Supplementary information

Instantaneous intraday changes in relative humidity as a key proxy for the mixing ratio of biogenic volatile organic compounds over vegetation under drought conditions

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S1. Seasonal measured CO₂ fluxes at Ramat Hanadiv
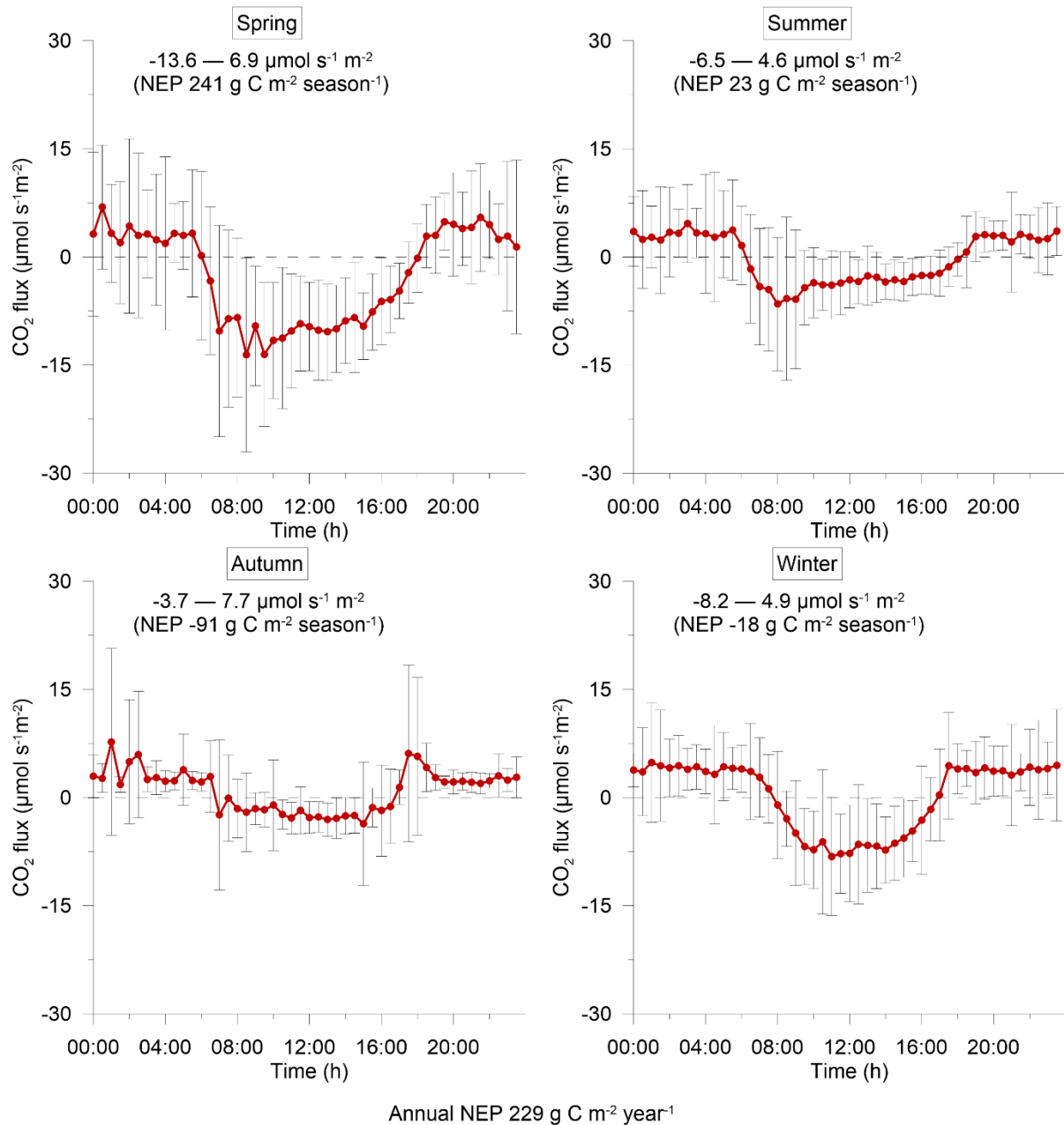
Figure S1. Seasonal measured CO₂ fluxes at Ramat Hanadiv. Presented are the mean diurnal profiles of the measured CO₂ fluxes at the Ramat Hanadiv measurement site (located 44.4 km southwest of the Shibli measurement site) between July 2015 and July 2017 (Li et al., 2018). Gray error bars indicate standard error of the mean. The range of mean hourly CO₂ fluxes and the mean seasonal net ecosystem production (NEP) are indicated individually for each season.

