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Cryptogamic organisms are a substantial source and sink for volatile organic compounds in the Amazon region

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Cryptogamic organisms such as bryophytes and lichens cover most surfaces within tropical forests, yet their impact on the emission of biogenic volatile organic compounds is unknown. These compounds can strongly influence atmospheric oxidant levels as well as secondary organic aerosol concentrations, and forest canopy leaves have been considered the dominant source of these emissions. Here we present cuvette flux measurements, made in the Amazon rainforest between 2016–2018, and show that common bryophytes emit large quantities of highly reactive sesquiterpenoids and that widespread lichens strongly uptake atmospheric oxidation products. A spatial upscaling approach revealed that cryptogamic organisms emit sesquiterpenoids in quantities comparable to current canopy attributed estimates, and take up atmospheric oxidation products at rates comparable to hydroxyl radical chemistry. We conclude that cryptogamic organisms play an important and hitherto overlooked role in atmospheric chemistry above and within tropical rainforests.

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Terrestrial vegetation emits between 700 and 1000 TgC per year of biogenic volatile organic compounds (BVOCs), with tropical forests accounting for roughly 70% of these emissions[1,2]. The Amazon basin hosts around 40% of the world's tropical forests, 10–20% of global biodiversity, and nearly 30% of all carbon in biomass from the world's forests[3]. Therefore, it is an important component of global water, energy, nutrient, and carbon cycles[4]. The isoprenoids, i.e., isoprene, monoterpenes and sesquiterpenes, are known to make up a large fraction of emitted BVOCs. These compounds serve the plants as antioxidants against stress-induced reactive oxygen species, temperature stress, and for communication[5]. Most BVOC emissions to the atmosphere are thought to occur as direct result of photosynthesis, primarily from the leaves of the forest canopy. BVOCs are highly reactive towards the atmosphere's primary oxidants hydroxyl radicals and ozone, so that BVOC lifetimes range typically from minutes to hours. Through these reactions, BVOCs can influence local ozone levels and produce secondary organic aerosol (SOA) particles which, in turn, affect cloud formation and climate[6]. The amount of BVOCs emitted also impacts the regional atmospheric oxidation capacity and therewith the lifetimes of globally relevant greenhouse gases (e.g., CH_4) and pollutants (CO)[7,8].

Bryophytes (i.e., mosses and liverworts) and lichens cover many terrestrial surfaces including plants, soils and rocks, and are known collectively as cryptogamic covers. In tropical forests, they grow on stems, branches and leaves[9], with coverage on stems and branches often reaching 100%[10] (see Fig. 1 and Supplementary Video 1), and with a large variety in species[9]. The physiological activity of cryptogams depends heavily on water availability, as they do not actively regulate their water status, but passively follow water conditions of their environment[9]. Cryptogams play an important role for forest microclimate[11], nutrient cycling[10] and the overall fitness of the host plant and surrounding vegetation[9,12]. They are known to emit N_2O[13], NO and HONO[14], and they exchange methane with the atmosphere due to symbiosis with methanotrophs and methanogens[15–17]. Cryptogams are estimated to fix 3.9 Pg of carbon per year, which corresponds to 7% of the net primary production of terrestrial vegetation[10]. Moreover, they take up around 49 Tg nitrogen per year which accounts for nearly half of the biological nitrogen fixation on land[10].

As cryptogams cover large areas of terrestrial surfaces they might play an important role for BVOC fluxes at ecosystem or global scale. Despite this potential importance, little is known about their BVOC emissions. Bryophyte and lichen BVOC exchange studies are limited to few boreal and mid-latitude species, which generally released relatively low levels of BVOCs compared to local vascular plants. For example, a subarctic moss was found to emit a total of 207 ng g_{dry}^{-1} h^{-1} BVOCs, comprised of isoprene, monoterpenes and some aromatic compounds, with these emissions being partly attributed to microbial activity[18,19]. A mid-latitude moss was found to emit around 13.2 ng g_{dry}^{-1} h^{-1} of acetaldehyde and low levels of monoterpenes and green leaf volatiles[20]. A recent study found evidence for bryophytes using volatile compound emissions as a means of communication[21]. Lichens have been shown to emit dimethyl sulfide, hydrogen sulfide[22] and low levels of monoterpenes and green leaf volatiles[20]; and to take up carbonyl sulfide[23], sulfur dioxide[24], and C_1-C_2 organic acids[25]. In several studies, gas uptake was found to be dependent on the ambient concentrations of the respective compounds[22,25] and on water content of the bryophytes/lichens[22,23].

Current atmospheric models consider tree canopies, grasses and crops as sources of BVOC emissions, disregarding potential contributions of bryophytes and lichens[1,2]. In models, the BVOC emissions are parameterized as a function of light, temperature, vegetation type and leaf area, with the underlying assumption that the emissions are predominately produced by the large vascular plants as a byproduct of photosynthesis. In this study, the atmospheric exchange of BVOCs between tropical bryophytes/lichens and the atmosphere is investigated, as well as their dependence on environmental parameters included in models. To ensure that the flux measurement results could be upscaled to larger areas, common, abundant and widespread species were selected. Samples consisting of a mix of bryophytes dominated by *Symbiezidium transversale* (Sw.) Trevis. were collected (see Supplementary Table 1), while lichen samples primarily contained species of the *Ramalinaceae* and *Graphidaceae* family (see Supplementary Table 2). The investigated taxa were common at the research site and are representative for the bryophytes and lichens throughout the Amazon rainforest (see methods for a detailed discussion on upscaling). Environmental conditions such as air chemical composition, light, humidity and temperature were kept close to natural by performing the experiments in the forest using sample and control cuvettes flushed with ambient rainforest air, so that both emission and uptake rates for a suite of BVOC could be determined (see methods). The extent of bryophyte and lichen coverage in the Amazon rainforest was determined using literature values and field observations at different sites of the Amazon rainforest to allow upscaling of emissions and uptake rates. The implications of bryophyte and lichen emissions for tropical/global BVOC budgets and atmospheric chemistry were assessed.

