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Drivers of biogenic volatile organic compound emissions in hygrophytic bryophytes

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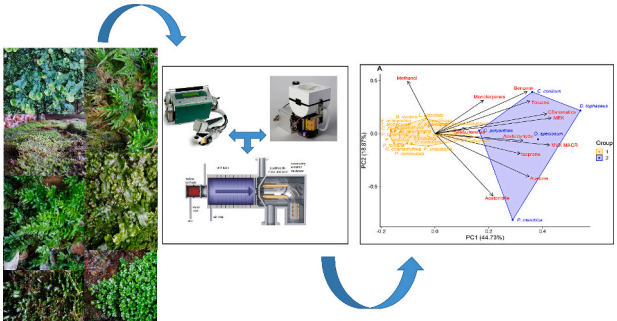
HIGHLIGHTS

- This study provides new information on BVOC emissions from bryophytes.
- We found a high and a low bryophyte BVOC emitter group.
- The emission of BVOCs from liverwort storage compounds was dominant, but emissions from mosses were also important.
- The most important driver for bryophyte BVOC emissions was species-specific variability.

GRAPHICAL ABSTRACT



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ABSTRACT

Bryophytes can both emit and take up biogenic volatile organic compounds (BVOCs) to and from the environment. Despite the scarce study of these exchanges, BVOCs have been shown to be important for a wide range of ecological roles. Bryophytes are the most ancient clade of land plants and preserve very similar traits to those first land colonisers. Therefore, the study of these plants can help understand the early processes of BVOC emissions as an adaptation to terrestrial life. Here, we determine the emission rates of BVOCs from different bryophyte species to understand what drives such emissions. We studied 26 bryophyte species from temperate regions that can be found in mountain springs located in NE Spain. Bryophyte BVOC emission presented no significant phylogenetic signal for any of the compounds analysed. Hence, we used mixed linear models to investigate the species-specific differences and eco-physiological and environmental drivers of bryophyte BVOC emission. In general, species-specific variability was the main factor explaining bryophyte BVOC emissions; but additionally, photosynthetic rates and light intensity increased BVOC emissions. Despite emission measurements

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reported here were conducted at 30°, and may not directly correspond to emission rates in natural conditions, most of the screened species have never been measured before for BVOC emissions and therefore this information can help understand the drivers of the emissions of BVOCs in bryophytes.

1. Introduction

Bryophytes, which include mosses, liverworts, and hornworts have been reported to emit several biogenic volatile organic compounds (BVOCs) to the environment, including isoprene, acetaldehyde, monoterpenes, sesquiterpenes, green leaf volatiles, and alcohols (Kesselmeier et al., 1999; Edtbauer et al., 2021; Ryde et al., 2022; Langford et al., 2023). BVOC emissions by bryophytes have been suggested to constitute a defence role against biotic and abiotic stress. For instance, oil bodies in several liverworts have been shown to contain terpene and aromatic compounds, and have been suggested to have a herbivore deterrent role against snails and other animals (Chen et al., 2018; Kanazawa et al., 2020). In terms of defence against abiotic stress, isoprene emission by bryophytes has been suggested to have a thermo-protection role (Hanson et al., 1999). This process consists of volatile release as a mechanism to cope with such stress by reducing the levels of damaging ROS within the leaf and thus increasing thermo-tolerance, and has been extensively observed in vascular plants (Loreto and Velikova, 2001; Affek and Yakir, 2002; Loreto and Fares, 2007; Sharkey et al., 2008).

Bryophytes are the most ancient clade of land plants (Wellman et al., 2003; Qiu et al., 2006; Ludwiczuk and Asakawa, 2020). Therefore, the study of these plants can help understand the processes of BVOC emissions by other plants, as their ability to emit certain VOCs might very well have evolved in bryophytes for the first time. For instance, Hanson et al. (1999) hypothesised that the correlated thermal and desiccation stress experienced by early land plants provided the selective pressure for the evolution of light-dependent isoprene emission in the ancestors of modern mosses. At the same time, bryophytes have developed numerous physiological and biochemical adaptations since diverging from the common ancestor they share with vascular plants (Roberts et al., 2012), leading to differences in how BVOC emissions from these species respond to environmental conditions (Langford et al., 2023).

Apart from temperature, other environmental drivers affecting bryophyte BVOCs emissions are light and UV radiation (Morén and Lindroth, 2000; Tiiva et al., 2007; Chen et al., 2018), hydric stress, including desiccation (Pressel et al., 2009; Tiiva et al., 2009; Faubert et al., 2010a; Chen et al., 2018), nutrient loading (Deakova, 2019), ozone exposure (Rinnan et al., 2013) and water availability (Janson and De Serves, 1998; Faubert et al., 2010a). Moreover, BVOC bryophyte emissions could be related to VOC-mediated plant-plant communication, which has been suggested to be involved in competition between moss species (Vicherová et al., 2020), or related to plant-ecosystem communication, such as by attracting pollinators (McCuaig et al., 2015). Regarding atmospheric chemistry, bryophytes have been found to be important, particularly in the boreal and tropical regions, where their emissions can represent a large fraction of the BVOCs emitted to the atmosphere (Edtbauer et al., 2021; Langford et al., 2023). For instance, Edtbauer et al., 2021 showed that up to 39 % of the total sesquiterpene emissions modelled for the Amazon forest could come from bryophytes. Despite the fact that bryophyte BVOC emissions have been shown to have myriad of roles, still, very little is known about such emissions.

There are two main routes for BVOC production and emissions in vascular plants. One is the so-called “de novo” route, where BVOCs are produced from recently photosynthesized carbon. This is the case for the emission of isoprene and some monoterepenes (Yang et al., 2021), for which their emission is temperature and light dependent (Ghirardo et al., 2010; Fasbender et al., 2018). The second route involves emissions from storage pools, such as oil bodies, resins and waxes, where BVOCs are released via volatilization, and such emissions are light independent but strongly temperature dependent (Kesselmeier and Staudt, 1999). This is true for many conifer trees, such as *Pinus sylvestris* (Monson et al., 1995) or black spruce (Lerdau et al., 1997). Within bryophytes, emissions from storage compounds can be expected in liverworts, as these have unique organelles, where terpenoids and aromatic compounds can be accumulated, and thus can be released to the environment (Ludwiczuk and Asakawa, 2020; Romani et al., 2022). Additionally, as BVOC emission can also be related to photosynthesis (Kesselmeier and Staudt, 1999), and thus light and temperature, higher isoprene emission at higher photosynthetically active radiation has been shown for *Sphagnum fallax* and *Polytrichum strictum* (Langford et al., 2023). Nevertheless, mosses which lack oil bodies are usually thought not to be important for BVOC emission (Nozaki et al., 2007). Furthermore, differences between the dynamics of BVOC emissions by vascular and bryophyte plants are expected given their morphological and physiological differences. Whereas in vascular plants water uptake and transpiration occurs in a controlled manner, this is not the case in bryophytes, as the latter are of poikilohydric nature (Proctor et al., 2007). Thus, it is expected that different bryophytes have not only a distinct blend and magnitude of BVOC emissions among them (Tiiva et al., 2009; Faubert et al., 2010b), but also, there are expected to be differences in the BVOC emission dynamics between bryophytes and vascular plants.

The objective of this study was to determine the emission rates of BVOC from 26 bryophyte species, and to understand what factors (e.g., photosynthesis, environmental conditions) drive such emissions. We selected a range of hygrophytic bryophytes from temperate regions that can be found in mountain springs. As many of these species have never been measured for BVOC emissions, this study can add information to our understanding on the drivers of the emissions of BVOCs by bryophytes.

2. Methodology

2.1. Species collection and environmental data

We collected 105 bryophytes samples (consisting of 26 different species, 16 mosses and 10 liverworts) across 51 semi-natural springs distributed in a south-to-north gradient across the NE of the Iberian Peninsula from September to November 2020. These springs comprised a very large gradient in terms of climate and water chemistry as shown in previous studies (Fernández-Martínez et al., 2019b). This large environmental gradient was selected in order to study the effect of environmental variability on bryophyte BVOC emissions. Only specimens in direct contact with spring water were collected, being either submerged or receiving the splash of the dripping water of the spring. Specimens were stored in a plastic container containing drops of water from the same spring of collection to ensure an optimal status before measurements. BVOC emissions from bryophyte specimens were analysed within 12 to 24 h after collection.

