



Measurement report: Moisture and light driven Volatile Organic Compound emissions of biocrusts from the Succulent Karoo, South Africa

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Abstract. Biological soil crusts (biocrusts) cover around 12 % of Earth's land surface and play critical roles in dryland ecosystems, yet their contribution to volatile organic compound (VOC) emissions remains poorly understood. Despite their extensive distribution, biocrusts are not currently included in global VOC emission inventories, possibly creating a significant gap in the understanding of atmospheric chemistry in arid regions. Here, we quantify VOC emissions and CO₂ fluxes from soil samples dominated by four different biocrust types, namely light cyanobacteria-, dark cyanobacteria-, chlorolichen-, and moss-dominated crusts and bare soil samples, collected from the Succulent Karoo, South Africa. Using a climate-controlled chamber, we measured biocrusts at high air humidity, during and after wetting with artificial rainwater, and during subsequent drying. Interestingly, VOC emissions were strongest in the absence of photosynthesis before wetting, when samples were exposed to humid air in the dark and in the light with strong emissions of ethanol, methanol, and acetone. After wetting most VOC emissions decreased, but some of them, like geosmin and 2-methylisoborneol, compounds associated with petrichor, increased. In general, moss-dominated biocrusts exhibited the highest isoprene and sulfur compound emissions. Dimethyl sulfide emission peaked during darkness, suggesting a light-dependent source or sink in moss dominated biocrusts. The emission of up to $75 \pm 48 \text{ nmol m}^{-2} \text{ s}^{-1}$ of total VOCs across the studied biocrust types highlights them as a significant, overlooked source of reactive VOCs to the atmosphere, potentially influencing atmospheric oxidation capacity and secondary organic aerosol formation, particularly in regions with low vascular vegetation cover.

1 Introduction

Biological soil crusts (biocrusts) are complex microbial communities colonizing the soil surface in drylands worldwide, covering ~12 % of Earth's land and ~30 % of dryland soils (Rodríguez-Caballero et al., 2018). They comprise photoautotrophs (cyanobacteria, algae, lichens, mosses) and heterotrophs (bacteria, fungi, archaea) (Maier et al., 2018; Weber et al., 2018). Their coverage is threatened by land-use intensification and climate change, with decreases of between 25-40 % estimated by the year 2070 (Rodríguez-Caballero et al., 2022). Clear changes are already being reported (Finger-Higgins et al., 2022; Herdy et al., 2026). Biocrust physiology is driven by water availability: they endure regular desiccation but resume photosynthesis within minutes after rehydration (Harel et al., 2004). Exposed to high radiation, they produce protective secondary metabolites (e.g., phenols, aldehydes) to manage oxidative stress and cellular water (Rajeev et al., 2013). While critical for soil stability, nutrient and carbon cycling (Weber et al., 2018, 2022), and vascular plant growth (Havrilla et al., 2019), their volatile organic compound (VOC) dynamics and atmospheric impacts remain poorly understood.

VOCs originate mainly from terrestrial vegetation (Guenther et al., 1995). They react with hydroxyl radicals (OH) and can contribute to tropospheric ozone (O₃) formation and therefore influence air quality and human health. Atmospheric oxidation of VOCs can also lead to the formation and growth of secondary organic aerosols (SOA), which in turn can act as cloud



condensation nuclei, modulate radiative forcing by cloud formation, and therefore influence the global climate (Scott et al., 2018; Tripathi et al., 2025). Many plants and other organisms, like insects, emit VOCs for intra- and interspecific communication (Degenhardt et al., 2009; Ueda et al., 2012; Dudareva et al., 2013) as well as protection against light, temperature, or oxidative stress. In bryophytes, which were among the first plants to colonize land, VOCs can be used as
 45 volatile cues in their competition for space (Vicheroová et al., 2020).

Globally the most important biogenic VOC is isoprene (C_5H_8), making up about half of the total BVOC emission with 450-600 Tg yr⁻¹ (Guenther et al., 2012; Sindelarova et al., 2022a). It's emission is light-dependent, usually synthesized *de novo* from recently assimilated carbon during photosynthesis (Delwiche and Sharkey, 1993; Karl et al., 2002). Isoprene has been observed to be emitted and taken up as an energy source by microorganisms in soils and in a moss (Cleveland and Yavitt,
 50 1997; Murrell et al., 2020; Crombie et al., 2025). Mosses have been observed to be more likely to emit isoprene than other land plant groups (Hanson et al., 1999). It is speculated that isoprene emission evolved in a common ancestor of land plants for thermal protection (Hanson et al., 1999; Vicheroová et al., 2020). The isoprenoids monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) are formed by multiple isoprene units. They can also be stored within a plant cell prior to emission or synthesized *de novo* (Dudareva et al., 2013; Bourtsoukidis et al., 2024). Most isoprenoids are chiral molecules occurring in two enantiomeric
 55 forms whose ratio can reflect the dominant biosynthetic pathway in the species, the tissue, or chemotype, possibly modulated by stress (Norin, 1996; Staudt et al., 2019; Byron et al., 2022; Daber et al., 2025; Byron et al., 2025; Schüttler et al., 2026).

Reduced sulfur containing VOCs, like dimethyl sulfide (DMS), can transform into sulfuric acid via oxidation in the atmosphere (Kanda and Tsuruta, 1995). Sulfuric acid, which has a low vapor pressure is considered the most important chemical compound in new particle formation (Kulmala et al., 2004). DMS is mainly produced by marine ecosystems by transformation of
 60 dimethylsulfoniopropionate (DMSP). However, it's emission is not limited to marine environments, with plants and microbes from soils and leaf litter being reported as sources (Berresheim and Vulcan, 1992; Kesselmeier and Hubert, 2002; Jardine et al., 2015). In addition to DMS, dimethyl disulfide (DMDS) can be emitted from wetlands and vegetation and can be bidirectionally exchanged with soils (Yi et al., 2010). There are also a few studies that found the organoselenium counterpart to DMS: dimethyl selenium (DMSe), in atmospheric samples, likely emitted by aquatic ecosystems (Jiang et al., 1983;
 65 Amouroux and Donard, 1996).

In contrast to the extensive literature on VOC emissions from vascular plants, emissions from cryptogamic organisms, and particularly biocrusts, have only recently started to be recognized, despite their importance in extensive dryland ecosystems. For example the communities growing on bark, as well as soils in Amazonia were found to be important sources of sesquiterpenes under certain humidity conditions (Bourtsoukidis et al., 2018; Edtbauer et al., 2021; Schüttler et al., 2026). In
 70 subarctic mosses and lichens, acetone, acetaldehyde and other low molecular weight molecules were the dominant VOCs emitted (Ryde et al., 2022). The emission of isoprene, monoterpenes and some aromatic compounds by subarctic peatland was partly attributed to microbial activity (Faubert et al., 2010; Tiiva et al., 2007). A mid-latitude moss was found to emit acetaldehyde and low levels of monoterpenes and green leaf volatiles (GLVs) like hexanal (Kesselmeier et al., 1999). Lichens have been shown to emit dimethyl sulfide and hydrogen sulfide (Gries et al., 1994) as well as to take up C1-C2 organic acids
 75 (Wilske and Kesselmeier, 1999). VOCs were shown to mediate intraspecific communication in moss biocrusts under rainfall (Wan et al., 2026). Apart from VOCs, bryophytes are known to exchange methane with the atmosphere due to symbiosis with methanotrophs and methanogens (Chen and Murrell, 2010; Angel et al., 2011; Lenhart et al., 2015). Biocrusts were also found to fix nitrogen and emit nitrous oxide (N_2O) (Lenhart et al., 2015), nitric oxide (NO), and nitrous acid (HONO) (Weber et al., 2015). In summary, while physically inconspicuous, biocrusts are potentially important drivers of regional atmospheric
 80 chemistry and climate through their emission and uptake of reactive volatiles and greenhouse gases.

In this study, four different biocrust types, dominated by light cyanobacteria, dark cyanobacteria, chlorolichens, and mosses, as well as bare uncolonized soil according to the criteria of Weber et al., 2018, were studied regarding to their VOC emission potential. The samples were collected in the South African Succulent Karoo region near Soebatsfontein, a globally significant



biodiversity hotspot for arid regions. The biocrusts were measured in the laboratory under controlled temperature and light conditions, representative of the source location. Gas was swept over the samples and measured for VOCs, CO₂, CO, and CH₄ during initially dry conditions, then moist, then after a rain wetting event, simulating conditions that typically arise during the passage of a rain front. This study aimed to screen for possible VOCs emitted by this understudied group of biocrusts and make an estimation of the relevance of the emitted quantities to the local atmospheric conditions.

2 Methods

2.1 Biocrust samples

Biocrust samples were collected in September 2023 by the research group of Bettina Weber, accompanied by Stefan Herdy and Rodrigo Paidano Alves, in Soebatsfontein, located in the Succulent Karoo, South Africa (research permit: FLORA 0008/2023; export permit: FLORA 0009/2023). Five different types of samples were collected and classified according to the method of Weber et al., (2018) as biocrust samples dominated by light cyanobacteria, dark cyanobacteria, chlorolichens, and mosses, as well as bare uncolonized soil. The samples were collected and dried at the location as described by Tamm et al., 2018 and Weber et al., 2012. The collected samples were kept in Ø 5,5 cm plastic petri dishes, sealed with a lid and tape, and stored in a freezer at -20°C at the University of Graz, Austria, before measurements.

2.2 Measurement set-up

Three replicates of each biocrust type were measured in parallel with a blank. A schematic of the measurement set-up is given in Fig. A1 in Appendix A. In preparation for the measurements, the samples were taken out of a -20°C freezer one day before the experiment took place and kept at room temperature overnight. On the following day, each sample was transferred to a glass petri dish and placed in a separate cuvette (glass bottle, 2.5 L volume) contained within a light and temperature-controlled climate chamber. The climate chamber was constructed at the Max-Planck-Institute for Chemistry in Mainz. The light from LED lamps (XLG-150-L-AB, poly klima® GmbH) could be regulated, reaching 0-1500 µmol m⁻² s⁻¹ photosynthetically active radiation (PAR) at a distance of 30 cm from the light source, and the temperature could be set between 18 - 50 °C using two thermoelectric Peltier assemblies (AR-AR-100-24, Adaptive, European Thermodynamics Ltd). The chamber was equipped with sensors for temperature and humidity conditions. The light intensity was set to approximately 480-500 µmol/m² s⁻¹ PAR, and controlled at each of the cuvette positions at the beginning of each measurement using a light sensor (Skye SKP 215/S quantum sensor connected to a Skye SKP 200 display meter; Skye Instruments Ltd., Llandrindod Wells, Powys, UK). Four 2.5 L glass cuvettes (three samples and one empty-blank) were placed inside the climate chamber, which was pre-conditioned to 25°C, which resulted in a temperature of 25.0 ± 0.2°C inside the chamber. Each of the three pre-conditioned samples on glass petri dishes was placed inside three randomly chosen cuvettes, whereas the fourth one was used as a blank or background cuvette. This latter cuvette contained no sample, but only an empty glass petri dish. Clean air was generated by a zero-air generator (VZA-138, Tofwerk AG) and continuously streamed through all four cuvettes. The chemical measurements were performed by sampling airflow sequentially between the cuvettes (each cuvette was measured for 5 minutes in turn). The zero-air generator removes about 80 % of the methane in ambient air, resulting in 0.29±0.05 ppmv. The air flow rate through each glass cuvette was set to 500 mL min⁻¹ resulting in an air residence time in each cuvette of 5 minutes. All tubing and connections were made from Teflon. By using clean zero air to flush the cuvettes, by design, only VOC emissions can be observed. In other experimental setups (Edtbauer et al., 2021; Schüttler et al., 2026), ambient air with a natural VOC composition has been used to also assess uptake processes.

The samples were subjected to five sequential treatment phases (see flowchart in Fig. A2 in Appendix A). **(1)** Samples were exposed to dry air in the dark for 1 hour. **(2)** The inflow air then was humidified to ~70 % relative humidity by bubbling through a reservoir filled with artificial rainwater (Fig. A1 in Appendix A). **(3)** After 10 hours of humid air exposure in the



dark, the light was switched on. (4) After 12 hours of moist air exposure in the light, the samples were manually wetted by slowly dripping artificial rainwater onto their surface. This was followed by a minimum 12-hour dry-out period, during which the lights remained on for the first 10 hours. (5) The lights were switched off after a total of 12 hours of illumination. The only exception was the first moss sample measurement, where light and dark cycles alternated every hour to investigate light dependent effects. Artificial rainwater (4.5–13.5 g per sample, depending on size; see Table A1 in Appendix A) was delivered via a valve system that allowed watering without opening the glass chambers, maintaining continuous air flow. The total water volume was controlled by adjusting the valve opening time. Watering was stopped when the samples were thoroughly moistened but not submerged, as determined by visual inspection. The artificial rainwater was comprised of the salts K_2CO_3 , Na_2CO_3 , $CaCO_3$, $FeSO_4 \times 7 H_2O$ and $MnSO_4 \times H_2O$ in a concentration of 8.7, 4.4, 5.0, 4.3 and 0.6 mg L⁻¹, respectively, dissolved in LC-MS grade water (Sigma Aldrich) (Tamm, 1953). The solution was autoclaved for 15 min at 121 °C. The pH was set to 6.5 with an HCl solution. The air flowing from the cuvettes was led via ¼ inch (0.625mm outer diameter) Teflon tubing into the measurement devices. Measurements proceeded sequentially with 5 minutes per cuvette, always starting and alternating with the background cuvette to bracket each sample by background readings. High time resolution was obtained using a PTR-TOF-MS (Vocus PTR-ToF-MS, ToFwerk AG and Aerodyne Research, Inc.) for VOC measurements and a PICARRO gas analyser for CO, CO₂, CH₄, and H₂O (PICARRO G2401-m, Picarro Inc., Sunnyvale-California, USA). For improved compound speciation, air was sampled onto adsorbent filled cartridges four times during each measurement: (A) at the beginning of the experiment (phase 1), (B) after 12 hours of humidification in (phase 3), (C) immediately after wetting with artificial rainwater in (phase 4), and (D) 12 hours after wetting and subsequent drying (phase 5). Air from the sample cuvettes and the background cuvette was collected using a handheld pump (Gilian GilAir Plus Personal Air Sampling Pump; Sensidyne) with a flow rate setting of 200 mL min⁻¹ for 4 min, collecting 800 mL in total. After completing a full 24-hour measurement cycle, the sample cuvettes were cleaned first with 90 % ethanol, then with LC-MS grade water, and heated at 110°C for at least 2 hours to dry. This was done before starting the next 24-hour measurement cycle with further samples. An overview of the conditions during measurements is given in Table A1 in Appendix A.

2.2.1 PTR-TOF-MS measurements

The time-resolved composition and abundance of VOCs was measured by a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (Vocus PTR-ToF-MS, ToFwerk AG and Aerodyne Research, Inc.). A PTR-MS instrument is highly sensitive to VOC compounds, whose proton affinity is higher than that of water (693 kJ mol⁻¹) (Lindinger et al., 1998). The Vocus-PTR-ToF-MS features a focusing ion-molecule reactor (FIMR), which increases the detection sensitivity compared to a typical PTR-MS. The PTR was operated under standard conditions with a drift tube pressure of 2.3 mbar, a reactor temperature of 90 °C, and a potential of 475 V along the FIMR. This results in an E/N of around 110 Td. The instrument was calibrated using a diluted calibration gas mixture (National Physical Laboratory, Teddington, USA) with acetaldehyde, methanol, ethanol, acetone, dimethyl sulfide, isoprene, 3-carene (a monoterpene), acetonitrile, methyl vinyl ketone (3-buten-2-one), butan-2-one, benzene, toluene, m-xylene, trimethylbenzene, and trichlorobenzene with a 1- or 3-point calibration before each measurement. The concentrations for compounds not included as standards were calculated using reaction rates and transmission curves. The ions used for the tentatively identified VOCs and the proton transfer reaction rates, if available, are summarized in Table C in the appendix. If no proton transfer reaction rate was found in the literature a value of $2.50 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used.

2.2.2 GC-MS

The custom-built cartridges were made of silica-coated stainless-steel tubes (89 mm x 5.33 mm I.D., SilcoNert 2000, SilcoTek) containing 150 mg of Tenax ® TA mesh range 80/100 (Supelco) and Carbograph ® 5 TD mesh range 40/60 (Lara srl.). The sorbents were sealed with quartz wool and stainless-steel tension springs (Sigma Aldrich). Prior to use, the cartridges were



conditioned at 300 °C for 1 hour while being flushed with pure nitrogen at 2 bar pressure (TC-20, Markes International). After
 165 sampling, the cartridges were stored in a freezer at -20 °C until analysis.
 Prior to measurement, the sampled cartridges were removed from the freezer and brought to ambient temperature before being
 desorbed using a thermal desorption unit (TD100-xr and UNITY xr, Markes International). The thermal desorption process
 consisted of two stages. In the first stage, the cartridges were dry-purged for 5 min with a flow rate of 50 ml min⁻¹ and then
 desorbed for 5 min at 250 °C. The desorbed samples were pre-concentrated onto a cold trap (Material Emissions, Markes
 170 International). In the second stage, the cold trap was first purged for 1 min at 10 °C and then injected at 250 °C for 5 min into
 the gas chromatograph (GC, Agilent Technologies 7250) using a split flow of 2 mL min⁻¹. The GC was equipped with a 60 m
 long chiral β-DEX™ 120 capillary column (Sigma Aldrich) with an inner diameter of 250 µm and a film thickness of 0.25 µm.
 Helium 5.0 was used as a carrier gas at 1.2 mL min⁻¹ flow rate. The GC oven temperature was initially held at 40 °C for 5 min,
 then ramped at 1.5°C min⁻¹ to 110 °C, followed by a ramp at 5°C min⁻¹ to 220 °C, where it was held for 2 minutes. Detection
 175 was performed using an Accurate Mass Quadrupole Time-of-Flight-Mass Spectrometer (Q-TOF, Agilent Technologies).
 The GC-TOF-MS peaks were integrated using chromatography analysis software Mass Hunter Quant (Agilent Technologies).
 Compounds were quantified using a gas standard calibration mixture (Apel-Riemer International, USA) diluted with air. Full
 details are available in (Schüttler et al., 2025)

2.2.3 Flux calculation

180 The VOC fluxes were calculated according to the following formula:

$$F_{a,g} = Q * \frac{C_t - C_0}{N_{a,g}}$$

where F_a is the flux rate (µmol m⁻² h⁻¹) per surface area and F_g is the flux rate (µmol g⁻¹ (DW) h⁻¹) per dry weight of the
 sample, Q is the flow rate through the sample cuvette (500 mL min⁻¹ equals 0.03 m³ h⁻¹), N_a is the surface area (0.00196 m²)
 of the 50 mm petri dish with the sample or N_g is the dry weight of the sample, C_t is the BVOC concentration in the chamber,
 185 and C_0 is the BVOC concentration outside the chamber. The data from each cuvette was averaged over the 5 min measurement
 intervals, excluding the first minute and last 20 seconds. The values of the background cuvette were interpolated from the
 sample before and after each sample cuvette and subtracted from each sample value.
 The measurement uncertainty of compounds within the calibration gas mixture of the PTR is 15 %, as has been previously
 calculated from the error of the dilution of the calibration gas, the calibration gas concentration, the precision of the instrument,
 190 and the error of the fit of the calibrations. Compounds not present in the calibration gas mixture have an estimated uncertainty
 of 50 % (Lindinger et al., 1998; Edtbauer et al., 2021).

2.4 Statistical analysis

The VOC data was analysed using the following packages in python (v 3.12.4): numpy (v 2.0.0), pandas (v 2.2.2), matplotlib
 (v 3.9.1), seaborn (v 0.13.2), statsmodel (v 0.14.5), scikit-learn (v 1.5.1), scikit-bio (v 0.5.9) and scipy (v 1.16.0). Data
 195 visualization was conducted using matplotlib and seaborn. The observations in this study stem from 15 physical samples (3
 replicates per biocrust type and bare soil) measured continuously over time across five experimental phases with three samples
 simultaneously within each measurement run (Table A1 in Appendix A). To account for non-independence of these repeated
 measures, statistical methods were chosen carefully. Associations between VOC compounds were assessed using Kendall's
 rank correlation coefficient (τ), which is robust to non-normality and outliers. Data was aggregated across measurement phases
 200 to avoid pseudo replication. To investigate compositional differences in the VOC composition among measurement phases
 and biocrust types, permutational multivariate analysis of variance (PERMANOVA; Anderson, 2001) on centred log-ratio
 (CLR)-transformed VOC class compositions (Aitchison distance), using scikit-bio with 999 permutations was performed. Zero
 values in the compositional data, arising when a VOC class contributed no measurable flux within a given observation, were



replaced with a small pseudo count (10^{-6}) prior to CLR transformation. Negative flux values, occasionally occurring due to background-subtraction noise around near-zero emissions, were set to zero prior to computing compositional proportions. To avoid pseudo-replication from repeated time points within the same physical sample, compositional data were averaged within each combination of sample replicate, measurement run, and phase (for the phase test) or sample replicate and measurement run (for the sample type test) prior to testing. As some physical samples were measured across multiple experimental runs (Table A1 in Appendix A), each measurement occasion was treated as a separate observational unit. Additionally, component analysis (PCA) was performed on the same CLR-transformed VOC class compositions using scikit-learn, with sample scores and compound loadings displayed as biplots for visualization. To analyse differences in VOC fluxes across measurement phases and sample types, linear mixed-effects models (LMMs) were fitted using the MixedLM implementation in statsmodels. To account for repeated measurements within the same physical sample, individual sample replicates ($n = 3$ per biocrust type and bare soil) were included as a grouping factor with random intercepts and random slopes for time within each measurement phase. An additional variance component was included to account for random intercepts per measurement run, controlling for possible batch effects across experimental runs. Fixed effects comprised measurement phase, time within phase, and sample type (biocrust type or bare soil). VOC flux data were log1p-transformed prior to modelling to address right-skewed residuals and heteroscedasticity identified in preliminary diagnostics. The log1p transformation, defined as $\log(1+\text{flux})$, requires flux values greater than -1 to remain defined. Negative flux values occurred occasionally due to background-subtraction noise around near-zero emissions and were set to zero, consistent with the study design in which only VOC emissions (positive flux values; no uptake) could be measured. Models were fitted by restricted maximum likelihood (REML) using the L-BFGS optimizer. Fixed-effect coefficients (β) represent the estimated change in the response variable (log1p-transformed VOC flux) associated with a given predictor level, relative to the reference level, while holding other model terms constant. Pairwise differences between phase levels were computed as linear contrasts of fixed-effect coefficients, with standard errors derived from the fixed-effects covariance matrix, and are reported as percent changes on the original scale ($100 \times (\exp(\beta) - 1)$), with 95 % confidence intervals obtained by back-transforming the confidence limits from the log1p scale. The same modelling framework was applied to test differences in specific VOC classes between sample types. All p-values for pairwise comparisons were adjusted for multiple testing using the Benjamini-Hochberg false discovery rate (FDR) procedure. Statistical significance was accepted if $p < 0.05$.