Fig. 1 Bryophytes and lichens on tree stems in the Amazon rainforest. The photo on the right hand side shows lichens on a tree stem while the other two photos display bryophytes on tree stems (pictures taken at the ATTO site).

Results

Bryophytes as strong sesquiterpenoid emitters. Over a time period of two years (November 2016 – November 2018), BVOC emissions of 10 bryophyte samples dominated by *Symbiezidium transversale* were measured. Although the samples in this study are referred to by the dominant species, tropical forest bryophytes grow in communities of intermixed species and they were sampled as such, to guarantee the representativeness of the measurements. Each sample was measured continuously for two days at a remote Amazon rainforest site[4] using proton transfer reaction mass spectrometry (PTR-MS)[26], see methods for details.

A common feature of all samples was the emission of sesquiterpenes (SQT, $C_{15}H_{24}$, m/z = 205.1951). Bryophyte SQT emissions followed a diel cycle with higher emissions during the day (Fig. 2a). SQT emissions were highly variable between different samples, ranging from around 5 to almost 400 µg m^{-2}_{tree} h^{-1}

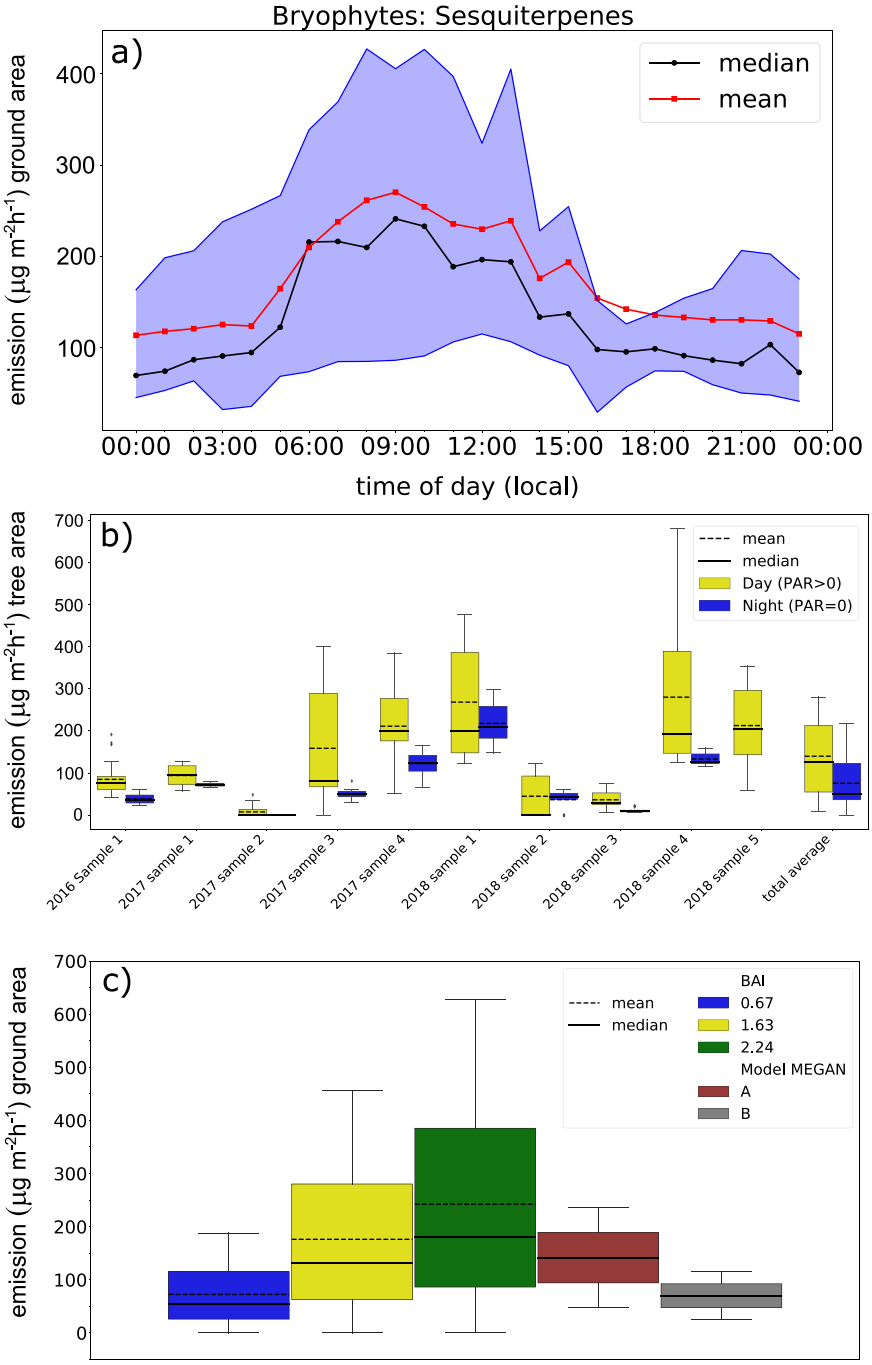

Fig. 2 Sesquiterpene (SQT) emissions from bryophytes of the Amazonian rainforest. a Diel cycle calculated from all 10 bryophyte samples. The blue shaded area extends from the 25th to 75th percentile. **b** SQT emission boxplots (per tree area) for the 10 different bryophytes samples. The range of emissions during daytime and nighttime is plotted in yellow and blue. The total average boxplots were calculated from all means of the individual samples. **c** SQT emissions of Amazon bryophytes per ground area for three different bryophyte area indexes (BAI). This is compared to SQT canopy emissions calculated with the MEGAN model (A: Acosta et al., 2014[1] and B: Bourtsoukidis et al., 2018[30]).The MEGAN boxplots were prepared by using the lower and upper limit for the emissions from the publications, therefore the mean equals the median. The boxes represent the 25th to 75th percentile, the whiskers the 5th to 95th percentile, and both the mean (dashed) and the median values (solid line) are shown.

(50–4500 ng $g_{dry}^{-1} h^{-1}$) (Fig. 2b). All samples with species identification and average emission rates per sample are listed in Supplementary Table 1 and Supplementary Data 1, respectively. Since the experiments were run under ambient conditions, the emission variability was in part the result of varying meteorology. However, high variability of SQT emissions between different samples of the same species even under controlled laboratory conditions has been reported in past studies of vascular plants[27–29].

The average (±standard deviation) daytime and nighttime emission of SQT from all samples was obtained by taking the mean of the mean emission values of the individual samples. This was done to give each sample equal weight in the total average (see Supplementary Discussion for comparison to median results). Average daytime emission amounted to 140 ± 100 μg m_{tree}^{-2} h^{-1} and the nighttime emission was 76 ± 70 μg m_{tree}^{-2} h^{-1}, yielding a total average emission of 108 ± 61 μg m_{tree}^{-2} h^{-1} (see Table 1 and Fig. 2b). This primary emission of bryophytes is related to the tree surface area.