The water chemistry of these springs is very constant throughout the year, and across years, because they drain water coming from aquifers. This is why in this study, we used the water chemistry analysed during the period 2013–2020 for previous studies (Fernández-Martínez et al., 2018, 2019b, 2021). We also recorded the geographic coordinates and the elevation at each spring, in order to extract climate data from gridded maps. We extracted monthly precipitation and temperature data from the digital Climatic Atlas of Catalonia (Pons, 1996; Ninyerola et al., 2000), available at http://www.opengis.grumets.cat/acdc/en_index.htm, for each spring. We then calculated mean annual temperature to use in our statistical analyses. We further calculated annual water

availability, as the monthly precipitation minus reference evapotranspiration following the Hargreaves method (Hargreaves, 1994). As a proxy of insolation, which could affect the physiological status of the bryophytes, we also recorded whether springs were under shade or not.

2.2. Methodology of measurements

In order to measure the BVOC emissions and photosynthetic rates of the collected bryophytes, a combination of analytical techniques was used.

To sample bryophyte gas exchange, we used a portable gas exchange measurement system (LI-6400-XT, LI-COR, Lincoln, USA) for determination of leaf CO_2 assimilation (A) with a needle leave chamber which was modified to fit the bryophyte species. For this we have used chemically inert perfluoroalkoxy (PFA) tubes and a Polytetrafluoroethylene (PTFE) film to place the bryophytes in the middle of the chamber supported by the PFTA film tray on top of the PFA tubes that we used for holding the tray structure. The LI-COR 6400-XT system provided 500 micromol s^{-1} of charcoal scrubbed air. The CO_2 and humidity of this air was then controlled via the silica gel, soda lime and CO_2 gas canisters which are part of the LI-COR 6400-XT system. Therefore, air was supplied at a known and constant relative humidity of 30 % and CO_2 mixing ratio of 400 ppm, as well as mostly-free of VOCs (i.e. as there was uptake of some oxygenated VOCs, we conclude that not all VOCs were removed by the charcoal filter). The outflow line of the chamber was split into a line going back to the Li_COR 6400-XT for the measurement of photosynthesis via infrared gas analysis, and another line connected to a Proton Transfer Reaction Mass Spectrometer (Ionicon GmbH, Innsbruck, Austria) for the online monitoring of the BVOC emissions. All tubing lines were made of chemically inert PFA material and were heated (50 °C) and isolated to avoid condensation and compound losses to tube walls.

The same procedure was followed on each day of measurements. First, the gas exchange measurement system was stabilized (stable temperature and CO_2 of 30 °C and 400 ppm of CO_2, respectively), and a control measurement was taken, without any bryophyte inside. The conditions used were 1000 μmol photon m^{-2} s^{-1} of photosynthetically active radiation (PAR) and 30 °C temperature. We chose these conditions to be able to derive the empirical emission factors needed for BVOC vegetation modelling (Guenther et al., 2012). These conditions were maintained for 20 min, while measuring photosynthesis and BVOC emissions during this time. Then, the cuvette was opened in order to rewet the bryophytes with their sampled spring water, as these light and temperature conditions can desiccate these species very fast. After rewetting, the bryophyte was placed back into the cuvette and, after stabilization of the measure signal, a decreasing light curve was performed. The light curve consisted of 1000, 500, 250, 100, 50, 25 and 0 μmol m^{-2} s^{-1} of radiation. Even though we did not detect drying in our samples when measuring photosynthesis during the light curve, decreasing water content of the bryophytes could have an impact on the photosynthesis measurements. However, as shown in Fig. S.I:1, light curves seem to work very well for all species, indicating that, if such an effect existed, its impact on our measurements were limited. Transpiration rates did not differ between light intensities, indicating that samples still had enough water to keep constant transpiration rates. Immediately after sampling, bryophytes were placed back into their sample spring water for leachate analysis and dry weight measurement.

2.3. Proton Transfer Reaction Mass Spectrometer (PTR-MS)

Measurements of BVOCs were performed using a PTR-MS (Ionicon Analytic GmbH, Austria) operated under standard conditions (2.2 mbar drift pressure, 600 V drift voltage, 127 Td) and H_3O^+ as reagent ion (Lindinger and Hansel, 1997). A catalytic converter (custom made with platinum pellets heated to 400 °C) was used to convert ambient VOCs to CO_2 + H_2O to determine the background signal for each compound. Background values were interpolated over the time of the measurements. Humidity dependent calibrations (using bubbled synthetic zero air to dilute the standard, regulated as close as possible to bryophyte humidity conditions) were performed using a gravimetrically prepared multicomponent standard, including methanol (*m/z* 33), acetonitrile (*m/z* 42), acetaldehyde (*m/z* 45), acetone (*m/z* 59), isoprene (*m/z* 69), methyl vinyl ketone + methacrolein (MVK+MACR) (*m/z* 71), methyl ethyl ketone (MEK) (*m/z* 73), benzene (*m/z* 79), toluene (*m/z* 93), benzaldehyde (*m/z* 107), α-pinene (*m/z* 137) and β-caryophyllene (*m/z* 205) (Riemer Environmental, Inc.). The PTR-MS technology allows for fast sampling at very low mixing ratios, but the system relies solely on mass-over-charge ratios (*m/z*) for compound specification. Thus, for detected masses such as *m/z* 33, *m/z* 42, *m/z* 45, *m/z* 59, *m/z* 71 and *m/z* 73, we relied on an identification which has been generally agreed on by reasonable exclusion of some BVOC species (Yáñez-Serrano et al., 2021).

2.4. Quantification of bryophyte fluxes

The equation used for the calculation of the BVOC fluxes was:

$$e = (u_i/g) \times (c_o c_i)$$

where u_i is the molar flux in the cuvette inlet in mol s^{-1}, g is the dry weight of the measured bryophyte sample in grams, c_o is the mixing ratio at the outlet of the cuvette and c_i is the mixing ratio at the cuvette inlet, both in mol mol^{-1}. Negative emissions were considered uptake.

Photosynthetic gas exchange was quantified using a differential infrared gas analyser (Licor 6400-XT system) as the differences of CO_2 and H_2O concentrations between empty and plant-containing cuvettes. Assimilation rate was calculated according to von Caemmerer and Farquhar (1981).

The bryophyte dry weight was determined by air-drying the samples for 48 h at 60 °C. The unit of mass used in this study is $gram_{dryweight}$, which from now on it will be referred to g for easier readability.

2.5. Statistical analysis

We investigated similarities and differences in the overall blend of BVOC emission among species using principal components (PCA) and cluster analyses using standard measurements at 1000 μmol m^{-2} s^{-1} of photosynthetically active radiation and 30 °C temperature. We then tested whether the emission of individual compounds, or the three main axes of the PCA describing BVOC emission, presented a phylogenetic signal within our subset of bryophyte species. To do so, we used the phylogenetic tree constructed in Fernández-Martínez et al., 2019a and the *phylosig* R function in *phytools* (Revell) R package. We then used linear mixed models (*nlme* R package) to investigate the relationship between bryophyte BVOC emission (12 compounds) and species-specific photosynthesis (i.e., average photosynthesis per species), sample-specific photosynthesis (i.e., deviation from the average photosynthesis of the species for a given sample at a given PAR), light intensity (photosynthetic photon flux density [PPFD]), and environmental drivers (climate [mean annual temperature and water availability], water chemistry [electrical conductivity, nitrate and phosphate concentration in water], elevation of the spring, and shadiness). All these above-mentioned predictors were included as fixed effects, while species was included as the random factor. We additionally included the first order interaction between mean photosynthesis per species, sample-specific photosynthesis and PPFD to further investigate the effect of these variables on BVOC emission. All response variables were log-transformed to achieve normality and homoscedasticity in model residuals. Water nitrate and phosphate concentration, and PPFD were also log-transformed due to the saturating nature of the relationship with BVOC emission. We used the *visreg* R package to plot effects plots and partial residuals plots to visualise model results.

3. Results

3.1. BVOC emission and absorption rates across bryophyte species

The emission rates of the different monitored BVOCs emitted by the screened species was highly variable among BVOC types and bryophyte species. Table 1 shows all of the BVOC emissions at 1000 μmol m^{-2} s^{-1} of PAR and 30 °C temperature. Despite the high variability among BVOCs emitted by the different species, a pattern of high and low emitters was found. To proceed with an accurate grouping between the species type, the BVOC type and BVOC magnitude, a principal components analysis was performed with the average blend of BVOC emission per bryophyte species. Two main groups of species emerged automatically allocated from the cluster analysis. Based on the magnitudes of the BVOC emissions by each group we classified them as a high emitter group (blue in Fig. 1) and a low emitter one (orange in Fig. 1).