S2. Mean diurnal profile of net measured CO₂, net measured water vapor, and relative humidity (RH) for DOY 306 to 313, 2016
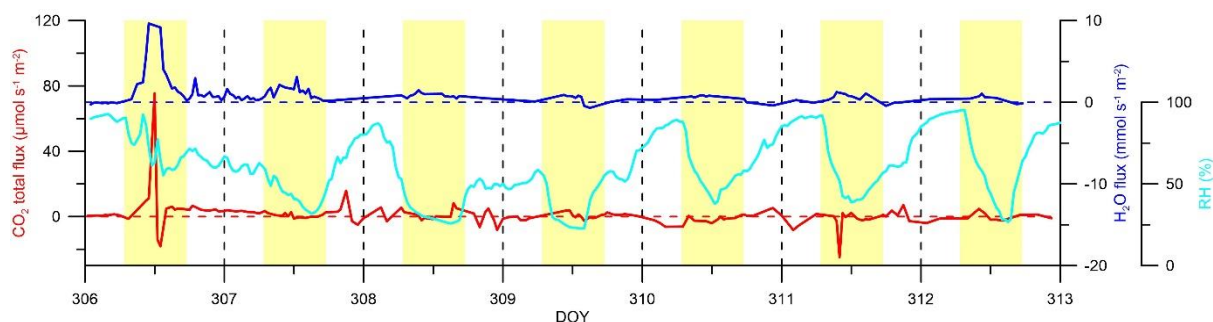
Figure S2. Mean diurnal profile of net measured CO_2, net measured water vapor (H_2O) and RH for DOY 306 to 313, 2016.

S3. Drought stress effect on biogenic volatile organic compound (BVOC) mixing ratios, analyzed by DDSI values (Sect. 3.3 in the main text) for DOY 306 and DOY 309–313

In Sect. 3.3 of the main text, it is noted that DDSI values, calculated using the ID and PF methods and displayed in Fig. 5, generally exhibited similar results, with a few exceptions. These exceptions resulted from cases in which a relatively high deviation of the observed mixing ratios from the corresponding second-order polynomial fitting occurred and could be quantified by the standard deviation of the observed mixing ratios from the second-order polynomial fitting used for the PF method. Figure 5 in the main text indicates, with red symbols, two cases—acetic acid on DOY 312 and ethanol on DOY 311—which gave opposite plus/minus signs for DDSI using the two methods. These two exceptions were associated with the top 5% of the calculated standard deviation of the observed mixing ratio from the corresponding second-order polynomial fitting used for the PF method.

S4. Diurnal profile of formic acid, formaldehyde, and acetic acid, together with corresponding RH, temperature and vapor pressure deficit (VPD), during DOY 310 and 312
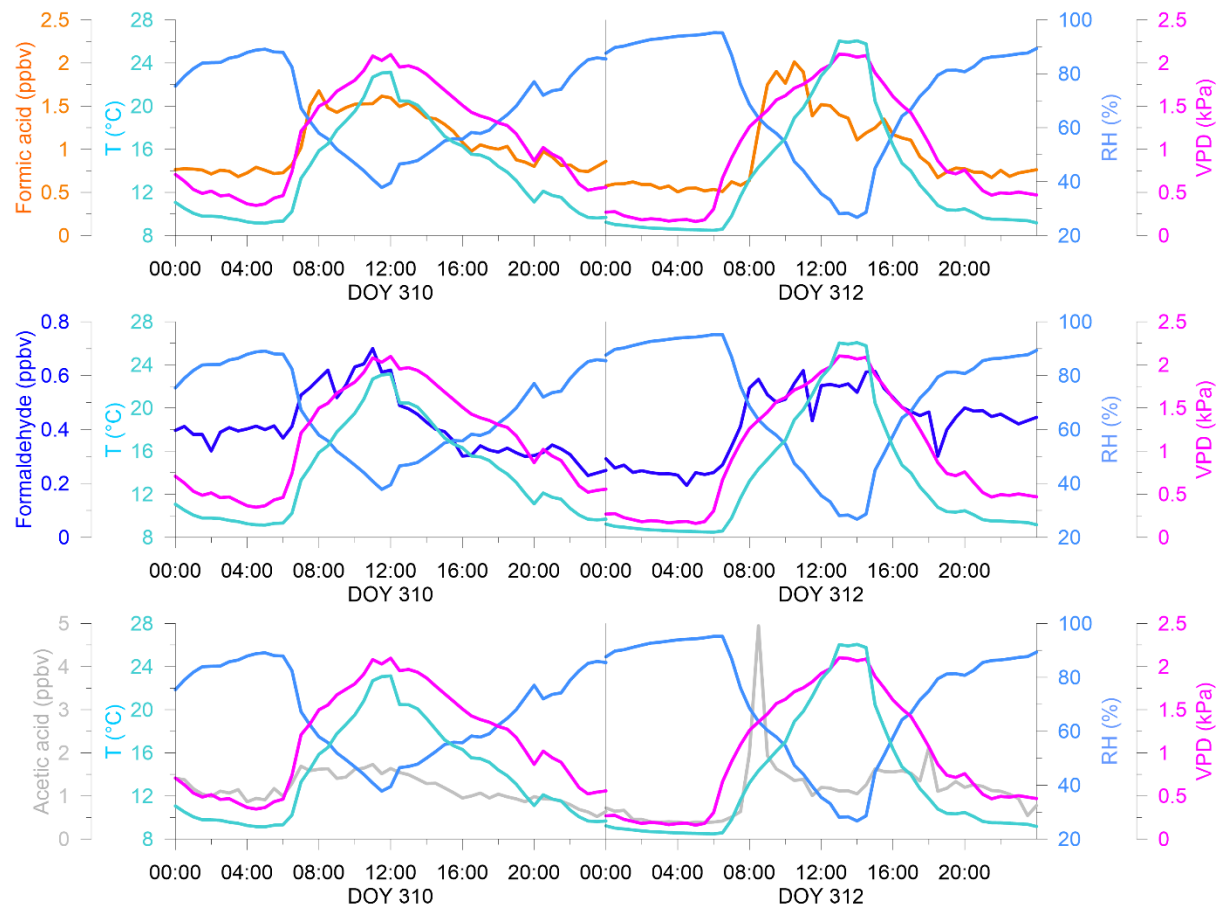
Figure S3. Diurnal profile of formic acid, formaldehyde, and acetic acid, together with corresponding RH, temperature (T) and VPD, during DOY 310 and 312.