To allow comparison of these emission fluxes with reported canopy emissions from the widely used Model of Emissions of Gases and Aerosols from Nature (MEGAN)[2], where emissions are related to the ground surface area, the results were converted to emission per ground area using Amazon rainforest stem area and leaf area to obtain a bryophyte area index (BAI). To account for uncertainty, three different bryophyte tree cover scenarios were used to calculate BAIs amounting to 0.67 $m_{tree}^2 m^{-2}$, 1.63 $m_{tree}^2 m^{-2}$, and 2.24 $m_{tree}^2 m^{-2}$ (see methods for further details). The average bryophyte SQT emissions per Amazon ground area amounted to 176 μg $m^{-2} h^{-1}$ (72-242 μg $m^{-2} h^{-1}$) (Fig. 2c). This is well within the range of Amazon canopy SQT emissions of 47 to 236 μg $m^{-2} h^{-1}$ calculated by MEGAN[1,30].

In addition to SQT emissions ($C_{15}H_{24}$), we quantified emissions of a second sesquiterpene type compound (SQT2, $C_{15}H_{22}$), of oxygenated sesquiterpenes (OSQT, $C_{15}H_{24}O$), and of diterpenes (DT, $C_{20}H_{32}$), which have rarely been observed to date[31–33]. The SQT2 emissions were largest, with a total average of 19.7 ± 11.7 μg m_{tree}^{-2} h^{-1} across all samples, which is approximately an order of magnitude lower than the SQT emissions. OSQT emissions were on average 13.2 ± 8.1 μg m_{tree}^{-2} h^{-1} (see Table 1 and Supplementary Fig. 2). As the rainforest air used for flushing the samples during the measurements contained ozone, albeit at low levels, OSQTs could be the result of a reaction of primarily emitted SQTs with ozone within the sampling setup. However, direct emission of oxygenated terpenoids has been observed previously and attributed to oxidation reactions occurring inside the plant cells[34]. We calculated the formation of OSQTs from reactions with ozone within the sampling setup and found indications that direct emissions are important to explain our observed OSQT emissions from bryophytes during the wet season (see Supplementary Discussion). DT emissions from the bryophyte samples amounted to 1 ± 1.1 μg m_{tree}^{-2} h^{-1} or 15.7 ± 18.6 ng g_{dry}^{-1} h^{-1} (Table 1) which is 3% of the average emission of a recent quantitative emission study of diterpenes, conducted on Mediterranean shrubs[31] and 2% of the average emissions of the first quantitative DT emission study on dominant coniferous trees in Japan[35]. SQT2, OSQT, and DT emissions were also normalized to ground area to allow a comparison with canopy emissions. This resulted in emissions amounting to 32.2 (13.2–44.2) μg $m^{-2} h^{-1}$ for SQT2s, 21.5 (8.8–29.5) μg $m^{-2} h^{-1}$ for OSQTs, and 1.5 (0.6–2.1) μg $m^{-2} h^{-1}$ for DTs (see Fig. 3).

The sum of SQTs, SQT2s, OSQTs and DT emissions yielded a total bryophytes sesquiterpenoid emission of 231 (95.1–318) μg $m^{-2} h^{-1}$. For comparison, the equivalent total sesquiterpenoid emission estimated by MEGAN for the Amazon canopy ranges from 47 to 236 μg $m^{-2} h^{-1}$ [1,30]. This result suggests that the sesquiterpenoid emissions of bryophytes in the Amazon rainforest are at least comparable, and potentially even larger than those of vascular plants.