As an example of the magnitude of BVOC emission and BVOCs blends, the liverwort *Conocephalum conicum* showed high emission of monoterpenes (27.9 ± 9.29 μg g^{-1} h^{-1}, mean ± standard error of the mean), and toluene (1.03 ± 0.19 μg g^{-1} h^{-1}), as well as considerable emissions of isoprene (3.71 ± 1.25 μg g^{-1} h^{-1}), acetone (3.39 ± 0.86 μg g^{-1} h^{-1}), MVK (0.55 ± 0.15 μg g^{-1} h^{-1}), MEK (0.39 ± 0.14 μg g^{-1} h^{-1}), benzene (0.24 ± 0.04 μg g^{-1} h^{-1}), and C_8 aromatics (0.58 ± 0.1 μg g^{-1} h^{-1}). At the same time, the moss *Oxyrrhynchium speciosum,* also classified as a high emitter, showed a different blend with highest emissions of isoprene (22.75 ± 15.16 μg g^{-1} h^{-1}), MVK (0.96 ± 0.3 μg g^{-1} h^{-1}), and C_8 aromatics (0.82 ± 0.38 μg g^{-1} h^{-1}), as well as high emissions of acetonitrile, acetaldehyde (1.33 ± 1.21 μg g^{-1} h^{-1}), acetone (3.78 ± 1.14 μg g^{-1} h^{-1}), MEK (0.47 ± 0.15 μg g^{-1} h^{-1}) and benzene (0.28 ± 0.19 μg g^{-1} h^{-1}).

Brachythecium rivulare, another species identified as high emitting, was the highest emitter of MEK and benzene. This species also presented high toluene emission, but low emissions for all other compounds. Additionally, *Apopellia endiviifolia* had high emissions of acetone, MEK and MVK + MACR, as well as high emissions of aromatics compounds (Table 1, Fig. 2).

Methanol uptake was the highest for *Philonotis marchica,* with an uptake of −28.83 μg g^{-1} h^{-1}, followed by *Palustriella commutata* and *Riccardia chamedryfolia* (−16.67 μg g^{-1} h^{-1}). All species showed methanol uptake except for *Philonotis fontana* and *Fontinalis antipyretica* which showed emission rather than uptake. Acetaldehyde showed a higher variability between species on uptake and emission. The highest uptake was shown by *P. commutata* (−1.38 ± 0.29 μg g^{-1} h^{-1}), and a high BVOC emitting species such as *C. conicum*, where some specimens showed acetaldehyde uptake (−0.17 ± 0.41 μg g^{-1} h^{-1}). Uptake of acetonitrile was highest by *Lophocolea bidentata* − 0.07 ± 0.04 μg g^{-1} h^{-1}, which interestingly also showed highest uptake of C8 aromatics (−0.15 ± 0.12 μg g^{-1} h^{-1}) and high uptake levels of methanol (−10.45 ± 5.64 μg g^{-1} h^{-1}) and acetaldehyde (−0.8 ± 0.68 μg g^{-1} h^{-1}). It is also important to note that *L. bidentata* had one of the highest monoterpene emissions, 4.67 ± 0.17 μg g^{-1} h^{-1} (Table 1, Fig. 2).

3.2. Drivers of bryophyte BVOC emissions

Total monoterpene emissions were the only compounds potentially presenting a significant phylogenetic signal (lambda ~1, *p*-value = 0.072, after Bonferroni correction for 14 tests). None of the other bryophyte BVOC emission categories presented significant phylogenetic signals, and neither did the other three main axes extracted through PCA (lambda ~0, *p*-value >0.05 for all BVOC compounds and PCA axes). Hence, for consistency, we used non-phylogenetically informed mixed linear models to investigate the species-specific differences and environmental drivers (climate, altitude, shade and water chemistry) of bryophyte BVOC emission.

The clustered image map shown in Fig. 3 separated the BVOCs into two main groups based on the similarity of their environmental drivers. The first one contained methanol, isoprene, monoterpenes, acetone, acetonitrile and MVK + MACR, and the second group contained acetaldehyde, benzene, toluene, MEK, and C_8 aromatics. This separation could be due to the lower standardised model coefficients observed for the latter group observed in Fig. 3. This could indicate the drivers observed do not have a strong impact on the bryophyte emissions of the latter group of compounds. In general, the main driver of the BVOC emissions by these species was the inter and intra-species variability; but additionally, the photosynthetic rates (Fig. 4) and the light availability (Fig. 5) increased the emissions of mainly the first group of compounds.

The emission of the first group of compounds showed a positive interaction between mean photosynthesis per species and the photosynthesis of the analysed samples at a given light intensity ($A_{sp} \times \Delta A$). Hence, species with higher photosynthetic capacity tended to emit larger quantities of these compounds with increasing photosynthesis. The deviation of photosynthesis from the species average (ΔA) showed that out of the more productive bryophyte species (Fig. 4), those that photosynthesize above the average emitted more isoprene, monoterpenes and acetone. In contrast, the less productive species, calculated as deviation from the average photosynthesis rate, decreased their emissions in such volatiles. Interestingly, the most important driver for methanol emission was the variability among species (conditional R^2 [fixed + random variability] – marginal R^2 [fixed effects]: R^2_c - R^2_m = 0.15 % of the variance explained, see SI model summary methanol). Furthermore, there was a higher uptake of methanol when higher photosynthetic rates were present, but mostly in species that have low productivity on average.

Similarly, the emission of the first group of BVOCs selected by the cluster map also increased with increasing PPFD. For instance, for isoprene, the more productive species (i.e. those presenting higher assimilation rates) produced more isoprene as PAR increased (Fig. 5). The less productive species followed the same pattern but at significantly lower rates. This relationship was also valid for acetone, as the response of more productive and less productive species was equal at low PAR levels, but at higher PAR levels, more productive species emitted more acetone. However, for MVK + MACR the relationship was opposite with less productive species emitting more MVK + MACR at higher light levels as compared to the more productive species. In the case of monoterpenes, there was very little variability, and most of it was explained by the differences between species. In any case, except for low PAR levels, there seemed to be a continuous emission independent of PAR, indicating the possibility of a storage release type of monoterpenes.

Mean annual temperature of the springs where the bryophytes were collected showed an influence on BVOC emissions (Fig. 6). Higher emission rates were found for those species acclimated to higher temperatures, even though these temperatures were consistently lower compared to the controlled conditions of 30 °C during this study. Nevertheless, 6–16 °C is the annual mean temperature, so, especially during summer, and with increasing global temperatures, many of these springs can experience temperatures of 30 °C and above. In fact, for methanol, higher uptake was observed from those species acclimated to higher temperatures as well. On the contrary, the nitrate levels at the springs where the bryophytes were collected showed a negative influence on BVOC emissions, with a small decrease in emissions when higher nitrate concentrations were present in the ecosystem (Fig. 7).

The drivers of BVOC emission were grouped in three main blocks based on the results from the clustered image map (Fig. 3): the first one consisted of PPFD, $\Delta A \times$ PPFD and $A_{sp} \times$ AA; the second one included elevation, mean annual temperature, A_{sp}, whether the spring was under shade or not, $A_{sp} \times$ PPFD, and nitrate and phosphate concentration in spring water; the third group of predictors included water availability, water conductivity and ΔA. While the first and third groups of variables were important predictors of BVOC emission, especially for the first group of compounds defined above, the second group of predictors generally presented low correlations with BVOC emission (see Fig. 3).

Table 1
BVOC average emission rates at 1000 μmol m^{-2} s^{-1} of PAR and 30 °C for the different bryophyte species screened. LW stands for liverwort and N# stands for replicates.

