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Instantaneous intraday changes in key meteorological parameters as a proxy for the mixing ratio of BVOCs over vegetation under drought conditions

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Abstract

Biogenic volatile organic compounds (BVOCs) exert a significant influence on photochemical air pollution and climate change, with their emissions strongly affected by meteorological conditions. However, the effect of drought on BVOC emissions is not well-characterized, limiting the predictive power of this feedback on climate change and air quality. This study hypothesized that under severe drought conditions, BVOC emissions will be more sensitive to instantaneous intraday variations in meteorological parameters than to the absolute values of those parameters. To test this hypothesis, we employed proton transfer reaction time-of-flight mass spectrometry to quantify the mixing ratios of a suite of soluble and insoluble VOCs, including isoprene, monoterpenes, sesquiterpenes, acetone, acetaldehyde, methanol, ethanol, formaldehyde, formic acid, acetic acid, 1,3-butadiene, dimethyl sulfide (DMS), and H_2S, under severe drought conditions in a natural Eastern Mediterranean forest in autumn 2016. Except for H_2S, which was used as a control, and to a certain extent DMS, all measured VOCs exhibited a strong response to changes in relative humidity, with lower mixing ratios observed around noon, suggesting inhibition of BVOC emission under the relatively high temperature and low relative humidity of drought conditions. Notably, our analysis revealed that instantaneous changes in meteorological conditions, especially in relative humidity, can serve as a better proxy for drought-related changes in BVOC emission rate than the absolute values of meteorological parameters. These findings are supported by direct flux measurements conducted in a mixed Mediterranean forest under drought conditions, in the same region, and presented as a companion article. The findings further highlight the importance of analyzing the effect of meteorological conditions on BVOC emissions under drought conditions on a daily—or shorter—timescale, and support biogenic emission sources for 1,3-butadiene.

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1 Introduction

Biogenic volatile organic compounds (BVOCs) are an important factor for accurate modeling of climate change and photochemical air pollution (Calfapietra et al., 2013; Curci et al., 2009; Peñuelas et al., 2009; Harper and Unger, 2018). BVOCs are thought to be emitted to protect the vegetation from biotic and abiotic stresses (Peñuelas and Munné-Bosch, 2005; Blande et al., 2007; Brilli et al., 2009; Berg et al., 2013), and for plant–plant and plant–animal communication (Baldwin et al., 2006; Filella et al., 2013; Trowbridge and Stoy, 2013). The emission rate of BVOCs depends on their rate of synthesis, physicochemical properties, and ambient conditions (Niinemets and Monson, 2013). Climate change leads to a significant change in the emission rate and composition of BVOCs. For instance, the emission rate of most BVOCs increases with temperature in an Arrhenius-type manner (Goldstein et al., 2004; Guenther et al., 1995; Monson et al., 1992; Niinemets et al., 2004; Tingey et al., 1990). However, drought can affect the emission and composition of BVOCs in a more complex manner (Fortunati et al., 2008; Peñuelas and Staudt, 2010; Holopainen and Gershenzon, 2010; Llusia et al., 2016; Schade et al., 1999), which is currently not well-characterized. Enhancing our understanding of the intricate mechanisms though which climate change influences BVOC emissions is crucial for improving model simulations and assessments of air quality and climate.

Drought affects the emission of BVOCs primarily via stomatal resistance, which is typically 2 orders of magnitude larger than cuticular resistance (Nobel, 1999). Hence, the effect of drought on BVOC emissions depends on environmental conditions, such as the level of the drought, and it is further complicated by plant types and properties, as well as the specific BVOC species. Soluble BVOCs such as alcohols and carboxylic acids, with Henry's law constants (H) on the order of 10^{-2}–10^{1} Pa m^3 mol^{-1}, are generally more sensitive to stomatal conductance than non-soluble BVOCs (Niinemets et al., 2004; Niinemets and Reichstein, 2003; Harley, 2013). However, these soluble

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species may be emitted at high rates under higher relative humidity (RH) during periods of drought (Filella et al., 2009; Loreto and Schnitzler, 2010).

The effect of drought on isoprene emission has been studied extensively and was shown to be delayed and/or smaller compared to its effect on photosynthesis rate (Tiiva et al., 2009; Niinemets, 2010; Zheng et al., 2017). Under moderate drought stress, only a moderate decrease or increase of isoprene was reported, but isoprene emission tends to decrease more significantly under more severe or prolonged drought stress (Pegoraro et al., 2005; Pegoraro et al., 2004; Sharkey and Loreto, 1993; Potosnak et al., 2014; Brilli et al., 2007). The effect of drought on the emission of other BVOCs, such as monoterpenes (MTs) and sesquiterpenes (SQTs), has been less extensively studied, but there is accumulating evidence of different responses to drought compared to isoprene, particularly for SQTs. SQT emission was shown to be less significantly reduced by moderate drought stress than that of MTs, isoprene, and some oxygenated BVOCs, with a potential rise close to the wilting point (Ormeño et al., 2007; Kreuzwieser et al., 2021; Hansen and Seufert, 1999; Bonn et al., 2019). According to Moradi et al. (2017), the effect of drought stress on terpenes such as MTs and SQTs also depends on the sensitivity of the specific plants to drought stress, where in more tolerant plants, either increased or stable emission rates of SQTs and MTs can occur under relatively prolonged stress.

The way in which meteorological conditions affect BVOC emission under drought conditions should be strongly related to their effect on stomatal conductance (Niinemets and Monson, 2013; Nobel, 2009). Under these conditions, stomatal conductance typically demonstrates morning and afternoon peaks, associated with the so-called midday depression (e.g., Li et al., 2019; Seco et al., 2017). Notably, these peaks are typically accompanied by a monotonic trend in RH and temperature. Hence, we hypothesize that stomatal conductance and consequently, BVOC emissions, are more sensitive to intraday variations in meteorological conditions than to the absolute values of those

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parameters. This hypothesis is also supported by the fact that the morning peaks in BVOC emissions often coincide with temperature and RH values that differ significantly from those associated with the afternoon peaks.

Previous studies in the Eastern Mediterranean have indicated that activity of the natural vegetation in this region tends to decrease under prolonged drought conditions in the absence of rain events (Maseyk et al., 2008; Rohatyn et al., 2018). Furthermore, Llusia et al. (2016) showed that during spring and summer in the Eastern Mediterranean, terpene emission rates are enhanced by warmer summer conditions but are strongly reduced under severe drought conditions. The Eastern Mediterranean is recognized as a global warming hotspot (Giorgi, 2006; IPCC, 2007; Lelieveld et al., 2012), associated with increasing drought conditions (Cook et al., 2016; Hoerling et al., 2012), particularly during the autumn (Li et al., 2019). Hence, we assumed that field measurements in this region during the autumn, under severe drought conditions, could be used to test our hypothesis and provide important insights into the effect of meteorological parameters on BVOC emission under drought.

2 Methods

2.1 Experimental site

The field measurements were carried out at the Beit Keshet Forest (Shibli) site (32.704680 N, 35.386608 E), located 36 km from the Eastern Mediterranean coast of northern Israel (see Fig. 1), at an elevation of 202 m above mean sea level. The site is approximately 1200 m × 900 m of moderate homogeneous slope, within a ca. 1000 ha forest covered by ~25% *Quercus calliprinos*, ~25% *Quercus ithaburensis*, ~20% *Pistacia terebinthus*, ~15% *Pistacia lentiscus*, ~10% *Pinus halepensis*, and ~5% *Pinus pinea*. Average canopy height is approximately 5 m. The site is exposed to a Mediterranean

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climate with an annual precipitation of 486 mm, and mean daily maximum and minimum temperatures of 27.4 °C and 15.0 °C, respectively.

2.2 Field measurements

The measurements at the Shibli site were performed between 6 Sep and 7 Nov 2016, and are described in more detail in (Li et al., 2019). The instrumentation setup included a platform for eddy covariance (EC) measurements of VOCs, ozone (O_3), carbon dioxide (CO_2) and water vapor (H_2O), sensible heat, latent heat, and momentum, as well as slower O_3 and NO_X measurements in an air-conditioned mobile laboratory which was located about 5 m from the EC tower, and another tower that was used for measurements of basic meteorological parameters. Note that due to a technical problem—a lack of synchronization resulting from the proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) data not being consistently recorded at the specified frequency of 10 Hz, VOC fluxes were not evaluated.