Sesquiterpenoid emissions from lichens. Lichens were also found to emit SQTs, although in lower amounts than bryophytes. In Fig. 4a) the emission of SQTs from ten separate lichen sample experiments is displayed as boxplots (see as well Supplementary Data 1). Lichen samples were wetted with ultrapure water after approximately one day of measurement. This was done for all samples except 2018 sample 3 and 4. Lichens (and also bryophytes) are poikilohydric, meaning that their water status adopts passively to the surrounding conditions. Under dry conditions

Table 1 Mean fluxes of the bryophyte samples. Daytime and nighttime fluxes as well as the mean of day and night fluxes are displayed per tree area and per sample dry weight. Positive flux values are emissions and negative flux values are uptake. Fluxes are displayed for sesquiterpenoids, oxygenated volatile organic compounds (OVOCs), subgroups of OVOCs (for details of the included compounds see Supplementary Data 2) and total VOC emission, uptake and balance (emission minus uptake).

Bryophytes	μg m_{tree}^{-2} h^{-1}			ng g_{dry}^{-1} h^{-1}		
	Day mean	Night mean	Total mean	Day mean	Night mean	Total mean
Sesquiterpenes	140.1 ± 99.51	76.08 ± 69.94	108.09 ± 60.81	2249.5 ± 1793.2	1203.0 ± 1303.3	1726.2 ± 1108.4
SQT2	22.8 ± 17.02	16.68 ± 16.05	19.74 ± 11.7	354.6 ± 306.6	253.8 ± 276.8	304.2 ± 206.5
OSQT	19.29 ± 14.57	7.08 ± 6.97	13.18 ± 8.07	298.3 ± 261.1	104.6 ± 126.1	201.4 ± 145.0
DT	1.64 ± 2.03	0.25 ± 0.51	0.95 ± 1.05	26.9 ± 36.1	4.5 ± 9.0	15.7 ± 18.6
OVOCs	−30.15 ± 18.96	−16.38 ± 9.78	−23.26 ± 10.67	−436.3 ± 303.3	−234.2 ± 201.4	−335.2 ± 182.0
Alcohols	−15.18 ± 16.99	−2.88 ± 1.36	−9.03 ± 8.52	−214.9 ± 220.0	−36.3 ± 19.8	−125.6 ± 110.4
Saturated carbonyls	−9.79 ± 6.28	−4.68 ± 2.28	−7.23 ± 3.34	−145.0 ± 122.7	−63.6 ± 43.7	−104.3 ± 65.1
Unsaturated carbonyls	0.62 ± 6.5	−3.16 ± 3.22	−1.27 ± 3.63	13.6 ± 113.3	−51.2 ± 62.7	−18.8 ± 64.8
Acids	−6.05 ± 6.37	−4.0 ± 3.2	−5.02 ± 3.57	−97.6 ± 116.4	−59.8 ± 63.4	−78.7 ± 66.3
Esters/dioxygenates	1.18 ± 2.93	−0.44 ± 0.6	0.37 ± 1.49	20.0 ± 50.7	−7.4 ± 11.6	6.3 ± 26.0
Other OVOCs (e.g., ethers, furans)	2.72 ± 3.33	0.06 ± 0.21	1.39 ± 1.67	41.2 ± 52.3	0.6 ± 2.9	20.9 ± 26.2
MVK, MACR, ISOPOOH	−3.3 ± 1.8	−0.84 ± 0.5	−2.07 ± 0.94	−51.3 ± 37.4	−12.3 ± 10.2	−31.8 ± 19.4
MEK	−0.36 ± 0.79	−0.44 ± 0.52	−0.4 ± 0.48	−2.3 ± 9.6	−4.2 ± 5.5	−3.2 ± 5.5
Total VOCs emission	850.74 ± 1131.3	360.22 ± 477.69	605.48 ± 614.01	14545.4 ± 20914.7	6173.4 ± 9281.5	10359.4 ± 11440.9
Total VOCs uptake	−29.78 ± 35.11	−11.34 ± 13.77	−20.56 ± 18.86	−445.4 ± 575.6	−163.1 ± 225.2	−304.2 ± 309.0
Total VOCs balance	820.97 ± 1121.59	348.88 ± 482.37	584.92 ± 610.46	14100.1 ± 20735.2	6010.2 ± 9335.7	10055.2 ± 11370.0