Species name	Division	N#	Methanol	Acetonitrile	Acetaldehyde	Acetone	Isoprene	MVK + MACR	MEK	Benzene	Toluene	C_8 aromatics	Total monoterpenes
			μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}	μg g^{-1} h^{-1}
Eucladium verticillatum	Moss	3	−5.36 ± 1.63	0.04 ± 0.03	−0.41 ± 0.15	0.63 ± 0.17	2.48 ± 2.12	0.41 ± 0.25	0.3 ± 0.17	0 ± 0.03	0.19 ± 0.1	0.11 ± 0.12	0.23 ± 0.16
Conocephalum conicum	LW	9	−3.27 ± 2.62	0.04 ± 0.04	−0.17 ± 0.41	3.39 ± 0.86	3.71 ± 1.25	0.55 ± 0.15	0.39 ± 0.14	0.24 ± 0.04	1.03 ± 0.19	0.58 ± 0.1	27.9 ± 9.29
Chiloscyphus polyanthos	LW	2	−5.94 ± 0.38	−0.03 ± 0.03	−0.34 ± 0.31	1.68 ± 1.36	1.53 ± 1.25	0.5 ± 0.38	0.19 ± 0	−0.06 ± 0.03	0.21 ± 0.2	0.21 ± 0.01	0.27 ± 0.15
Oxyrrhynchium speciosum	Moss	9	−1.76 ± 8.7	0.12 ± 0.09	1.33 ± 1.21	3.78 ± 1.14	22.75 ± 15.16	0.96 ± 0.39	0.47 ± 0.15	0.28 ± 0.19	0.09 ± 0.12	0.82 ± 0.38	0.85 ± 0.37
Apopellia endiviifolia	LW	14	−5.74 ± 3.55	0.01 ± 0.02	0.51 ± 0.86	3.9 ± 0.65	2.66 ± 0.66	0.75 ± 0.25	0.65 ± 0.24	0.14 ± 0.07	0.25 ± 0.17	0.37 ± 0.18	0.79 ± 0.26
Philonotis marchica	Moss	1	−28.83	1.09	3.10	9.91	4.49	0.62	0.26	−0.02	−0.02	0.34	1.17
Scapania undulata	LW	1	−0.23	0.00	2.59	1.77	0.11	0.21	0.15	0.03	0.05	0.04	0.19
Didymodon tophaceus	Moss	6	−13.04 ± 2.13	0.02 ± 0.04	0.37 ± 0.54	1.84 ± 0.73	1.44 ± 0.95	0.52 ± 0.45	0.6 ± 0.36	0.25 ± 0.24	0.8 ± 0.54	0.3 ± 0.15	0.56 ± 0.31
Brachythecium rivulare	Moss	8	−2.44 ± 1.07	−0.02 ± 0.01	0.08 ± 0.41	0.73 ± 0.17	0.62 ± 0.29	0.14 ± 0.11	0.75 ± 0.71	0.35 ± 0.33	0.63 ± 0.52	0.12 ± 0.13	0.19 ± 0.18
Plagiochila porelloides	LW	2	−5.11 ± 0.63	−0.04 ± 0.02	−1.22 ± 0.3	0.33 ± 0.03	0.26 ± 0.13	0.09 ± 0.07	0.05 ± 0.05	0.03 ± 0.03	0.08 ± 0.01	0.1 ± 0.02	0.2 ± 0.1
Lunularia cruciata	LW	4	−5.22 ± 2.94	0.03 ± 0.02	1.29 ± 1.07	0.75 ± 0.2	2.47 ± 1.55	0.31 ± 0.17	0.15 ± 0.01	0.08 ± 0.02	0.12 ± 0.02	0.2 ± 0.03	1.39 ± 0.35
Marchantia polymorpha	LW	2	−5.26 ± 0.81	−0.01 ± 0	0.05 ± 0.49	0.36 ± 0.02	0.03 ± 0.03	−0.09 ± 0.01	0 ± 0.01	0 ± 0	0.02 ± 0.01	0.04 ± 0	1.69 ± 0.11
Palustriella commutata	Moss	5	−20.37 ± 3.85	−0.03 ± 0.01	−1.38 ± 0.29	1.65 ± 0.38	2.83 ± 2.01	0.18 ± 0.17	0.3 ± 0.13	0.1 ± 0.08	0.62 ± 0.47	0.41 ± 0.17	0.71 ± 0.41
Cratoneuron filicinum	Moss	5	−2.84 ± 3.72	−0.03 ± 0.01	−0.71 ± 0.2	0.44 ± 0.13	0.59 ± 0.55	−0.06 ± 0.06	0 ± 0.02	0.01 ± 0.02	0.03 ± 0.04	0.07 ± 0.07	0.39 ± 0.33
Lophocolea bidentata	LW	2	−10.45 ± 5.64	−0.07 ± 0.04	−0.8 ± 0.68	0.62 ± 0.38	0.57 ± 0.21	0.16 ± 0.18	0.16 ± 0.16	0 ± 0.01	0.03 ± 0	−0.15 ± 0.12	4.67 ± 0.17
Philonotis fontana	Moss	1	1.99	−0.01	−0.06	2.23	0.57	0.02	0.06	−0.03	0.04	0.03	0.09
Riccardia chamedryfolia	LW	1	−16.67	−0.01	−0.43	0.44	−0.12	0.08	−0.02	0.00	0.02	−0.01	0.10
Fontinalis antipyretica	Moss	2	0.92 ± 0.85	−0.02 ± 0.02	−0.13 ± 0.45	0.57 ± 0.24	−0.01 ± 0.34	0.04 ± 0.08	0.03 ± 0.04	0.05 ± 0.02	0.05 ± 0.02	−0.01 ± 0.07	0.11 ± 0.01
Bryum pseudotriquetrum	Moss	4	−3.94 ± 1.47	−0.02 ± 0.01	−0.39 ± 0.47	1.49 ± 0.36	1.02 ± 1.12	0.29 ± 0.24	0.37 ± 0.35	0.01 ± 0.05	0.04 ± 0.04	0.7 ± 0.72	0.08 ± 0.1
Rhynchostegium riparioides	Moss	6	−5.54 ± 1.44	−0.01 ± 0.01	−0.19 ± 0.25	0.45 ± 0.2	0.64 ± 0.61	0.04 ± 0.06	0.04 ± 0.03	0.01 ± 0.01	0.16 ± 0.13	0.04 ± 0.06	0.11 ± 0.07
Plagiomnium undulatum	Moss	10	−13.66 ± 3.82	−0.03 ± 0.01	−0.71 ± 0.3	1.67 ± 0.89	0.61 ± 0.35	0.15 ± 0.1	0.15 ± 0.09	0.04 ± 0.04	0.12 ± 0.08	0.21 ± 0.12	0.95 ± 0.72
Fissidens taxifolius	Moss	2	−7.04 ± 1.37	−0.04 ± 0.01	−0.05 ± 0.08	0.64 ± 0.15	0.54 ± 0.48	0.06 ± 0.02	0.03 ± 0.05	−0.03 ± 0.03	0 ± 0.01	0.03 ± 0.1	0.15 ± 0.02
Porella platyphylla	LW	2	−3.37 ± 0.85	−0.02 ± 0	−0.26 ± 0.04	0.11 ± 0.06	−0.05 ± 0	−0.03 ± 0	−0.03 ± 0.01	−0.01 ± 0	0 ± 0.01	−0.05 ± 0.02	0.88 ± 0.09
Thamnobryum alopecurum	Moss	6	−5.74 ± 1.81	−0.04 ± 0.01	−0.88 ± 0.33	0.67 ± 0.22	0.55 ± 0.27	0.11 ± 0.05	0.04 ± 0.03	−0.02 ± 0.03	0.03 ± 0.04	0.14 ± 0.07	0.21 ± 0.09
Fissidens grandifrons	Moss	2	−3.17 ± 1.15	0.01 ± 0	0.29 ± 0.28	1.6 ± 1.82	1.46 ± 1.05	0.25 ± 0.08	0.2 ± 0.07	0.16 ± 0.16	0.21 ± 0.2	0.15 ± 0.16	0.13 ± 0.07
Plagiomnium rostratum	Moss	1	−12.09	0.01	0.74	0.90	0.44	0.14	0.05	0.01	0.03	0.04	0.47