When fluxes are presented in the text, they are the mean $\pm$ their standard deviation.

2.5 Upscaling the emission fluxes to the ecosystem scale

In order to gauge the relative importance of the biocrust types and the overall biocrust impact on the overlying atmosphere, we upscaled the laboratory derived fluxes according to ecosystem observations and rainfall conditions. At Soebatsfontein, biocrusts cover approximately 27 % of the 2 837 ha surface area (Weber et al., 2018). For upscaling the total VOC emissions from this site, we assumed that the biocrust covered area consisted of 55.6 % light cyanobacteria, 18.5 % dark cyanobacteria, 3.7 % moss, 3.7 % chlorolichen, and 18.5 % cyanolichen dominated biocrusts, based on the average community composition reported by Rodríguez-Caballero et al. (2022) for four sites within this region. Cyanolichen-dominated crusts were assumed to emit VOCs at the same rate as dark cyanobacterial crusts, as they were not included in the laboratory emission measurements (here chlorolichen were measured).

Continuous field measurements of biocrust wetness (expressed as precipitation equivalents in mm) were used to estimate active emission periods over a full year (Weber et al., 2016, 2018). Biocrusts were considered metabolically active when their surface wetness exceeded thresholds of 0.3 mm or 0.1 mm, respectively, in two independent upscaling scenarios. For each biocrust type, the mean VOC flux measured 0.2–12.2 hours after wetting in the here presented laboratory experiments was multiplied by the cumulative duration of active wet periods and by the respective areal coverage to obtain rough annual ecosystem-scale emission estimates.



3 Results

3.1 Respiration and photosynthesis

In general, for all biocrust samples, as shown in Figure 1, the net CO₂ fluxes were close to zero before the samples were wetted. This shows that very little to no photosynthesis or respiration occurred in the first three phases of the experiment. This includes the 12 hour exposure to humid air in phase 2 (dark) and 3 (light) at approximately 75 % relative humidity (see Fig. A3 for temperature and humidity during the measurements). After wetting of the samples in phase 4, the CO₂ flux showed net uptake in all biocrust types except the moss in the light. Also, CO was taken up by all samples except one moss sample (see Figure B1 in Appendix B). The net CO₂ flux became positive during darkness, indicating ongoing respiration and the stop of photosynthesis. The CO₂ fluxes of light cyanobacteria, dark cyanobacteria and the lichen dominated biocrust sample were very similar, decreasing exponentially to an equilibrium value of circa $-2 \mu\text{mol m}^{-2} \text{s}^{-1}$. For bare soil samples, the changes in fluxes were less pronounced, attaining an uptake flux for CO₂ of $-1 \mu\text{mol m}^{-2} \text{s}^{-1}$, half that of the encrusted soils. During close examination under the magnifying lens, a greenish tinge, could be observed in the bare soil samples. For the mosses, the respiration appeared to be exceeding photosynthesis, even in the light periods, so that CO₂ showed net emissions even after wetting. It should however be noted that the mosses previously had been subjected to a different light regime of alternating one-hour periods of light and dark (described in Sect. 3.3; Figure 8).

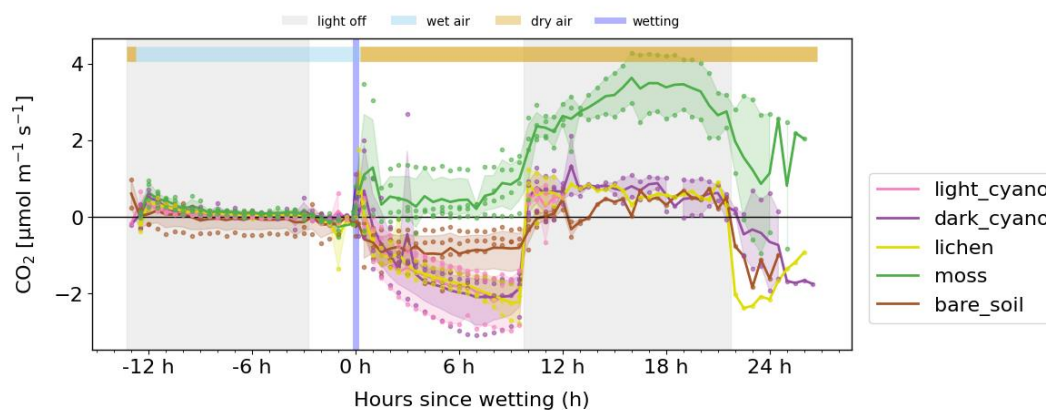


Figure 1: Net CO₂ flux during the measurements 2-7 for the different sample types. The lines represent the mean emission, shaded areas the 95 % confidence interval; dots are the individual measurement points of each replicate.

3.2 VOC emissions

The variability of VOC emission flux magnitude was greater than that of CO₂ fluxes between the three replicates of the same biocrust type. Nonetheless, there were distinct VOC emission patterns observed for the different biocrust types associated with the experimental procedures described above.

The VOC composition differed significantly (PERMANOVA; Table D2 in Appendix D) between the phase of the measurement (light, wetness) and sample type (biocrust or bare soil). Phase explained a substantially larger proportion of compositional variance ($R^2 = 0.503$, pseudo- $F = 23.8$, $p < 0.01$) than sample type ($R^2 = 0.518$, pseudo- $F = 4.3$, $p < 0.01$). The separation by measurement phase and the associated parameters was also reflected by PCA analysis (Figure B2 in Appendix B). The highest total emissions were observed in the moss-dominated samples (linear mixed-effects model; $\beta = 2.33$, corresponding to $121 \text{ nmol m}^{-2} \text{s}^{-1}$ difference; $p < 0.01$; Table D1 in Appendix D). Pairwise comparisons among phases showed that total VOC emissions in phase 1 (dark, dry air), phase 3 (light, humid air), and phase 4 (light, after wetting) were significantly lower than in phase 2 (dark, humid air; linear mixed-effects model; $\beta = -1.21, -2.48$, and -2.86 , corresponding to a 70 %, 92 %, and 94 % decrease, respectively; all $p < 0.05$; FDR-adjusted; Table D1 in Appendix D). The exceptional role



of moss-dominated samples was also reflected by a PCA analysis, where the data were separated by measurement phase (Figure B3 in Appendix B). The VOC flux composition of moss-dominated biocrusts clearly differed from all other biocrust types during the different wetting phases, whereas emissions of biocrusts dominated by light cyanobacteria were often similar to those of lichen-dominated crusts (comparison had no significant difference; PERMANOVA; Table D2 in Appendix D).

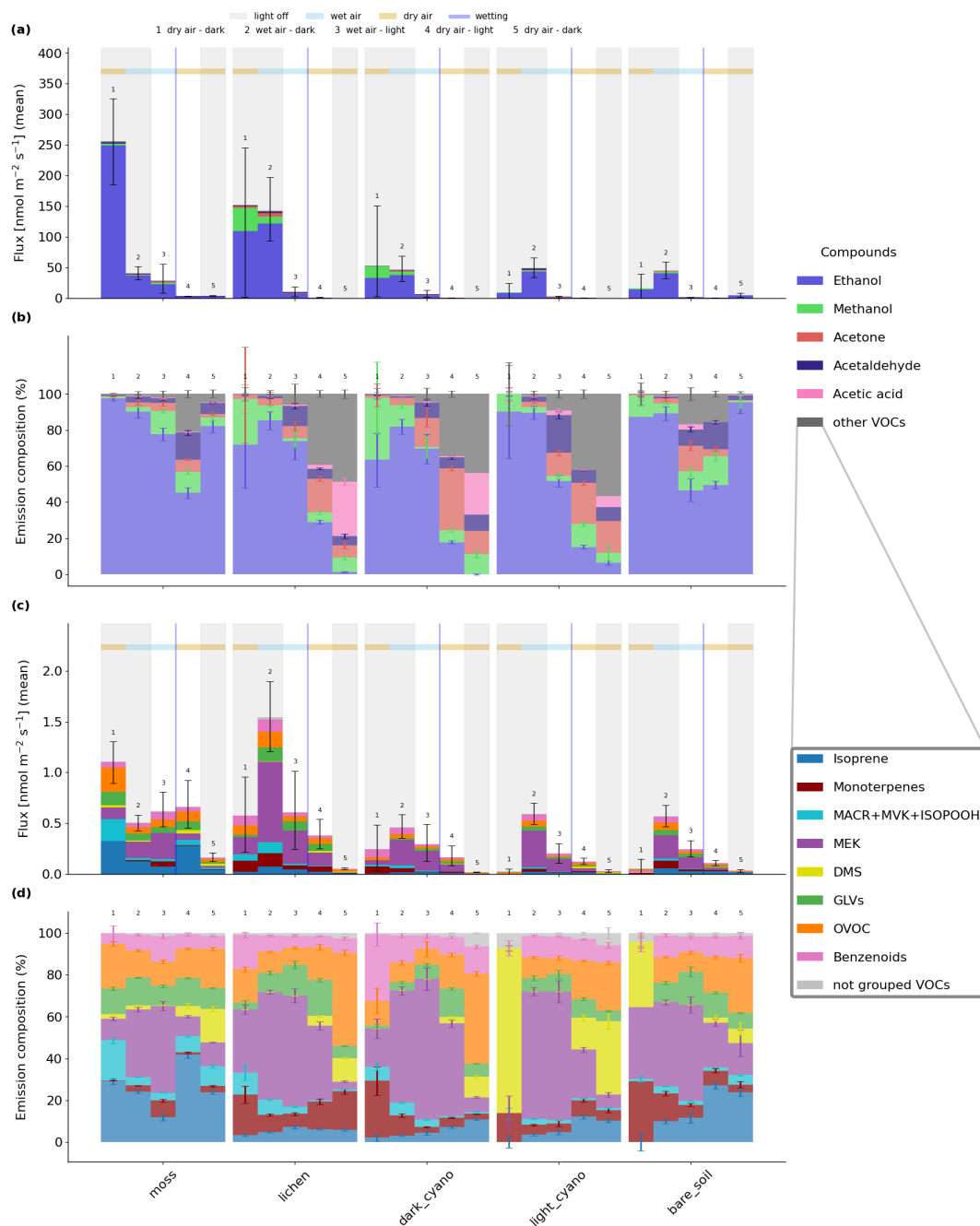
While CO₂ uptake through photosynthesis increased after wetting, VOC emissions were higher under dry conditions. Ethanol, methanol, and acetone (Figure 2a) dominated the emissions with fluxes approximately 100 times higher than those of other less volatile VOCs (Figure 2b; Figure B4 in the Appendix B shows the composition over time). Emissions of low molecular weight compounds, including ethanol, methanol, acetone, acetaldehyde, and acetic acid fell below 10 nmol m⁻² s⁻¹ after wetting.

The quantitatively highest emitted VOC was ethanol (mean of 190±121 nmol m⁻² s⁻¹ before wetting for all samples and 5.6±8.8 nmol m⁻² s⁻¹ after wetting; Figure 2), followed by methanol (mean of 16.5±16.8 nmol m⁻² s⁻¹ before wetting for all samples and 0.7±1.3 nmol m⁻² s⁻¹ after wetting), acetone (mean of 6.8±6.4 nmol m⁻² s⁻¹ before wetting for all samples and 0.7±0.5 nmol m⁻² s⁻¹ after wetting) and acetaldehyde (mean of 3.18±1.57 nmol m⁻² s⁻¹ before wetting for all samples and 0.5±0.5 nmol m⁻² s⁻¹ after wetting).

The mean VOC flux detected by PTR-MS, excluding low molecular weight compounds (Figure 2c,d), was 2.5±1.8 nmol m⁻² s⁻¹ (0.3±0.2 pmol g⁻¹ DW h⁻¹) before wetting (phase 1-3) and 0.7±0.5 nmol m⁻² s⁻¹ (0.09±0.08 pmol g⁻¹ DW h⁻¹) afterwards (phase 4-5). Mean emissions before and after wetting for each individual compound are shown in Table C2 in Appendix C.

While the total emission of VOC was lower after wetting, some compounds, like dimethyl sulfide (DMS) and geosmin increased or started to be emitted after the wetting event. Bare soil samples also emitted VOCs, although at lower rates than lichen- and moss-dominated biocrust samples, but at the same magnitude as cyanobacteria-dominated biocrusts (bare soil samples were only statistically significant compared to moss-dominated biocrusts, *p* < 0.01). Green leaf volatiles (GLV) showed higher emissions by moss- and lichen-dominated biocrusts compared to bare soil and cyanobacterial biocrusts (not statistically significant by linear mixed-effects model; *β* = 0.036, corresponding to 0.04 nmol m⁻² s⁻¹ difference; *p* > 0.05). The composition of the GLVs is shown in Figure B5 in Appendix B and summarized in Table C2 in Appendix C: The compounds pentanal, hexanal, cyclohexene, hexadienal, cyclohexanone, hexanoic acid, and nonenal (see Table C1) were grouped as GLVs. Note that the identification of these compounds is tentative, as no standard was used. Oxygenated VOCs (OVOC) other than the oxidation products of isoprene (MACR+MVK+ISOPOOH: methacrolein, methyl vinyl ketone, and isoprene hydroxy hydroperoxides), methyl ethyl ketone (MEK), ethanol, methanol, acetone, acetaldehyde, and acetic acid are shown in Figure B6 in Appendix B.

Benzenoid compounds like toluene, styrene, trimethylbenzene, xylenes were grouped together and are shown in Figure B7 in Appendix B. The GC measurements also verified peaks for toluene, styrene, different xylenes and trimethylbenzenes, and benzene with NIST library match factors above 750.



310

Figure 2 Mean VOC emission of the four biocrust types and bare soil ($n = 3$) measured by PTR-ToF-MS. Measurements (2-7) are grouped by phases of the experiments; Emission rates of (a) total VOCs mainly composed of low molecular weight compounds ethanol, methanol, acetone, acetaldehyde, and acetic acid and (c) the less volatile compounds, with 95 % confidence intervals shown as error bars. Mean proportional contributions of the total VOCs (b) and less volatile compounds (d) are shown in percent with the error bars representing the standard error of the mean. MACR+MVK+ISOPOOH refers to $m/z = 71.0497$ in the PTR, usually being methacrolein, methyl vinyl ketone, and isoprene hydroxy hydroperoxides; MEK refers to $m/z = 73.0242$ in the PTR, methyl ethyl ketone or other C4 carbonyls; DMS is dimethyl sulfide; GLVs are identified green leaf volatiles; OVOC are identified oxygenated VOCs.

315



3.2.1 Isoprene and Monoterpenes

320 All biocrusts emitted isoprene and monoterpenes. The moss samples emitted notably higher amounts of isoprene, while the lichen-, light cyanobacteria-, and dark cyanobacteria-dominated biocrusts as well as bare soil emitted more monoterpenes (Figure 3). Monoterpene emission was highest in the first part of the experiments, starting low after introduction to the cuvette, and increasing rapidly during exposure of the samples to humid air in the dark. Monoterpene emissions peaked ~3 hours after insertion into the sample cuvettes (~2 hours after exposure to humid air), similar for all samples except for mosses, which

325 peaked ~1 hour earlier and reached lower monoterpene flux values. Thereafter, the monoterpenes decreased, exhibiting a small peak during and after wetting. In one of the lichen-dominated samples, this increase of monoterpene emissions already started before wetting when the light was switched on. The same light dependence was observed for the isoprene emissions of the moss-dominated biocrusts that increased with light and dropped during darkness.

The isoprene emission in mosses was a factor 10 higher than for the other sample types, while the monoterpenes were lowest

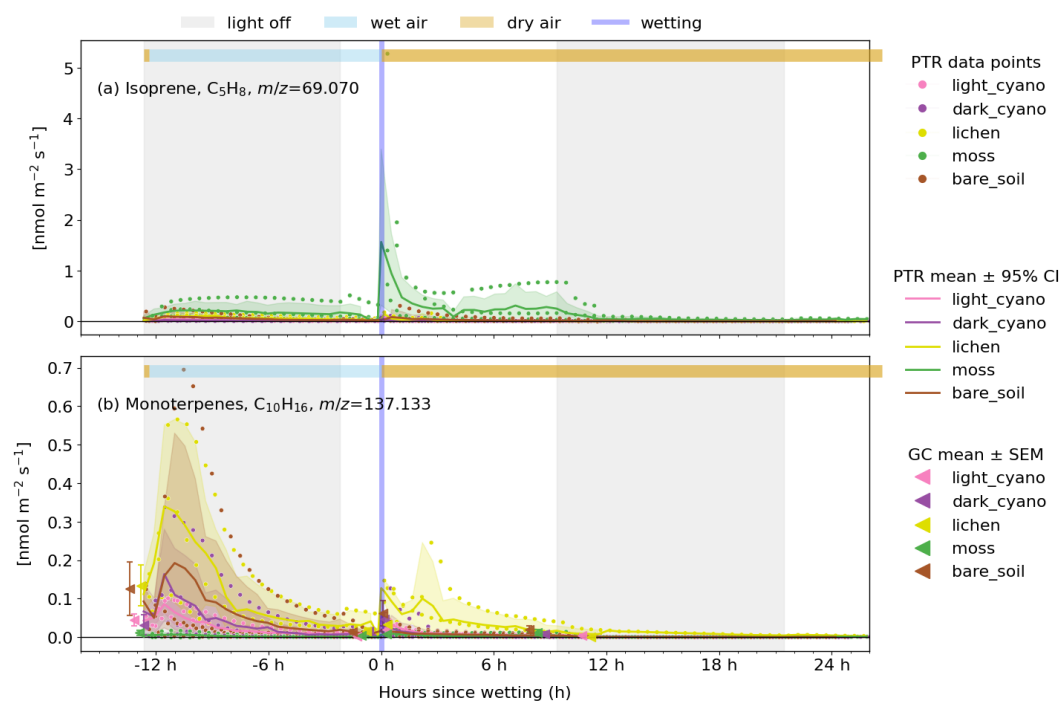
330 for the moss-dominated biocrusts. The highest peak for isoprene was observed immediately after wetting. For the other four sample types the pattern of isoprene emission was similar to the monoterpene emission, but did not decrease as much after the wetting. The isoprene and monoterpene emissions became close to zero at the end of the drying period for all sample types, even though respiration and photosynthesis were still active (Figure 1). The isoprene emission of the moss made up around 90 % of its carbon investment in total isoprenoid VOC emissions, as shown in Figure 4. The total isoprenoids comprised

335 isoprene, monoterpenes, sesquiterpenes, geosmin and 2-methylisoborneol. For the other biocrusts, the carbon investment into isoprene as compared to total isoprenoids still made up around 20-60 %, while investing about the same amount of carbon into heavier isoprenoids like monoterpenes.

The speciation of the monoterpenes by GC-MS in Figure 5 shows a different composition for each biocrust, with the largest difference between the moss samples compared to the lichen- and cyanobacteria-dominated crusts. The other monoterpene

340 emissions were dominated by *p*-cymene. Of the chiral monoterpenes detected, the (–)-enantiomers of camphene, α -pinene, and β -pinene and the (+)-enantiomer of limonene were dominating across all samples.

The GC-MS measurements of the speciated monoterpenes were broadly consistent with the PTR measurements (see triangular markers for GC data in Figure 3 showing PTR-data and diamond markers for PTR data in Figure 5 showing GC monoterpene data).



345

Figure 3: Time series of the mean isoprenoid VOC fluxes during the measurement of four different biocrust types and bare soil (n = 3). Measurements comprise (a) isoprene and (b) monoterpenes. The lines represent the mean emission, shaded areas the 95 % confidence interval; dots are the individual measurement points of each replicate of PTR measurement; triangular markers represent the mean GC measurements and the vertical lines the standard error of the mean (SEM).