S5. **Principal component analysis (PCA) of ambient meteorological parameters, including their gradient with time, and mixing ratios of VOCs**
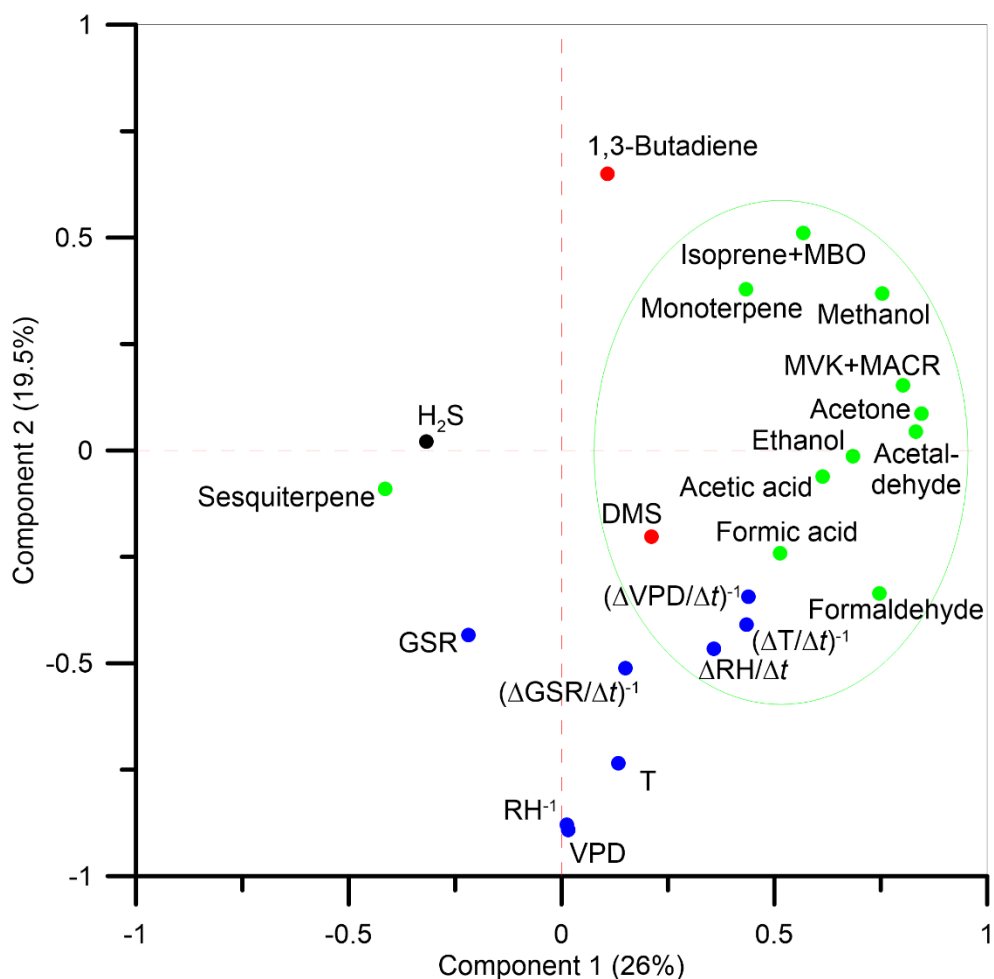
Figure S4. PCA (Wold et al., 1987) of ambient meteorological parameters, including their gradient with time, and mixing ratios of VOCs. The color of the label indicates ambient meteorological parameters (blue), BVOCs (green), AVOC (H_2S; black), and either BVOCs or AVOCs (dimethyl sulfide (DMS) and 1,3-butadiene; red). T, temperature; RH, relative humidity; VPD, vapor pressure deficit; GSR, global solar radiation; MBO, 2-methyl-3-buten-2-ol; MVK+MACR, methyl vinyl ketone and methacrolein. Note that the inverse of RH is presented rather than RH.