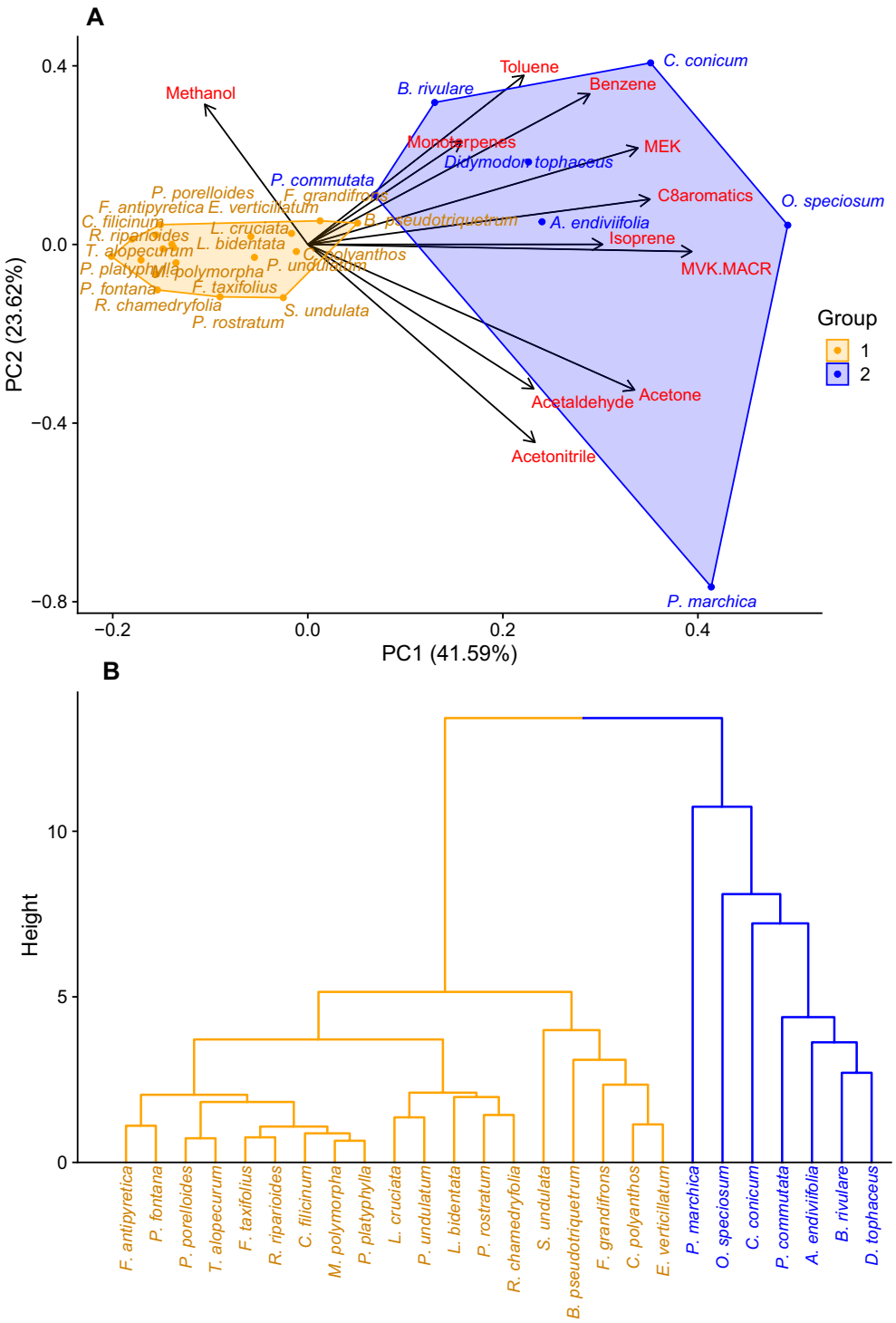

Fig. 1. Panel A shows the results of a principal components analysis performed with the average blend of BVOCs emission per bryophyte species at 1000 μmol m^{-2} s^{-1} of photosynthetically active radiation and 30 °C temperature. The two groups of species emerging from the cluster analysis (panel B) are highlighted in orange and blue.

Nonetheless, bryophytes in springs located at higher elevation presented higher isoprene emissions compared to those at lower elevations, but lower benzene and acetonitrile emissions (Fig. 3).

The second group of compounds identified by the cluster image map generally presented very weak correlations with all of the studied drivers of BVOC emission, thus suggesting that the emission of these compounds by the screened bryophytes is less affected by the monitored drivers than the emissions of the first group of compounds. Nevertheless, this second group of BVOCs decreases their emissions with higher elevation, nitrate (Fig. 7) and phosphate levels, but show higher emissions with higher climatic temperature, such as MEK and C8 aromatics having higher emissions from bryophytes inhabiting springs at warmer temperatures (Fig. 6) and higher water availability (for benzene and C8 aromatics).

4. Discussion

In general, liverworts, and particularly thalloid liverworts, seemed to

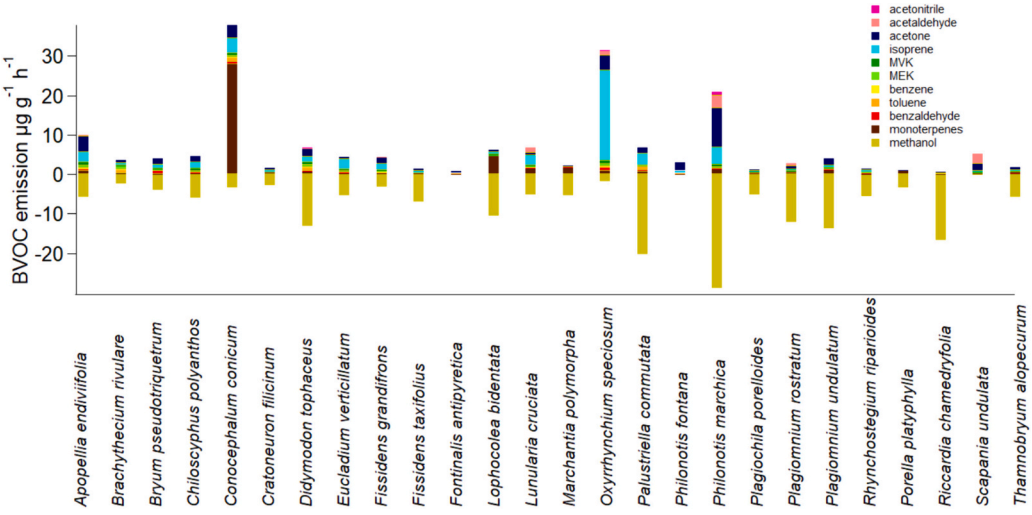

Fig. 2. BVOC emission by the different bryophyte species screened at 1000 µmol m^{-2} s^{-1} of photosynthetically active radiation and 30 °C temperature.

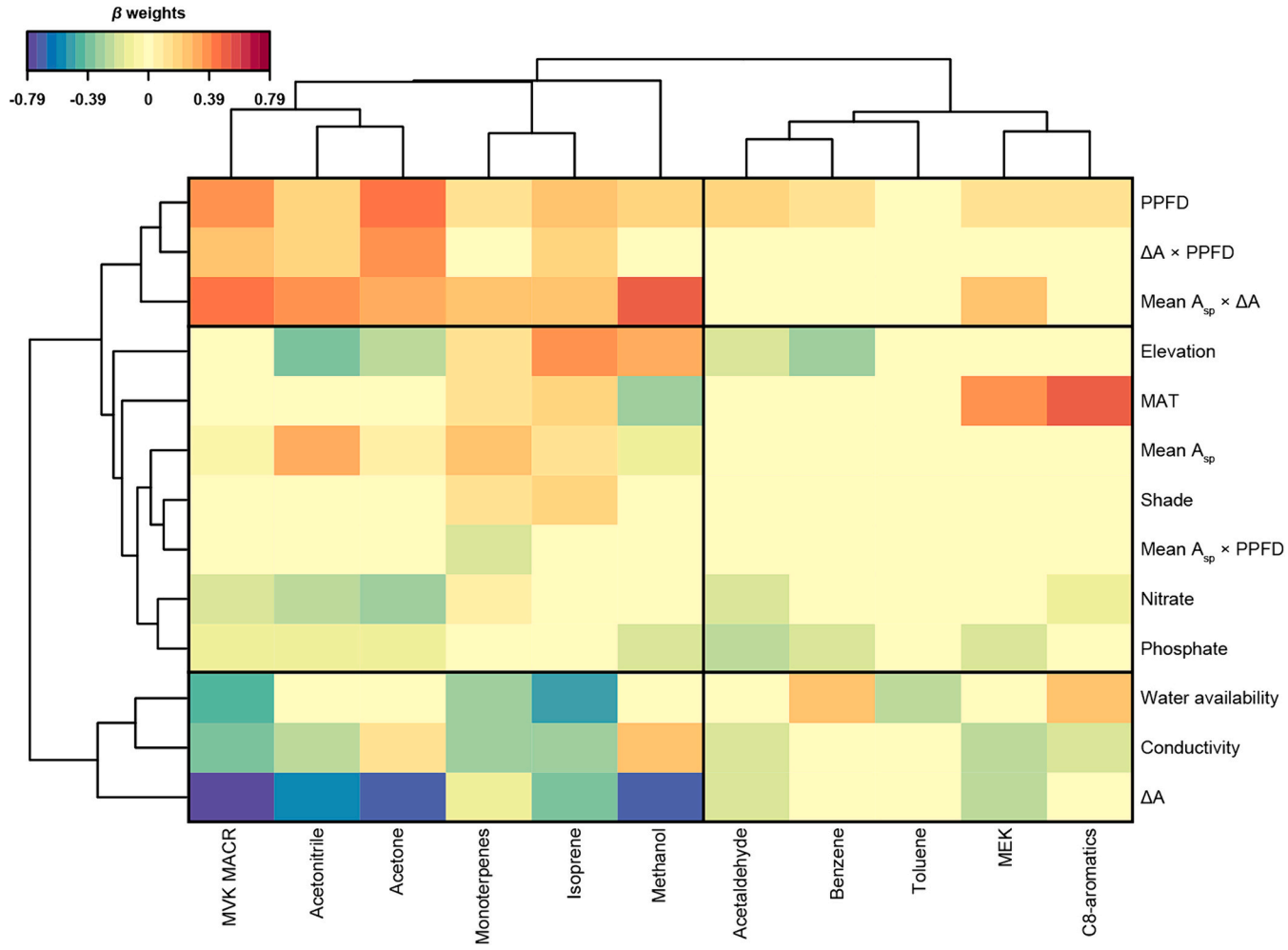

Fig. 3. Clustered image map showing the relationship between different BVOC compounds (bottom) and all predictor variables included in our models. Beta weights indicate standardised model coefficients. *Acronyms:* A_{sp} indicates the average photosynthesis per species; ΔA indicates the difference between the average photosynthesis per species and the photosynthesis recorded for a given sample at a particular light intensity; PPFD stands for photosynthetic photon flush density; MAT stands for mean annual temperature.