350

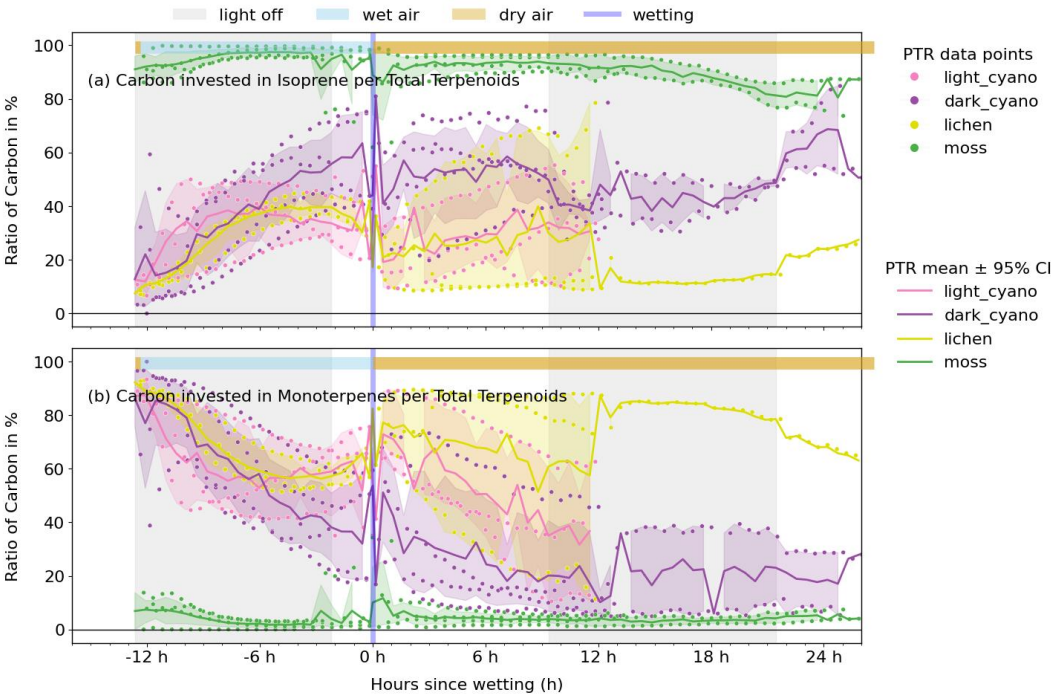


Figure 4: Time series of the mean carbon invested by different biocrust types and bare soil ($n = 3$) in (a) isoprene and (b) monoterpenes per total isoprenoids VOC carbon flux. Measurements comprise four different biocrust types. The lines represent the mean contribution, shaded areas the 95 % confidence interval.

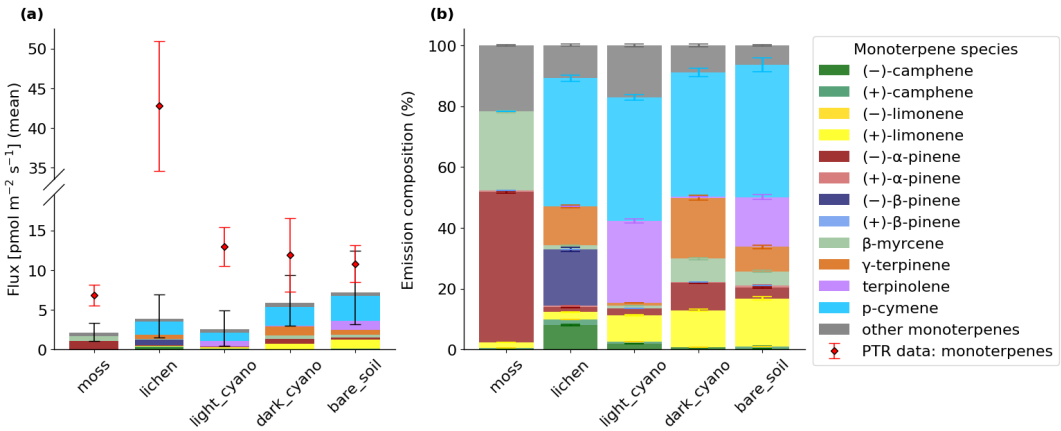


Figure 5 Monoterpene mean emission composition of different biocrust types and bare soil ($n = 3$) over the complete measurement cycle (i.e., cycle of dry, high air humidity, wet, and drying conditions). Results shown as (a) stacked bar plot with mean values per biocrust type and 95 % confidence interval of the total monoterpene emission based on the GC measurements. The red diamond shape markers show mean total monoterpene fluxes based on PTR measurements ± 1 hour around the GC measurement points with standard error. In (b) mean monoterpene emission composition of each biocrust type and bare soil is shown in percent, with the error bars representing the standard error.

3.2.2 Petrichor associated emissions after wetting: geosmin and 2-methylisoborneol

For PTR and GC measurements, the isoprenoids geosmin ($C_{12}H_{22}O$, $m/z = 183.1749$) and 2-methylisoborneol ($C_{11}H_{20}O$, $m/z = 169.1587$) were observed to be emitted in small amounts after wetting (Figure 6), especially by the moss-, lichen- and



365 dark-cyanobacteria dominated crusts. Geosmin and 2-methylisoborneol had a match factor of up to 750 and 500, respectively, with the NIST library in the GC measurement. These compounds are considered part of the “petrichor”, the smell of dry soil after rain (Bear and Thomas, 1964; Gerber and Lechevalier, 1965). Other sesquiterpenes also peaked during wetting (see Figure B8 in the Appendix B), but were mostly below the limit of detection for the GC measurement. Other compounds, correlating with geosmin and 2-methylisoborneol, were $m/z = 141.1270$ ($C_9H_{16}O$), $m/z = 99.0441$ ($C_5H_6O_2$), 370 and $m/z = 136.022$ (C_7H_5NS) tentatively identified as nonenal or nonenone, furfuryl alcohol, and benzothiazole respectively ($r = 0.75$, 0.73 , and 0.61 for Kendall τ correlation with geosmin and $r = 0.79$, 0.56 , and 0.55 with 2-methylisoborneol, respectively; all $p < 0.05$; Figure B9 in Appendix B; Table D3 in Appendix D). An additional time series plot of these substances can be found in the Appendix B in Figure B8. Another common compound associated with petrichor, isopropylmethoxypyrazine, has neither been detected in GC nor in PTR measurements.

375

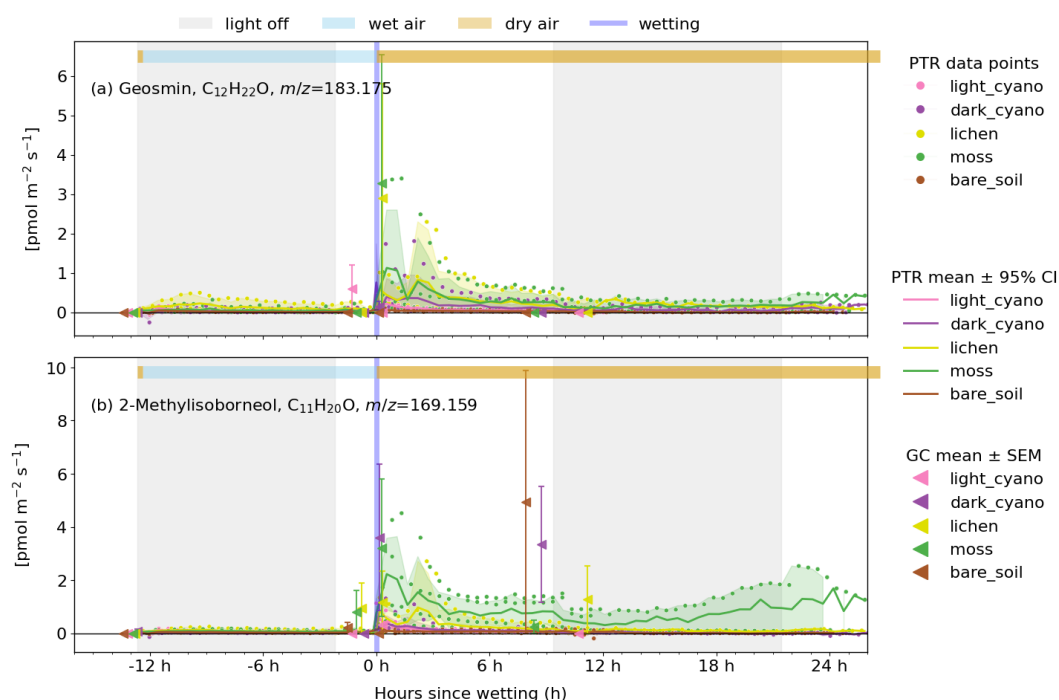


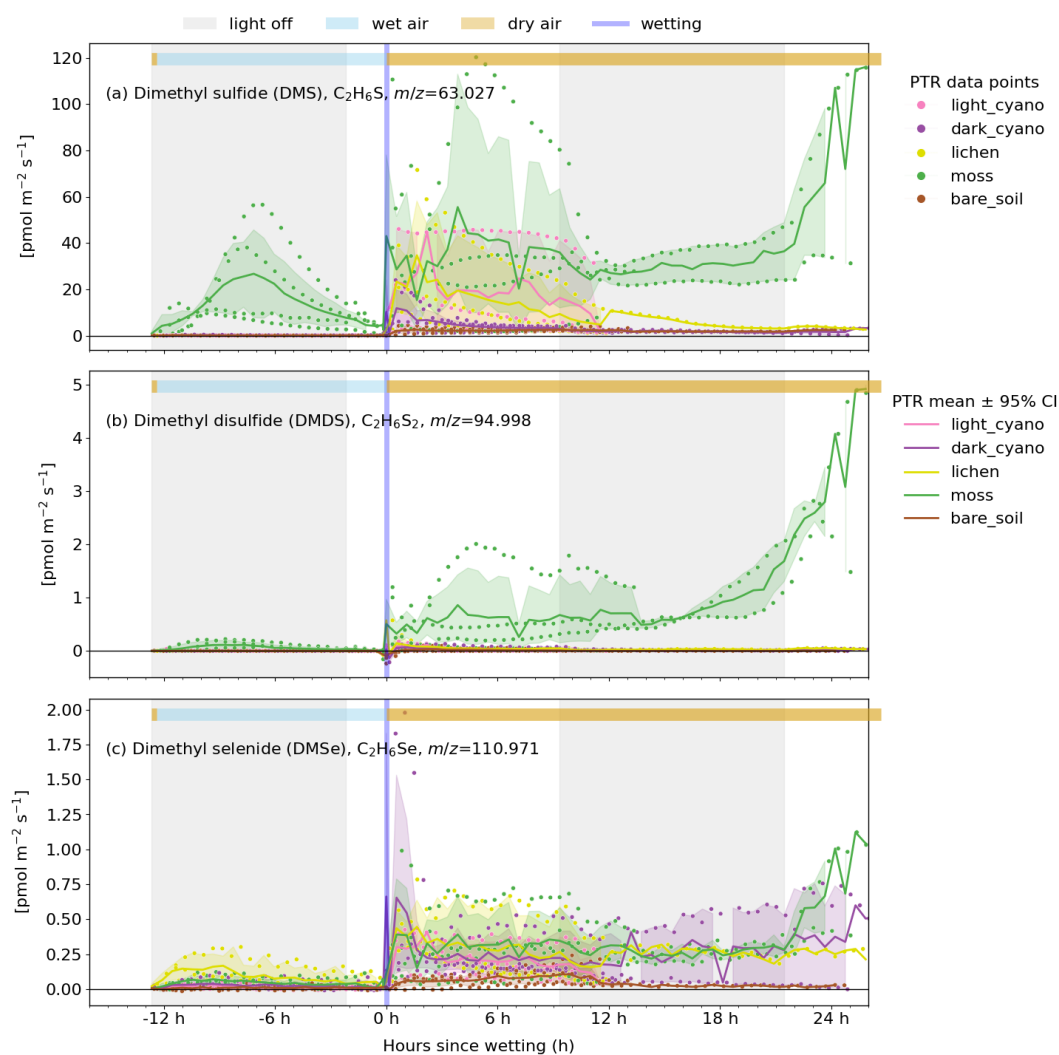
Figure 6 Time series of the mean fluxes of VOCs associated with petrichor during the measurement of different biocrust types and bare soil ($n = 3$) for (a) geosmin and (b) 2-methylisoborneol. The lines represent the mean emission, shaded areas the 95 % confidence interval; triangular markers represent the mean GC measurements and the vertical lines the standard error of the mean.

380 3.2.3 Sulfur and Selenium compounds

The emissions of sulfur compounds were strongest in the moss-dominated biocrusts (see Figure 7). For the moss samples, emission of DMS was already observed before wetting, under high air humidity conditions, with a peak in emissions after ~5 hours of exposure to high air humidity in the dark. A second burst of DMS emission was observed after wetting, and emission even increased at the end of the drying period. However, one needs to consider that the moss samples had already 385 been measured and activated through wetting during measurement 1 (compare Table A1 in Appendix A) and subsequently dried afterwards. Lichen-, light cyanobacteria-, and dark cyanobacteria-dominated biocrusts, as well as bare soil only emitted DMS after wetting. DMS emission then continued throughout the following light period. During the subsequent dark period, only the lichen and moss samples continued to emit DMS. Generally, DMS showed the highest emission rates of sulfur and selenium compounds.



390 For dimethyl disulfide (DMDs) the difference between moss and the other biocrust types was even stronger, although the temporal pattern of emissions was similar to DMS (Figure 7). As DMDs emits two sulfur atoms per molecule, contributed up to 15 % to the total sulfur emission in moss samples during the drying period of phase 5 (see Figure 7). Interestingly, we also observed dimethyl selenide emissions after wetting, with highest emission rates by the dark cyanobacteria-dominated biocrusts. This compound DMSe, is chemically related to DMS, since selenium is in the same group of the periodic table. The temporal patterns of the DMSe emissions in relation to the light and water treatments are similar, although the fluxes are by a factor of 100 lower.



400 **Figure 7** Time series of the mean sulfur and selenium VOC emissions during the measurement of the different biocrust sample types and bare soil ($n = 3$) for (a) dimethyl sulfide (DMS), (b) dimethyl disulfide (DMDs), and (c) dimethyl selenide (DMSe). The lines represent the mean emission, shaded areas the 95 % confidence interval.

3.3 Impact of one-hour light-dark cycles on the moss dominated biocrusts

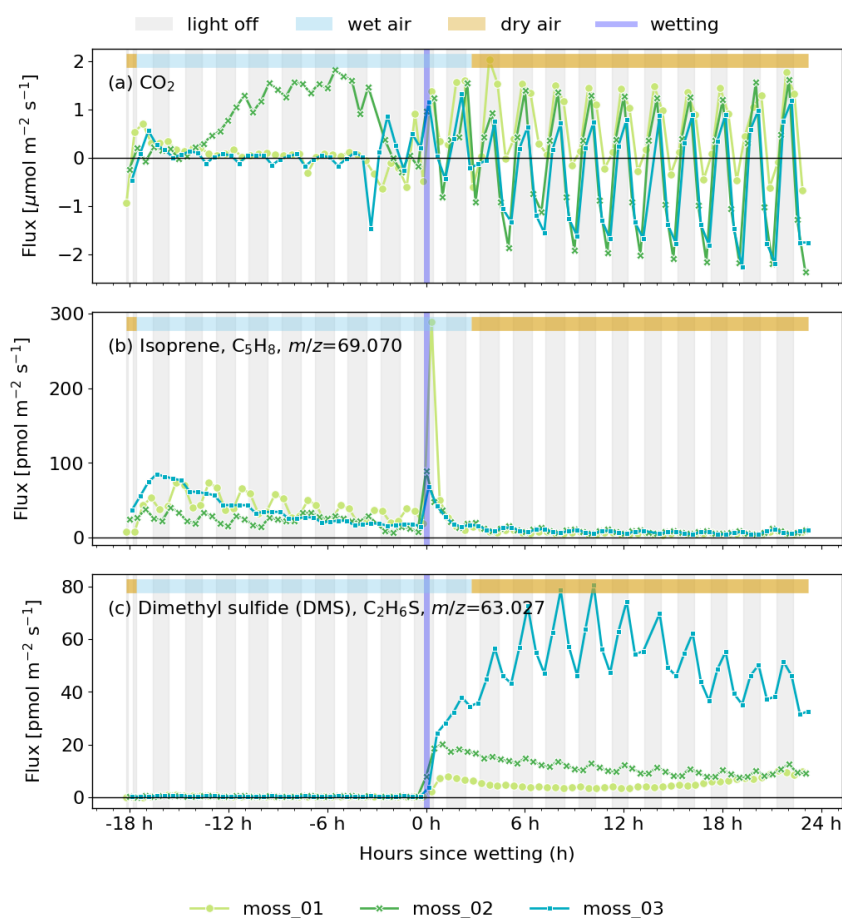
For the moss samples, an additional test was performed to examine the photosynthetically related emission of VOCs in more detail. In the first measurement of the three moss dominated samples (Figure 8), the light was switched on and off at an hourly



405 interval (see Table A1). This allowed observation of the rapid adaption of the fluxes from night- to daytime conditions under constant temperature. The three moss replicates did not behave in the same way during this measurement. The second replicate moss_02 showed higher respiration rates at high air humidity before wetting compared to the other two moss samples. After wetting, the amplitude of the CO₂ uptake flux increased, and thereafter all three moss dominated samples showed a clear pattern of photosynthesis occurring in the light and increased CO₂ emission during darkness.

410 The total emission of isoprene was higher at high air humidity alone before wetting, than it was after wetting. Two of the samples (moss_01 and moss_02) showed a clear trend of increased emission during the time in the light as compared to dark conditions (Figure B11 in Appendix B). The wetting led to a brief burst of emission, while afterwards the emission was lower. In stark contrast to isoprene, DMS only started to be emitted from mosses 2 and 3 after wetting, and emissions increased in the dark rather than the light. While all moss samples started emitting DMS after wetting, sample moss_03, and to a smaller degree also moss_02, showed a dependence on light with increased emissions during darkness. At the same time, moss_01 seemed to emit DMS continuously after rewetting with less dependence on light. DMDS and DMSe emission patterns were similar to DMS and monoterpene emissions (Figure B10 in Appendix B).

415



420 **Figure 8** Time series of the fluxes of (a) CO₂, (b) Isoprene and (c) DMS during the measurement of moss dominated biocrust samples with light switched on and off at an hourly interval. The markers represent a measurement point of each moss dominated biocrust replicate.



3.4 Methane

Methane emissions and uptake were monitored by the PICARRO instrument. Before wetting no net methane flux was registered. After wetting, methane was taken up at a rate of $-0.52 \pm 0.01 \text{ nmol m}^{-2} \text{ s}^{-1}$ in the light (Figure B12 in Appendix B).

425 It was briefly emitted by moss and dark cyanobacteria samples ~12 hours after the wetting during darkness. In general, the fluxes were low, which might also be due to the low concentrations in the input air (below ambient atmospheric concentrations), as the zero-air generator removes methane partly from the incoming air.

3.5 Upscaling emissions

With the emission values of the 15 samples of four different biocrust types and bare soil, studied under artificial conditions, a
 430 first-order upscaling of the measured emissions to the ecosystem scale was performed as described in Sect. 2.5. For the Succulent Karoo site near Soebatsfontein, the upscaling yielded total VOC emissions of 0.64 Mg yr^{-1} using a biocrust wetness activity threshold of 0.3 mm, and 0.98 Mg yr^{-1} using a threshold of 0.1 mm. If biocrusts occupy roughly 12 % of the global land surface ($148.94 \text{ million km}^2$; Rodriguez-Caballero et al., 2018) and exhibit comparable emission rates worldwide, these emissions could be as high as 0.61 Tg yr^{-1} corresponding to approximately 0.07 % of the estimated global annual biogenic
 435 VOC emissions of 835.4 Tg yr^{-1} (Wang et al., 2024). Compared to the annual transferred sulfur from the oceans to the atmosphere of $28.1 \text{ Tg (S) yr}^{-1}$ (Lana et al., 2011), biocrust could emit up to $0.0138 \text{ Tg (S) yr}^{-1}$ (using a biocrust wetness activity threshold of 0.1 mm) contributing 0.05 % of emissions.

4 Discussion

Biocrusts covering the soils of arid environments, such as these studied here from the Succulent Karoo (South Africa -aridity
 440 index: 0.08), irregularly undergo wetting by rain and desiccation events. In this study, we explore the VOC emission behaviour of four different biocrusts types and bare soil exposed to low and high air humidity, followed by a wetting event in relation to CO_2 uptake and changing light conditions.

4.1 Respiration and photosynthesis

After wetting, lichen and both cyanobacteria biocrusts, but also the bare soil samples showed photosynthetic uptake of CO_2 in
 445 the light. The latter is intriguing, as photosynthesis would not be expected for bare soil samples. As these “bare soil” samples have been collected from uncrusted areas in the field, they are not expected to be sterile, and respiration in the dark could easily be explained by a wealth of bacteria and fungi also colonizing these samples (Maier et al., 2018). The low rates of net photosynthesis could only be explained by the presence of some photosynthesizing organisms. As a greenish tinge, likely caused by an initial cyanobacterial colonization, could be observed in these samples the bare soil samples could indeed not be
 450 “bare”.

Under the standard measurement routine, the moss samples showed lower respiration rates, but no CO_2 uptake in the light (Figure 1). This might have been caused by some stress during the first experiment with hourly dark and light intervals, where the samples still showed positive net photosynthesis rates (Figure 8a). High respiration rates of moss-dominated biocrusts from the same site have also been observed during earlier in-depth CO_2 gas exchange studies, where soil respiration rates were
 455 observed to be particularly high, likely due to high fungal and bacterial abundance and physiological activity (Weber et al., 2012; Maier et al., 2018). The observation of CO uptake (Figure B1) can be explained as in the microbiome of lichen and moss biocrusts a high abundance of CO dehydrogenases were found (Tian et al., 2023) and bacteria are known for oxidizing CO (King and Weber, 2007). The speedy recovery of the metabolism of the biocrusts after wetting is consistent with previous studies (Garcia-Pichel and Belnap, 1996; Harel et al., 2004; Ohad et al., 2010; Rajeev et al., 2013), as they are used to
 460 desiccation and have to rapidly adapt when water is present. The net photosynthesis of up to $2 \mu\text{mol m}^{-2} \text{ s}^{-1}$ uptake of CO_2 for



the lichen- and cyanobacteria-dominated biocrusts was similar to rates found by Tamm et al., 2018 for biocrusts from the same location.