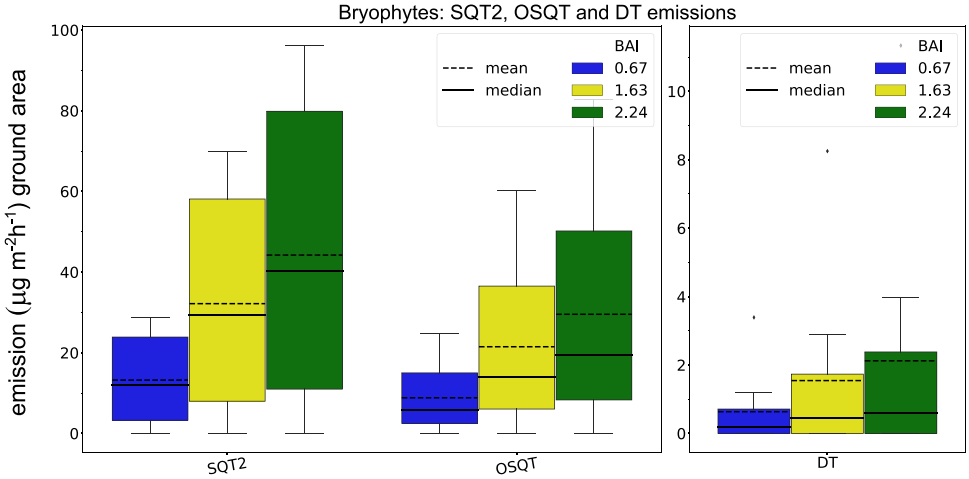

Fig. 3 Bryophytes emissions of SQT2s ($C_{15}H_{22}$), OSQTs ($C_{15}H_{24}O$), and DTs ($C_{20}H_{32}$). Emissions are per Amazon rainforest ground area for different bryophyte area indices (BAI). The boxes represent the 25th to 75th percentile, the whiskers the 5th to 95th percentile, and both the mean (dashed) and the median values (solid line) are shown.

they dry out and are physiologically inactive, and after rehydration they become physiologically active again. Thus, water is the parameter most relevant for their physiological activity. Lichens generally take up less water than bryophytes and thus tend to dry out quicker. Whereas the bryophyte samples were mostly wet when they were collected and thus could be measured in that state, the lichens were mostly very dry and thus wetting them during the experiment seemed plausible. In future experiments, we plan to investigate the VOC emissions under varying water contents. Samples in the dry season displayed increased SQT emissions upon wetting (see Supplementary Fig. 3). In analogy to the bryophyte measurements, emissions were normalized to Amazon ground area for comparison to canopy emissions. The same values for coverage on stems, leaves and lianas were applied and the resulting emissions per Amazon ground area are displayed in boxplots (Fig. 4b). Lichens in contrast to bryophytes displayed a prominent seasonal difference in emission strength of SQTs (see Supplementary Fig. 4). Dry season emissions were around one order of magnitude higher than emissions during the wet season (Fig. 4b).

Emissions of SQTs per unit ground area obtained from the measured emissions per tree area (see Table 2 and methods) for the dry season were 68.8 (28.3–94.6) $\mu g\, m^{-2} h^{-1}$ (non-wetted), 126 (51.7–173) $\mu g\, m^{-2} h^{-1}$ (wetted) and for the wet season 5.3 (2.2–7.3) $\mu g\, m^{-2} h^{-1}$ (non-wetted), and 7.4 (3–10.1) $\mu g\, m^{-2} h^{-1}$ (wetted). To generate a representative annual average emission, we assumed that during the dry season the lichens were in the non-wetted state for 80% of the time and for 20% of the time the wetted emission value was applicable, while for the wet season the numbers were applied in the opposite way (i.e., 80% wetted, 20% non-wetted). This yields an average emission of 43.6 (17.9–59.9) $\mu g\, m^{-2} h^{-1}$. An alteration of the assumed time fractions in a wetted and non-wetted stage did not have a substantial effect. SQT2s, OSQTs and DTs were emitted from lichens as well and amounted to a sum of 4.8 (2–6.6) $\mu g\, m^{-2} h^{-1}$. Thus, the total sesquiterpenoid emissions from lichens amount to 48.4 (19.9–66.5) $\mu g\, m^{-2} h^{-1}$.

In summary, both bryophytes and lichens emit sesquiterpenoids. Bryophytes dominate with an emission of 231 (95.1–318) $\mu g\, m^{-2} h^{-1}$, while lichens add another 48.4 (19.9–66.5) $\mu g\, m^{-2} h^{-1}$, yielding a total cryptogam sesquiterpenoid emission of 279 (115–384) $\mu g\, m^{-2} h^{-1}$ per ground area. Thus, the range of cryptogam sesquiterpenoid emissions calculated by us is even higher than the range of the Amazon canopy emissions estimated by MEGAN ranging from 47 to 236 $\mu g\, m^{-2} h^{-1}$ [1,30].

Lichens and bryophytes as sinks of isoprene oxidation products and other OVOCs. The reactive BVOC emissions from the rainforest are rapidly oxidized in the atmosphere by oxidants such as ozone and OH radicals, forming more polar, oxygenated species that are collectively termed oxygenated volatile organic compounds (OVOCs). OVOCs are abundant in the Amazon rainforest[36]. Strong insolation and humidity favor high OH production rates which promotes oxidation of primary BVOC emissions into more oxygenated forms[37,38]. The measured OVOCs were categorized into eight subgroups (see Supplementary Data 2 and 3), because the uptake and emission behavior appeared to differ depending on their chemical functionality.

Bryophytes showed an uptake of all OVOC groups for most of the measurements, which was more pronounced during day than night and stronger during the dry season than the wet season (see Fig. 5a). Exclusively uptake was observed for acids, saturated carbonyls, alcohols and the signal corresponding to the sum of methyl vinyl ketone (MVK), methacrolein (MACR) and isoprene-hydroxy-hydroperoxides (ISOPOOH).

Lichens, on the other hand, mainly emitted OVOCs, especially during dry season, despite alcohols and acids being taken up. During the wet season, the overall emissions were lower, and for non-wetted samples, OVOC uptake dominated over emission (Fig. 5b).