present the largest emissions of monoterpenes (*C. conicum, Lunularia cruciata, Marchantia polymorpha*). This is consistent with the fact that thalloid liverworts have oil vacuoles, unique organelles where BVOC accumulate (Ludwiczuk and Asakawa, 2020), that may respond to environmental changes to emit monoterpenes. Thus, monoterpene emissions from liverworts are expected to be originated in storage

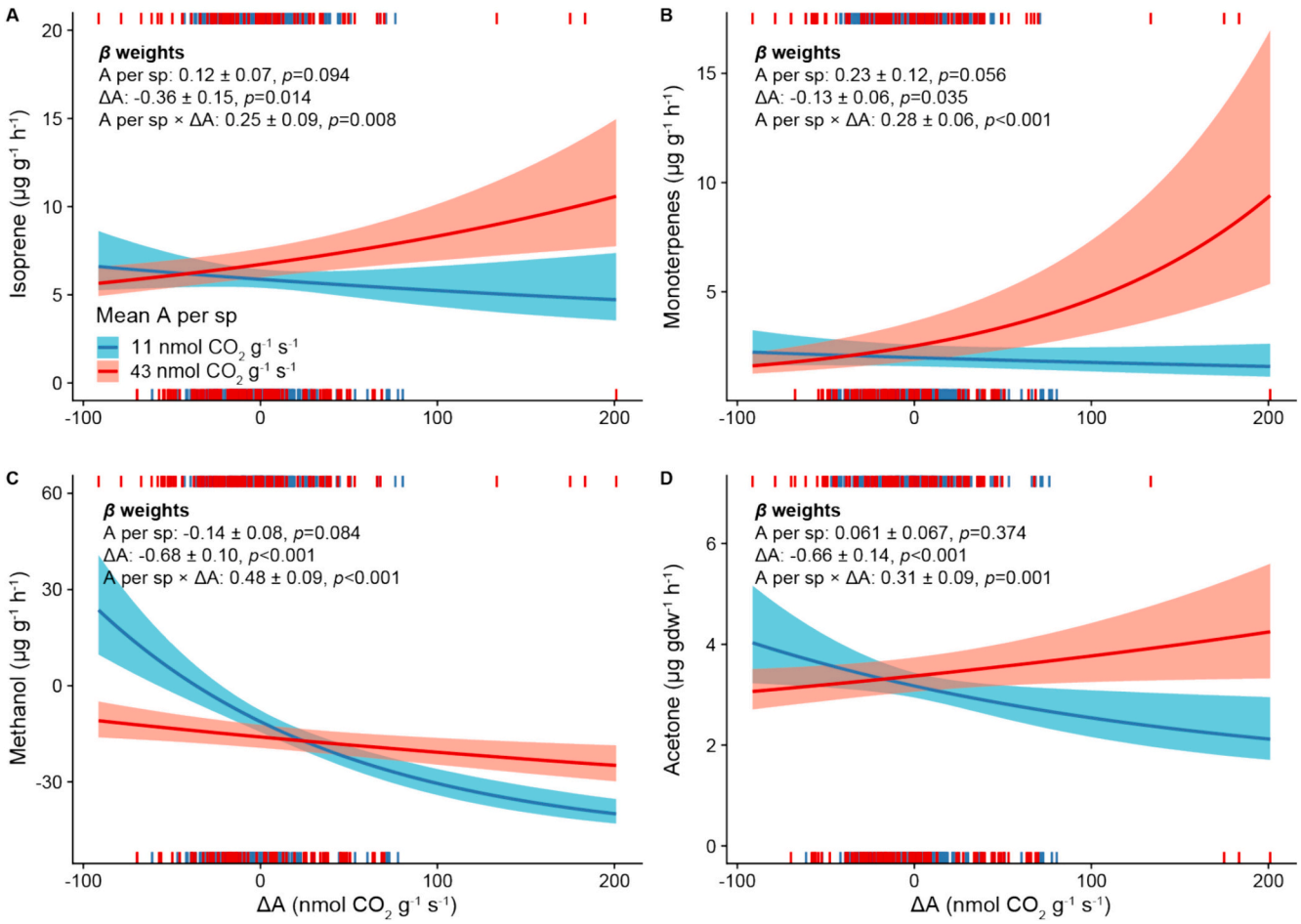

Fig. 4. Effect plots showing the relationship between different BVOC compounds (y-axes) and the difference between the average photosynthesis per species and the photosynthesis recorded for a given sample at a particular light intensity (ΔA, x-axis) as a function of the average photosynthesis of the species (high and low photosynthesis in red and blue, respectively). Beta weights indicate standardised model coefficients.

compounds. Further, when collecting these species, small fractures in their thalli occurred, for which we cannot discard the possibility that some of these emissions are the result of broken tissues. Nevertheless, *C. conicum* has been reported to strongly emit a variety of BVOCs (Ludwiczuk et al., 2013) and the usual proxy for plant mechanical damage, hexenol, was not detected to increase concomitantly (data not shown). That demonstrates that the changes in BVOCs emissions were actual biological responses not driven by tissue fractures in these thalloid liverworts.

Most of these monoterpene emissions from bryophytes are commonly thought to come from the volatilization from oil bodies (Ludwiczuk and Asakawa, 2020). In contrast, leafy liverworts (except for L. *bidentata*), and mosses presented low monoterpene emissions. Mosses have usually been thought not to be important for BVOC emission due to the lack of such oil bodies (Nozaki et al., 2007). This is most likely due to the targeting of monoterpenes with respect to other compounds, which, as shown in this study, mosses may not emit in great amounts. However mosses have been shown to also emit isoprenoids (Saritas et al., 2001; Ludwiczuk and Asakawa, 2020). For instance, in this study, *O. speciosum*, was shown to be the bryophyte with the highest isoprene emissions, even though it had negligible emissions of monoterpenes. This isoprene emission is remarkably high and at the level of other vascular 'high emitter' tropical plant species (Mu et al., 2022). Thus, our results indicate that mosses can be as important as liverworts and some vascular plants in the emission of BVOCs. Our results also indicate the multiple origins of BVOC emissions from bryophytes, not only from storage compounds, but also from recently photosynthesized carbon, as is visible for isoprene emissions (Langford et al., 2023).

Our results also indicate that, in fact, isoprene emission was very widely present across species, with only a few species that did not show isoprene emission. Isoprene has been shown to increase plant thermotolerance, so thermal and correlated desiccation stress experienced by early land plants could have provided the selective pressure for the evolution of light-dependent isoprene emission (Hanson et al., 1999) as an early adaptive trait for plants colonising terrestrial ecosystems, where isoprene emission had a relatively strong phylogenetic signal (Fernández-Martínez et al., 2018). However, given that as not all bryophytes are isoprene emitters (Ryde et al., 2022), this trait may have been lost, probably because as bryophytes radiated into different habitats, the isoprene emission capacity was lost multiple times in favour of other thermal protective mechanisms in bryophyte species (Hanson et al., 1999; Fernández-Martínez et al., 2018). The general lack of phylogenetic relatedness in terms of BVOC emission found in our study further suggests that the local environment of these species may have played a very important role in the microevolution (evolutionary change within a species, especially over a short period) of their emission traits as also suggested by others (Roberts et al., 2012; Langford et al., 2023). In any case, more research is needed to shed light not only on the evolution of isoprene, but also for other BVOCs.