4.2 General VOC emission trends of biocrusts

The results of this study show that biocrusts and bare soil emitted a variety of VOCs (Figure 2), suggesting they could play a significant role in the local atmospheric VOC chemistry of the Succulent Karoo. Additionally, VOC emissions changed over the course of the measurements in response to changes in water availability and light conditions. The greatest difference was observed when comparing the VOC release before (phase 1-3) and after the wetting (phase 4-5). While the respiration and photosynthetic activity seemed to mainly start after the wetting, VOC emissions were already present before wetting of the samples under high air humidity conditions alone. Surprisingly, total VOC emissions were lower in the light after wetting (phase 4) than in the dark when the samples were exposed to humid air (phase 2). This could be due to partial activation caused by high air humidity alone, which activated VOC emissions, but was insufficient for positive rates of net photosynthesis. Water vapour alone has previously been shown to activate respiration and sometimes even photosynthesis in lichens with green algal photobionts (Lange et al., 2006), whereas cyanobacteria almost exclusively need liquid water to be activated (Lange et al., 1993). Therefore, even though in this study almost no net photosynthesis was observed under humid air conditions prior to wetting, other biological processes might have been activated at lower water content thresholds, particularly in accompanying bacteria (Truu et al., 2017). The common emission of low molecular weight compounds and others hints towards the occurrence of common bacteria and other organisms found in all samples. The differences between the studied biocrusts and bare soil are biggest when comparing moss with the other samples. During succession, moss- and lichen-dominated biocrusts develop on light and then dark cyanobacterial predecessors (Weber et al., 2018). Overall, biodiversity within the biocrusts increases along the successional stages and reveals bacterial compositions characteristic for the different biocrust types, which could cause the higher and different emissions (Maier et al., 2018).

The sharp and short increase of emissions for some compounds during and immediately after wetting could be due to an abiotic effect, during which the soil pore space is replaced by water and the gases in the spaces are released (Monard et al., 2021; Pugliese et al., 2023).

The total mean VOC emissions before and after wetting of the moss ($1.75 \pm 0.99 \text{ nmol m}^{-2} \text{ s}^{-1}$, $175 \pm 158 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$, or $4.7 \pm 3.7 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$ and $1.35 \pm 1.79 \text{ nmol m}^{-2} \text{ s}^{-1}$, $128 \pm 238 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$, or $0.79 \pm 2.61 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$, respectively) and lichen biocrusts ($4.34 \pm 2.15 \text{ nmol m}^{-2} \text{ s}^{-1}$, $452 \pm 400 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$, or $6.7 \pm 5.5 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$ and $0.32 \pm 0.26 \text{ nmol m}^{-2} \text{ s}^{-1}$, $452 \pm 400 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$, or $0.05 \pm 0.11 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$, respectively), are within the same magnitude as emission rates found in previous. Total VOC emissions found for subarctic mosses and lichens, including low molecular weight compounds, were slightly higher (15.5 and $14.2 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$, respectively; Ryde et al., 2022). In this study moss and lichen samples were measured directly after collection in the field without monitoring their wetness. For tropical epiphytic communities in the Amazon rainforest, higher emission values of $953 \pm 995 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$ ($10 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$) for mosses and lower values $274 \pm 310 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$ ($0.5 \text{ } \mu\text{g g}^{-1} \text{ (DW) h}^{-1}$) for lichens were reported (Edtbauer et al., 2021). The values here are overall mean values of non-wetted and wetted samples from several seasons. The rates normalized by dry weight (DW) from within this study could even be larger, as the dry-weight measurements likely included mineral material from the soil underneath and embedded in the biocrusts, inflating the mass used for normalization compared to studies measuring largely mineral-free epiphytic or peatland associated tissues. In studies where low molecular weight compounds were not part of the total VOC flux reported, for example because GC measurements could not capture such molecules, fluxes were much lower $207 \text{ ng g}^{-1} \text{ (DW) h}^{-1}$ for subarctic moss (Faubert et al., 2010; Tiiva et al., 2007) or mid-latitude moss that emitted $13.2 \text{ ng g}^{-1} \text{ (DW) h}^{-1}$ of acetaldehyde and low levels of monoterpenes and green leaf volatiles like hexanal (Kesselmeier et al., 1999).



4.3 Low molecular weight compounds: Ethanol, methanol, acetone, acetaldehyde, and acetic acid

Ethanol, seen as the highest emitted compound in this study, is usually a product of anaerobic fermentation only found in plant emissions if they are under anoxic conditions (Kimmerer and Kozłowski, 1982; Kimmerer and Macdonald, 1987). Ethanol also had the highest relative abundance in emissions seen in the mosses *Syntrichia caninervis* and *Didymodon vinealis* from an arid environment, especially before wetting the samples (Wan et al., 2026). Also in lichen thalli, when exposed to a high water content, ethanol emission of up to $15 \text{ pmol g}^{-1} (\text{DW}) \text{ s}^{-1}$ has been observed (Wilske et al., 2001) as well as in thawing permafrost soils (Kramshøj et al., 2018). The occurrence of the ethanolic fermentation in lichens may be a feature of their poikilohydric lifecycle. An alternative explanation for the unexpectedly high ethanol emissions before wetting the samples could be aerobic fermentation via the Crabtree effect, documented in various yeast species, whereby excess sugar availability triggers ethanol production even under oxygenated conditions (Crabtree, 1929; Dashko et al., 2014). Humidity-induced partial rehydration may mobilize storage sugars sufficiently to trigger this overflow metabolism in Crabtree-positive yeasts, if they were present within the samples, but in order to prove this, additional measurements would be needed. If such emissions of ethanol occur in the field, then this can have important consequences for the atmospheric budgets of acetaldehyde and in turn peroxy acetyl nitrate (PAN) (Grosjean and Miguel, 1988; Millet et al., 2012).

Methanol is a typical microbial VOC, but it has also been seen in emissions from plant roots (Steeghs et al., 2004), from flowering plants (MacDonald and Fall, 1993), released from plant leaves upon growth, when the cell walls are expanding (Hüve et al., 2007) and released from pectin and/or lignin in plant cell walls (Schink and Zeikus, 1980; Fall and Benson, 1996; Galbally and Kirstine, 2002). In plant litter, methanol was found to be the most dominant VOC emitted during microbial decomposition, making up to 78 % to 99 % of net emissions (Gray et al., 2010) and up to 26 % of Aleppo Pine litter emissions (Viros et al., 2021). Acetone and methanol emissions in a similar magnitude (up to 0.387 and $4.62 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively) have been described from agricultural soils (Schade and Custer, 2004). Soil can switch between releasing methanol when dry and consuming methanol when wet (Bourtsoukidis et al., 2018). The high methanol emission rates of biocrusts and bare soil could be explained by the wealth of microbial organisms with them (Maier et al., 2018).

In experiments where uptake was monitored along with emission values, because ambient air instead of zero air was used for flushing the sample cuvettes or chambers, an uptake for ethanol and most carbonyl substances was observed (Edtbauer et al., 2021; Wilske et al., 2001). Similarly, uptake rates for methanol and acetic acid (maximum uptake rates from $-0.8 \text{ nmol m}^{-2} \text{ s}^{-1}$ to $-0.6 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively) were found, while acetaldehyde and ethanol were emitted or taken up in the range of $-0.04 \text{ nmol m}^{-2} \text{ s}^{-1}$ to $+0.02 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Asensio et al., 2007). In our experiment, as per design, uptake rates could not be monitored. The lower emission values after wetting could also be due to the transition of highly soluble compounds into the liquid phase of the VOC free rain water.

4.4 Isoprenoids emissions: isoprene and monoterpenes

Although isoprenoid emissions accounted only for a minor fraction of total VOC emissions, their reactivity and potential role in atmospheric oxidation processes, as well as their potential relevance as communication compounds for organisms and during particle production make them an interesting study subject. The higher emission of isoprene by moss-dominated biocrusts, compared to the other biocrust types, aligns with previous studies that identified significant isoprene emissions for various moss species (Hanson et al., 1999). It has been hypothesized that isoprene emission evolved in the predecessors of mosses as protection against damage by high temperatures (Hanson et al., 1999; Vicheroová et al., 2020). Isoprene is associated with *de novo* emissions directly related to photosynthesis in vascular plants (Guenther et al., 2006). However, the relationship with light and temperature was recently found to be different in moss as compared to vascular plants (Langford et al., 2023). Remarkably, in measurement 1 of the moss samples (Figure 8b), they showed isoprene emission in the light at high air humidity when CO_2 was barely taken up, but little emission in the light periods after wetting when photosynthetic uptake of CO_2 was strongest.



Biosynthetic genes of isoprenoids are widespread among soil bacteria and fungi, and soils have also been found to be a possible
 545 sink for isoprene (Crombie et al., 2025; Murrell et al., 2020; Schüttler et al., 2026; Pugliese et al., 2026). Therefore, isoprene
 might have mixed sources and sinks within the samples.

Monoterpene emission peaked when the biocrusts were exposed to humid air. Although photosynthesis and respiration were
 not as active during humid air, as after wetting (Figure 1), the increase to 25°C inside the climate chamber, compared to the
 room temperature of around 21°C, might have stimulated the emission from storage pools and the humidity from the air might
 550 have already activated biological processes. The monoterpene speciation varied between sample types (Figure 5), representing
 possibly different storage pools and/or metabolic pathways related to the different dominating organisms in the biocrusts.
 Monoterpene emissions from plants are known to be temperature driven (Bourtsoukidis et al., 2024). Since lichen- and light
 cyanobacteria-dominated biocrust, showed a second peak after wetting, there might also be new synthesis of monoterpenes or
 an enhanced emission after wetting.

555 4.5 Petrichor associated emission of sesquiterpenoids

The sesquiterpenoid geosmin, known as the smell of wet earth (Gerber and Lechevalier, 1965), has been shown to be emitted
 by fungi, actinobacteria and cyanobacteria (Izaguirre et al., 1982; Watson, 2004; Baubin et al., 2023), but was also found in
 bryophytes (Asakawa et al., 2013). Similarly, 2-methylisoborneol is also reported to have a musty, earthy smell. Both are
 associated with “petrichor”, the smell of dry soil after rainfall (Bear and Thomas, 1964; Gerber and Lechevalier, 1965). The
 560 emission of those two compounds points towards microbial activation of actinobacteria and/or cyanobacteria after wetting.

The other compounds correlating well with geosmin and 2-methylisoborneol (Figure B9) were nonenal or nonenone ($C_9H_{16}O$,
 $m/z = 141.1270$), previously identified in truffles (Federico et al., 2015), furfuryl alcohol ($C_5H_6O_2$, $m/z = 99.0441$), and
 benzothiazole (C_7H_5NS , $m/z = 136.022$), occurring rarely but not never in nature (Le Bozec and Moody, 2009) although mostly
 attributed to anthropogenic sources (Liao et al., 2018).

565 The human nose is extremely sensitive to geosmin with an odour threshold reported to be as low as 9.5 pptv (Polak and Provasi,
 1992), approximately 80 000 times lower than that of ethanol. Despite their relatively low proportion relative to the total VOC
 emissions (below 0.1 %), they can dominate the perceived smell of the Succulent Karoo after rainfall.

In South African natural water sources, concentrations of up to 3170 ng L⁻¹ geosmin were found (Wnorowski and Scott, 1992;
 Kwon et al., 2021). It was found that African elephants are, as humans, sensitive to the smell of geosmin and use it to navigate
 570 to water sources (Wood et al., 2022). It was proposed to use geosmin-degrading bacteria (Chislock et al., 2021) to re-orient
 elephant traffic away from villages (Gunawardana, 2024). Geosmin also serves as a powerful attractant for mosquitoes,
 influencing egg-laying behaviour (Melo et al., 2020).

4.6 Sulfur and selenium compounds: is there a night-time source of DMS emissions by mosses?

Sulfur and selenium containing VOCs (DMS, DMDS, and DMSe) showed contrasting behaviour to isoprenoid emissions
 575 during the treatments. DMS, DMDS, and DMSe emission increased after wetting of the samples, while monoterpenes and
 isoprene were also emitted before wetting and prior to photosynthetic uptake of CO₂. However, the delayed peak of DMS
 emission by the moss-dominated biocrusts (Figure 7), could suggest a *de novo* synthesis linked to microbial growth phases. In
 a rainforest soil rewetting experiment, an immediate DMS pulse after rewetting of up to 55 pmol m⁻² s⁻¹ has been observed
 (Pugliese et al., 2023) that was in the same order of magnitude as the emission of mosses observed in this study immediately
 580 after wetting (approximately 40 pmol m⁻² s⁻¹; Figure 7; Figure 8). The same immediate burst of DMS upon rewetting has been
 observed in a chamber study with soil crusts from the Negev desert (Ghirardo et al., 2026). This could mean that a different,
 possibly stress related mechanism was active. Gries et al., 1994 found DMS (0.005–0.025 pmol g⁻¹ (DW) s⁻¹) emitted by
 different lichen species and a cyanobacterium (*Nostoc commune*), while COS (not measured in this study) was taken up. DMS
 can be produced by the DMSP pathway as in marine biota, but was also found to originate from methanethiol, especially in



585 soils (Carrión et al., 2015, 2017). However, in this study no concurrent emission of methanethiol with DMS was found. The increase in DMS emission during darkness in the moss samples (Figure 8) suggests either a production in the organisms that are only active during dark periods, a light-dependent sink suppressed in dark conditions, or a delayed emission of the compound after a one-hour light period. However, the sharp increase after the lights were switched off hints at an increased emission mechanism during dark periods or an inhibition of a production mechanisms during light periods. Elevated DMS
 590 concentrations have been reported from below a forest canopy during night time, which could indicate that a mechanism in soil organisms or biocrusts is active during the night (Berresheim and Vulcan, 1992; Jardine et al., 2015).

4.7 Other VOC emissions

Apart from the low molecular weight compounds, isoprenoids and sulfur containing VOC, a variety of green leaf volatiles (GLVs), oxygenated VOC (OVOC), and benzenoids were also emitted.

595 4.7.1 OVOC

In an experiment, during which ambient air was used to flush through sample cuvettes, uptake of most OVOC was observed for mosses and lichen in a tropical forest (Edtbauer et al., 2021). In the current study, as no uptake was monitored, some OVOCs were emitted. Highest OVOC emission rates were observed for methyl ethyl ketone and other C4 carbonyls (MEK, $m/z=73.065$), that are known to be emitted from both biogenic and anthropogenic sources (Yáñez-Serrano et al., 2016) and
 600 were shown to emitted by Mediterranean shrubland soils (max seasonal average of $78 \mu\text{g m}^{-2} \text{h}^{-1}$) (Asensio et al., 2008). It was followed by $m/z=71.050$ being associated with methacrolein (MACR), methyl vinyl ketone (MVK), and isoprene hydroxy hydroperoxides (ISOPOOH). They are both known to be taken up and emitted by plants (Tani et al., 2010, 2020) and were taken up by Amazonian rainforest soil (Schüttler et al., 2026).

4.7.2 GLVs

605 Green leaf volatiles (GLVs) are typically C6 or C9 aldehydes synthesized by the lipoxygenase (LOX) pathway, that can undergo isomerization, dehydrogenation, and esterification in plants (Hatanaka et al., 1987; Feussner and Wasternack, 2002; Ameye et al., 2018). They were emitted in larger quantities by lichen and moss samples compared to cyanobacteria and bare soil samples (Figure B5). GLVs were emitted over the entire measurement, but decreased over time. GLVs are known to be markers for stress in plants (Ameje et al., 2018). In an experiment with mosses and lichens, they were mainly emitted during
 610 the first hours after insertion into sample cuvettes (Edtbauer et al., 2021) but excluded from the analysis as they were assumed to a result of the sample transfer from tree to cuvette. Hexanoic acid has also been identified in subarctic lichens and mosses (Ryde et al., 2022) and (E)-2-hexenal was shown to be exchanged in soils (Asensio et al., 2007).

4.7.3 Benzenoids

Most emitted hydrocarbons, other than isoprene and monoterpenes, were benzenoids. These emissions could result from the
 615 desorption of previous adsorption or from microbial production. Although benzenoid emissions are typically associated with anthropogenic source, they have been observed for plants (Heiden et al., 1999; Misztal et al., 2015), cyanobacteria (Żyska-Haberecht et al., 2019), and oceanic phytoplankton (Rocco et al., 2021). Benzenoids have been proposed as potential indicators for predicting the successional stage of biocrusts (Zhao et al., 2023). For example, styrene has been observed to be synthesized by the microorganism *Pseudomonas putida* (García-Franco et al., 2024), and toluene emission has been observed in the moss
 620 *Warnstorfia exannulata* (Faubert et al., 2010). Previous studies have attributed aromatic compounds, such as styrene and toluene, to aromatic monoterpene fragments (Edtbauer et al., 2021). A typical aromatic monoterpene is *p*-cymene contributing up to 61 % to total monoterpene emissions in GC measurements in this study. In moss-dominated biocrusts no *p*-cymene emission was detected, but they still showed benzenoid emissions. Therefore, not all benzenoid emissions should be attributed



to aromatic monoterpene fragments. The GC measurements agree relatively well with the PTR flux magnitude (Figure B6 in Appendix B). Note that the GC measurements are calibrated relative to *p*-cymene, as no authentic standard was used. Styrene, trimethylbenzene, and toluene correlated relatively well before and after wetting with monoterpenes (Kendall's $\tau = 0.57, 0.90$, and 0.72 before wetting and $r = 0.30, 0.49$, and 0.35 after wetting, respectively; all $p < 0.05$; Figure B9 in Appendix B; Table D3 in Appendix D), so reported fluxes may partly reflect aromatic monoterpenes. However, benzene did not correlate well ($r = 0.16$ before wetting and $r = 0.27$; $p < 0.05$ for both; Figure B9 in Appendix B; Table D3 in Appendix D).

630 4.8 Methane

Methane (CH_4) is an important greenhouse gas, and microbes play a major role in both emission and uptake (Nazaries et al., 2013). The uptake of methane observed by us after wetting (Figure B12 in Appendix B) is in agreement with most studies of dryland soils that point to CH_4 consumption (methanotrophy) of up to -0.45 to $-0.92 \text{ nmol m}^{-2} \text{ s}^{-1}$ by undisturbed soils in an arid environment (Angel and Conrad, 2009) and up to $-1.45 \text{ nmol m}^{-2} \text{ s}^{-1}$ by Mediterranean biocrusts (Lafuente et al., 2020). The lower rates of $-0.52 \pm 0.01 \text{ nmol m}^{-2} \text{ s}^{-1}$ observed by us during phase 4 after wetting could be a result of the initially lower methane concentrations in the air used for flushing; thus, the values should only be used qualitatively. CH_4 consumption is usually achieved by methanotrophs at the anoxic/oxic interface (Kolb et al., 2003), here possibly initiated by the wetting which removed air from the pores of the samples.

Emission of methane has also been observed in biocrust communities in low rates of approximately $0.01 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Richardson et al., 2022).

4.9 Upscaling and relevance of VOC emissions by biocrusts

Atmospheric models consider vegetation as VOC source, but biocrusts and cryptogamic covers are not included (Edtbauer et al., 2021; Guenther et al., 2012; Sindelarova et al., 2022b). Although an estimate is highly tentative with the data from this study only covering 3 replicates of four biocrust types and bare soil from one sampling area, it indicates that biocrusts could account for a small (0.07%) but measurable fraction of global annual BVOC emissions (835.4 Tg yr^{-1} ; Wang et al., 2024). As this upscaling approach assumes the same biocrust emission values for all global biocrust covers, it might actually be higher for biocrusts in less arid regions, as they would be active for larger periods across a year due to higher humidity. However, the emissions by biocrusts could be more relevant locally in arid and semi-arid regions, where they are most abundant and vascular plants are scarce. Another uncertainty of this upscaling is the measurement under artificial conditions. Thus, to better assess biocrust relevance, field studies under natural conditions should be performed in the future.

5 Conclusion

Biocrusts of the Succulent Karoo emit a variety of VOCs including oxygenated VOCs, isoprenoids, and sulfur-containing compounds in amounts of total emissions of up to $75 \pm 48 \text{ nmol m}^{-2} \text{ s}^{-1}$ as mean across the four biocrust types studied. Remarkably, the total VOC emission from biocrusts was highest under high air humidity conditions in the absence of liquid water, and was dominated by ethanol, methanol, and acetone. Monoterpenes and benzenoids peaked during humid-air exposure, possibly due to already activated metabolism of some organisms within the samples. Immediately after wetting, the VOC blend shifted and geosmin and 2-methylisoborneol, associated with “petrichor” and microbial activation, were emitted along a secondary monoterpene peak for some biocrust types. Different biocrusts types had some overlap in their VOC composition, but there were qualitative and quantitative differences hinting at different physiological processes, phylogenetic groups, or functions of emitted VOCs. Biocrusts dominated by moss showed higher emission of isoprene and sulfur compounds, possibly due to higher biodiversity of the organisms within this crust type and a possibly different emission strategy. Enhanced DMS and DMDS emission in darkness by the moss samples following wetting pointed towards a diel



pattern and a potential yet unknown night-time source of DMS from dryland soils, although the underlying mechanism (dark
production versus light-dependent sinks) remains to be resolved. Biocrusts could be shaping the VOC budget in arid regions
665 like the Succulent Karoo, which, despite being seemingly sparse in vegetation, is now found capable of emitting reactive VOCs
to the atmosphere and similar in flux magnitude and composition to previous studies on soil, mosses, lichens, and other
cryptogamic covers. Within this study, biocrusts from one location, but representative of biocrust communities globally were
studied. Per design only emissions were explored, while there could also be uptake of VOCs. In the future biocrust samples
from different locations should be analysed under controlled laboratory conditions as well as in the field. Isotopic and genomic
670 approaches are needed to apportion sources among mosses, lichens, cyanobacteria, and associated microbes and further test
the underlying mechanisms of nocturnal DMS release. Compared to vascular plants, VOC emissions from biocrusts are sparse.
Understanding the contribution of dryland biocrusts under different light, humidity, and wetting is critical for improving
regional and global atmospheric chemistry models, especially under projected rainfall change due to climate change, land
degradation and land use change.