The VOC measurements were performed using a PTR-ToF-MS 8000 (Ionicon Analytik GmbH, Innsbruck, Austria; see (Graus et al., 2010; Jordan et al., 2009), as described in more detail in Dayan et al. (2020). Ambient air was pulled at a rate of about 35 L min^{-1} through a PFA Teflon tube (3/8 inch outer diameter, 5/16 inch inner diameter) and was directed to PTR-ToF-MS for sampling at a rate of 0.5 L min^{-1} through a 1/16 inch outer diameter polyether ether ketone tube. The measured data were recorded in a computer at a frequency of 10 Hz. The background (zero) and sensitivity (span) calibrations were performed every 3 h and weekly, respectively. Zero air for background calibration was obtained through a catalytic converter which was heated to 350 °C. Gas standards (Ionicon Analytik GmbH) were used for the sensitivity calibration. The raw hdf5 data files of the PTR-ToF-MS were preprocessed using PTRwid processing suite in the IDL environment (Holzinger, 2015). The EC

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measurements were performed at 10 Hz using a 3D anemometer (R3-100, Gill Instruments, Hampshire, UK). A fast closed-path dry chemiluminescent O_3 sensor (FOS V2.0.1, Sextant, New Zealand) and an open-path CO_2/H_2O gas analyzer (IRGA; LI-7500, LI-COR, Lincoln, NE, USA) were used to quantify the fluxes of O_3 and CO_2/H_2O, respectively.

O_3 mixing ratios were measured using a model 49i (Thermo Environmental Instruments Inc., Waltham, MA, USA) with a limit of detection of 1.0. Complementary meteorological measurements included wind speed and direction using an R.M. Young wind monitor 05103, temperature (T) and RH using a Campbell HC2S3 probe, and net radiation using a Kipp & Zonen CMP11 probe. The FOS, IRGA and sonic 3D data were recorded to a CR3000 data logger (Campbell Scientific, Logan, UT, USA) at a frequency of 10 Hz. T, RH, net radiation, O_3, and NO_X mixing ratio were recorded by a CR1000 data logger (Campbell Scientific) at 1 min time resolution.

2.3 Flux evaluation and partitioning

Flux evaluation and partitioning are described in more detail in (Li et al., 2019). Briefly, the fluxes of CO_2, H_2O, and O_3 were evaluated using the EddyPro 6.2.0 software (LI-COR), and partitioning of the fluxes to stomatal and non-stomatal flux was performed using the electric circuit analogy (Chamberlain and Chadwick, 1953). Daytime carbon assimilation (A) was evaluated by subtracting the respiration flux from the net measured CO_2 flux, individually for each diurnal cycle. The daytime respiration flux was evaluated by extrapolating the nighttime measured CO_2 flux, which presumably represents solely the respiration flux, according to Reichstein et al. (2005).

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2.4 Modeling of BVOC emission rate

BVOC emission rates were evaluated using the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGANv2.1; (Guenther et al., 2012), with an updated algorithm for the parameterized drought stress (Wang et al., 2022)). The major driving variables input into the model were species composition, light, leaf area index, vegetation cover fraction, T, and soil moisture. The model was configured using actual meteorological data measured onsite. Vegetation cover fraction and leaf area index inputs were determined using remote sensing (MOD44B and TERRA/MODIS, respectively). Root fraction was estimated based on soil samples collected in the region of the measurements. The wilting point was estimated based on the soil type as discussed for the specific measurement region in Ravikovitch et al. (1960).

Figure 1. Regional satellite image including the Shibli site. Background imagery from © Microsoft Bing Maps.

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3 Results and discussion

3.1 Identified VOCs used for the analyses

The following analyses rely on the assumption that the BVOC mixing ratios which were measured over the studied vegetation can be used as a proxy for their emission rate from the vegetation, and that this, in turn, will enable us to study the effect of meteorological conditions on the BVOC emission rate. However, considering that the correlation between meteorological conditions and mixing ratios can be indirectly affected by the impact of meteorological conditions on the mixing height and chemical loss rate, we also focus on VOCs that presumably originated predominantly from anthropogenic sources as a control.

Anthropogenic VOCs (AVOCs) presumably include 1,3-butadiene (m/z = 55.055) (Knighton et al., 2009) and hydrogen sulfide (H_2S) (m/z = 34.995) (Li et al., 2014); however, our analyses indicated that the former is predominantly emitted from biogenic sources during the measurements. BVOCs presumably include MTs (m/z = 137.133, m/z = 95.086, m/z = 81.070), isoprene + 2-methyl-3-buten-2-ol (MBO) (m/z = 69.071; m69), dimethyl sulfide (DMS) (m/z = 63.062), acetone (m/z = 59.049), acetaldehyde (m/z = 45.033), the sum of methyl vinyl ketone and methacrolein (MVK + MACR) (m/z = 71.048) (Janson and Serves, 2001; Karl et al., 2003; Park et al., 2013; Kanda and Tsuruta, 1995), ethanol (m/z = 47.0497), methanol (m/z = 33.032), formic acid (m/z = 47.0133), acetic acid (m/z = 61.029), and SQTs (m/z = 205.195) (Jordan et al., 2009; Park et al., 2013). This classification is based on the correlation of the VOCs with meteorological parameters, as described in Sect. 3.3 and 3.4, as well as on our previous analysis of measurements in a mixed Mediterranean vegetation site in Ramat Hanadiv (located 44.4 km southwest of the Shibli site (Dayan et al., 2020)). Table 1 compares the observed BVOC mixing ratios with the predicted emission rates for the different BVOCs based on the MEGAN simulations. The mixing ratios are presented for day of year (DOY)

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306 and 309–313, for which high-quality measurements are available. It is remarkable to note that the SQT levels are higher than those of the MTs by about 1.5 orders of magnitude, emphasizing the relevance of the measurement site in studying the effects of drought on atmospheric chemistry via changes in SQT emission.

Table 1. Comparison of mean and standard deviation of BVOC emission rates as predicted by MEGAN and the observed mixing ratios, for day of year (DOY) 306 and 309–313. The values are scaled on a white–red color scale, individually for each column in the table.

Compounds	MEGAN ($mg\ m^{-2}\ h^{-1}$)		Measurement (ppbv)	
	Mean	Standard deviation	Mean	Standard deviation
Isoprene+MBO	3.887E-03	1.656E-02	0.081	0.029
Total MTs	11.142	10.815	0.144	0.078
Myrcene	0.534	0.518		
Sabinene	1.112	1.079		
Limonene	1.631	1.583		
3-Carene	0.541	0.525		
t-β-Ocimene	1.631	1.583		
β-Pinene	1.705	1.655		
α-Pinene	3.262	3.166		
Other MTs	0.726	0.705		
Total SQTs	1.217	1.967	2.718	0.694
α-Farnescene	0.152	0.246		
β-Caryophyllene	0.304	0.492		
Other SQTs	0.761	1.229		
Total MT+SQT	12.359	12.782	2.863	0.772
Methanol	4.802	8.171	2.740	1.333
Acetone	2.406	1.579	2.875	0.652
Bidirectional VOCs	1.786	4.069		
Stress VOCs	1.348	2.587		
Other VOCs	1.403	0.921		
DMS	0.000	0.000	0.078	0.029
Acetaldehyde	0.000	0.000	1.521	0.426

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3.2 Spatial heterogeneity in the measured VOCs' mixing ratios

Spatial non-homogeneity in the measured VOCs' mixing ratios for different wind directions can affect the interpretation of the effect of changing meteorological conditions on the measured mixing ratios. Such non-homogeneity may result from heterogeneous spatial transport of the measured VOCs from outside the investigated measurement area, or to non-homogeneity in the emission of the BVOCs within the study area due to spatial variations in the vegetation cover and type and/or soil properties.

Figure 2 presents, individually for each of the investigated VOCs, the percentage of time that the daytime-investigated VOCs' mixing ratios (Fig. 2b-o) and time (Fig. 2a) fall in a specific range for 12 equally sized wind direction ranges. Figure 2a clearly demonstrates the role of sea and land breezes in determining the wind direction during the day: in the morning, air masses mostly originated from the eastern and southern sectors, while in the afternoon, they originated mostly from the western sector. This may lead to difficulty in interpreting the reason for changes in the measured BVOC mixing ratios for different wind directions, considering that both wind direction and meteorological conditions, such as solar radiation, T, and RH, change with time in a systematic manner during the day. Sea and land breezes can also cause systematic differences in the air moisture in the measurement area, for different wind directions and time, directly affecting the BVOCs' emission rates and mixing ratios. Note that the sea breeze has been shown to transport moisture from the Eastern Mediterranean Sea to over tens of kilometers from the coast (Li et al., 2019; Derimian et al., 2017; Naor et al., 2017).

Overall, Fig. 2 demonstrates a weak association between the measured VOCs and wind direction. DMS, H_2S, MVK + MACR, and formic acid showed no clear association with wind direction during the daytime. For 1,3-butadiene, isoprene + MBO, and MT, elevated daytime mixing ratios originated predominantly from the southwestern sector. SQT, acetone, acetaldehyde, ethanol, formaldehyde, and acetic acid were associated with somewhat elevated mixing ratios for the

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227 northeastern sector during the daytime. In Sect. 3.3 and 3.4, the association of the measured VOCs
228 with meteorological parameters is investigated.