Most of the studied species are semi-aquatic and live around the edges of springs, receiving drops of water but not being fully submerged. However, two of the study species typically live underwater, these being *F. antipyretica*, which mostly lives in low-speed streams, and *Rhynchostegium riparioides,* which typically lives in turbulent waters. These two

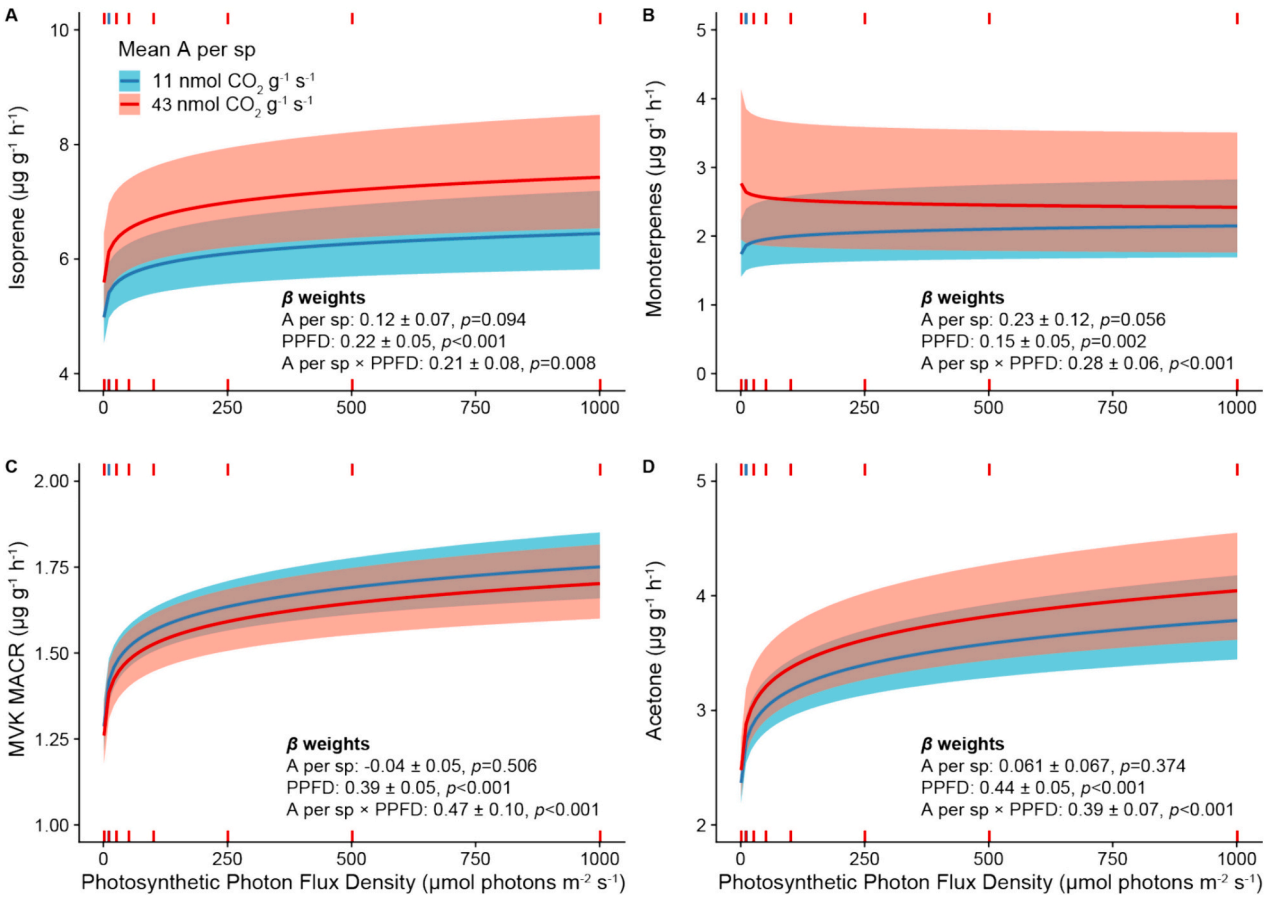

Fig. 5. Effect plots showing the relationship between different BVOC compounds (y-axes) and photosynthetic photon flux density (PPFD, x-axis) as a function of the average photosynthesis of the species (high and low photosynthesis in red and blue, respectively). Beta weights indicate standardised model coefficients.

species are the ones presenting the lowest rates of emission of BVOCs, and among those with the lowest uptake rates of methanol as well. Producing BVOCs is costly in terms of the carbon balance of the plant, for which these species may have evolved in a way to avoid BVOCs emission as much as possible as they would have little use underwater, i.e. isoprene thermo-tolerance protection is no longer needed in aquatic environments (Vickers et al., 2009), so these species may have lost this trait with time.

Temperature is a key driver for BVOC emissions by vegetation. On the one side, higher temperatures can stimulates metabolic activity, including photosynthesis, leading to higher plant BVOC emissions originated from recently photosynthesized carbon (Fasbender et al., 2018). It also increases the volatile release from storage compartments in plants, such as oil bodies (Kesselmeier and Staudt, 1999). On the other side, high temperatures can cause stress, and volatile release can be a mechanism to cope with such stress by reducing the levels of damaging ROS within the leaf and thus increasing thermo-tolerance (Loreto and Velikova, 2001; Affek and Yakir, 2002; Loreto and Fares, 2007; Sharkey et al., 2008; Yáñez-Serrano et al., 2019), although this comes at a very high carbon and energetic cost (Harvey et al., 2015) and depending on the severity of the temperature stress, it can lead to irreversible damage to plants (Yáñez-Serrano et al., 2019). In addition, volatiles such as isoprene may contribute to the stabilization of cell membranes and integrated membrane proteins (Singsaas et al., 1997; Sharkey and Yeh, 2001; Peñuelas and Munné-Bosch, 2005; Behnke et al., 2007; Velikova et al., 2011), although it has been shown more recently that the isoprene content in thylakoid membranes may be too low to affect the membrane dynamics (Harvey et al., 2015). In this study, we found higher BVOC emission rates for those bryophytes living in springs with higher mean annual temperatures as compared to those inhabiting environments with lower annual temperatures, probably as an acclimation mechanism to cope with heat and desiccation stress. In fact, it has been shown that many mosses and liverworts are able to withstand desiccation and rehydration (Proctor et al., 2007). For instance, for the liverwort *Southbya nigrella* it was showed that oil bodies remain intact during dehydration, but can change drastically in shape and consistency during rehydration (Pressel et al., 2009). During drying, some of the soluble carbohydrates in the bryophyte cell are likely converted to oil body terpenoids, and these oil bodies could act as a store of carbon (Marschall et al., 1998), thus using BVOCs as mechanisms to cope with desiccation (Chen et al., 2018). This desiccation process may be a limitation to our study, as it was a processed which could not be controlled. New experimental designs should aim to target desiccation and its role in BVOC emissions.

At the same time, higher bryophyte BVOC emissions could be related to VOC-mediated plant-plant communication which was suggested to be involved in competition between moss species (Vicherová et al., 2020), or bryophyte-ecosystem communication, such as with pollinators as a means of increasing pollination (McCuaig et al., 2015). In fact, bryophytes have been shown to emit BVOCs that are sex-specific and play a role in microarthropod-mediated bryophyte reproduction, and have a similar chemical diversity (i.e. types of BVOCs species emitted) to that found in vascular plants, (Rosenstiel et al., 2012). Another biotic role for the emissions of BVOCs by bryophytes is as a means of defence against herbivores and pathogens, in particular with isoprenoid emissions (Asakawa et al., 2013; Chen et al., 2018).

The springs where the bryophytes were located differed in terms of elevation. This could imply a difference in the radiation regime that these bryophytes experience. UV-B radiation stress has harmful effects on aquatic liverworts (Martínez-Abaigar et al., 2006), and despite the