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Appendix A Flow Chart, Measurement Overview and Humidity and Temperature in the climate chamber

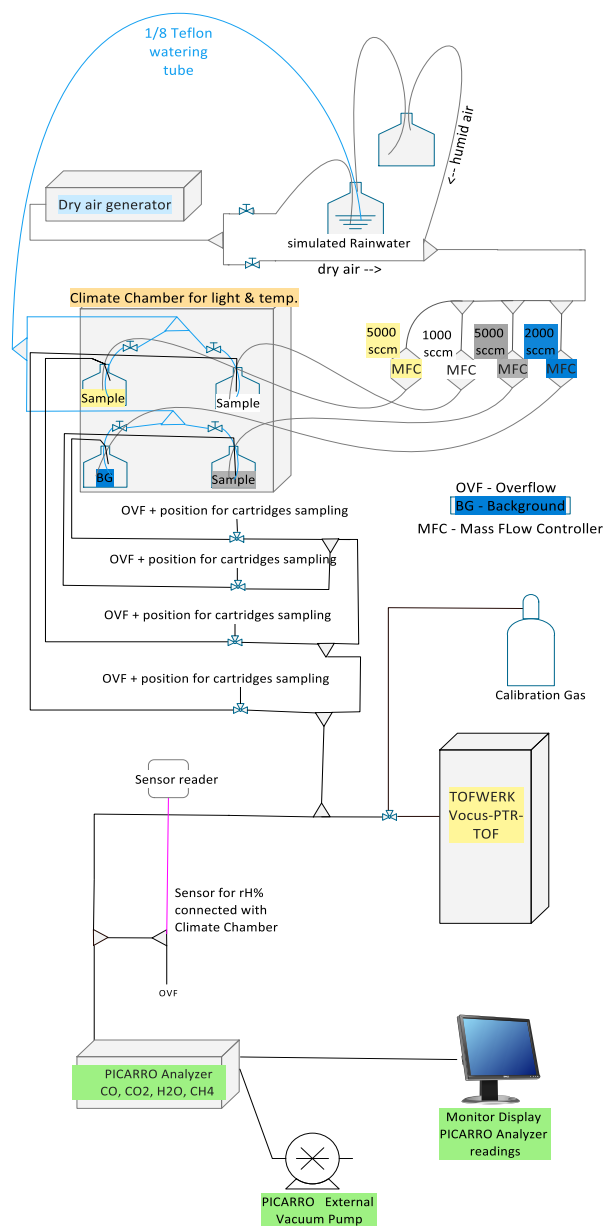
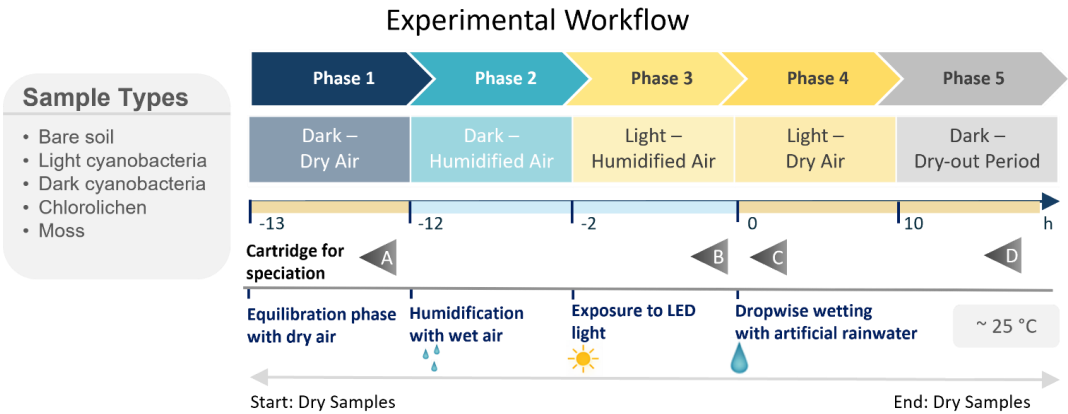


Figure A1 Set-up for the measurements.



680 **Figure A2** Flow Chart with the phases of the experimental workflow for measurement 2-7 including the times adsorbent cartridges for speciation via GC-MS were taken (A, B, C and D).

685 **Table A1** Overview of measurement conditions in chronological order with the light regime, temperature, amount of water used for wetting for each sample in each cuvette, sample number, relative wetness at the start of the measurement, remaining wetness after the measurement, dry weight of the sample in gram, and note for measurement.

No	Light Regime	Amount wetted per sample [g]	Sample No	Relative wetness at start of measurement	Remaining relative wetness after measurement	Dry weight [gr]	Note
1	1 h on / 1 h off	13.05	moss_01	15.7 %	46.9 %	18.6	Faster light change
			moss_02	4.6 %	54.9 %	15.9	
			moss_03	82.1 %	78.0 %	8.5	
2	12 h off / 12 h on	4.5	dark_cyano_01	0.9 %	4.9 %	5.9	
			lichen_01	1.4 %	11.0 %	15.9	
			light_cyano_01	0.9 %	5.1 %	10.2	
3	12 h off / 12 h on	13.5	dark_cyano_02	0.0 %	27.5 %	26.6	
			lichen_03	0.8 %	21.3 %	12.8	
			moss_02	0.0 %	44.4 %	15.9	
4	12 h off / 12 h on	9	bare_soil_03	0.8 %	41.7 %	12.4	No adsorbent cartridges taken
			dark_cyano_03	27.9 %	17.9 %	14.7	
			moss_03	0.5 %	100.1 %	8.5	
5	12 h off / 12 h on	9	bare_soil_02	0.8 %	16.0 %	22.6	
			lichen_03	0.8 %	21.3 %	12.8	
			light_cyano_02	0.4 %	64.5 %	8.3	
6	12 h off / 12 h on	9	bare_soil_01	0.7 %	56.8 %	15.2	
			light_cyano_03	0.6 %	30.5 %	25.3	
			moss_01	0.5 %	51.9 %	18.6	
7	12 h off / 12 h on	4.5	bare_soil_03	39.2 %	45.0 %	12.4	Repetition of measurement 4
			dark_cyano_03	13.2 %	20.1 %	25.3	
			moss_03	73.5 %	45.2 %	8.5	

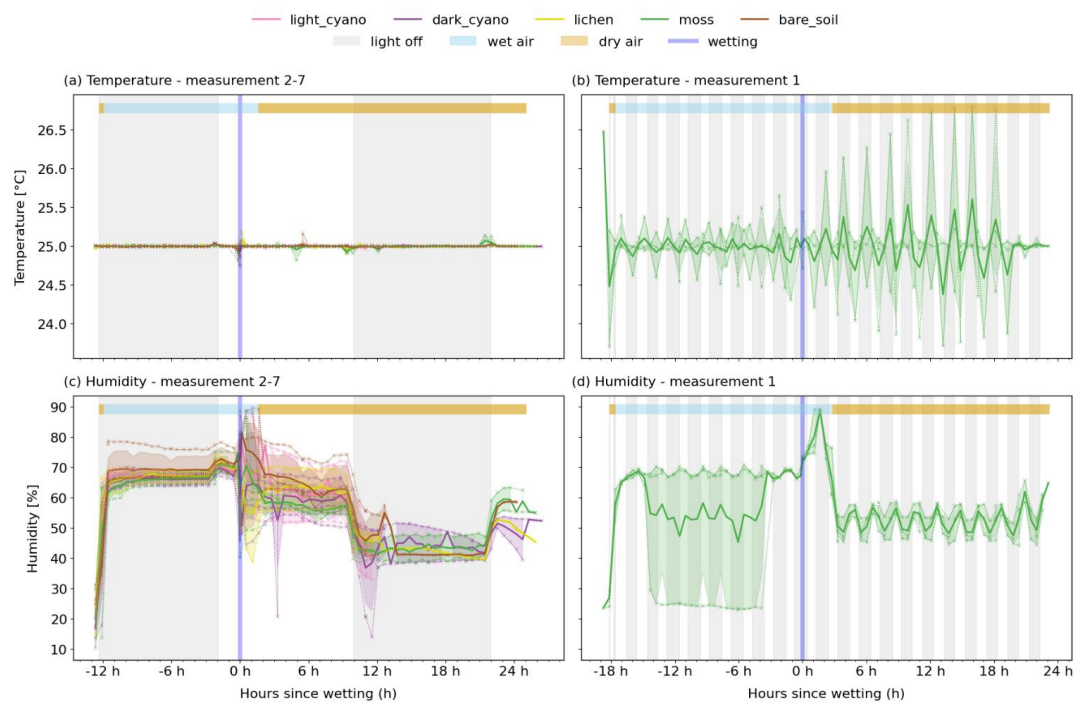
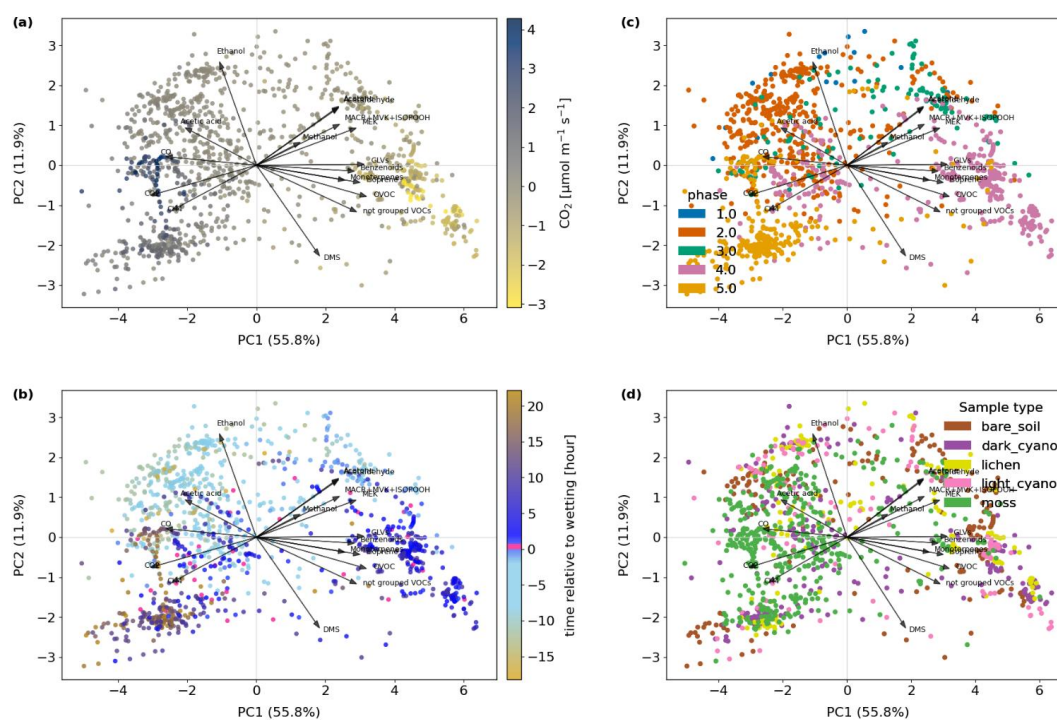
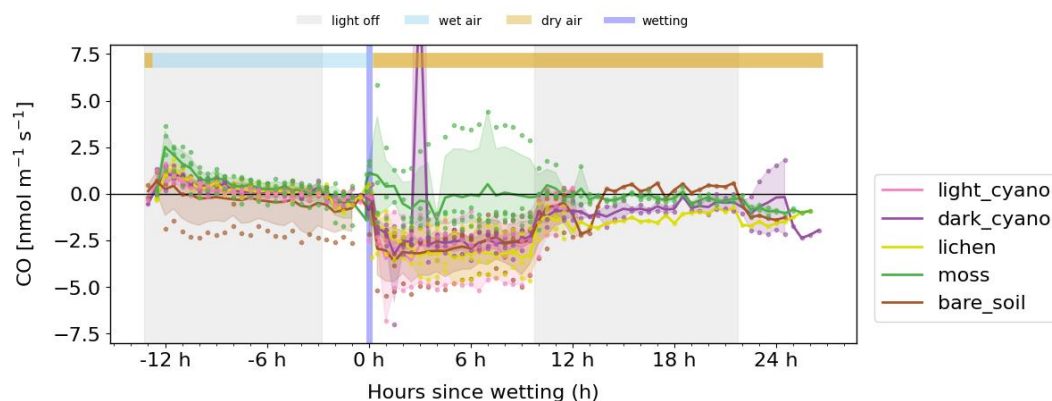


Figure A3 (a) Air temperature and (c) humidity inside the climate chamber as mean values with 95 % confidence interval during the experiments with each sample type during measurements 2-7 and during measurement 1 in (b) and (d).

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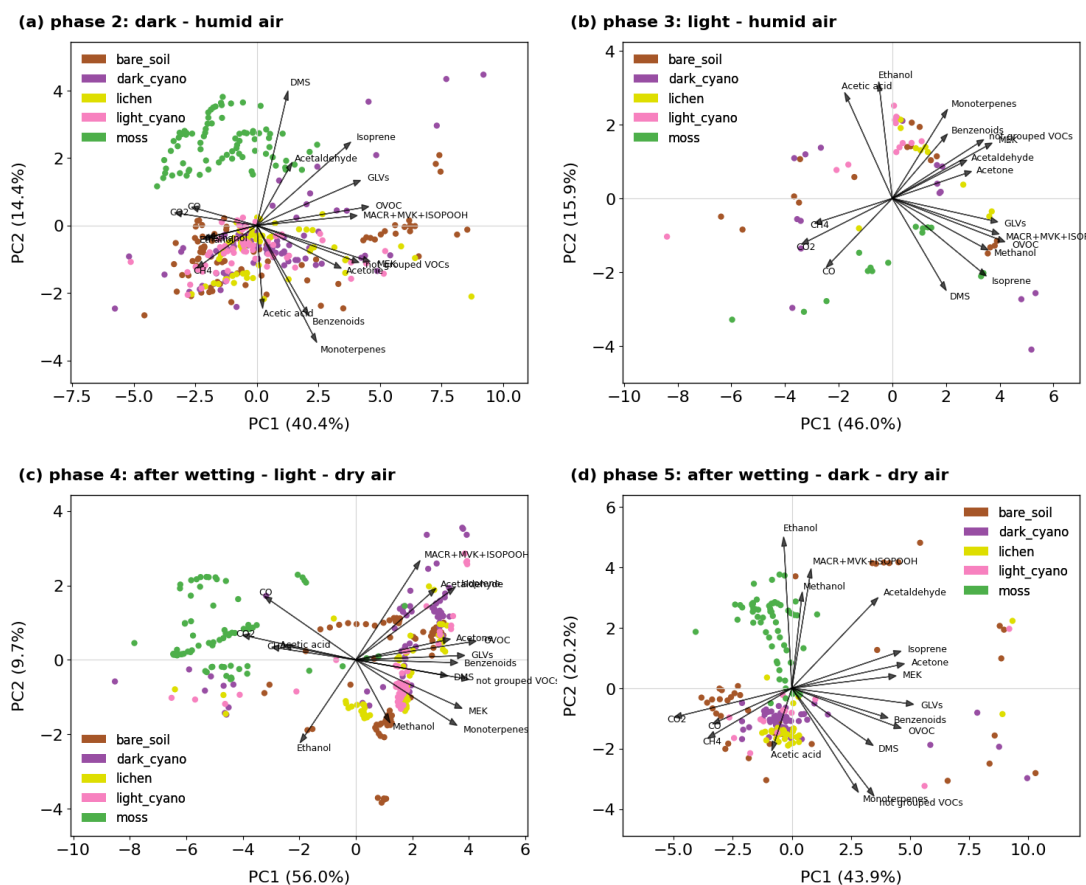
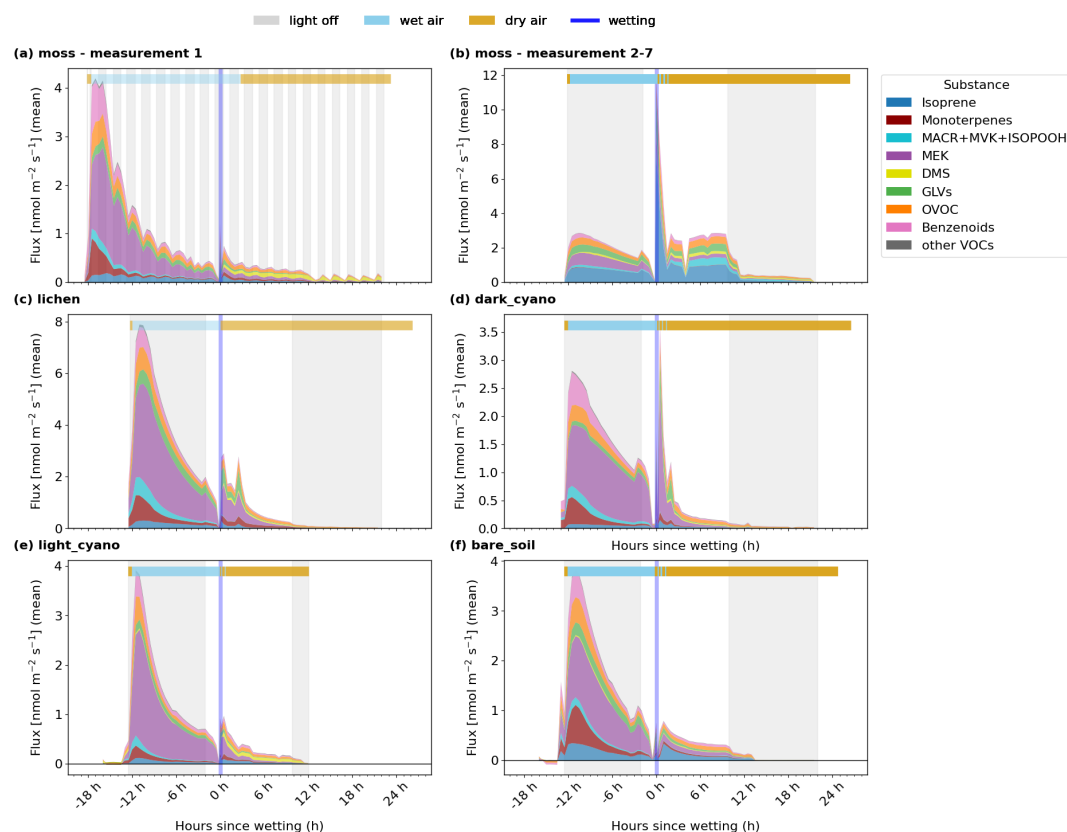
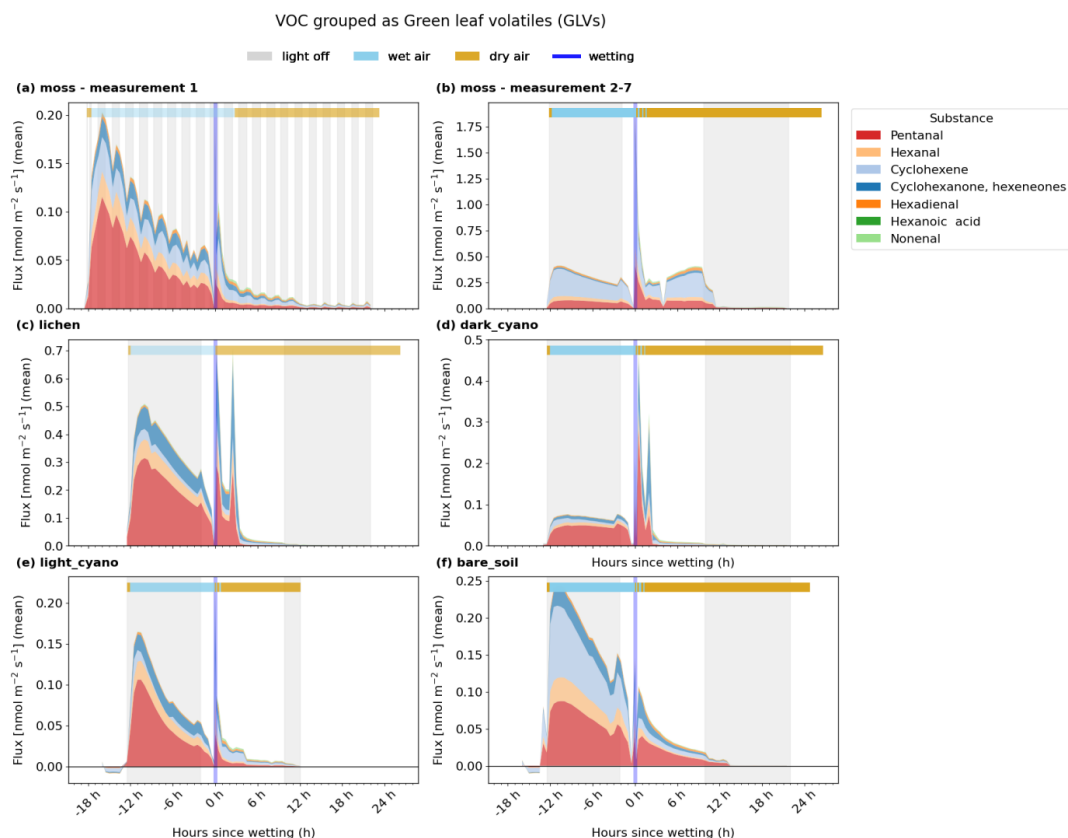


Figure B3 PCA Biplot of PC1 and PC2 of VOC fluxes coloured by sample type with arrows corresponding to the scores of the different VOCs and VOC classes with data from phase (a) 2, (b) 3, (c) 4, and (d) 5 of the measurements.



705 **Figure B4** Time series of stacked areas for selected VOCs for each sample type (a) moss in measurement 1, (b) moss in measurements 2-7, (c) lichen, (d) dark cyanobacteria, (e) light cyanobacteria, and (f) bare soil samples. Stacked areas are coloured by the individual compound.



