gas fluxes in terrestrial ecosystems*.
- Kaplan, J.O., Folberth, G. & Hauglustaine, D.A. (2006) Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations. *Global Biogeochemical Cycles*, 20, 1–16.
- Kovalchuk, A., Raffaello, T., Jaber, E., Kerö, S., Ghimire, R., Lorenz, W.W. et al. (2015) Activation of defence pathways in Scots pine bark after feeding by pine weevil (*Hylobius abietis*). *BMC Genomics*, 16, 352–1–15.
- Kreuzwieser, J., Harren, F.J.M., Laarhoven, L.J.J., Boamfa, I., Te lintel-Hekkert, S., Scheerer, U. et al. (2001) Acetaldehyde emission by the leaves of trees—correlation with physiological and environmental parameters. *Physiologia Plantarum*, 113, 41–49.
- Kreuzwieser, J., Kühnemann, F., Martis, A., Rennenberg, H. & Urban, W. (2000) Diurnal pattern of acetaldehyde emission by flooded poplar trees. *Physiologia Plantarum*, 108, 79–86.
- Kreuzwieser, J., Scheerer, U. & Rennenberg, H. (1999) Metabolic origin of acetaldehyde emitted by poplar (*Populus tremula* × *P. alba*) trees. *Journal of Experimental Botany*, 50, 757–765.
- Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H.E., Nieminen, T. et al. (2013) Direct observations of atmospheric aerosol nucleation. *Science*, 339, 943–946.
- Kulmala, M., Nieminen, T., Nikandrova, A., Lehtipalo, K., Manninen, H.E., Kajos, M.K. et al. (2014) CO₂-induced terrestrial climate feedback mechanism: from carbon sink to aerosol source and back. *Boreal Environment Research*, 19, 122–131.
- Lerdau, M., Litvak, M. & Monson, R. (1994) Plant chemical defense: monoterpenes and the growth-differentiation balance hypothesis. *Trends in Ecology and Evolution*, 9, 52–57.
- Llusà, J. & Peñuelas, J. (1998) Changes in terpene content and emission in potted Mediterranean woody plants under severe drought. *Canadian Journal of Botany*, 76, 1366–1373.
- Loreto, F. & Schnitzler, J.P. (2010) Abiotic stresses and induced BVOCs. *Trends in Plant Science*, 15, 154–166.
- Lüpke, M., Leuchner, M., Steinbrecher, R. & Menzel, A. (2016) Impact of summer drought on isoprenoid emissions and carbon sink of three Scots pine provenances. *Tree Physiology*, 36, 1382–1399.
- Lüpke, M., Leuchner, M., Steinbrecher, R. & Menzel, A. (2017) Quantification of monoterpene emission sources of a conifer species in response to experimental drought. *AoB PLANTS*, 9, plx045.
- Lusebrink, I., Erbilgin, N. & Evenden, M.L. (2013) The Lodgepole × Jack Pine hybrid zone in Alberta, Canada: a stepping stone for the mountain pine beetle on its journey east across the boreal forest? *Journal of Chemical Ecology*, 39, 1209–1220.
- Lusebrink, I., Erbilgin, N. & Evenden, M.L. (2016) The effect of water limitation on volatile emission, tree defense response, and brood success of *Dendroctonus ponderosae* in two pine hosts, lodgepole, and jack pine. *Frontiers in Ecology and Evolution*, 4, 2.
- Mäki, M., Heinonsalo, J., Hellen, H. & Back, J. (2017) Contribution of understorey vegetation and soil processes to boreal forest isoprenoid exchange. *Biogenosciences*, 14, 1055–1073.
- McDowell, N.G. (2011) Mechanisms linking drought, hydraulics, carbon metabolism, and vegetation mortality. *Plant Physiology*, 155, 1051–1059.
- Niinemets, Ü., Loreto, F. & Reichstein, M. (2004) Physiological and physicochemical controls on foliar volatile organic compound emissions. *Trends in Plant Science*, 9, 180–186.
- Niinemets, Ü. & Monson, R. (Eds.) (2013) *Biology, controls and models of tree volatile organic compound emissions*, 1st edition. Dordrecht, the Netherlands: Springer Science+Business Media.
- OFEV (Ed.) (2019) La canicule et la sécheresse de l'été 2018. Impacts sur l'homme et l'environnement. Office fédéral de l'environnement, Berne. État de l'environnement n° 1909: 91 p.
- Ormeño, E., Mévy, J.P., Vila, B., Bousquet-Mélou, A., Greff, S., Bonin, G. et al. (2007) Water deficit stress induces different monoterpene and sesquiterpene emission changes in Mediterranean species. Relationship between terpene emissions and plant water potential. *Chemosphere*, 67, 276–284.