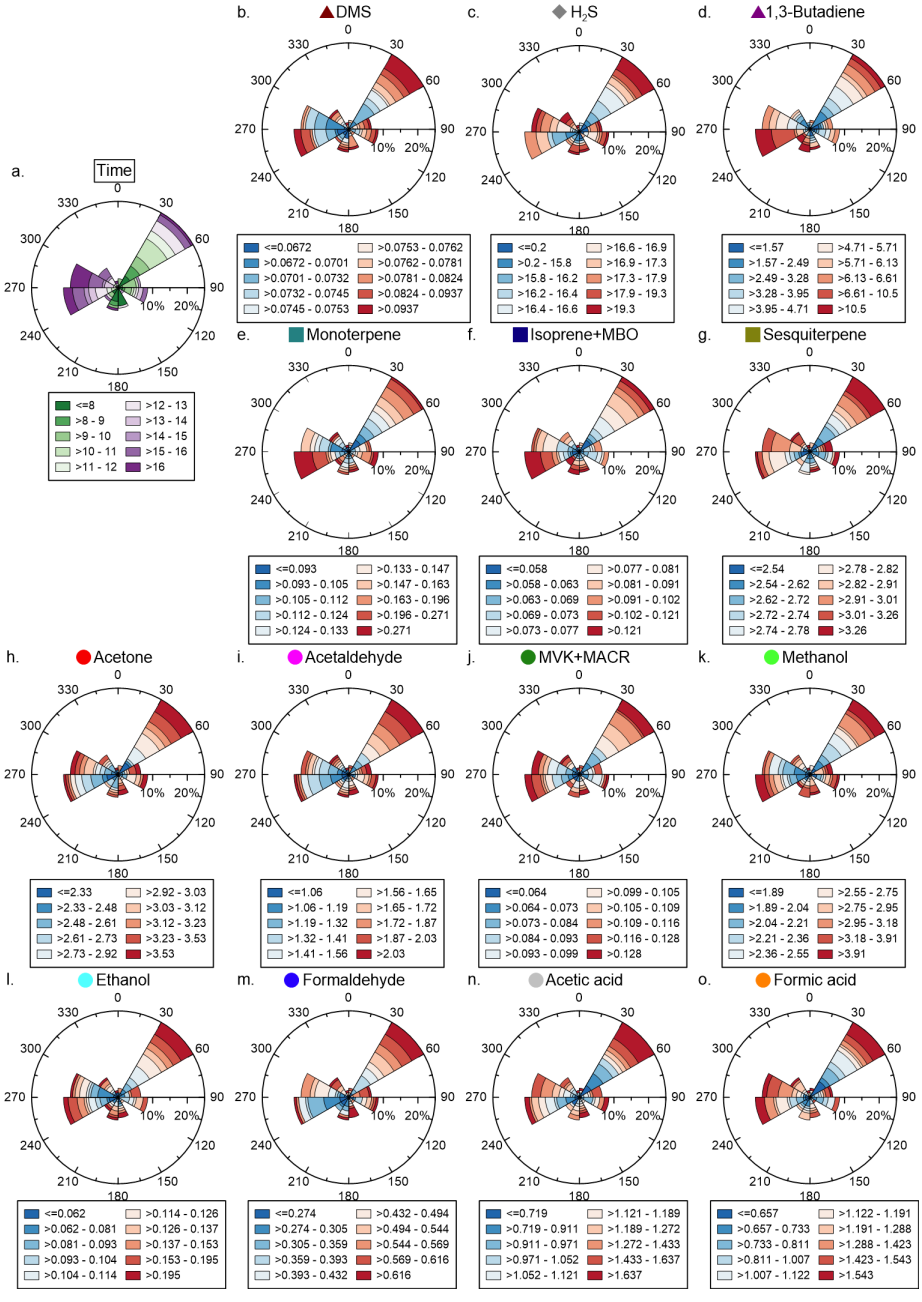

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Figure 2. Mixing ratio vs. wind direction for selected VOCs during the daytime. Presented is the percentage of time for which the measured mixing ratios of VOCs fall in a specific range, specified by an evenly distributed color scale, individually for each of 12 wind sectors. Circular symbols represent presumed soluble BVOCs, square symbols represent presumed insoluble BVOCs, rhombus symbols represent presumed AVOCs, and triangular symbols represent either presumed AVOCs or insoluble BVOCs. See more information on VOC solubility in Table 2.

3.3 Drought effect on vegetation activity and measured VOC mixing ratios

The Eastern Mediterranean region experiences a notable scarcity of rainfall during the summer, leading to drought conditions at the end of the summer and beginning of autumn. For instance, the mean integrated precipitation amounts between May/June and September/October for the years 2013–2023, recorded at the Tavor Kadoorie station located 2 km from the measurement site near Shibli, is only 14.1 mm. It is remarkable that in 2016, daily precipitation was consistently below 1.1 mm for 157 days until DOY 306, the first day included in our analysis. The drought that develops at the end of summer and in early autumn affects BVOC emissions in the Eastern Mediterranean (Li et al., 2019; Llusia et al., 2016; Rohatyn et al., 2018). To verify drought conditions during the field measurements, we used calculated stomatal CO_2 flux as a proxy for vegetation activity in the footprint area. Figure 3 presents the ecosystem gross primary production (GPP) CO_2 flux, net measured water flux, and RH for DOY 283–313 (9 Oct–8 Nov; Fig. 3a), and for DOY 306 – 313 (1 Nov–8 Nov), the measured ecosystem GPP CO_2 flux and net water vapor flux (Fig. 3b), and measured T, RH, and vapor pressure deficit (VPD) (Fig. 3c). The analyses presented herein focus on DOY 306 and DOY 309–313, for which high-quality VOC measurements are available. Both DOY 283–313 and DOY 306–313 were characterized by apparently low vegetation activity with a mean daytime stomatal CO_2 flux of 4.16 and 0.70 μmol s^{-1} m^{-2}, respectively. As indicated in Fig. 3c, DOY 306–313 was characterized by low RH, down to

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less than 30%, with a daily minimum at 12:30 h. These low RH levels corresponded with relatively high T and VPD values.

Low vegetation activity during the summer and autumn is typical for the Eastern Mediterranean and particularly for the measurement area (Li et al., 2019). For instance, the calculated mean diurnal net CO_2 flux during the autumn in Ramat Hanadiv (located 44.4 km southwest of the site) was 1.0 µmol s^{-1} m^{-2} in 2015–2016, compared to 0.2 and -2.6 µmol s^{-1} m^{-2} in the winter and spring, respectively. The corresponding mean seasonal net ecosystem production (NEP) for the measurement period is 21.6 g C m^{-2}, significantly lower than the mean seasonal NEP in Ramat Hanadiv during the spring (241 g C m^{-2}; see Fig. S1).

DOY 306 was an exception. On this day, a rain event was recorded, resulting in relatively high stomatal CO_2 and evapotranspiration fluxes between 10:00 and 12:00 h, while GPP dropped back from 15.84 to 0.01 µmol s^{-1} m^{-2} at 13:00 h (Fig. 3b). The relatively high evapotranspiration flux on that day was followed by a positive CO_2 flux, which can be explained by the enhanced respiration (see Fig. S2). Relatively high stomatal CO_2 flux also occurred on DOY 311, which can be attributed to the relatively high RH on this specific day (Figs. 3b, 3c).

No clear diurnal pattern was observed for the stomatal CO_2 flux, which was nearly zero during all or most of the day, between DOY 306 and DOY 311. Therefore, it was not possible to use CO_2 flux as a proxy for vegetation activity during the day. Instead, we used the meteorological parameters as potential proxies for the regulation of BVOC emission under drought stress, via their effect on stomatal conductance (Sect. 1). Based on the data presented in Fig. 3c, minimum daily RH was lower than 35% for all days except DOY 306, with a minimum daily RH of 55%, and reached as low as 18% on DOY 313. While day-to-day changes in T were relatively more moderate than those in RH, day-to-day changes in VPD were also relatively large (Fig. 3c). We hypothesized that these day-to-day and

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intraday changes in RH and VPD can be used as good proxies for the observed changes in BVOC mixing ratios under drought conditions. In the following, we investigate the response of the measured VOC mixing ratios to changes in RH, T, VPD, and global solar radiation (GSR) as proxies for the effect of meteorological conditions on BVOC emissions under drought stress.