710 **Figure B5** Time series of the mean VOCs fluxes grouped to GLVs for (a) moss samples during measurement 1 and during measurement 2-7 (b) moss, (c) lichen, (d) dark cyanobacteria, (e) light cyanobacteria, and (f) bare soil samples. Stacked areas are coloured by the individual compound.

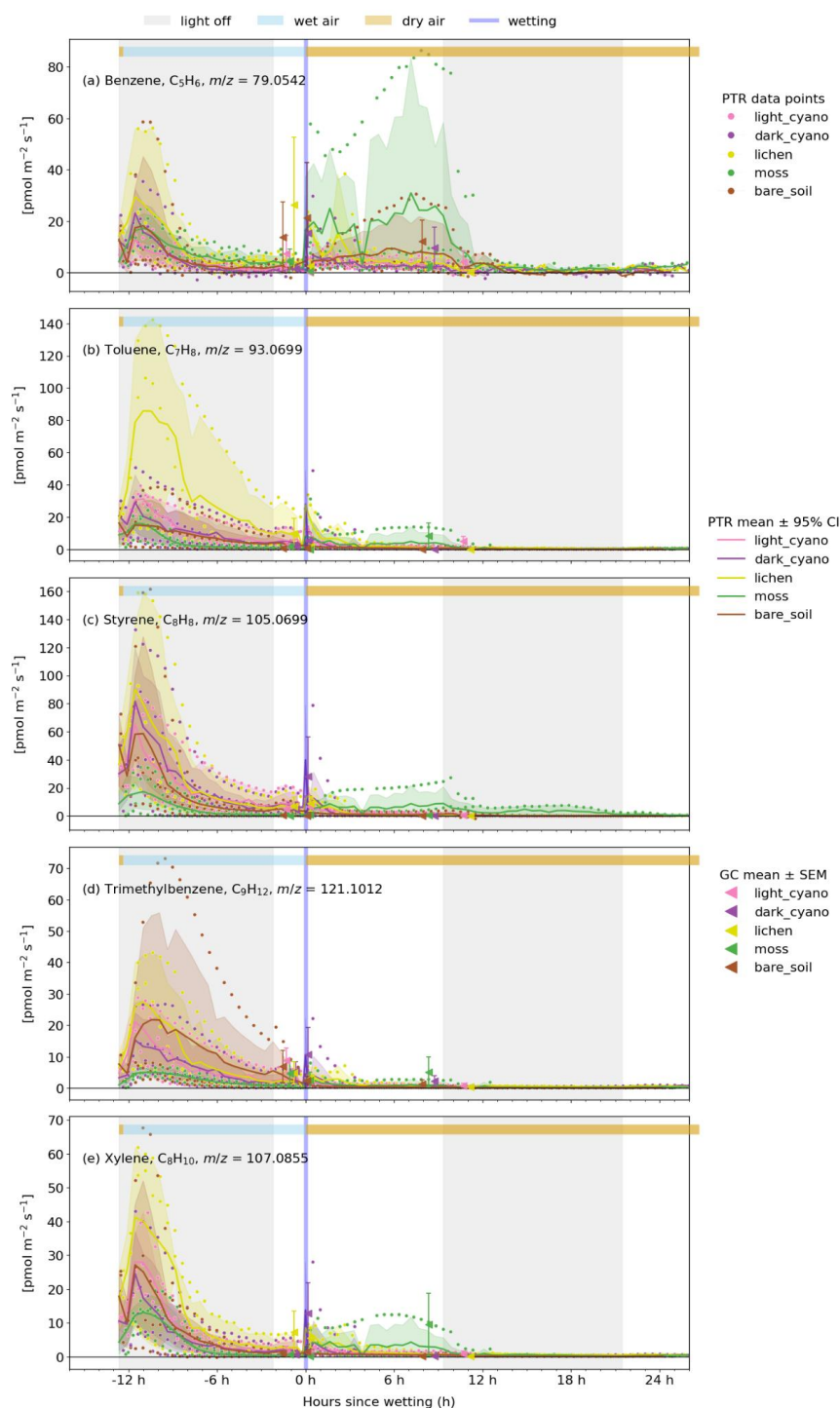


Figure B6 Time series of the mean benzenoid VOCs fluxes during the measurements for the different biocrust sample types for (a) benzene, (b) toluene, (c) styrene, (d) trimethylbenzene, and (e) xylene. The lines represent the mean emission, shaded areas the 95 % confidence interval; dots are the individual measurement points of each replicate connected with thin dotted lines; triangular markers represent the mean GC measurements and the vertical lines the standard error of the mean.

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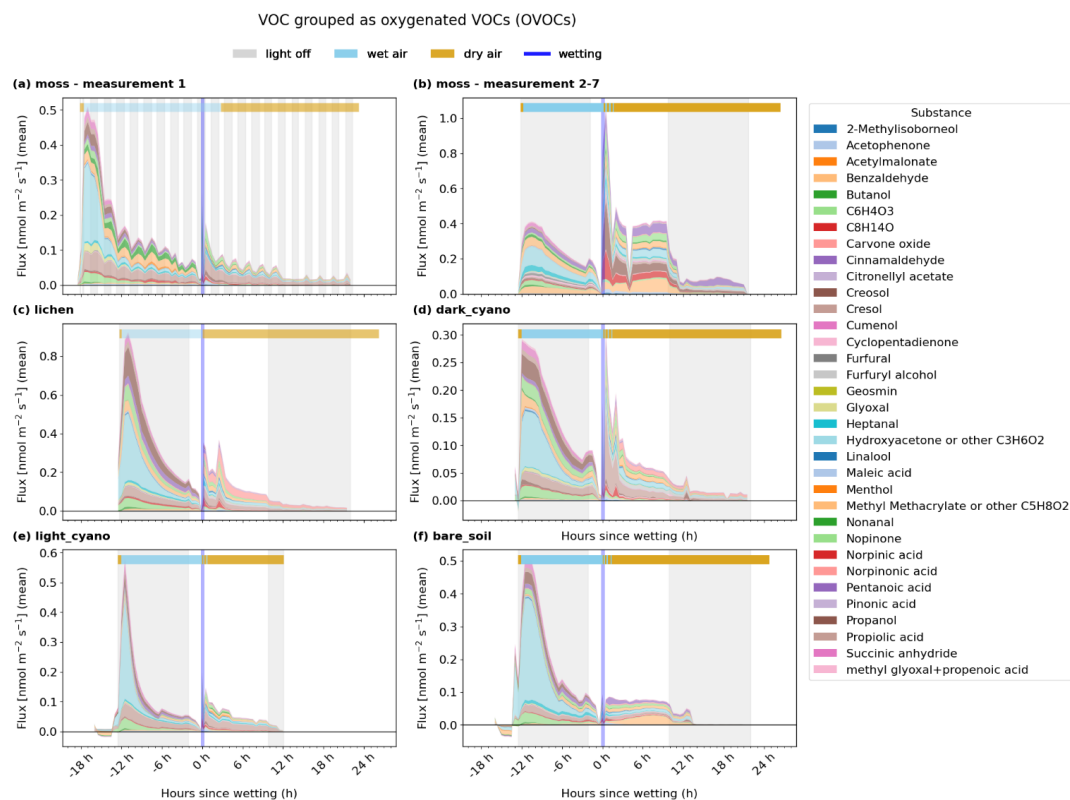


Figure B7 Time series of the mean oxygenated VOCs (OVOCs) fluxes for (a) moss samples during measurement 1 and during measurement 2-7 (b) moss, (c) lichen, (d) dark cyanobacteria, (e) light cyanobacteria, and (f) bare soil samples. Stacked areas are coloured by the individual compound.

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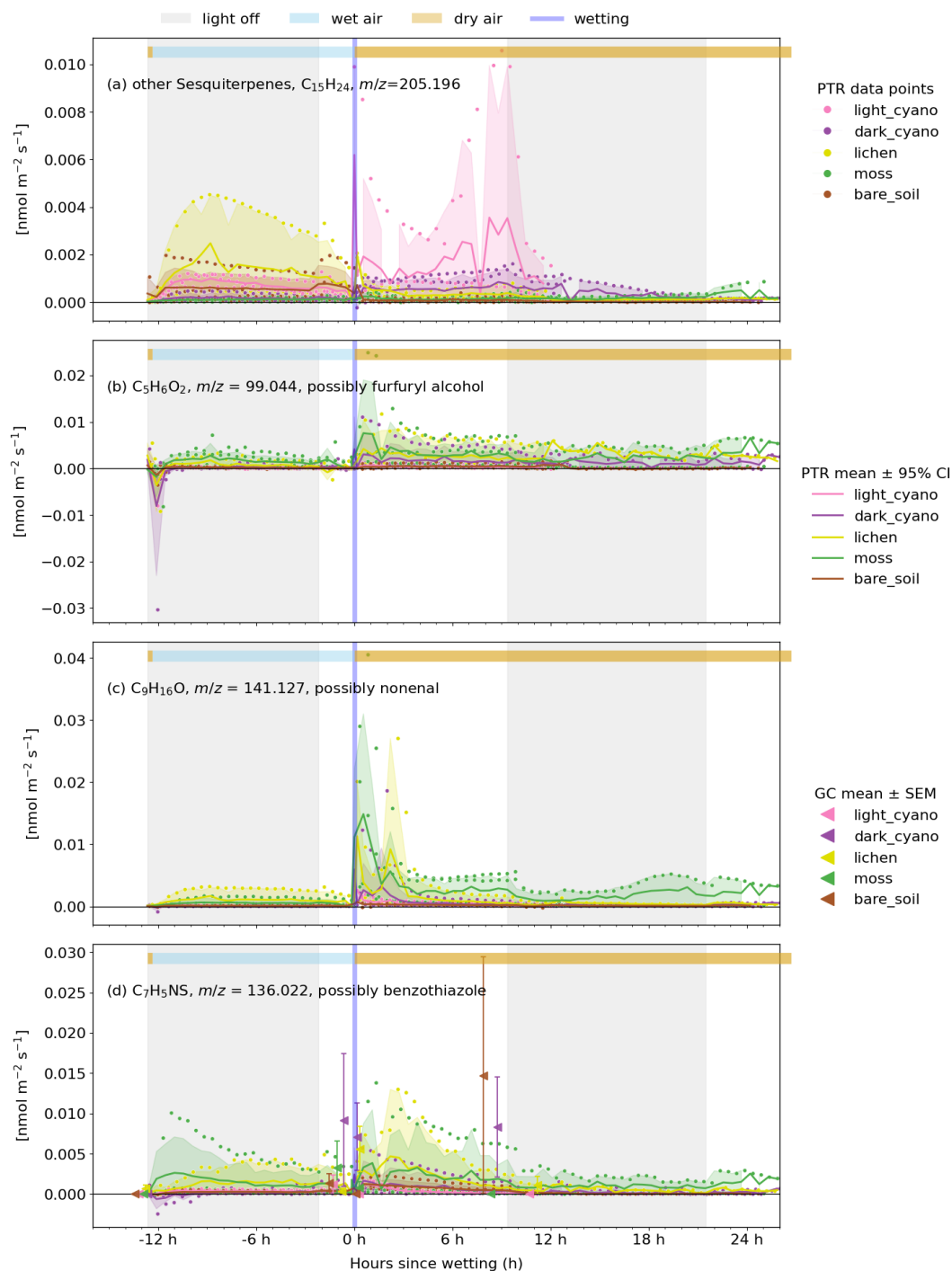
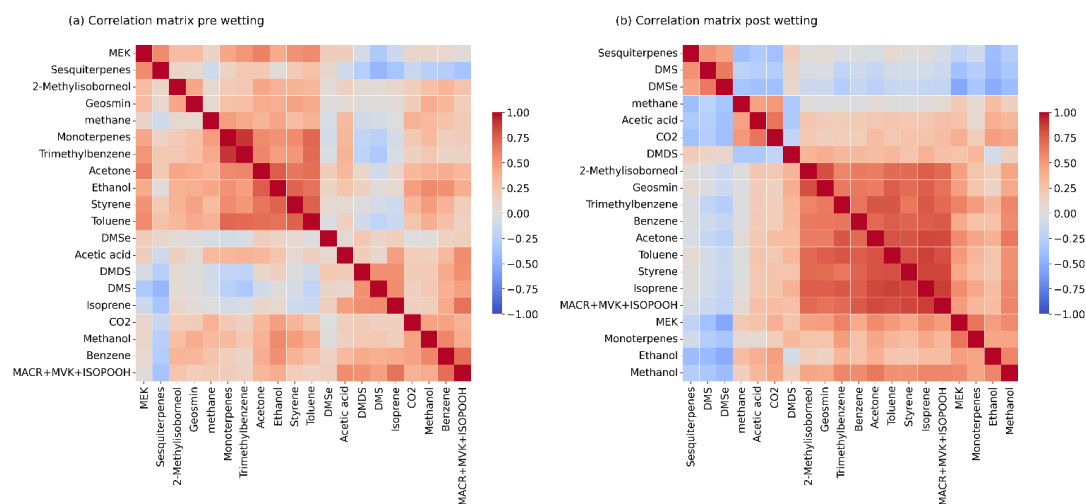


Figure B8 Time series of the mean fluxes of (a) sesquiterpenes, and compounds correlating well with the VOCs associated with petrichor (b) furfuryl alcohol, (c) nonenal, and (d) benzothiazole during the measurements for the different biocrust sample types. The lines represent the mean emission, shaded areas the 95 % confidence interval; dots are the individual measurement points of each replicate connected with thin dotted lines; triangular markers represent the mean GC measurements and the vertical lines the standard error of the mean.



730 **Figure B9** Kendall's τ correlation heatmap of selected substances before (phase 1-3) and after wetting (phase 4-5).

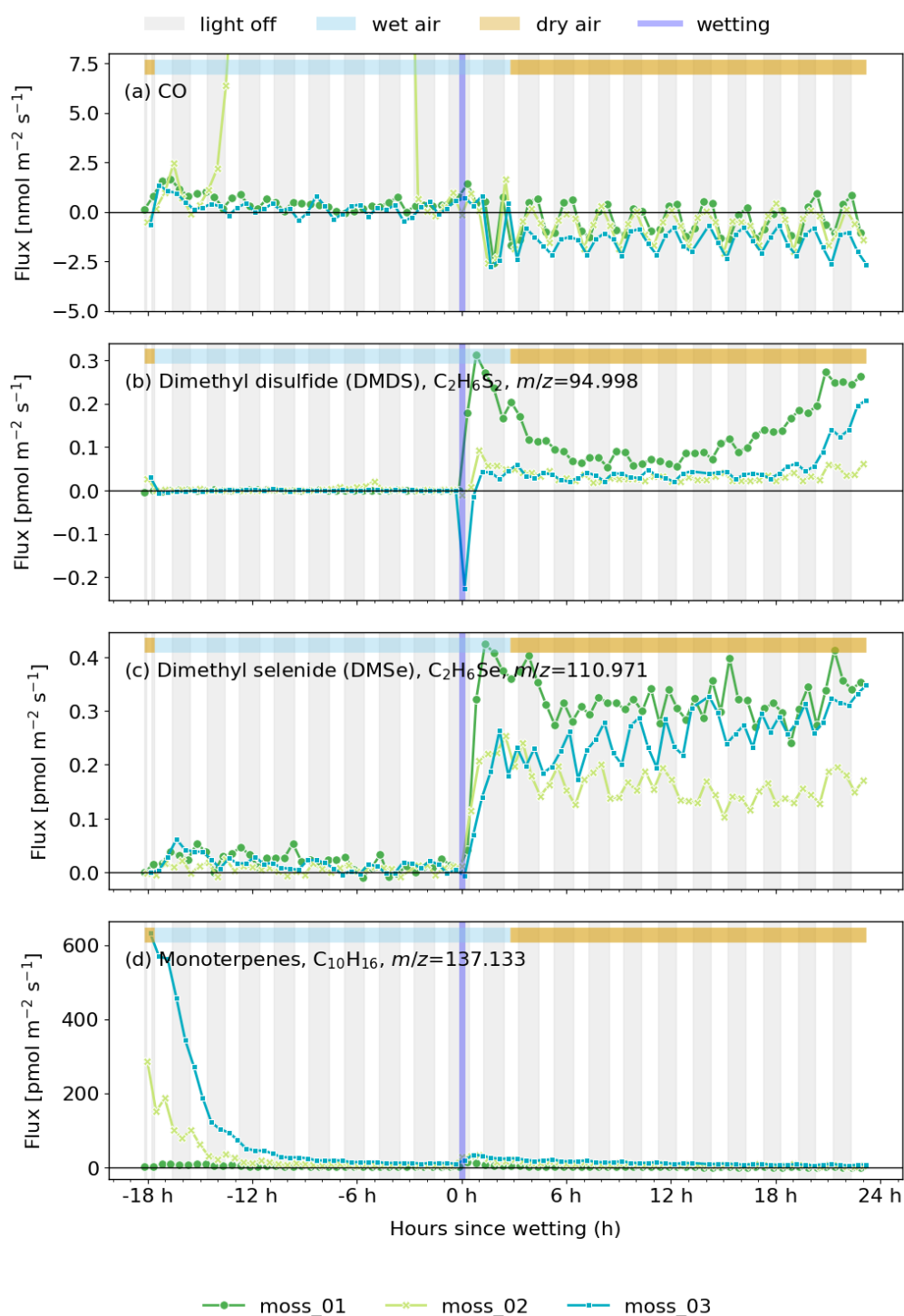


Figure B10 Time series of the fluxes of (a) CO, (b) DMDS, (c) DMSe, and (d) Monoterpenes during the first measurement with moss dominated biocrust in the 1-hour light on/off regime. The dots represent a measurement point of each moss dominated biocrust replicate.

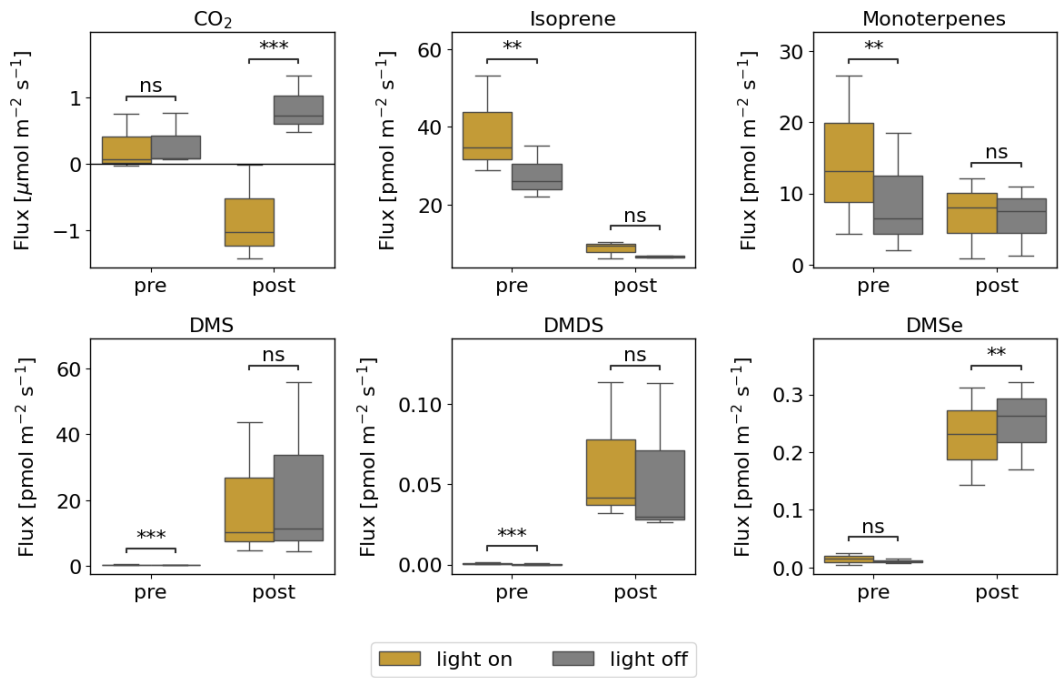


Figure B11 Boxplots of CO₂ and selected VOCs split in pre and post wetting and light conditions in measurement 1 for the moss dominated biocrust samples. Significance stars indicate differences based on OLS between light off and light on for pre and post wetting. P-values were adjusted per panel using the Benjamini–Hochberg FDR; stars follow the conventional thresholds (* p < 0.05, ** p < 0.01, *** p < 0.001; “ns” not significant).

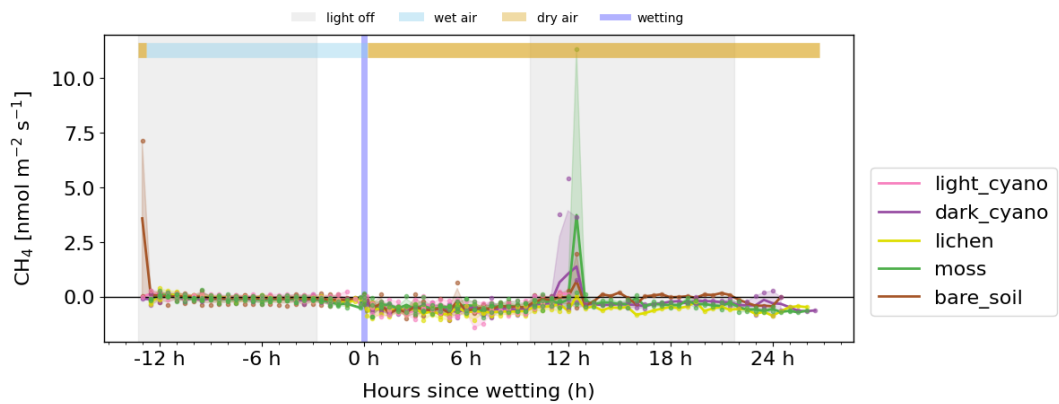


Figure B12 Time series of the mean flux of methane during the measurements for the different biocrust sample types. The lines represent the mean emission, shaded areas the 95 % confidence interval; dots are the individual measurement points of each replicate connected with thin dotted lines.