- Paasonen, P., Asmi, A., Petäjä, T., Kajos, M.K., Äijälä, M., Junninen, H. et al. (2013) Warming-induced increase in aerosol number concentration likely to moderate climate change. *Nature Geoscience*, 6, 438–442.
- Phillips, M.A. & Croteau, R.B. (1999) Resin-based defenses in conifers. *Trends in Plant Science*, 4, 184–190.
- Pinheiro, J., Bated, D., DebRoy, S. & Sarkar, D. & R Core Team. (2021) nlme: linear and nonlinear mixed effect models. R Package Version, 3.1-152. <https://CRAN.R-project.org/package=nlme>
- Reid, M.L., Sekhon, J.K. & LaFramboise, L.M. (2017) Toxicity of monoterpene structure, diversity and concentration to mountain pine beetles, *Dendroctonus ponderosae*: beetle traits matter more. *Journal of Chemical Ecology*, 43, 351–361.
- Rhoades, D.F. (1990) Analysis of monoterpenes emitted and absorbed by undamaged boles of lodgepole pine. *Phytochemistry*, 29, 1463–1465.
- Rigling, A., Brühlhart, H., Bräker, O.U., Forster, T. & Schweingruber, F.H. (2003) Effects of irrigation on diameter growth and vertical resin duct production in *Pinus sylvestris* L. on dry sites in the central Alps, Switzerland. *Forest Ecology and Management*, 175, 285–296.
- van Rij, J., Wieling, M., Baayen, H. & van Rij, H. (2020) Interpreting time series and autocorrelated data using GAMMs. R. package version, 2.4.
- Rissanen, K., Hölttä, T. & Bäck, J. (2018) Transpiration directly regulates the emissions of water-soluble short-chained OVOCs. *Plant Cell and Environment*, 41, 2288–2298.
- Rissanen, K., Hölttä, T., Bäck, J., Rigling, A., Wermelinger, B. & Gessler, A. (2021) Drought effects on carbon allocation to resin defences and on resin dynamics in old-grown Scots pine. *Environmental and Experimental Botany*, 185, 104410.
- Rissanen, K., Hölttä, T., Vanhatalo, A., Aalto, J., Nikinmaa, E., Rita, H. et al. (2016) Diurnal patterns in Scots pine stem oleoresin pressure in a boreal forest. *Plant Cell and Environment*, 39, 527–538.
- Rissanen, K., Vanhatalo, A., Salmon, Y., Bäck, J. & Hölttä, T. (2020) Stem emissions of monoterpenes, acetaldehyde, and methanol from Scots pine (*Pinus sylvestris* L.) affected by tree water relations and cambial growth. *Plant, Cell & Environment*, 43, 1751–1765.
- Salmon, Y., Dietrich, L., Sevanto, S., Hölttä, T., Dannoura, M. & Epron, D. (2019) Drought impacts on tree phloem: from cell-level responses to ecological significance. *Tree Physiology*, 39, 173–191.
- Schade, G.W. & Goldstein, A.H. (2001) Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation. *Journal of Geophysical Research Atmospheres*, 107, ACH 2-1–ACH 2-8.
- Schade, G.W., Goldstein, A.H. & Lamanna, M.S. (1999) Are monoterpene emissions influenced by humidity? *Geophysical Research Letters*, 26, 2187–2190.
- Schaub, M., Haeni, M., Hug, C., Gessler, A. & Rigling, A. (2016) Tree measurements 2002–2016 from the long-term irrigation experiment Pfynwald, Switzerland. Dataset <https://doi.org/10.16904/11>
- Schönbeck, L., Gessler, A., Schaub, M., Rigling, A., Hoch, G., Kahmen, A. et al. (2020) Soil nutrients and lowered source:sink ratio mitigate effects of mild but not of extreme drought in trees. *Environmental and Experimental Botany*, 169, 103905.

- Schönbeck, L., Grossiord, C., Gessler, A., Gisler, J., Meusbürger, K. & D'Odorico, P. et al. (2021) Photosynthetic acclimation and sensitivity to short- and long-term environmental changes. *bioRxiv*, 2021.01.04. 425174.
- Sevanto, S. (2018) Drought impacts on phloem transport. *Current Opinion in Plant Biology*, 43, 76–81.
- Seybold, S.J., Huber, D.P.W., Lee, J.C., Graves, A.D. & Bohlmann, J. (2006) Pine monoterpenes and pine bark beetles: a marriage of convenience for defense and chemical communication. *Phytochemistry Reviews*, 5, 143–178.