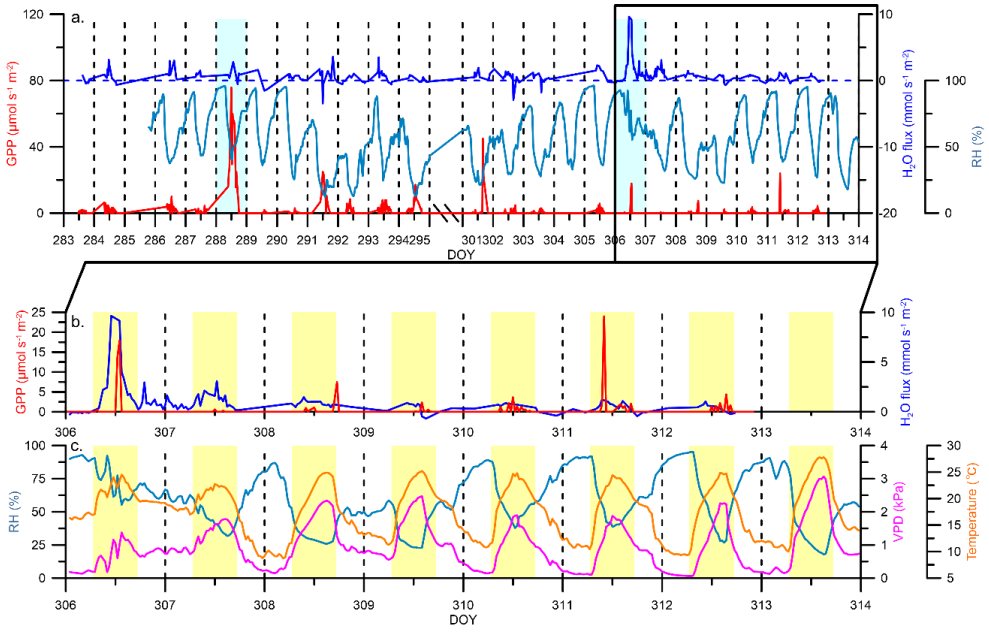

Figure 3. Drought and rain effects on vegetation activity. (a) Measured H_2O flux (blue), ecosystem gross primary production (GPP) CO_2 flux (red), and RH (cyan) on DOY 283–313. Shaded blue rectangle represents rain event. (b) Measured ecosystem GPP CO_2 flux and net H_2O flux on DOY 306–313. (c) Measured T, VPD, and RH on DOY 306–313. Yellow shading represents daytime.

Figure 4 presents the mean measured daytime time series of the various investigated VOCs, together with the corresponding T, RH, and GSR. In general, the VOCs showed an increase in mixing ratios following sunrise at ~06:00 h until around 08:00–10:00 h, along with the increasing T, as can be expected for BVOCs, including soluble BVOCs under drought, during periods of relatively high RH (e.g., Filella et al., 2009; Loreto and Schnitzler, 2010). This increase was followed by either a sharp

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decrease or moderation in the mixing ratios of most presumed BVOCs. For most of the presumed BVOCs, an increase in mixing ratios was observed after around 13:00 h. This contradicts the expectation of an increase in BVOCs during the daytime with temperature (Niinemets and Monson, 2013), suggesting a reduction in stomatal conductance and reduced BVOC emissions under severe drought conditions around noontime (Bourtsoukidis et al., 2014; Loewenstein and Pallardy, 1998). SQT and ethanol were exceptional, with no increase in the mixing ratios after 13:00 h for the former, and a late increase in the mixing ratios, starting at around 15:00 h, for the latter. Formic acid was also exceptional in showing a gradual increase in the mean mixing ratios from sunrise to around 12:30 h. Overall, Fig. 4 indicates a drought stress-induced anomaly in the BVOC mixing ratios, which were expected to correlate with GSR and T, resulting in a daytime increase from morning to afternoon.

To systematically characterize the midday depression in VOC mixing ratios, we calculated both the morning decreasing rate of VOCs between 08:30 and 12:30 h and their afternoon increasing rate from 12:30 h to sunset (17:30 h). We chose 08:30 h to initiate the calculation because most of the BVOC species showed an increase in concentration before this time point, as would be expected for increases in T and GSR under non-drought stress conditions (see Sect. 1). We chose 12:30 h as the turning time point because at this time, the sum over the normalized mixing ratios of each individual presumed BVOC was lowest between sunrise and sunset, corresponding with the lowest mean daytime RH. Accordingly, the intensity of the daytime drought stress index (DDSI) in the VOC mixing ratios was evaluated according to the following equation:

$$\mathrm{DDSI} = -\sum_{t=8.5,0.5}^{12.5} \frac{C_{t+0.5}-C_t}{C_t} + \sum_{t=13.0,0.5}^{17.5} \frac{C_{t+0.5}-C_t}{C_t} \qquad \text{Eq.1}$$

where DDSI represents the intensity of the midday depression and C_t is the mixing ratio at time point t. We repeated the DDSI calculation using a second-order polynomial fitting (DDSI-PF) approach. According to this calculation, DDSI-PF is the difference between the value of this polynomial fitting

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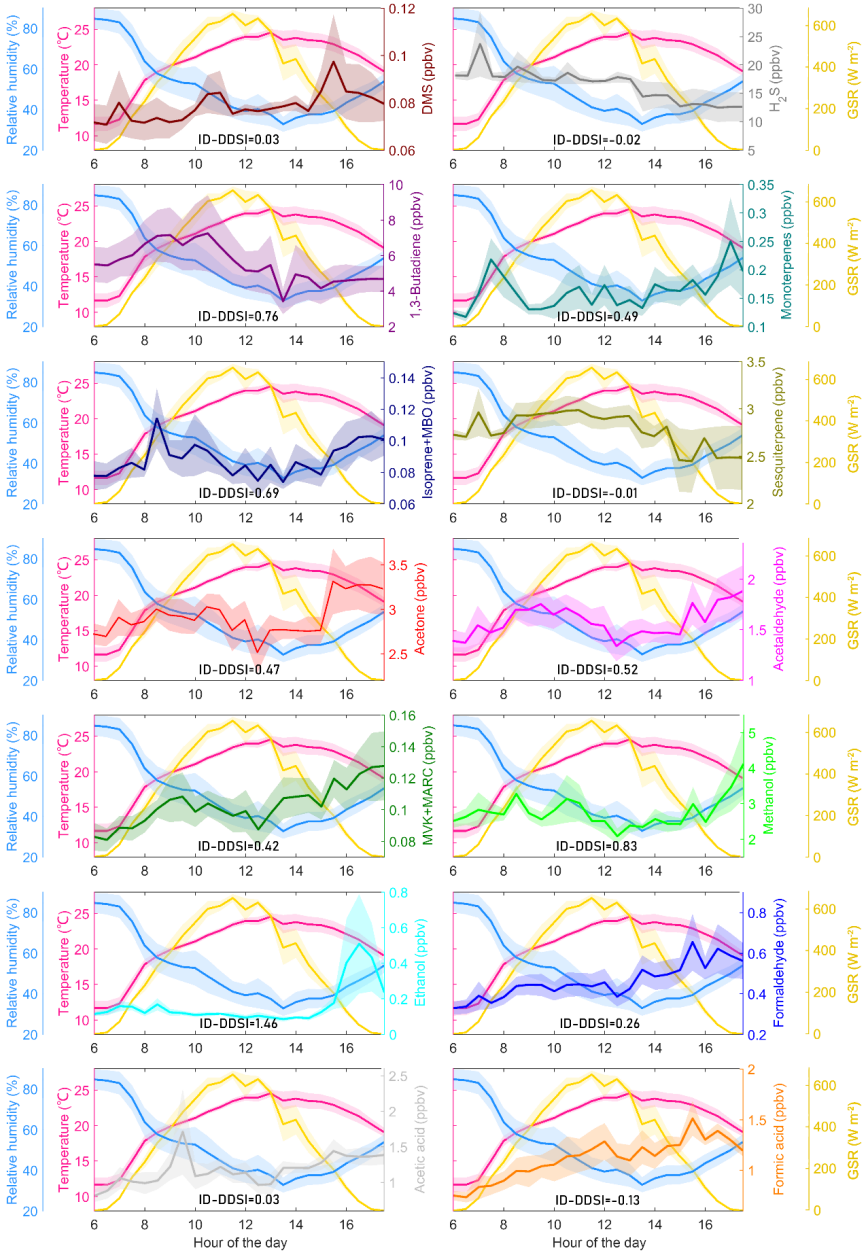
315 at 12:30 h and the corresponding value at 12:30 h of a linear line between 08:30 h and sunset (i.e.,
316 17:30 h). Whereas the former DDSI method (termed in the following as integrated differential [ID]



341 **Figure 4.** Daytime diurnal profiles of the measured VOC species and several meteorological factors (temperature, T;
342 relative humidity, RH; and global solar radiation, GSR). The colors for the VOC species are as in Fig. 2. The DDSI for

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each VOC species specifies the intensity of the apparent effect of drought on the decrease in BVOC emission rate during the daytime, excluding DOY 306 (see Sect. 3.3).

DDSI) provides a more rigorous measure of the daytime drought effect, the PF method provides a better indication of the pattern of reduced mixing ratios around noontime under drought conditions.