Appendix C Masses used and mean fluxes from PTR and GC measurements

750 **Table C1** List of tentatively identified volatile organic compounds (VOCs) emitted by the biocrusts in discernible amounts, measured with the PTR-TOF-MS with the measured mass to charge ratio $(m/z)_{\text{measured}}$, the exact ion mass $(m/z)_{\text{exact}}$, the mass accuracy in ppm, the formula, the potential compound, used k rate and respective reference.

$(m/z)_{\text{measured}}$	$(m/z)_{\text{exact}}$	Mass accuracy [ppm]	Formula	Potential compound	k rate $10^{-9} [\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}]$	k rate reference
33.0335	33.0335	0.27	CH ₄ O	Methanol*		
45.0335	45.0335	0.20	C ₂ H ₄ O	Acetaldehyde	3.60	(Lindinger et al., 1998)
47.0491	47.0491	0.88	C ₂ H ₆ O	Ethanol*		
59.0491	59.0491	0.70	C ₃ H ₆ O	Acetone*		
61.0284	61.0284	0.10	C ₂ H ₄ O ₂	Acetic acid	3.00	(Lindinger et al., 1998)
61.0648	61.0648	0.14	C ₃ H ₈ O	Propanol	2.80	(Lindinger et al., 1998)
63.0263	63.0263	0.04	C ₂ H ₆ S	Dimethyl sulfide*		
69.0699	69.0699	0.34	C ₅ H ₈	Isoprene*		
71.0128	71.0128	0.62	C ₃ H ₂ O ₂	Propiolic acid		
71.0491	71.0491	0.58	C ₄ H ₆ O	MACR+MVK*+IS OPOOH		
73.0284	73.0284	0.08	C ₃ H ₄ O ₂	Methyl glyoxal, propenoic acid		
73.0648	73.0648	0.12	C ₄ H ₈ O	MEK*, C4 carbonyl		
75.0441	75.0441	0.59	C ₃ H ₆ O ₂	Hydroxyacetone	3.00	Used value is for ethyl formate (Španěl and Smith, 1998)
75.0804	75.0804	0.55	C ₄ H ₁₀ O	Butanol	2.31	Calculated according to (Sekimoto et al., 2017) as referred to in (Pagonis et al., 2019)
79.0542	79.0542	0.34	C ₅ H ₆	Benzene*		
81.0335	81.0335	0.11	C ₅ H ₄ O	Cyclopentadienone		
83.0855	83.0855	0.32	C ₆ H ₁₀	Cyclohexene	1.96	Calculated according to (Sekimoto et al., 2017) as referred to in (Pagonis et al., 2019)
87.0804	87.0804	0.48	C ₅ H ₁₀ O	Pentanal	3.60	(Španěl et al., 1997)
93.0699	93.0699	0.25	C ₇ H ₈	Toluene*		
94.9984	94.9984	0.33	C ₂ H ₆ S ₂	DMDS	2.60	(Španěl and Smith, 1998)
95.0491	95.0491	0.43	C ₆ H ₆ O	Phenol	2.7	(Španěl and Smith, 1997)
97.0284	97.0284	0.06	C ₅ H ₄ O ₂	Furfural	3.90	(Wang et al., 2004a)
97.0648	97.0648	0.09	C ₆ H ₈ O	Hexadienal		
99.0441	99.0441	0.45	C ₅ H ₆ O ₂	Furfuryl alcohol		
99.0804	99.0804	0.42	C ₆ H ₁₀ O	Cyclohexanone, hexeneones	4.00	(Wang et al., 2004b)
101.0233	101.0233	0.20	C ₄ H ₄ O ₃	Succinic anhydride		
101.0597	101.0597	0.06	C ₅ H ₈ O ₂	Methyl Methacrylate or other C ₅ H ₈ O ₂		
101.0961	101.0961	0.08	C ₆ H ₁₂ O	Hexanal	3.70	(Španěl et al., 1997)



103.0754	103.0754	0.43	C ₅ H ₁₀ O ₂	Pentanoic acid	2.90	(Španěl and Smith, 1998)
105.0699	105.0699	0.22	C ₈ H ₈	Styrene	2.24	Calculated according to (Sekimoto et al., 2017) as referred to in (Pagonis et al., 2019)
107.0491	107.0491	0.39	C ₇ H ₆ O	Benzaldehyde	3.7	(Španěl et al., 1997)
107.0855	107.0855	0.25	C ₈ H ₁₀	Xylene*		
109.0648	109.0648	0.08	C ₆ H ₄ O ₂	Cresol	2.20	(Wang et al., 2004b)
110.9707	110.9707	0.43	C ₂ H ₆ Se	DMSe		
115.1117	115.1117	0.36	C ₇ H ₁₄ O	Heptanal	3.70	(Španěl et al., 1997)
117.0182	117.0182	0.30	C ₄ H ₄ O ₄	Maleic acid		
117.0910	117.0910	0.05	C ₆ H ₁₂ O ₂	Hexanoic acid		
121.0648	121.0648	0.07	C ₈ H ₈ O	Acetophenone	4.30	(Španěl et al., 1997)
121.1012	121.1012	0.19	C ₉ H ₁₂	Trimethylbenzene*		
125.0233	125.0233	0.16	C ₆ H ₄ O ₃	C ₆ H ₄ O ₃		
127.1117	127.1117	0.33	C ₈ H ₁₄ O	C ₈ H ₁₄ O	4.80	(Španěl et al., 1997)
133.0648	133.0648	0.07	C ₉ H ₈ O	Cinnamaldehyde		
133.1012	133.1012	0.17	C ₁₀ H ₁₂	Cymene		
135.1168	135.1168	0.20	C ₁₀ H ₁₄	Cymene	2.45	Calculated according to (Sekimoto et al., 2017)
136.0215	136.0215	0.34	C ₇ H ₅ NS	Benzothiazole		
137.0961	137.0961	0.06	C ₉ H ₁₂ O	Cumenol		
137.1325	137.1325	0.17	C ₁₀ H ₁₆	Monoterpenes (3- carene*)		
139.0754	139.0754	0.32	C ₈ H ₁₀ O ₂	Creosol		
139.1117	139.1117	0.30	C ₉ H ₁₄ O	Nopinone		
141.1274	141.1274	0.06	C ₉ H ₁₆ O	Nonenal	4.80	(Španěl et al., 2002)
143.1430	143.1430	0.29	C ₉ H ₁₈ O	Nonanal	4.20	(Smith et al., 2003)
145.0132	145.0131	0.35	C ₅ H ₄ O ₅	Acetylmalonate		
155.1430	155.1430	0.27	C ₁₀ H ₁₈ O	Linalool	3.40	(Španěl et al., 1997)
157.1587	157.1587	0.05	C ₁₀ H ₂₀ O	Menthol	3.10	(Španěl and Smith, 1997)
167.1067	167.1067	0.26	C ₁₀ H ₁₄ O ₂	Carvone oxide		
169.1587	169.1587	0.05	C ₁₁ H ₂₀ O	2-Methylisoborneol	2.67	Molecular properties from (Bhatia et al., 2022), Calculated according to (Su and Chesnavich, 1982)
171.1016	171.1016	0.17	C ₉ H ₁₄ O ₃	Norpinonic acid		
173.0808	173.0808	0.20	C ₈ H ₁₃ O ₄	Norpinic acid		
183.1743	183.1743	0.23	C ₁₂ H ₂₂ O	Geosmin	2.73	Molecular properties from (Bhatia et al., 2022), Calculated according to (Su and Chesnavich, 1982)
185.1172	185.1172	0.11	C ₁₀ H ₁₆ O ₃	Pinonic acid		
199.1693	199.1693	0.22	C ₁₂ H ₂₂ O ₂	Citronellyl acetate		
205.1951	205.1951	0.11	C ₁₅ H ₂₄	Sesquiterpenes		

*part of calibration gas



Table C2 Mean fluxes from PTR measurements for selected VOCs, tentatively identified, per sample type in $\text{pmol m}^{-2} \text{s}^{-1}$ with standard deviation for before wetting (phase 1-3) and after wetting (phase 4-5); negative values occur due to background subtraction.

Class	Tentative Substance	Mean flux and standard deviation in $\text{pmol m}^{-2} \text{s}^{-1}$									
		moss		lichen		dark_cyano		light_cyano		bare_soil	
		Before wetting	After wetting	Before wetting	After wetting	Before wetting	After wetting g	Before wetting	After wetting	Before wetting	After wetting g
Low molecular weight OVO C	Ethanol	54429 ± 106952	1802 ± 3574	100640 ± 160463	161 ± 1234	32245 ± 70995	41 ± 462	26863 ± 50086	37 ± 156	26676 ± 50279	1492 ± 5941
	Methanol	2560 ± 11173	227 ± 377	10871 ± 23146	367 ± 60	5005 ± 14348	21 ± 44	1062 ± 3289	31.28 ± 35.46	1838 ± 5442	84 ± 100
	Acetone	1033 ± 1636	118 ± 170	4622 ± 5849	107 ± 404	1735 ± 2410	84 ± 561	807 ± 1287	55.70 ± 107.34	748 ± 1108	21 ± 30
	Acetaldehyde	1133 ± 1499	263 ± 629	1524 ± 1869	32 ± 100	467 ± 917	16 ± 61	862.06 ± 1371.56	17.74 ± 31.77	276 ± 454	102 ± 253
	Acetic acid	70 ± 74	8 ± 15	254 ± 297	25 ± 48	40 ± 52	5 ± 14	103.98 ± 180.17	-4.86 ± 16.41	100 ± 143	-5 ± 11
Isoprenoids	Isoprene	140.90 ± 162.7	120.0 ± 381.1	61.2 ± 46.5	14.5 ± 28.9	13.6 ± 14.5	6.8 ± 13.3	12.2 ± 14.1	12.6 ± 14.9	35.4 ± 54.2	20.9 ± 45.5
	Monoterpenes	24.0 ± 81.4	5.39 ± 6.74	112.7 ± 141.4	31.9 ± 44.3	38.8 ± 72.3	3.9 ± 13.9	17.8 ± 24.7	8.29 ± 9.46	51.3 ± 122.9	5.05 ± 7.12
	Sesquiterpenes	0.36 ± 0.41	0.47 ± 0.40	1.26 ± 1.56	0.32 ± 0.33	0.16 ± 0.13	0.48 ± 0.45	0.76 ± 0.41	1.77 ± 2.70	0.55 ± 0.64	0.09 ± 0.24
	Geosmin	0.07 ± 0.09	0.19 ± 0.37	0.12 ± 0.14	0.28 ± 0.39	0.03 ± 0.05	0.15 ± 0.27	0.02 ± 0.03	0.07 ± 0.06	0.01 ± 0.03	0.03 ± 0.03
	2-Methylisoborneol	0.30 ± 0.64	0.51 ± 0.70	0.08 ± 0.07	0.25 ± 0.41	0.03 ± 0.02	0.09 ± 0.17	0.03 ± 0.04	0.14 ± 0.17	-0.01 ± 0.09	0.05 ± 0.07
GLVs	Cyclohexene	28.98 ± 41.95	17.25 ± 67.25	7.08 ± 5.58	3.24 ± 5.03	1.78 ± 1.47	1.18 ± 2.54	0.93 ± 3.48	2.60 ± 4.27	11.53 ± 20.44	1.61 ± 2.71
	Pentanal	19.53 ± 16.11	9.44 ± 23.98	67.18 ± 48.49	12.62 ± 42.14	10.82 ± 12.58	4.28 ± 25.40	11.86 ± 12.82	1.92 ± 5.25	12.01 ± 13.68	3.50 ± 5.79
	Hexadialenal	3.33 ± 3.66	2.17 ± 5.74	1.44 ± 0.64	1.37 ± 1.54	0.34 ± 0.21	0.55 ± 1.08	0.36 ± 0.62	0.58 ± 0.61	0.52 ± 0.65	0.52 ± 0.43
	Cyclohexanone, hexeneones	4.12 ± 3.16	2.48 ± 6.57	20.02 ± 11.47	11.07 ± 35.27	1.65 ± 1.89	2.75 ± 15.99	3.45 ± 3.70	1.74 ± 6.20	3.75 ± 5.57	1.61 ± 3.14
	Hexanal	6.99 ± 6.28	3.44 ± 11.21	15.14 ± 10.20	4.13 ± 14.10	1.59 ± 1.46	1.04 ± 5.07	3.14 ± 3.28	1.14 ± 4.09	4.50 ± 6.11	0.75 ± 1.62
	Hexanoic acid	9.68 ± 17.04	3.74 ± 8.12	11.76 ± 9.60	4.70 ± 12.00	1.69 ± 2.02	1.21 ± 4.78	1.85 ± 3.14	0.94 ± 2.32	1.83 ± 3.83	0.61 ± 1.32
	Nonenal	0.72 ± 1.06	1.82 ± 3.85	0.97 ± 1.18	1.53 ± 3.81	0.11 ± 0.18	0.68 ± 2.06	0.10 ± 0.08	0.51 ± 0.61	0.05 ± 0.15	0.21 ± 0.17
	MACR+MVK+ISOP OOH	45.12 ± 82.10	26.20 ± 74.30	91.70 ± 128.68	1.70 ± 3.87	24.50 ± 42.78	0.76 ± 2.33	10.41 ± 19.59	0.98 ± 1.16	11.34 ± 21.97	1.49 ± 2.73
	MEK	186.16 ± 223.48	32.93 ± 57.98	674.34 ± 656.14	78.53 ± 186.93	229.98 ± 281.96	37.25 ± 193.90	220.54 ± 266.79	23.96 ± 55.97	153.97 ± 156.43	16.15 ± 22.35
OVO C	Propionic acid	1.79 ± 2.17	0.36 ± 0.77	4.48 ± 4.98	0.19 ± 0.62	1.45 ± 1.96	0.04 ± 0.51	1.05 ± 1.59	0.02 ± 0.29	1.16 ± 1.61	-0.04 ± 0.21
	Methyl glyoxal, propenoic acid	0.93 ± 0.97	0.44 ± 0.49	1.52 ± 1.56	0.43 ± 0.37	0.52 ± 0.78	0.25 ± 0.26	0.25 ± 0.89	0.13 ± 0.19	0.38 ± 0.87	0.11 ± 0.23
	Hydroxyacetone or other C3H6O2	17.77 ± 27.66	4.21 ± 7.09	33.82 ± 52.99	3.41 ± 1.76	10.17 ± 22.59	1.65 ± 1.30	11.27 ± 32.74	1.36 ± 0.85	18.84 ± 40.26	1.28 ± 1.70
	Butanol	0.74 ± 1.58	0.01 ± 0.02	0.95 ± 1.69	0.00 ± 0.01	0.18 ± 0.38	0.00 ± 0.02	0.18 ± 0.46	0.01 ± 0.05	0.19 ± 0.48	0.00 ± 0.01
	Cyclopentadienone	1.10 ± 1.47	0.39 ± 0.92	0.57 ± 0.53	0.17 ± 0.24	0.19 ± 0.26	0.09 ± 0.32	0.18 ± 0.22	0.09 ± 0.07	0.27 ± 0.26	0.06 ± 0.08
	Furfural	1.01 ± 1.83	0.17 ± 0.63	0.51 ± 0.49	0.09 ± 0.18	0.17 ± 0.20	0.04 ± 0.09	0.02 ± 0.38	0.04 ± 0.06	0.06 ± 0.37	0.03 ± 0.06
	Furfuryl alcohol	1.47 ± 2.10	1.95 ± 3.16	0.65 ± 1.75	3.13 ± 2.93	-0.09 ± 3.46	1.73 ± 2.20	-0.05 ± 0.94	0.44 ± 0.32	-0.07 ± 0.66	0.38 ± 0.53
	Succinic anhydride	3.14 ± 3.83	0.76 ± 0.98	5.31 ± 5.59	0.61 ± 0.98	2.16 ± 3.11	0.28 ± 0.71	1.98 ± 2.94	0.25 ± 0.27	2.06 ± 2.82	0.24 ± 0.41
	Methyl Methacrylate or other C5H8O2	8.95 ± 6.46	3.70 ± 5.60	9.65 ± 7.94	4.64 ± 7.78	2.76 ± 2.74	1.56 ± 1.26	0.11 ± 6.41	1.66 ± 1.31	0.27 ± 5.36	1.48 ± 1.52
	Pentanoic acid	15.71 ± 32.58	5.98 ± 11.00	9.60 ± 6.96	1.23 ± 2.99	1.53 ± 1.82	0.43 ± 1.34	1.86 ± 2.74	0.40 ± 0.81	1.50 ± 3.76	1.57 ± 3.48
	Benzaldehyde	10.21 ± 14.71	7.97 ± 23.59	3.83 ± 5.42	0.60 ± 1.64	0.47 ± 0.95	0.24 ± 0.44	0.80 ± 2.10	0.67 ± 1.07	0.24 ± 2.97	5.35 ± 13.04
	Cresol	4.33 ± 5.37	0.91 ± 1.54	7.26 ± 7.80	0.75 ± 3.42	2.77 ± 4.01	0.72 ± 7.39	2.53 ± 3.94	0.05 ± 0.41	2.67 ± 3.92	0.15 ± 0.55
	Heptanal	3.48 ± 3.28	1.60 ± 4.16	2.87 ± 2.20	1.17 ± 4.02	0.32 ± 0.17	0.39 ± 1.03	0.86 ± 0.94	1.42 ± 2.13	1.50 ± 1.63	0.48 ± 0.74
	Maleic acid	0.78 ± 0.91	0.19 ± 0.27	1.35 ± 1.46	0.20 ± 0.30	0.58 ± 0.86	0.08 ± 0.22	0.47 ± 0.68	0.09 ± 0.12	0.49 ± 0.65	0.09 ± 0.13