MVK, MACR, and ISOPOOH, which are all measured on mass 71 in PTR mass spectrometry (m/z 71.049)[39], are oxidation products of isoprene, the most abundant BVOC in the Amazon rainforest. Mass 71 was, in contrast to other OVOCs, always taken up by bryophytes and lichens. Uptake was stronger in the dry season than during the wet season and followed a diel cycle (Fig. 5c, d). The reason for the stronger uptake during the day is most likely that MVK, MACR and ISOPOOH are produced from OH oxidation mainly during the day and only very small concentrations are available for uptake during the night. In both seasons, uptake during the day was ≈4 $\mu g\, (m^2 h)^{-1}$ (ground area) for bryophytes and ≈13 $\mu g\, (m^2 h)^{-1}$ (ground area) for lichens (see Fig. 5c, d). We calculated the in-canopy (height 30 meters) loss rate of mass 71 due to uptake by bryophytes and lichens, and compared it with the loss rate of mass 71 due to OH oxidation calculated from the background concentrations of mass 71 (for details see Supplementary Methods). Because there is no significant OH available for reactions during the night, only the daytime values (6:00 till 18:00) were considered relevant for the loss percentage. Depending on the constituents of mass 71,

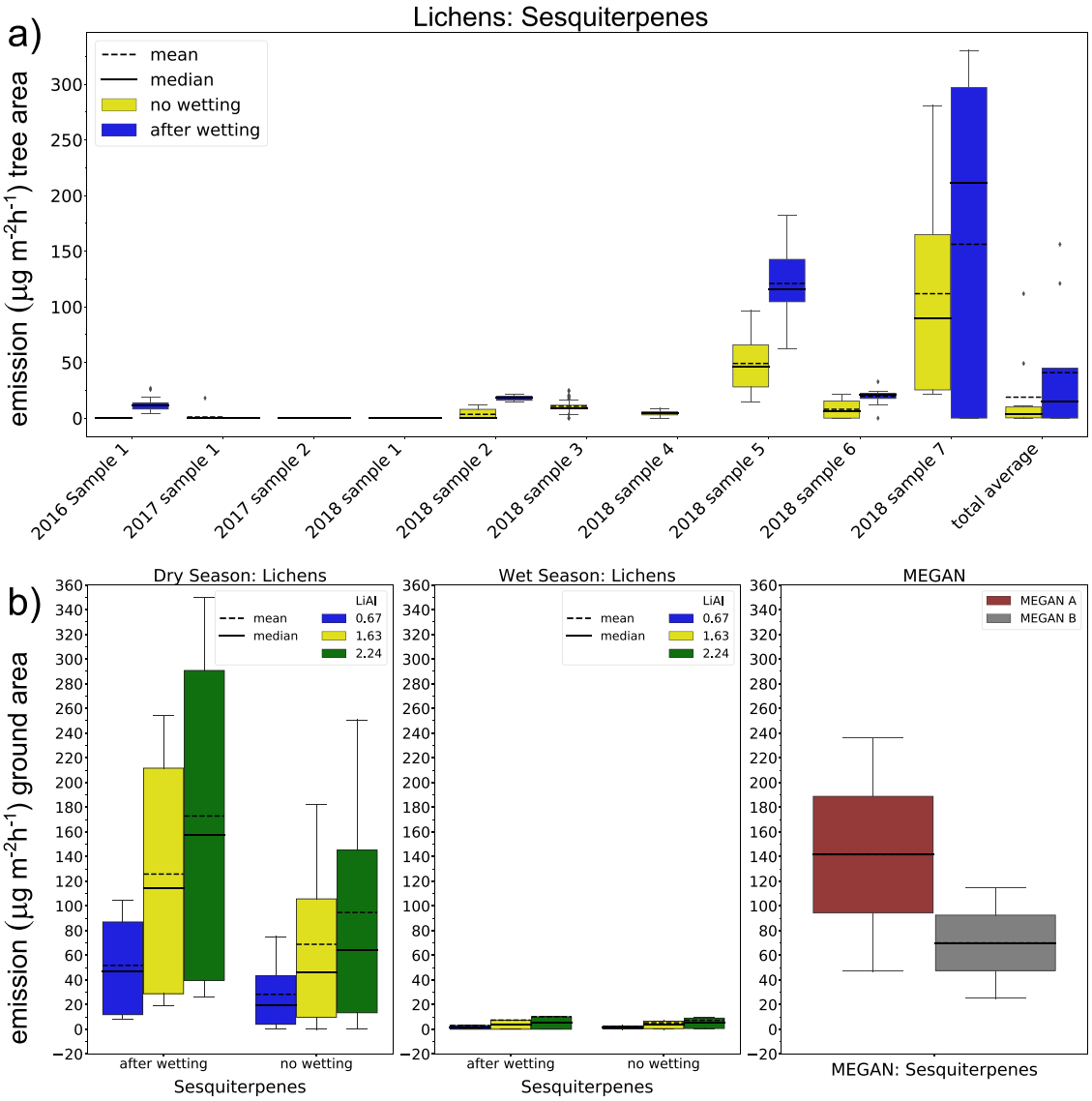

Fig. 4 Sesquiterpene (SQT) emissions from lichen samples of the Amazonian rainforest. a SQT emissions of the 10 individual lichen samples. Emissions before wetting are shown in yellow and after the sample was wetted in blue. The samples 2018 3 and 4 were not wetted. Emissions are shown per tree surface area. The total average boxplots were calculated from all means of the individual samples. **b** Emissions of SQTs from lichens per ground area. Emission in the dry and wet season for wetted and non-wetted conditions are given for three different lichen area indices (LiAI). The plot on the right is SQT emissions from the canopy calculated with the MEGAN model (A: Acosta et al., 2014[1] and B: Bourtsoukidis et al., 2018[30]). The MEGAN boxplots were made by using the lower and upper limit for the emissions from the publications, therefore the mean equals the median The boxes represent the 25th to 75th percentile, the whiskers the 5th to 95th percentile, and both the mean (dashed) and the median values (solid line) are shown.

the OH loss rate would be different, because MVK, MACR and ISOPOOH have different reaction rates with OH. Assuming mass 71 to be exclusively MVK, MACR or ISOPOOH respectively, we obtained an uptake loss of 96–145% (MVK), 66–100% (MACR), or 20–30% (ISOPOOH) of OH oxidation for bryophytes and lichens together. In reality, mass 71 could be expected to be a mix of the three, so that 20–30% for ISOPOOH (see Fig. 5e, f) represents a lower limit of the importance of the uptake loss compared to the OH loss within the canopy.