Figure 5 presents the DDSI values for all investigated VOCs and individually for each measurement day, based on the ID approach (Eq. 1) and using the DDSI-PF approach. The ID and PF approaches showed generally similar results, with a few exceptions, as explained in Sect. S3 and indicated in the figure. All BVOCs showed a negative DDSI on DOY 306, except for formaldehyde based on the PF method, and SQT and acetic acid, with nearly neutral DDSI, based on both methods. It should be emphasized that a negative DDSI does not mean that the BVOC emissions are not affected by the drought, because it is possible that with no drought effect, the calculated DDSI would be more negative, reflecting the general BVOC emission enhancement with T. Hence, interpretation of the drought stress on BVOC emissions in Fig. 5 should mainly focus on the trend in the DDSI following the rain event on DOY 306, and in response to the day-to-day changes in meteorological conditions.

In general, most of the BVOCs showed a gradual increase or higher DDSI than on DOY 306, during the days following DOY 306. However, this trend is masked to some extent, mostly due to the negative DDSI on DOY 310 for all presumed BVOCs except ethanol. As indicated in Fig. 3, this day was characterized by higher RH and lower VPD than the other investigated days, except for DOY 311. However, while on the latter day, RH values remained low (below 38%), on DOY 310, RH values increased sharply at around 12:00 h. Hence, the relative higher RH around noon on DOY 310 apparently facilitated the negative DDSI for all investigated BVOCs, except ethanol, on this day (Fig. 5). Negative DDSI was also observed on DOY 313 for MT and on DOY 312 for formic acid and acetic acid, and to a lesser extent for formaldehyde and SQT. DOY 312 was characterized by low RH, corresponding with relatively high VPD and T (Fig. 3). However, RH reached minimum values well

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after 12:30 h on this day (Fig. 3), while remaining relatively high in the morning. This resulted in a strong peak of acetic acid, formic acid, and formaldehyde at around 08:30–09:30 h (see Fig. S3), followed by a later decrease of acetic acid and formic acid when RH dropped below 27%, and a later decrease of formaldehyde after 14:00 h. As will be discussed below, differing from all other investigated BVOCs, SQT mixing ratios reached their highest levels around noontime, corresponding with low DDSI during most of the measurement days (Fig. 4).

Formic acid is the most soluble species among the investigated BVOCs, followed by acetic acid and formaldehyde (Table 2). Figure 5 demonstrates that all three of these species corresponded with negative DDSI on DOY 310. Formic acid also corresponded with negative DDSI on DOY 312, whereas acetic acid and formaldehyde corresponded with negative DDSI on this day, depending on the DDSI calculation method. These negative DDSIs on DOY 310 and 312 resulted from an increase in their mixing ratios before noontime, along with a sharp decrease in RH (Fig. S3). This suggests that those soluble species, particularly formic acid, were accumulated in the leaves at high partial pressure during the day or days before being emitted in large quantities under the relatively moderate T and RH before noontime of DOY 310 and DOY 312. The phenomenon of high emission rate of soluble species under drought stress during relatively high RH in the morning has been demonstrated in other studies (Filella et al., 2009; Loreto and Schnitzler, 2010). This further suggests that the emission of soluble species is not necessarily more limited than that of non-soluble BVOCs during drought periods, as long as at least low vegetation activity is maintained part of the time. This is supported by the fact that pressure buildup of compounds inside the leaf can compensate for stomatal closure (Loreto and Schnitzler, 2010).

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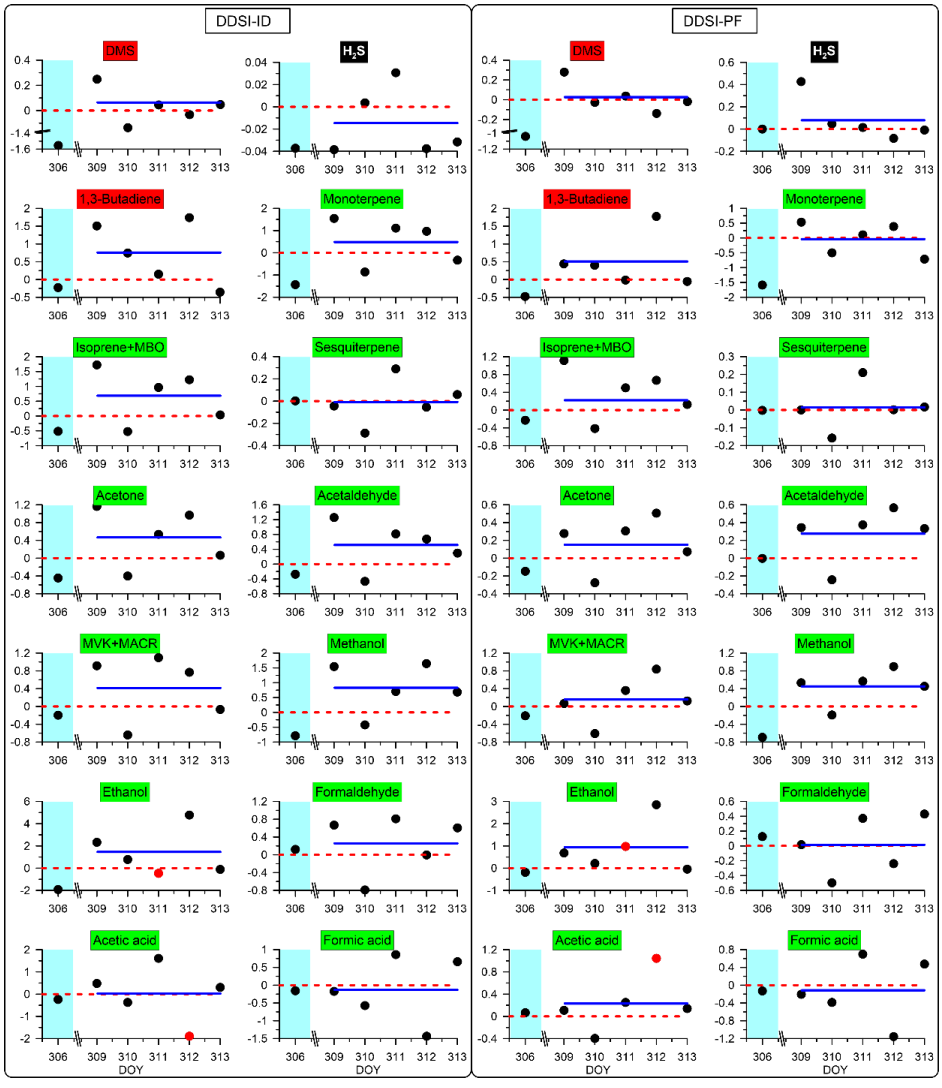

Figure 5. Drought stress effect on BVOC mixing ratios. Presented are the DDSI values (Sect. 3.3) for DOY 306 and DOY 309–313, individually for each investigated VOC, vs. DOY. Green, black, and red species names refer to presumed BVOCs, AVOCs, and either BVOCs or AVOCs, respectively. Horizontal blue and dashed red lines indicate mean and zero DDSI, respectively. Red circles indicate opposite plus/minus signs for DDSI using the ID and PF methods. These two exceptions were associated with the top 5% of the calculated standard deviation of the observed mixing ratios from the corresponding second-order polynomial fitting, which was used for the PF method.

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Table 2 summarizes the mean DDSI for the investigated VOCs, excluding the rainy day (DOY 306), using the two methods, together with the VOCs' H values, scaled by color. The depletion rate of the BVOC mixing ratios during the daytime due to drought stress can also be affected by chemical reactions, mainly involving OH and O_3. Hence, the table also presents the rate constants of the investigated VOCs with the main oxidants, OH and O_3, scaled by color, for comparison. Comparison of the DDSI and these rate constants revealed no clear association between the two, suggesting a relatively minor effect of the chemical reactions on the calculated DDSI values (Sect. S6). All investigated BVOCs were associated with mean positive DDSI according to both methods, except for SQT and formic acid, which showed either a slight negative or approximately neutral DDSI. Enhancement in SQT emission under severe drought conditions, close to the wilting point, to protect the plant from oxidative stress has been demonstrated (e.g., Bonn et al., 2019). While a slight negative DDSI does not reflect a no-drought constraint on the BVOC emissions, the apparently more moderate response to drought of the relatively more soluble species, including formic acid, acetic acid, and formaldehyde (Table 2), seems to contradict the expectation of a strong stomatal response of soluble BVOCs to stomatal conductance (Niinemets et al., 2004; Niinemets and Reichstein, 2003; Gabriel et al., 1999). This trend results from the relatively strong response of the soluble BVOCs to higher RH on DOY 310 and on DOY 312 before noon, as explained above. Among all investigated BVOCs, the relatively soluble methanol and ethanol were associated with the highest DDSI values. Methanol was shown to be more responsive to stomatal conductance under drought than other oxygenated BVOCs, including the soluble formic acid and acetic acid (Filella et al., 2009). Interestingly, the DDSI for 1,3-butadiene was relatively high. While 1,3-butadiene is frequently used as a proxy for anthropogenic emissions (e.g., Chang et al., 2014; Khan et al., 2018; Lewandowski et al., 2015), there are indications of this species' emission from biogenic origin as well. Huang et al. (2020) reported emission of 1,3-butadiene in dynamic chamber experiments from both soil and leaves, somewhat higher for the former.