Acetophenone	1.00 ± 0.58	1.06 ± 1.49	0.78 ± 0.57	0.45 ± 1.15	0.34 ± 0.18	0.18 ± 0.50	0.43 ± 0.55	0.44 ± 0.98	0.19 ± 0.51	0.36 ± 0.59
	4.22 ± 5.15	0.95 ± 1.33	7.15 ± 7.75	0.80 ± 1.30	3.00 ± 4.40	0.33 ± 0.94	2.56 ± 3.77	0.36 ± 0.43	2.71 ± 3.63	0.36 ± 0.59
C6H4O3	2.82 ± 4.63	4.13 ± 9.20	2.31 ± 1.28	1.78 ± 5.27	0.32 ± 0.17	0.55 ± 1.63	0.46 ± 0.56	1.21 ± 2.77	0.33 ± 1.15	0.62 ± 0.97
	-0.00 ± 0.11	0.06 ± 0.17	-0.11 ± 0.11	-0.01 ± 0.14	-0.02 ± 0.06	0.04 ± 0.07	-0.00 ± 0.07	0.05 ± 0.07	-0.00 ± 0.07	0.05 ± 0.09
Cinnamaldehyde	0.46 ± 0.73	0.45 ± 0.89	0.03 ± 0.18	0.23 ± 0.19	-0.02 ± 0.11	0.13 ± 0.15	0.01 ± 0.05	0.17 ± 0.14	-0.00 ± 0.15	0.13 ± 0.11
	3.53 ± 5.29	9.20 ± 20.13	1.02 ± 1.16	1.02 ± 1.63	0.88 ± 1.10	0.46 ± 1.40	0.38 ± 0.73	0.79 ± 0.97	0.10 ± 0.99	0.31 ± 1.34
Creosol	4.66 ± 7.16	4.38 ± 7.51	10.17 ± 10.32	2.89 ± 4.98	3.89 ± 6.91	1.34 ± 3.44	0.72 ± 1.10	1.32 ± 1.95	2.12 ± 2.33	1.17 ± 1.16
	3.72 ± 5.19	1.37 ± 6.15	0.34 ± 0.35	0.29 ± 0.68	0.32 ± 0.38	0.22 ± 0.30	0.05 ± 1.34	0.71 ± 1.16	-0.05 ± 1.28	0.23 ± 0.41
Nonanal	0.07 ± 0.09	0.02 ± 0.04	0.12 ± 0.15	0.01 ± 0.05	0.05 ± 0.09	0.00 ± 0.04	0.04 ± 0.06	0.00 ± 0.03	0.03 ± 0.07	0.00 ± 0.03
	0.55 ± 0.76	0.87 ± 1.43	1.16 ± 0.99	0.98 ± 1.86	0.36 ± 0.47	0.34 ± 0.87	0.25 ± 0.29	0.54 ± 0.75	0.54 ± 0.67	0.28 ± 0.31
Acetylmalonate	0.99 ± 1.36	0.65 ± 1.31	0.25 ± 0.33	0.17 ± 0.33	0.34 ± 0.42	0.24 ± 0.30	-0.10 ± 0.92	0.72 ± 1.09	-0.27 ± 1.04	0.19 ± 0.22
	0.20 ± 0.35	0.39 ± 0.43	0.10 ± 0.07	0.72 ± 0.67	0.02 ± 0.08	0.27 ± 0.23	0.04 ± 0.07	0.32 ± 0.22	0.06 ± 0.07	0.33 ± 0.37
Carvone oxide	0.30 ± 0.64	0.51 ± 0.70	0.08 ± 0.07	0.25 ± 0.41	0.03 ± 0.02	0.09 ± 0.17	0.03 ± 0.04	0.14 ± 0.17	-0.01 ± 0.09	0.05 ± 0.07
	0.48 ± 1.34	0.65 ± 0.70	1.53 ± 1.47	11.04 ± 12.50	0.07 ± 0.16	2.06 ± 2.95	0.09 ± 0.11	0.40 ± 0.25	0.23 ± 0.17	0.46 ± 0.40
Norpionic acid	0.46 ± 1.21	0.38 ± 0.28	0.08 ± 0.06	0.42 ± 0.44	0.03 ± 0.08	0.13 ± 0.13	0.01 ± 0.13	0.12 ± 0.10	-0.08 ± 0.27	0.08 ± 0.09
	0.01 ± 0.08	0.08 ± 0.09	0.07 ± 0.20	0.19 ± 0.17	0.06 ± 0.23	0.12 ± 0.11	-0.01 ± 0.12	0.08 ± 0.09	0.03 ± 0.11	0.07 ± 0.09
Geranyl formate	0.07 ± 0.09	0.02 ± 0.19	0.12 ± 0.28	0.01 ± 0.28	0.03 ± 0.03	0.15 ± 0.15	0.02 ± 0.02	0.07 ± 0.07	0.01 ± 0.01	0.03 ± 0.03
	0.09 ± 0.09	0.37 ± 0.36	0.14 ± 0.12	0.39 ± 1.04	0.05 ± 0.01	0.27 ± 0.27	0.03 ± 0.02	0.06 ± 0.24	0.03 ± 0.06	0.03 ± 0.19
Menthhol	0.15 ± 0.99	0.34 ± 0.26	0.10 ± 0.06	0.96 ± 0.21	0.09 ± 0.02	0.23 ± 0.09	0.08 ± -0.03	0.15 ± 0.10	0.12 ± -0.17	0.19 ± 0.04
	2.99 ± 0.64	0.64 ± 0.06	0.06 ± 0.21	0.21 ± 0.06	0.04 ± 0.04	0.08 ± 0.08	-0.03 ± 0.12	0.10 ± 0.08	-0.17 ± 0.48	0.04 ± 0.09
Citronellyl acetate	8.96 ± 12.56	7.27 ± 16.63	9.97 ± 13.48	4.55 ± 5.73	5.06 ± 8.28	2.31 ± 3.53	0.52 ± 7.17	3.49 ± 2.98	1.75 ± 12.50	4.61 ± 7.56
	8.44 ± 20.00	1.94 ± 3.88	35.91 ± 42.26	2.81 ± 5.44	10.40 ± 12.39	1.44 ± 4.87	6.35 ± 12.82	2.25 ± 2.54	4.09 ± 11.48	0.78 ± 0.87
Benz enoi ds	2.19 ± 2.29	7.26 ± 40.20	2.45 ± 2.47	0.48 ± 0.99	0.97 ± 1.08	0.63 ± 2.66	0.59 ± 1.10	0.21 ± 0.38	0.64 ± 1.56	0.15 ± 0.92
	21.45 ± 35.04	2.94 ± 5.44	27.86 ± 40.61	1.79 ± 3.90	23.80 ± 30.48	1.69 ± 7.81	15.17 ± 21.70	1.98 ± 3.05	11.78 ± 29.63	1.04 ± 1.57
Xylene	5.44 ± 13.30	1.63 ± 3.00	15.96 ± 20.41	1.75 ± 2.42	7.00 ± 10.47	1.12 ± 3.19	5.61 ± 11.23	1.71 ± 1.74	5.29 ± 15.05	0.55 ± 0.47
	5.27 ± 9.62	0.79 ± 1.09	11.78 ± 14.95	1.27 ± 1.66	7.14 ± 8.55	1.01 ± 2.75	6.33 ± 8.96	1.22 ± 1.21	9.95 ± 20.54	0.46 ± 0.56
Trimethylbenzene	0.53 ± 1.12	0.15 ± 0.17	2.79 ± 2.88	0.81 ± 1.28	0.97 ± 1.13	0.30 ± 0.65	1.08 ± 0.98	0.41 ± 0.38	1.02 ± 1.08	0.22 ± 0.24
Cymenene	10.65 ± 15.36	29.57 ± 26.90	0.03 ± 0.07	12.27 ± 14.41	0.09 ± 0.12	3.53 ± 3.76	6.63 ± 13.77	16.95 ± 17.20	5.31 ± 10.11	2.37 ± 1.71
	0.64 ± 3.18	0.56 ± 0.90	-0.00 ± 0.01	0.05 ± 0.07	0.00 ± 0.00	0.03 ± 0.04	0.02 ± 0.05	0.10 ± 0.20	0.32 ± 0.89	0.02 ± 0.09
Sulfu r and selen ium	0.04 ± 0.04	0.28 ± 0.19	0.09 ± 0.08	0.28 ± 0.18	0.02 ± 0.03	0.27 ± 0.29	0.17 ± 0.27	0.20 ± 0.13	0.14 ± 0.24	0.07 ± 0.06

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Table C3 Fluxes from GC measurements per sample type in pmol m⁻² s⁻¹ with standard deviation for time points A before wetting and before treatment with humid air, B immediately before wetting, C immediately after wetting, and D after the subsequent dry out of the samples.

Class	Substance	RT [min]	Time point	moss	lichen	dark_cyano	light_cyano	bare_soil
Monot erpenes	(-)-α-pinene	35.281	B	19.2	0.397 ± 0.688	0.934	0.0171 ± 0.0295	1.36 ± 1.17
			C	19.243 ± 0.828	1.42 ± 2.38	11.07 ± 9.35	3.74	0.632 ± 0.877
			D	10.0 ± 11.2		8.7 ± 12.3		18.4
	(+)-α-pinene	35.893	B	0.095 ± 0.134	0.247 ± 0.391	0	0	1.53 ± 2.49
			C	0	0.153 ± 0.266	0.268 ± 0.340	0.0139 ± 0.0241	0.082 ± 0.142
			D	0.153 ± 0.265		0.0089 ± 0.0179	0.073 ± 0.104	
tricyclene		36.477	B					1.382 ± 0.009
			C					



		D	1.46		26.7	
unknown	36.664	B		1.79 ± 2.24		0.00126
monoterpene		C		0.7818 ± 0.0457	0.111 ± 0.193	
(best match:		D				
β-ocimene)						
(-)-camphene	37.790	B	0.0149 ± 0.0211	3.98 ± 7.28	0.334 ± 0.473	0.653 ± 0.187
		C	0.121 ± 0.243	2.30 ± 1.40	1.03 ± 1.14	0.321 ± 0.279
		D	0.0780 ± 0.0781	0.221 ± 0.271	0.0156 ± 0.0271	0
unknown	38.196	B		9.9 ± 17.1		0
monoterpene		C	1.39 ± 2.41	0	8.1 ± 14.0	0
(best match:		D	13.4 ± 18.9		12.4	
β-ocimene)						
β-myrcene	38.289	B	0	0	2.81	0.449 ± 0.777
		C	7.6 ± 13.3	2.30 ± 3.26	6.32	0.694 ± 0.982
		D	7.8 ± 13.6		12.7 ± 18.0	13.4 ± 18.9
(+)-camphene	38.319	B	0	1.07 ± 1.30		0
		C	0.0546 ± 0.0649	1.059 ± 0.287	0.100 ± 0.141	1.78 ± 2.52
		D	0.1031 ± 0.0477	0.3992 ± 0.0974	0.470 ± 0.381	0.971
sabinene	38.540	B			0.0255 ± 0.0330	0.0185 ± 0.0262
		C				0
		D	13.4			
3-carene	38.915	B		0	0	1.35
		C	1.3719 ± 0.0581			
		D			0	27.2
(-)-β-pinene	40.271	B	0	0	0	0
		C		63.7	0	0
		D	0		0	0
(-)-α-phellandrene	40.667	B				0
		C	1.22 ± 1.72	0.113		0
		D			2.31	2.43
α-terpinene	42.286	B		0	0.001 ± 0.002	0.006 ± 0.005
		C	0.0001 ± 0.0002	0.125 ± 0.217	0.200 ± 0.282	0.0001 ± 0.0002
		D	0.0002 ± 0.0004	0	0.001 ± 0.001	0.459 ± 0.556
p-cymene	43.819	B	0	9.4 ± 18.7	22.3 ± 15.8	2.43 ± 3.35
		C	0	35.7 ± 45.2	35.6 ± 46.8	19.8 ± 34.3
		D	0	0	2.23 ± 3.56	0
(+)-limonene	44.502	B	2.90	1.91 ± 2.82	14.7 ± 12.1	1.27 ± 1.15
		C	0	1.47 ± 2.08	11.7 ± 13.7	11.8
		D	0.421 ± 0.729	0	2.09	19.09 ± 8.59
unknown	45.212	B				0
monoterpene		C		0	0.0795	5.29
(best match α-phellandrene)		D	0.141 ± 0.200		0.0285	0.00521
γ-terpinene	47.908	B		44.4		
		C			44.71 ± 1.96	1.39
		D				24.6 ± 32.9
unknown	36.664	B		1.79 ± 2.24		0.00126
monoterpene		C	0	0.7818 ± 0.0457	0.111 ± 0.193	0
(best match β-ocimene)		D	0		0	
Petrich or	geosmin	66.124	B	0	0	0
		C	1.96 ± 4.39	2.90 ± 4.11	0.139 ± 0.240	0
		D	0	0	0	0



	2-methylisoborneol	56.536	B	0.80 ± 1.39	0.95 ± 2.13	0	0	0.204 ± 0.353
			C	1.38 ± 3.10	1.17 ± 2.02	3.61 ± 4.76	0.314 ± 0.544	0
			D	0.139 ± 0.369	1.26 ± 2.19	3.35 ± 4.36	0	4.94 ± 9.88
Benzenoids	benzene	12.951	B	4.55 ± 7.88	26.4 ± 64.6	1.42 ± 2.47	7.3 ± 12.6	13.7 ± 23.8
			C	4.32 ± 5.84	2.48 ± 4.29	15.27 ± 9.20	0	21.4 ± 37.1
			D	2.80 ± 2.72	0	9.7 ± 16.0	4.23 ± 7.32	12.2 ± 16.3
	toluene	18.082	B	1.90 ± 2.72	9.5 ± 23.3	1.61 ± 2.79	2.20 ± 3.81	0.78 ± 1.36
			C	0	1.74 ± 3.01	5.37 ± 9.29	0.68 ± 1.17	0.77 ± 1.34
			D	4.8 ± 12.0	0	0	5.05 ± 4.81	0
	<i>p</i> -xylene	24.624	B	0.103 ± 0.178	1.27 ± 1.99	0.253 ± 0.247	0.0531 ± 0.0920	0.111 ± 0.192
			C	0.0215 ± 0.0549	0.754 ± 0.677	1.23 ± 2.14	0.083 ± 0.143	0.303 ± 0.514
			D	0.92 ± 2.35	0	0.0753 ± 0.0951	0.0279 ± 0.0483	0.099 ± 0.198
	<i>m</i> -xylene	26.141	B	0.209 ± 0.363	4.21 ± 7.78	0.184 ± 0.319	0.436 ± 0.754	0.77 ± 1.33
			C	0	2.70 ± 2.61	6.99 ± 6.62	0.533 ± 0.924	0.471 ± 0.816
			D	2.61 ± 5.13	0.0541 ± 0.0938	0.0083 ± 0.0166	0	0
	ethylbenzene	27.318	B	0.285 ± 0.494	2.31 ± 4.01	0.163 ± 0.231	0.78 ± 1.35	0.094 ± 0.124
			C	0.044 ± 0.108	1.66 ± 1.58	2.60 ± 4.50	0.361 ± 0.366	0.689 ± 0.804
			D	1.59 ± 3.43	0	0.0295 ± 0.0590	0.94 ± 1.32	0
	<i>o</i> -xylene	28.376	B	0	2.14 ± 2.34	0.127 ± 0.180	0.313 ± 0.543	0
			C	0	0.454 ± 0.407	2.85 ± 4.03	0.0209 ± 0.0363	0.077 ± 0.133
			D	1.76 ± 3.87	0	0	0.286 ± 0.404	0
	styrene	29.624	B	0.305 ± 0.528	6.7 ± 15.0	4.93 ± 8.53	5.34 ± 9.10	0.486 ± 0.842
			C	0.45 ± 1.09	8.74 ± 8.92	28.2 ± 48.8	6.81 ± 5.95	0.0100 ± 0.0174
			D	0.58 ± 1.01	0.165 ± 0.285	0	0.550 ± 0.953	0
	benzene, 1,3,5-trimethyl-	35.196	B	4.26 ± 7.15	1.07 ± 1.58	4.60 ± 4.49	0.551 ± 0.636	0.81 ± 1.40
			C	1.10 ± 2.86	0.649 ± 0.582	0.59 ± 1.02	0.95 ± 1.65	0.0549 ± 0.0481
			D	0.299 ± 0.787	0.204 ± 0.354	0.135 ± 0.270	0	0.245 ± 0.490
	benzene, 1,2,4-trimethyl-	38.504	B	0.210 ± 0.347	1.69 ± 3.39	0.338 ± 0.498	3.92 ± 2.89	3.00 ± 3.68
			C	0	1.479 ± 0.901	4.82 ± 7.88	0.467 ± 0.407	1.17 ± 1.15
			D	1.64 ± 3.24	0	0.90 ± 1.81	0.436 ± 0.755	0.53 ± 1.05
	benzene, 1,2,3-trimethyl-	38.522	B	0.200 ± 0.347	2.16 ± 3.28	0.438 ± 0.758	4.39 ± 3.49	3.05 ± 3.98
			C	0	1.135 ± 0.955	5.23 ± 7.58	0.77 ± 1.03	1.16 ± 1.14
			D	1.72 ± 3.21	0.217 ± 0.376	1.20 ± 1.76	0.349 ± 0.605	0.52 ± 1.04
	phenol	58.38	B	8.6 ± 14.9	36.0 ± 80.5	0	14.1 ± 24.4	35.0 ± 36.3
			C	31.2 ± 51.4	43.1 ± 52.0	37.3 ± 53.2	0	33.9 ± 58.6
			D	14.4 ± 30.5	11.2 ± 19.4	35.8 ± 53.1	0	38.5 ± 73.1
GLVs	pentanal	15.116	B	5.65 ± 9.79	7.2 ± 12.5	0	0	0
			C	0.197 ± 0.522	0.218 ± 0.378	0	0	1.02 ± 1.76
			D	0	0	0	0	0
	hexanal	24.468	B	6.18 ± 9.55	3.29 ± 5.70	2.00 ± 2.66	0.350 ± 0.607	0.108 ± 0.186
			C	4.18 ± 3.74	0.566 ± 0.981	0.77 ± 1.33	2.62 ± 4.55	0.85 ± 1.47
			D	0.98 ± 2.17	0.61 ± 1.06	0.516 ± 0.734	0.190 ± 0.328	0
	hexanoic acid	58.785	B	0	0	0	0	0
			C	0	0	0	0	0
			D	0	0	30.0 ± 60.1	0	1.50 ± 3.00



760 Appendix D Statistical test results

765 **Table D1** Fixed-effect coefficients from linear mixed-effects models testing differences in VOC flux ($\log_{10}$ -transformed, $\text{nmol m}^{-2} \text{s}^{-1}$) among measurement phases, sample type, and time within phase. Models included random intercepts and random slopes for time within phase by sample replicate, and a random intercept for measurement run. β represents the coefficient on the $\log_{10}$ scale; CI: 95% confidence interval; p-values were derived from Wald z-tests and adjusted for multiple comparisons using the Benjamini-Hochberg false discovery rate (FDR). Significance: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Reference level for phase:		phase 1 phase 2	phase 1 phase 3	phase 1 phase 4	phase 1 phase 5	phase 2 phase 3	phase 2 phase 4	phase 2 phase 5	phase 3 phase 4	phase 3 phase 5	phase 4 phase 5
Total VOCs	β -coefficient	1.21	-1.27	-1.65	2.59	-2.48	-2.86	1.38	-0.38	3.86	4.24
	95% CI	0.3–2.1	-2.2–0.3	-2.6–0.7	1.7–3.5	-2.9–2.1	-3.1–2.6	1.1–1.7	-0.77–0.01	3.5–4.3	3.9–4.5
	p value (adj)	0.01*	0.01*	***	***	***	***	***	0.054	***	1***
GLV	β -coefficient	0.047	0.035	0.027	0.002	-0.012	-0.02	-0.044	-0.008	-0.033	-0.025
	95% CI	0.025–0.068	0.012–0.058	0.005–0.049	-0.020–0.024	-0.021–0.003	-0.026–0.013	-0.051–0.038	-0.017–0.002	-0.042–0.023	-0.032–0.018
	p value (adj)	***	0.005**	0.02*	0.8	0.02*	***	***	0.12	***	***
Reference level for sample type:		lichen bare soil	lichen dark cyano	lichen light cyano	lichen moss	bare soil dark cyano	bare soil light cyano	bare soil moss	dark cyano light cyano	dark cyano moss	light cyano moss
Total VOCs	β -coefficient	-0.295	-0.056	-0.657	2.239	0.239	-0.362	2.534	-0.601	2.295	2.896
	95% CI	-2.4–1.8	-1.6–1.5	-2.4–1.1	0.6–3.9	-2.2–2.6	-3.1–2.4	1.2–3.9	-2.1–0.9	0.3–4.3	0.6–5.2
	p value (adj)	0.94	0.94	0.79	0.047*	0.94	0.94	0.002**	0.79	0.06	0.049*

Reference level for sample types:		cyanobacteria and bare soil	cyanobacteria, lichen, and bare soil
		moss and lichen	moss
Total VOCs	β -coefficient	1.53	2.33
	95% CI	0.37–2.69	0.81–3.84
	p value (adj)	0.010**	0.003**
GLV	β -coefficient	0.036	
	95% CI	-0.005–0.078	
	p value (adj)	0.087	

770 **Table D2** Permutational multivariate analysis of variance (PERMANOVA) results of global and pairwise comparisons using 999 permutations per test for measurement phase and sample type. P-values of pairwise comparisons were adjusted for multiple comparisons within each factor (phase, sample type) using the Benjamini-Hochberg false discovery rate (FDR) procedure; R^2 indicates the proportion of total compositional variance explained by the grouping factor; N denote the number of observations in each group.

Factor	Group A	Group B	Pseudo-F	p-value	p-value adjusted (FDR)	N _{Group A}	N _{Group B}
Phases ($R^2 = 0.503$)			23.82	0.001		N = 99	
Phase	1	2	10.10836	0.001	0.001	15	21
Phase	1	3	7.186443	0.001	0.001	15	21
Phase	1	4	20.480147	0.001	0.001	15	21
Phase	1	5	26.950259	0.001	0.001	15	21
Phase	2	3	24.54491	0.001	0.001	21	21
Phase	2	4	40.27097	0.001	0.001	21	21
Phase	2	5	14.689778	0.001	0.001	21	21



Phase	3	4	9.194698	0.001	0.001	21	21
Phase	3	5	44.171642	0.001	0.001	21	21
Phase	4	5	43.505163	0.001	0.001	21	21
Sample types ($R^2 = 0.518$)			4.30	0.001		N = 21	
Sample type	bare_soil	dark_cyano	3.144301	0.092	0.175	4	4
Sample type	bare_soil	lichen	0.88108	0.491	0.614	4	3
Sample type	bare_soil	light_cyano	0.4355	0.883	0.898	4	3
Sample type	bare_soil	moss	8.836223	0.002	0.020	4	7
Sample type	dark_cyano	lichen	1.604382	0.217	0.310	4	3
Sample type	dark_cyano	light_cyano	2.324638	0.105	0.175	4	3
Sample type	dark_cyano	moss	5.627805	0.008	0.033	4	7
Sample type	lichen	light_cyano	0.316896	0.898	0.898	3	3
Sample type	lichen	moss	6.717467	0.013	0.033	3	7
Sample type	light_cyano	moss	7.464444	0.013	0.033	3	7

775 **Table D3** Kendall's rank correlation coefficients (τ) between petrichor associated molecules geosmin and 2-methylisoborneol, and monoterpenes with benzenoid compounds; correlations were computed on imputed, aggregated flux data (see Methods); p-values were adjusted for multiple comparisons using the Benjamini-Hochberg false discovery rate (FDR) procedure within each period.

Period	Compound A	Compound B	τ	p-value	p-value adjusted (FDR)
pre	Geosmin	Nonenal	0.455	< 0.001	< 0.001
pre	Geosmin	Benzothiazole	0.321	0.002	0.003
pre	Geosmin	Furfuryl alcohol	0.222	0.03	0.03
pre	2-Methylisoborneol	Nonenal	0.478	< 0.001	< 0.001
pre	2-Methylisoborneol	Benzothiazole	0.404	< 0.001	< 0.001
pre	2-Methylisoborneol	Furfuryl alcohol	0.254	0.015	0.018
post	Geosmin	Nonenal	0.752	< 0.001	< 0.001
post	Geosmin	Benzothiazole	0.614	< 0.001	< 0.001
post	Geosmin	Furfuryl alcohol	0.733	< 0.001	< 0.001
post	2-Methylisoborneol	Nonenal	0.793	< 0.001	< 0.001
post	2-Methylisoborneol	Benzothiazole	0.554	< 0.001	< 0.001
post	2-Methylisoborneol	Furfuryl alcohol	0.563	< 0.001	< 0.001
pre	Monoterpenes	Benzene	0.438	< 0.001	< 0.001
pre	Monoterpenes	Toluene	0.662	< 0.001	< 0.001
pre	Monoterpenes	Trimethylbenzene	0.649	< 0.001	< 0.001
pre	Monoterpenes	Styrene	0.706	< 0.001	< 0.001
post	Monoterpenes	Benzene	0.379	0.003	0.003
post	Monoterpenes	Toluene	0.669	< 0.001	< 0.001
post	Monoterpenes	Trimethylbenzene	0.623	< 0.001	< 0.001
post	Monoterpenes	Styrene	0.416	0.001	0.001

Data availability

The data used to support the findings in this study are publicly available on the EDMOND repository and can be accessed with the following DOI: <https://doi.org/10.17617/3.ALNDM6> (Edtbauer et al., 2026)



Author contributions

JS: Conceptualization, Data Curation, Formal analysis, Visualization, Writing – original draft

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790 **Competing interests**

The authors declare that they have no conflict of interest.

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