Comparison with NO_x mixing ratios at the rainforest site indicated that a higher fraction of mass 71 was taken up when NO_x values were lower (see Supplementary Fig. 11). It is known that decreasing NO_x leads to an increase in ISOPOOH formation, whereas increasing NO_x favors formation of MVK and MACR[40]. Therefore, we conclude that the observed uptake is likely to be dominated by ISOPOOH. Uptake of ISOPOOH by plant leaves has been reported recently[41].

Dependence of fluxes on environmental/meteorological variables. Detailed analysis of emission/uptake through General Linear Mixed Models (see methods) corroborated the observed differences in emission/uptake between bryophytes and lichens and revealed an influence of environmental factors (see Table 3). In the following we present the model results for SQTs, as they are by far the dominating sesquiterpenoid emission, and mass 71. Model results for SQT2s, OSQTs and DT can be found in the supplement. Emissions of SQTs from bryophytes increased with photosynthetically active radiation (PAR), temperature (T) and relative humidity (RH), whereas season was not relevant. This

Table 2 Mean fluxes of the lichen samples. Mean fluxes of wetted and non-wetted lichen samples during the dry and the wet season and the mean overall (both seasons, non-wetted, wetted). Positive flux values are emissions and negative flux values are uptake. Fluxes are given per tree area and per sample dry weight for sesquiterpenoids, oxygenated volatile organic compounds (OVOCs), subgroups of OVOCs (for details of the included compounds see Supplementary Data 3) and total VOC emission, uptake and balance (emission minus uptake).

Lichens	μg m^{-2}_{tree} h^{-1}					ng g^{-1}_{dry} h^{-1}				
	Dry season		Wet season		All seasons	Dry season		Wet season		All seasons
	Non-wetted mean	Wetted mean	Non-wetted mean	Wetted mean	Mean (non-wetted and wetted)	Non-wetted mean	Wetted mean	Non-wetted mean	Wetted mean	Mean (non-wetted and wetted)
Sesquiterpenes	42.23 ± 51.16	77.14 ± 72.49	3.24 ± 4.06	4.53 ± 9.07	26.74 ± 22.01	126.2 ± 147.0	237.9 ± 235.4	22.7 ± 24.1	33.2 ± 66.3	89.8 ± 68.7
SQT2	1.54 ± 1.72	2.79 ± 2.01	0.0 ± 0.0	0.0 ± 0.0	0.9 ± 0.72	5.1 ± 7.0	8.9 ± 8.9	0.0 ± 0.0	0.0 ± 0.0	2.9 ± 2.9
OSQT	3.34 ± 2.22	5.02 ± 3.72	0.0 ± 0.0	0.0 ± 0.0	1.84 ± 0.96	10.2 ± 7.5	15.2 ± 11.6	0.0 ± 0.0	0.0 ± 0.0	5.6 ± 3.2
DT	0.5 ± 0.86	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.35	1.4 ± 2.4	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.5 ± 0.9
OVOCs	78.39 ± 364.84	106.21 ± 290.65	−8.03 ± 77.85	17.94 ± 88.66	48.35 ± 153.17	276.1 ± 928.4	341.5 ± 743.8	−167.6 ± 408.0	−10.0 ± 448.9	123.8 ± 421.1
Alcohols	−4.88 ± 36.06	−11.92 ± 24.72	8.92 ± 43.8	2.66 ± 46.1	−1.19 ± 23.95	0.3 ± 77.6	−23.3 ± 51.0	−6.2 ± 218.2	−42.3 ± 249.9	−19.7 ± 107.0
Saturated carbonyls	6.64 ± 64.71	17.76 ± 57.71	−24.6 ± 32.09	7.02 ± 15.16	4.78 ± 27.39	35.1 ± 155.0	63.9 ± 141.3	−188.7 ± 237.5	20.3 ± 67.0	9.7 ± 73.0
Unsaturated carbonyls	82.83 ± 168.02	72.77 ± 127.14	0.01 ± 0.94	3.44 ± 4.57	41.79 ± 68.42	238.1 ± 451.5	209.9 ± 340.7	−0.3 ± 7.7	24.8 ± 33.9	126.1 ± 184.3
Acids	−30.76 ± 28.01	0.78 ± 21.84	4.22 ± 20.84	8.93 ± 26.77	−8.23 ± 15.79	−73.1 ± 55.9	8.2 ± 51.5	−8.4 ± 113.0	16.5 ± 126.8	−22.7 ± 56.8
Esters/dioxygenates	9.76 ± 25.93	15.97 ± 24.12	3.36 ± 5.34	1.57 ± 0.88	6.46 ± 10.67	30.5 ± 67.3	49.6 ± 62.7	29.9 ± 52.7	7.6 ± 1.0	23.2 ± 28.1
Other OVOCs (e.g., ethers, furans)	23.96 ± 42.01	20.94 ± 35.87	3.57 ± 5.48	1.75 ± 1.13	12.73 ± 17.2	66.2 ± 115.1	57.7 ± 98.4	32.4 ± 53.5	8.3 ± 1.9	38.8 ± 47.4
MVK, MACR, ISOPOOH	−9.82 ± 6.19	−10.87 ± 3.07	−1.34 ± 0.2	−4.32 ± 0.36	−6.88 ± 2.5	−23.7 ± 9.5	−27.5 ± 3.5	−9.1 ± 4.5	−24.5 ± 12.7	−22.9 ± 6.4
MEK	0.66 ± 1.69	0.78 ± 2.15	−2.18 ± 2.18	−3.1 ± 2.83	−1.12 ± 1.35	2.7 ± 4.1	2.9 ± 5.1	−17.1 ± 17.3	−20.8 ± 23.4	−8.7 ± 9.7
Total VOCs emission	293.95 ± 462.93	292.17 ± 407.09	42.41 ± 46.15	42.83 ± 49.63	168.17 ± 190.69	847.8 ± 1264.2	856.6 ± 1121.8	242.7 ± 168.3	224.5 ± 206.4	538.9 ± 524.8
Total VOCs uptake	−106.25 ± 116.25	−63.62 ± 75.04	−45.94 ± 37.16	−49.8 ± 41.78	−73.38 ± 50.12	−240.9 ± 194.3	−140.2 ± 116.6	−350.8 ± 316.2	−390.3 ± 308.2	−301.6 ± 149.6
Total VOCs balance	187.7 ± 507.06	228.55 ± 442.72	−3.53 ± 61.91	−6.96 ± 63.52	94.8 ± 209.24	606.9 ± 1311.2	716.5 ± 1171.2	−108.0 ± 321.2	−165.7 ± 341.0	237.3 ± 555.4