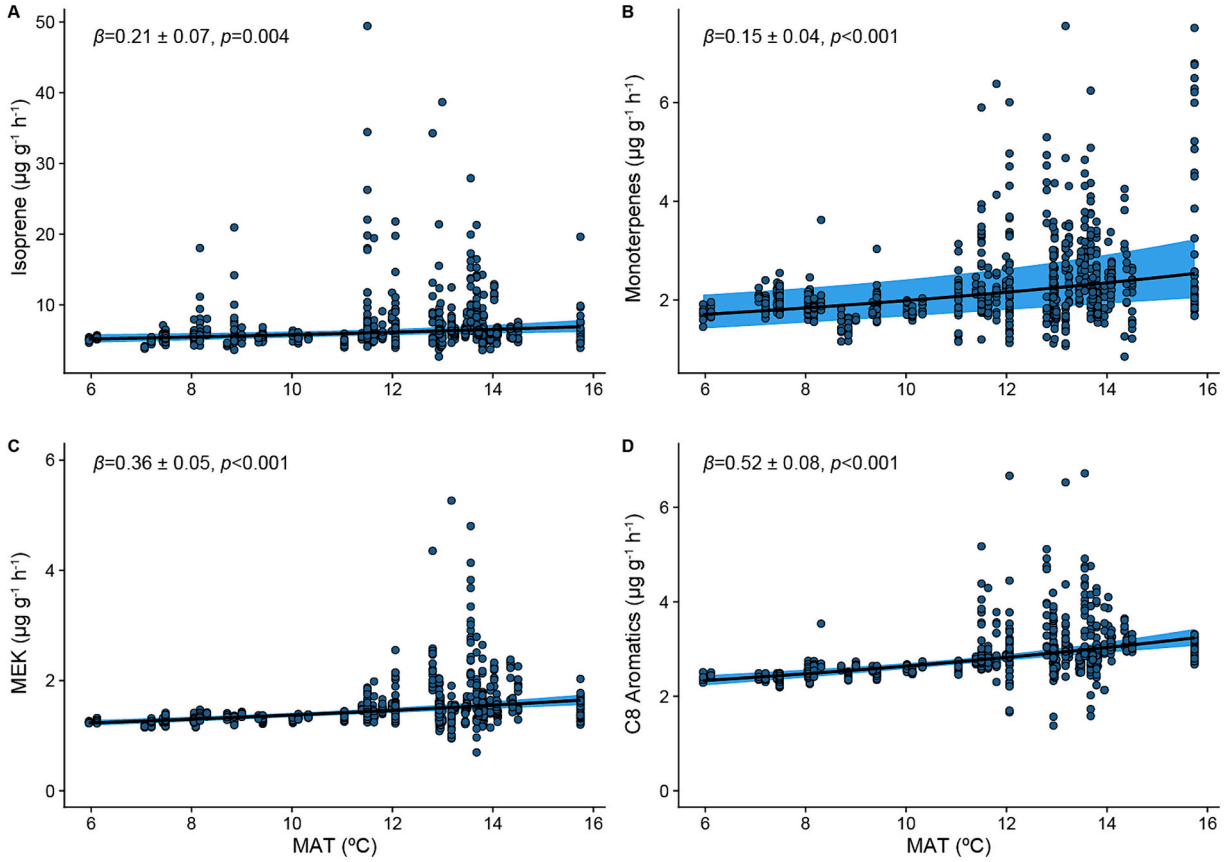

Fig. 6. Partial residuals plots showing the relationship between different BVOC compounds (y-axes) and mean annual temperature (MAT, x-axis) of the springs where they were collected. Beta weights indicate standardised model coefficients.

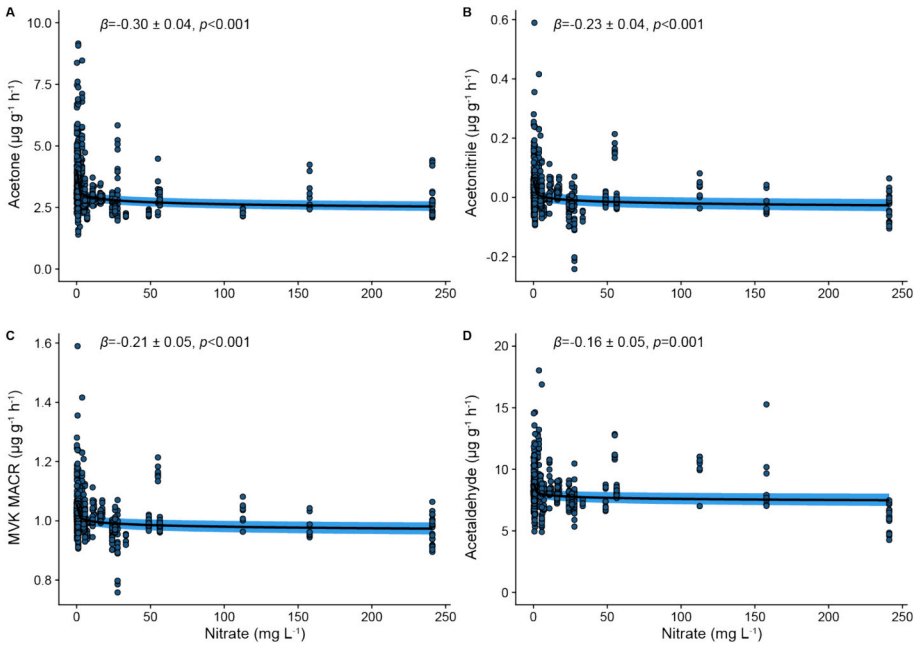

Fig. 7. Partial residuals plots showing the relationship between different BVOC compounds (y-axes) and water nitrate concentration of the springs where they were collected. Beta weights indicate standardised model coefficients.

fact that no significant overall UV-B effect was established for subarctic peatland (including bryophytes) BVOCs emissions, it was observed to affect at least toluene and 1-octene emissions by doubling and tripling their emissions respectively (Faubert et al., 2010b). In Malaysia, higher isoprenoid emissions were observed at higher elevation sites, suggesting an evolutionary constraint at the family level, although further

confirmation is needed (Koid et al., 2022). In this sense, our study supports this idea, as isoprene and monoterpene emission were positively correlated with elevation (Fig. 3). Furthermore, given the higher levels of UV radiation during early stages of terrestrialization, stored BVOCs emissions may have played a role in the UV absorption in bryophytes, particularly liverworts as they are known to produce secondary metabolites, including isoprenoids, which are stored in oil bodies, under UV-B stress (Chen et al., 2018).

Although water nutrient concentrations have been shown to have a positive influence on bryophyte nutrient concentrations (Fernández-Martínez et al., 2021), the effect of water chemistry on BVOC emissions for this study was small. This is most likely due to the fact that the most important determinant factor for BVOC emissions was the inter and intraspecific variability, possibly overshadowing the impact of other drivers. A negative role of nitrate on BVOC emissions was found and may indicate that species with higher nitrogen concentrations need to emit less BVOCs to defend themselves, or is because photosynthesis is more efficient and so they have less volatile by-products, as previously suggested for vascular plants (Fernández-Martínez et al., 2018). However, it could also be related to the fact that excess N can be toxic to bryophytes, causing damage to cell membranes and solute leakage, and subsequent reduced growth and even shoot death (Pearce et al., 2003). Bryophytes with lower photosynthetic rates could then reduce their productivity and their associated emission of BVOCs.

In this study, a very strong inter and intraspecific variability was found, being by far the dominant drivers in BVOC emissions. Ryde et al., 2022 found, similarly, species-specific VOC emissions, however, they found this emission to be connected to the genetic species relatedness, which contrasts with our results, where we found no connection between the evolutionary history of the studied bryophytes and their BVOC emissions. Lastly, it is important to acknowledge that the emissions reported here were conducted at 30 °C for modelling purposes, but the rates could not easily be related to emission rates under natural conditions. In any case, the great variability between and within species, indicates the need for further research as we cannot model bryophyte VOC emissions with one, common set of emission capacities (Ryde et al., 2022).

5. Conclusions

In this study we shed more light into the "omitted" natural VOC sources by showing the dynamics of BVOCs emissions of 26 hygrophytic bryophytes species including liverworts and mosses. A high and a low BVOC emitter group were identified. Additionally, BVOC emissions were classified as more constitutive emissions and more induced emissions, based on the influence that the ent drivers had on their emissions. We demonstrate that mosses can be as important as liverworts in terms of BVOC emissions, although the significant role of storage compound release from liverworts is demonstrated. In this study, a very strong inter and intraspecific variability was found, by being by far the dominant driver in BVOC emissions, but photosynthetic rates, PAR, temperature, and water chemistry were also important. On the contrary, we found no general connection between phylogenetic relatedness and BVOC emissions. BVOC emissions by bryophytes should be further explored so that the drivers and ecological roles of such emissions can be better described, and hence to assess the overall impact of bryophyte BVOC emissions on the ecosystem and the atmosphere.

CRediT authorship contribution statement

A.M. Yáñez-Serrano: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **J. Corbera:** Methodology, Conceptualization. **M. Portillo-Estrada:** Writing – review & editing, Resources, Conceptualization. **I.A. Janssens:** Writing – review & editing, Resources. **J. Llusià:** Writing – review & editing, Methodology. **I. Filella:** Writing – review & editing, Methodology. **J. Peñuelas:** Writing – review & editing, Supervision, Methodology, Conceptualization. **C. Preece:** Writing – review & editing, Methodology, Data curation, Conceptualization. **F. Sabater:** Writing – review & editing, Methodology, Data curation. **M. Fernández-Martínez:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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

Data availability

Data and code to perform analyses presented in this study can be openly found at Figshare: https://doi.org/10.6084/m9.figshare.24511306.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174293.

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