- Smith, R.H. (1965) Effect of monoterpene vapors on the western pine beetle. *Journal of Economic Entomology*, 58, 509–510.
- Staudt, M., Byron, J., Piquemal, K. & Williams, J. (2019) Compartment specific chiral pinene emissions identified in a Maritime pine forest. *Science of the Total Environment*, 654, 1158–1166.
- Staudt, M., Ennajah, A., Mouillot, F. & Joffre, R. (2008) Do volatile organic compound emissions of Tunisian cork oak populations originating from contrasting climatic conditions differ in their responses to summer drought? *Canadian Journal of Forest Research*, 38, 2965–2975.
- Staudt, M., Rambal, S., Joffre, R. & Kesselmeier, J. (2002) Impact of drought on seasonal monoterpene emissions from *Quercus ilex* in southern France. *Journal of Geophysical Research Atmospheres*, 107, ACH 15-1–ACH 15-9.
- Sturgeon, K.B. (1979) Monoterpene variation in ponderosa pine xylem resin related to western pine beetle predation. *Evolution*, 33, 803–814.
- Taipale, R., Ruuskanen, T.M., Rinne, J., Kajos, M.K., Hakola, H., Pohja, T. et al. (2008) Technical note: quantitative long-term measurements of VOC concentrations by PTR-MS—measurement, calibration, and volume mixing ratio calculation methods. *Atmospheric Chemistry and Physics*, 8, 6681–6698.
- Thoss, V. & Byers, J.A. (2006) Monoterpene chemodiversity of ponderosa pine in relation to herbivory and bark beetle colonization. *Chemoecology*, 16, 51–58.
- Tingey, D.T., Turner, D.P. & Weber, J.A. (1991) Factors controlling the emissions of monoterpenes and other volatile organic compounds. In: Sharkey, T.D., Holland, E.A. & Mooney, H.A. (Eds.) *Trace gas emissions by plant*. San Diego: Academic Press Inc., pp. 93–119.
- Tingey, M.D.T. (1980) Influence of light and temperature on monoterpene emission rates from slash pine. *Plant Physiology*, 65, 797–801.
- Vanhatalo, A., Aalto, J., Chan, T., Hölttä, T., Kolari, P., Rissanen, K. et al. (2020) Scots pine stems as dynamic sources of isoprenoid and methanol emissions. *Frontiers in Forests and Global Change*, 2, 95.
- Vanhatalo, A., Chan, T., Aalto, J., Korhonen, J.F., Kolari, P., Hölttä, T. et al. (2015) Tree water relations can trigger monoterpene emissions from Scots pine stems during spring recovery. *Biogeosciences*, 12, 5353–5363.
- Vanhatalo, A., Ghirardo, A., Juurola, E., Schnitzler, J.P., Zimmer, I., Hellén, H. et al. (2018) Long-term dynamics of monoterpene synthase activities, monoterpene storage pools and emissions in boreal Scots pine. *Biogeosciences*, 15, 5047–5060.
- Velikova, V., Sharkey, T.D. & Loreto, F. (2012) Stabilization of thylakoid membranes in isoprene-emitting plants reduces formation of reactive oxygen species. *Plant Signaling & Behavior*, 7, 139–141.
- Warneke, C., Karl, T., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W. et al. (1999) Acetone, methanol, and other partially oxidized volatile organic emissions from dead plant matter by abiological processes: significance for atmospheric HO(X) chemistry. *Global Biogeochemical Cycles*, 13, 9–17.
- Weber, P., Bugmann, H. & Rigling, A. (2007) Radial growth responses to drought of *Pinus sylvestris* and *Quercus pubescens* in an inner-Alpine dry valley. *Journal of Vegetation Science*, 18, 777–792.
- Wood, S. (2017) *Generalized additive models: an introduction with R*, 2nd edition. Chapman and Hall/CRC.
- Wu, C., Pullinen, I., Andres, S., Carriero, G., Fares, S., Goldbach, H. et al. (2015) Impacts of soil moisture on de novo monoterpene emissions from European beech, Holm oak, Scots pine, and Norway spruce. *Biogeosciences*, 12, 177–191.
- Ziemann, P.J. & Atkinson, R. (2012) Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chemical Society Reviews*, 41, 6582–6605.
- Zweifel, R., Etzold, S., Sterck, F., Gessler, A., Anfodillo, T., Mencuccini, M. et al. (2020) Determinants of legacy effects in pine trees—implications from an irrigation-stop experiment. *New Phytologist*, 277, 1081–1096.

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