S6. Effect of chemical oxidation on the observed daily trends in BVOC concentrations

In Sect. 3.3 of the main text, we introduce the DDSI term, which reflects the apparent effect of meteorological conditions on BVOC emission rates under drought. We further introduce two methods for DDSI calculation, termed as DDSI-ID and DDSI-PF. Here we test to what extent the oxidation of BVOCs by OH and O_3 affects the calculated DDSI values, using the chemical rates of the different investigated VOCs with these main daytime oxidants. Overall, the examination indicated that chemical kinetics could account, on average, for up to 5% of the evaluated DDSI values (see Sect. 3.3 in the main text). Notably, dimethyl sulfide, monoterpene, and sesquiterpene exhibited chemical kinetic effects of up to 20–30% of the DDSI value, whereas H_2S exhibited a DDSI value near zero, both when calculated with and without accounting for its chemical oxidation.

Table S1. 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. The second column of the DDSI values, in brackets, in addition to Table 2 in the main text, takes into consideration the chemical kinetics' lifetime effect.

	H for solubility in water at 298.15 K [mol m^{-3} Pa^{-1})]	DDSI-ID		DDSI-PF		OH rate constant at 25℃ [cm^3 molecule^{-1} s^{-1}]	O_3 rate constant at 25 [cm^3 molecule^{-1} s^{-1}]
Isoprene	1.29E-04	0.686	(0.648)	* 0.221	(0.349)	9.99E-11	1.28E-17
Monoterpene **	1.68E-04	0.485	(0.890)	*-0.038	(0.156)	1.36E-10	1.08E-16
Sesquiterpene **	3.54E-04	-0.007	(0.007)	* 0.014	(-0.042)	2.44E-10	1.20E-14
Acetone	2.58E-01	0.466	(0.413)	0.152	(0.140)	1.75E-13	
Acetaldehyde	1.43E-01	0.515	(0.292)	0.275	(0.253)	1.49E-11	
MVK Methyl vinyl ketone	2.60E-01	0.415	(0.409)	0.155	(0.136)	1.88E-11	
Methanol	2.17E+00	0.833	(0.833)	0.452	(0.416)	8.96E-13	
Ethanol	1.97E+00	1.460	(1.461)	0.936	(0.722)	3.21E-12	
Formaldehyde	3.28E+01	0.257	(0.254)	0.016	(0.012)	8.49E-12	
Acetic acid	7.52E+01	0.026	(0.026)	0.230	(0.209)	7.40E-13	
Formic acid	5.93E+03	-0.131	(-0.131)	-0.115	(-0.102)	4.50E-13	
DMS	5.60E-03	0.034	(0.047)	0.027	(0.033)	4.84E-12	
H_2S	1.00E-03	-0.015	(-0.013)	0.079	(0.088)	4.80E-12	
Butadiene	1.00E-04	0.758	(0.747)	* 0.509	(0.503)	6.65E-11	6.33E-18

*These DDSI values were calculated based on the effect of the BVOC's oxidation by O_3 and OH on its lifetime, while others, in the same column, accounted only for the effect of oxidation by OH on the BVOC's lifetime.

**The rate constants for monoterpenes are averaged values of α-pinene, β-pinene, limonene, D-limonene, and myrcene, and for sesquiterpenes, averaged values of α-farnesene, β-caryophyllene, and humulene. The H value for monoterpene 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 monoterpenes, according to the MEGAN model); while the H value for sesquiterpene was based on the relative emission rates of α-farnesene and β-caryophyllene (together accounting for 38% of the total sesquiterpenes in MEGAN).

DMS, dimethyl sulfide.

References

Li, Q., Gabay, M., Rubin, Y., Fredj, E., and Tas, E.: Measurement-based investigation of ozone deposition to vegetation under the effects of coastal and photochemical air pollution in the Eastern Mediterranean, Sci Total Environ, 645, 1579-1597, 10.1016/j.scitotenv.2018.07.037, 2018.

Wold, S., Esbensen, K., and Geladi, P.: Principal Component Analysis, Chemometr Intell Lab, 2, 37-52, Doi 10.1016/0169-7439(87)80084-9, 1987.