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Asensio et al. (2007) also reported a high emission rate compared to other BVOCs. Thus, emission of 1,3-butadiene from both the soil and vegetation might have contributed to its observed mixing ratios.

Table 2. Henry's law constant (H), calculated DDSI for the daytime on DOY 306 and DOY 309–313, and oxidation rate constant of each VOC species. Mean DDSI values for the investigated VOCs, evaluated based on the ID and PF methods (Sect. 3.3), are presented, with red, blue, and no shading indicating positive, negative, and approximately neutral DDSI, respectively. The rate constants of each VOC with OH and O_3 are also presented, individually scaled on a normalized white–red scale.

	Henry's law constant for solubility in water at 298.15 K (mol m^{-3} Pa^{-1})	DDSI-ID	DDSI-PF	OH rate constant at 25°C (cm^3 $molecule^{-1}$ s^{-1})	O_3 rate constant at 25°C (cm^3 $molecule^{-1}$ s^{-1})
Isoprene	1.29E-04 [a]	0.686	0.221	9.99E-11	1.28E-17
MT *	1.68E-04 [a+b]	0.485	-0.038	1.36E-10	1.08E-16
SQT *	3.54E-04 [c]	-0.007	0.014	2.44E-10	1.20E-14
Acetone	2.58E-01 [a]	0.466	0.152	1.75E-13	
Acetaldehyde	1.43E-01 [a]	0.515	0.275	1.49E-11	
MVK **	2.60E-01 [b]	0.415	0.155	1.88E-11	
Methanol	2.17E+00 [a]	0.833	0.452	8.96E-13	
Ethanol	1.97E+00 [a]	1.460	0.936	3.21E-12	
Formaldehyde	3.28E+01 [a]	0.257	0.016	8.49E-12	
Acetic acid	7.52E+01 [a]	0.026	0.230	7.40E-13	
Formic acid	5.93E+03 [a]	-0.131	-0.115	4.50E-13	
DMS	5.60E-03 [b]	0.034	0.027	4.84E-12	
H_2S	1.00E-03 [b]	-0.015	0.079	4.80E-12	
1,3-Butadiene	1.00E-04 [b]	0.758	0.509	6.65E-11	6.33E-18

*The rate constants for MTs are averaged values of α-pinene, β-pinene, limonene, D-limonene, and myrcene, and for SQTs, averaged values of α-farnesene, β-caryophyllene, and humulene. The H value for MT was based on the relative emission rates of myrcene, sabinene, limonene, 3-carene, t-β-ocimene, α-pinene, and β-pinene (together accounting for 93% of the total MTs, according the MEGAN model); while the H value for SQT was based on the relative emission rates of α-farnesene and β-caryophyllene (together accounting for 38% of the total SQTs in MEGAN).

**The H value and OH/O_3 rate constants are for MVK only, while the DDSI-ID and DDSI-PF values are for MVK + MACR.

a. (Niinemets and Reichstein, 2003); b. (Sander, 2023); c. (Copolovici and Niinemets, 2015).

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3.4 Meteorological parameters as a proxy for variations in BVOC mixing ratio under drought conditions

To investigate the effect of meteorological parameters on BVOC mixing ratios, we tested the correlation of the investigated VOC mixing ratios to RH, T, GSR and VPD. Table 3 shows the Pearson correlation coefficient (R) between these meteorological parameters and the measured mixing ratios of the various investigated VOCs, during the daytime of the investigated periods (DOY 306 and DOY 309–313). Considering that the rain event on DOY 306 could significantly affect the results, we also present the corresponding R values for the same period, excluding DOY 306. To further focus the analysis on the drought effect, we repeated it with exclusion of the early morning measurements (before 08:30 h) as well, considering the relatively high RH values during the early morning. We chose 08:30 h because most of the BVOC species showed an increase in concentration before this time point, as would be expected for increases in T and GSR under drought conditions when RH is relatively high (Filella et al., 2009; Loreto and Schnitzler, 2010). Finally, for the same reason, we also excluded the late afternoon (later than 15:30 h), when a less severe drought effect is expected.

Table 3 suggests that GSR is the best proxy for the effect of drought on the BVOC mixing ratios. Whereas under non-drought conditions, a positive correlation between solar radiation and BVOC emissions is expected (Staudt et al., 2000; Guenther et al., 1995), Table 3 demonstrates a negative R for all BVOCs with GSR, except for SQT. The anticorrelation tended to be stronger when calculated after 08:30 h, and to a lesser extent between 08:30 and 15:30 h. The lower correlation of RH and T, compared to GSR, with the BVOC mixing ratios may arise from the fact that under severe drought, the effect of RH may tend to be a dominant factor in restricting BVOC emissions, whereas under less severe drought, T tends to enhance BVOC emissions (Sect. 1). Therefore, because of the

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general anticorrelation between RH and T, neither shows a dominant impact on the BVOC mixing ratios when calculated over the whole investigation period.

Interestingly, 1,3-butadiene showed a very high correlation with RH. This may reinforce our previous assumption that it is emitted from a biogenic origin, such as the soil or vegetation, at the measurement site. According to Asensio et al. (2007), an increase in soil temperature above 25 ºC can lead to a significant decrease in 1,3-butadiene emission; during our measurements, the soil temperature probably reached higher values during most of the daytime. Because soil temperature tends to anticorrelate with atmospheric RH, a decrease in RH during the daytime can be expected to result in a decrease in 1,3-butadiene emission rates. This may be further indicated by the higher correlation of 1,3-butadiene with RH when the morning period is excluded (see Table 3).

Table 3. Pearson correlation coefficient (R) for the correlation between the quantified VOCs' mixing ratios and RH, T, GSR, and VPD during the daytime of DOY 306 and DOY 309–313. The values are also presented for the same period, excluding measurements before 08:30 h, and before 08:30 and after 15:30 h.

Periods / VOCs	All measurement days				Without the rainy day (DOY 306)				After 08:30 h and without the rainy day (DOY 306)				Between 08:30 h and 15:30 h, without the rainy day (DOY 306)			
	R(RH)	R(T)	R(GSR)	R(VPD)	R(RH)	R(T)	R(GSR)	R(VPD)	R(RH)	R(T)	R(GSR)	R(VPD)	R(RH)	R(T)	R(GSR)	R(VPD)
DMS	-0.271	0.092	0.070	0.254	-0.247	0.070	-0.067	0.225	-0.314	0.112	-0.242	0.234	-0.326	0.154	-0.227	0.262
MT	0.216	-0.014	-0.205	-0.166	0.024	-0.068	-0.224	-0.011	-0.263	0.371	-0.185	0.346	-0.278	0.517	-0.148	0.432
Acetone	0.019	-0.018	-0.163	-0.034	0.081	-0.015	-0.242	-0.086	0.055	0.013	-0.301	-0.024	0.082	0.048	-0.269	-0.021
Isoprene+MBO	0.395	-0.059	-0.188	-0.367	0.151	-0.103	-0.121	-0.191	0.242	-0.101	-0.155	-0.193	0.309	-0.098	-0.101	-0.228
Acetaldehyde	-0.067	0.021	-0.027	0.025	-0.048	0.033	-0.071	0.002	0.040	-0.042	-0.131	-0.027	0.093	-0.040	-0.071	-0.049
MVK+MACR	0.086	0.118	-0.086	-0.075	-0.004	0.111	-0.063	-0.005	0.142	-0.035	-0.176	-0.097	0.170	-0.023	-0.145	-0.105
H_2S	-0.043	-0.239	0.061	-0.064	0.028	-0.239	0.038	-0.130	-0.022	-0.036	0.354	-0.006	-0.047	-0.097	0.327	-0.020
1,3-Butadiene	0.665	-0.123	-0.121	-0.569	0.612	-0.300	-0.026	-0.545	0.730	-0.470	0.020	-0.642	0.735	-0.473	0.054	-0.647
SQT	-0.073	-0.011	0.237	0.020	-0.064	-0.008	0.245	0.006	0.067	-0.082	0.298	-0.077	0.041	-0.154	0.265	-0.096
Methanol	0.187	-0.124	-0.219	-0.220	0.046	-0.179	-0.305	-0.133	-0.083	-0.013	-0.289	0.045	-0.074	0.055	-0.214	0.078
Ethanol	-0.068	0.006	-0.198	0.048	-0.047	0.013	-0.227	0.030	-0.074	-0.020	-0.289	0.031	-0.071	0.029	-0.241	0.053
Formaldehyde	-0.395	0.178	-0.026	0.319	-0.291	0.204	-0.097	0.224	-0.127	-0.004	-0.264	0.067	-0.103	0.012	-0.248	0.064
Acetic acid	-0.039	0.059	-0.037	-0.003	0.017	0.065	-0.049	-0.051	0.357	-0.295	-0.162	-0.316	0.387	-0.307	-0.151	-0.334
Formic acid	-0.160	0.266	-0.048	0.109	-0.170	0.260	-0.036	0.109	0.360	-0.301	-0.286	-0.357	0.378	-0.295	-0.280	-0.364

We further hypothesized that the intensity of the instantaneous intraday variations in the meteorological parameters may play a role in the BVOC emissions, and therefore can be used as a

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proxy for BVOC emissions, rather than the values of the meteorological parameters themselves. To test this, Fig. S4 presents a principal component analysis (PCA) (Wold et al., 1987) for all investigated VOCs, T, RH, VPD, and GSR, as well as the linear regression slope coefficients of these meteorological parameters ($\frac{\Delta T}{\Delta t}, \frac{\Delta RH}{\Delta t}, \frac{\Delta VPD}{\Delta t}, \frac{\Delta GSR}{\Delta t}$, respectively); Fig. 6 presents a PCA for the same parameters, excluding $\frac{\Delta T}{\Delta t}$, $\frac{\Delta VPD}{\Delta t}$ and $\frac{\Delta GSR}{\Delta t}$. Both figures demonstrate that $\frac{\Delta RH}{\Delta t}$ has the highest association with the BVOC mixing ratios; this is more clearly demonstrated in Fig. 6. This figure clearly indicates that all BVOCs except SQT correlated with component 1 (32.3%) together with $\frac{\Delta RH}{\Delta t}$,

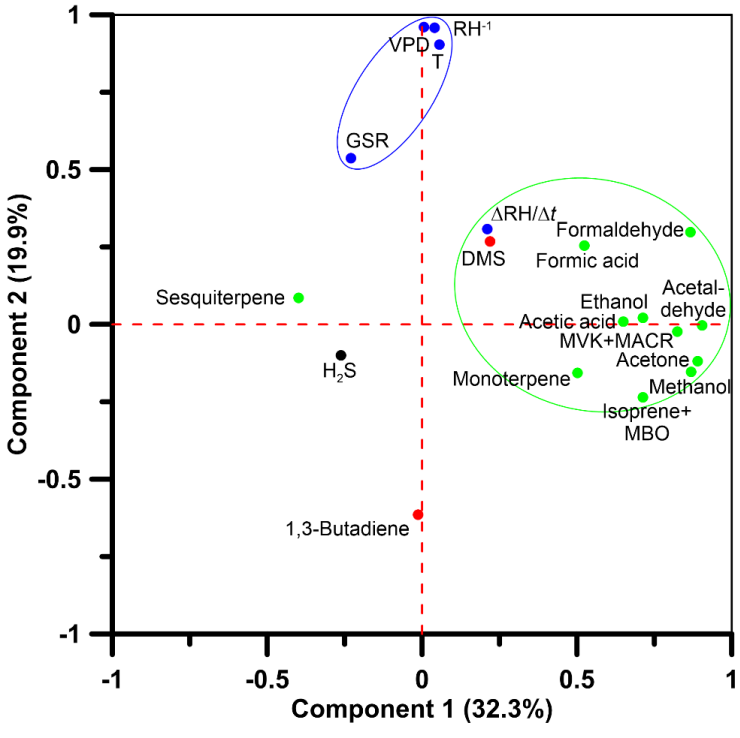

Figure 6. PCA of ambient meteorological parameters, including meteorological parameters and the temporal derivative of RH, and the measured mixing ratios of VOCs. Colors indicate ambient meteorological parameters (blue), BVOCs (green), AVOCs (black), and either BVOCs or AVOCs (red). Note that the inverse of RH is presented rather than RH.

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indicating a dominant role for $\frac{\Delta \boldsymbol{RH}}{\Delta \boldsymbol{t}}$ in the BVOC mixing ratios, rather than any of the meteorological parameters. The weak correlation of SQT with $\frac{\Delta \boldsymbol{RH}}{\Delta \boldsymbol{t}}$ may result from this species' tendency to be emitted at a higher rate close to the wilting point, as suggested by Bonn et al. (2019).

The effect of meteorological conditions on the rate of BVOC emissions is expected to show day-to-day variations, particularly for this specific study, considering the relief in drought stress on DOY 306 and 310 and before noontime on DOY 312. To investigate the response of the mixing ratios to meteorological parameters on a daily basis, we evaluated the regression coefficient for the mixing ratios vs. each of T, RH, GSR, and VPD, as well as their temporal derivatives ($\frac{\Delta T}{\Delta t}, \frac{\Delta RH}{\Delta t}, \frac{\Delta GSR}{\Delta t}, \frac{\Delta VPD}{\Delta t}$, respectively), individually for each measurement day. Figure 7 shows the 30-min-based Pearson correlation coefficients (PCC(R)) for the investigated VOCs, separately for each day and individually for soluble (H > 0.1) and insoluble (H < 0.1) species (Murphy and Morrison, 2014).

The figure demonstrates a higher correlation for BVOC mixing ratios with the instantaneous change in the meteorological parameters, than with the meteorological parameters themselves. Exceptional is $\frac{\Delta GSR}{\Delta t}$, which appears, similar to GSR, to be a poor proxy for BVOC emissions. This reinforces the notion that the apparently dominant role played by GSR in the BVOCs' emission (see Table 3) results only from the fact that RH and T tend to anticorrelate and cancel out each other's effects during the measurements, as explained above. Figure 7 further emphasizes the important role of the temporal gradient of the tested meteorological parameters, particularly $\frac{\Delta RH}{\Delta t}$, in the emission of BVOCs under drought conditions, which was also captured without performing the analysis on a daily basis (Fig. 6).

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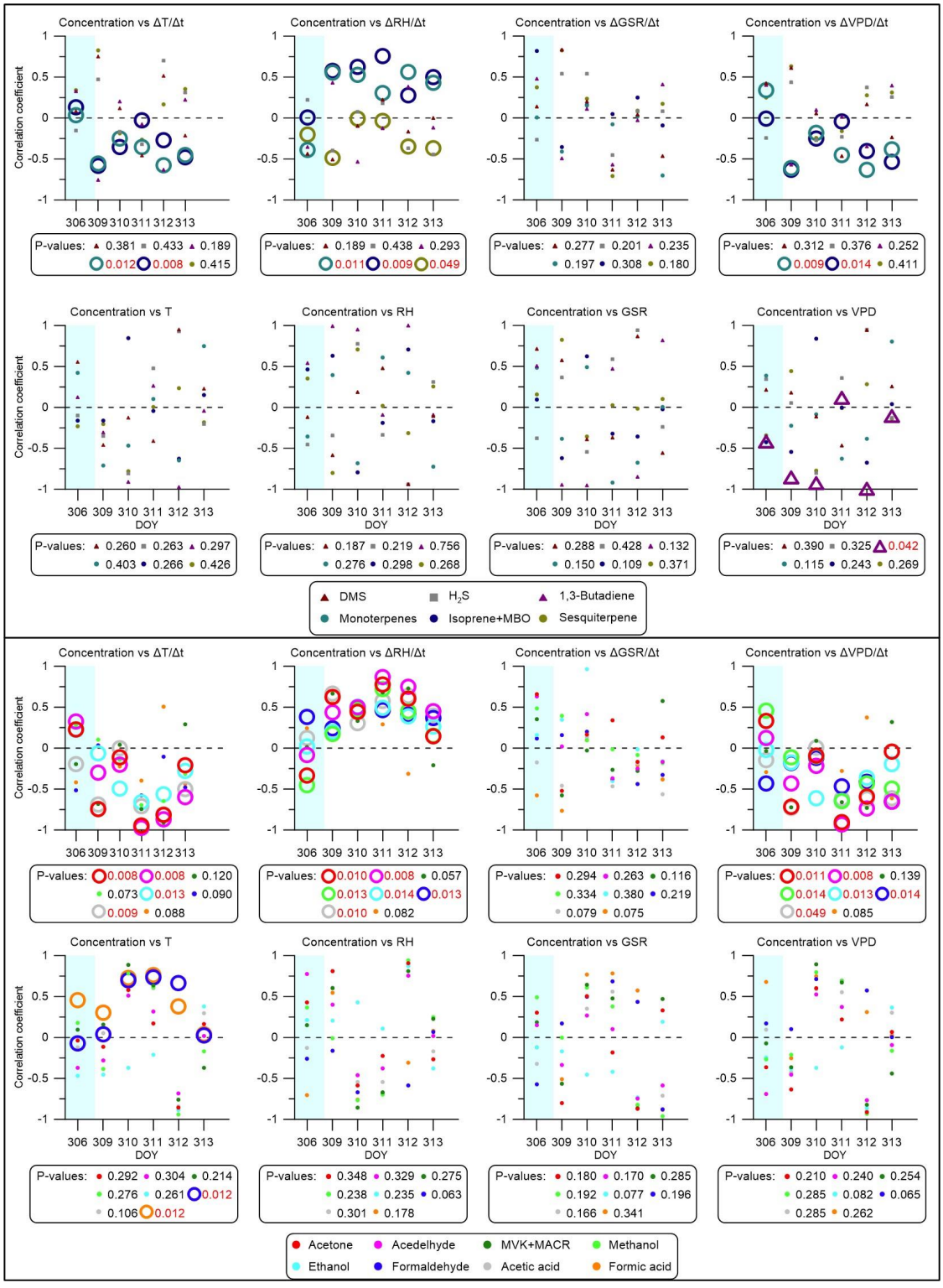

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Figure 7. Daytime correlation coefficient between mixing ratios and meteorological parameters and their temporal derivatives for relatively non-soluble (upper panel) and soluble (lower panel) VOCs (see H values in Table 2). The colors of the symbols are unique to each VOC species. Circles represent presumed BVOCs, squares represent presumed AVOC (H_2S), and triangles represent either BVOCs or AVOCs, including DMS and 1,3-butadiene. Large empty symbols and values in red indicate statistically significant correlations ($P < 0.05$), with *P*-values calculated excluding measurements on the rainy day (DOY 306); blue shaded rectangle indicates rain event.

Table 4 summarizes the results shown in Fig. 7 and indicates, individually for each VOC, whether any of the correlation types presented in Fig. 7 are statistically significant, based on the null hypothesis of R = 0 ($P < 0.05$) using a one-sample t-test. The *P*-value calculation was based on the DOY 309–313 data, excluding DOY 306 during which a rain event occurred.

Overall, Table 4 clearly indicates that the temporal gradients of the meteorological parameters correspond with a much higher number of cases (23 out of 26) for which the correlation or anticorrelation with the BVOC mixing ratios were found to be statistically significant, compared to the meteorological parameters themselves (3 out of 26). Out of these 23 cases, the anticorrelation of SQT with $\frac{\Delta RH}{\Delta t}$ is exceptional, reflecting an increase in its emission rate with increasing drought stress, in agreement with the analysis presented in Table 3. Table 4 suggests that under the studied conditions, $\frac{\boldsymbol{\Delta RH}}{\boldsymbol{\Delta t}}$ is the best proxy for the emission of BVOCs under drought stress. The ranking for the various tested meteorological parameters serving as good predictors for BVOC emission rates under drought conditions is as follows: $\frac{\Delta RH}{\Delta t} > \frac{\Delta VPD}{\Delta t} > \frac{\Delta T}{\Delta t} > T > VPD > \frac{\Delta GSR}{\Delta t} > GSR = RH.$

There was no significant difference in the results for the soluble vs. non-soluble BVOCs. However, both formaldehyde and formic acid, which are among the most soluble BVOCs included in our study (see Table 2), corresponded with a significant correlation ($P < 0.05$) with T, while among these two species, only formaldehyde also showed a significant correlation with $\frac{\boldsymbol{\Delta RH}}{\boldsymbol{\Delta t}}$. These results are in line with our previous findings that relatively elevated RH during periods of drought stress can

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enhance the emission rate of soluble BVOCs with increasing T, as was demonstrated for DOY 306 and 310, and for DOY 312 before noon (Sect. 3.3).

The statistically significant anticorrelation of SQT mixing ratios with $\frac{\Delta RH}{\Delta t}$ under drought conditions may agree with Bonn et al. (2019), who found that a sharp increase in SQT emission occurs close to the wilting point, apparently to protect the plant against oxidative damage. The increase in SQT emission rate in response to drought stress is further supported by Caser et al. (2019), who found that drought can induce the mechanism of SQT synthesis.

Table 4. Correlation of the investigated VOCs with various meteorological parameters. Presented is the number of VOCs for which a non-statistically significant and statistically significant R with various meteorological conditions and their temporal derivatives ($\frac{\Delta T}{\Delta t}$, $\frac{\Delta RH}{\Delta t}$, $\frac{\Delta VPD}{\Delta t}$, $\frac{\Delta GSR}{\Delta t}$ and $\frac{\Delta RH}{\Delta t}$ are the temporal derivatives of T, RH, VPD, GSR and RH, respectively) was observed. Red and blue shading indicate positive and negative correlation, respectively. Darker color (red or blue) indicates statistically significant correlation ($P < 0.05$), while light color indicates a non-statistically significant correlation, with $0.1 > P > 0.05$.

	T	$\frac{\Delta T}{\Delta t}$	RH	$\frac{\Delta RH}{\Delta t}$	VPD	$\frac{\Delta VPD}{\Delta t}$	GSR	$\frac{\Delta GSR}{\Delta t}$
DMS								
H_2S								
1,3-Butadiene								
MT								
Isoprene+MBO								
SQT								
Acetone								
Acetaldehyde								
MVK+MACR								
Methanol								
Ethanol								
Formaldehyde								
Acetic acid								
Formic acid								
	2	*6+3*	*1*	*8+2+1*	*2+1*	*8+1*	*1*	*2*

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4. Summary and conclusions

We investigated the effect of meteorological conditions on BVOC mixing ratios under drought. Under the drought conditions in this study, the instantaneous changes in meteorological conditions, $\frac{\Delta RH}{\Delta t}$, $\frac{\Delta VPD}{\Delta t}$ and $\frac{\Delta T}{\Delta t}$, were found to be better proxies for the mixing ratios of the investigated BVOCs at the canopy scale than the absolute values of RH, T, VPD and GSR. In particular, $\frac{\Delta RH}{\Delta t}$ was associated with a positive correlation for 10 out of 11 of the investigated presumed BVOCs. These findings are consistent with those presented in the companion paper by Li et al. (2023), which is based on direct flux measurements from branches of natural vegetation in the same region. For 8 out of the 11 investigated VOCs, a statistically significant positive correlation was observed between $\frac{\Delta RH}{\Delta t}$ and the BVOC mixing ratios. SQT showed an anticorrelation with $\frac{\Delta RH}{\Delta t}$, in line with previous studies indicating an increase in its emission rate under severe drought conditions, close to the wilting point.

Our analyses reinforce previous studies indicating enhanced emission rates of soluble species under higher RH during drought periods, including formaldehyde, formic acid, and acetic acid, resulting in a lower DDSI than for the non-soluble BVOCs. Moreover, formic acid and formaldehyde showed a significant positive correlation with T in the daily-basis analysis; the latter also showed a significant positive correlation with $\frac{\Delta RH}{\Delta t}$. The dramatic effect of relatively high RH during a drought period emphasizes the need to analyze the results on a timescale of 1 day or less, for cases in which significant day-to-day or intraday changes in meteorological conditions occur. Moreover, applying the analysis to the whole investigation period, rather than on a daily scale, resulted in GSR being the best proxy for most of the BVOC mixing ratios, with a negative correlation to them. This resulted from the large changes in RH during the drought period, leading to opposite effects of RH and T, which tend to be anticorrelated, on BVOC emissions. Namely, under high RH, BVOC emission rates could increase

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with increasing T, whereas under low RH, the BVOC emission rates decreased with increasing T and decreasing RH.

The strong correlation of 1,3-butadiene with RH, when calculated over the whole campaign period during the daytime (see Table 3), reinforces findings from previous studies indicating a biogenic source for this compound, from both vegetation and soil. Considering the frequent use of 1,3-butadiene as a proxy for anthropogenic emissions, such studies should take into account its potentially significant biogenic emission.

Overall, our study aligns with previous findings on the effect of drought on BVOC emission rates. Notably, we revealed that instantaneous changes in meteorological conditions may serve as a more adequate proxy for BVOC emissions during drought than the absolute values of those parameters. These insights are highly relevant for the enhancement of air quality and climate models. However, it is important to note that the present study did not thoroughly investigate the impact of chemical loss and changes in mixing layer height on BVOC mixing ratios. Similarly, the study conducted by Li et al. (2023), which led to similar findings based on direct flux measurements, did not assess the influence of drought on BVOCs at the ecosystem level. Therefore, additional research is needed to better understand the effects of instantaneous changes in meteorological conditions on BVOC emissions, and how these affect BVOC concentration at the canopy level.

Author contribution. ET designed the experiments, MG carried out the field measurements and performed the data acquisition together with CD. PM and EF led the calibration, quality control, and data processing. AG set up the MEGANv2.1 model. QL and ET led the analyses with contributions from all co-authors. QL and ET prepared the manuscript with contributions from AG.

Competing interests. The authors declare that they have no conflict of interest.

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