was different for lichens, where season and RH had a significant effect, and T a marginal effect ($p = 0.09$). Lichens also showed a different response to the environmental factors in the two seasons (see Supplementary Fig. 12).

Similar to SQT emissions, mass 71 uptake increased with PAR and T but showed a decrease with RH. The response to environmental factors varied between seasons, which led to evident seasonal differences, mainly in bryophyte mass 71 uptake (see Supplementary Fig. 12).

This analysis indicates that PAR, T and RH are parameters influencing fluxes from bryophytes and lichens, and these parameters could also be used in models to drive cryptogamic emissions.

The results of this analysis also helped elucidate the previously described variability between samples. As shown in Table 3, the variance in bryophyte SQT emissions was largely explained by the random factor (sample) and not by selected environmental factors (PAR, T and RH). For lichens, the random factor was less dominant, but still contributed significantly to the total explained variability (see Table 3). This implies the importance of other variables that have not yet been accounted for in this analysis. One of these variables could be the water content of the sample, as it is highly relevant for the physiological activity of cryptogams[9], which was not monitored during this study, since water content is not a parameter readily available for model input. As our results indicate, different or additional parameters are needed to fully account for the variation in fluxes of BVOCs by cryptogams, as compared to the ones used for vascular plants in MEGAN[2]. Measurements under controlled laboratory conditions are needed to identify the role of the abiotic factors water status, temperature, and light intensity, but also of biotic factors, like age and stress for emission patterns and to define potential model parameterizations.

Total VOC emissions from tropical bryophytes and their OH and ozone reactivity. Apart from the aforementioned OVOC and sesquiterpenoid species, all bryophyte samples emitted a variety of other BVOCs (see Supplementary Data 2). The chemical variety within bryophyte sesquiterpene and monoterpene emissions is shown in Fig. 6a).

The total BVOC emissions from the bryophyte samples amounted to $10.4 \pm 11.4\ \mu g\ g^{-1}_{dry}\ h^{-1}$, which is high compared to most plant species that do not emit isoprene. Compared to previously reported values for a boreal moss they were more than an order of magnitude higher[18,19]. It should be noted, however, that little data on total bryophyte VOC emissions exists for comparison.

The relevance of BVOC emissions from bryophytes for atmospheric chemistry can be assessed by measuring the total OH sink of the emitted substances, named the total OH reactivity emission (TOHRE, see Methods)[42,43]. Average TOHRE of the samples was $1.82*10^{-4} \pm 1.79*10^{-4}\ m^3 g^{-1}_{dry} s^{-2}$, and therefore in the same order of magnitude as the measured TOHRE of a boreal pine tree and one order of magnitude lower than of boreal spruce and birch trees[43]. In contrast to the only two other TOHRE studies, the bryophyte emissions did not exhibit any significant unattributed OH reactivity fraction[42,43]. Bryophyte TOHRE was approximately 2/3 due to monoterpene-attributed reactivity emissions and 1/3 to sesquiterpene-attributed reactivity emissions (Fig. 6b). Contributions from OVOCs were negative (i.e., uptake) and are therefore not shown in Fig. 6.

The total ozone sink caused by the bryophyte VOC emissions, i.e., the total ozone reactivity, was calculated to be $3.24*10^{-9} \pm 2.99*10^{-9}\ m^3 g^{-1}_{dry} s^{-2}$. As shown in Fig. 6c), sesquiterpenes were the main drivers of ozone reactivity emissions (79% of the calculated ozone reactivity in the non-stressed state). Owing to their rapid reaction with ozone, atmospheric degradation of the bryophyte

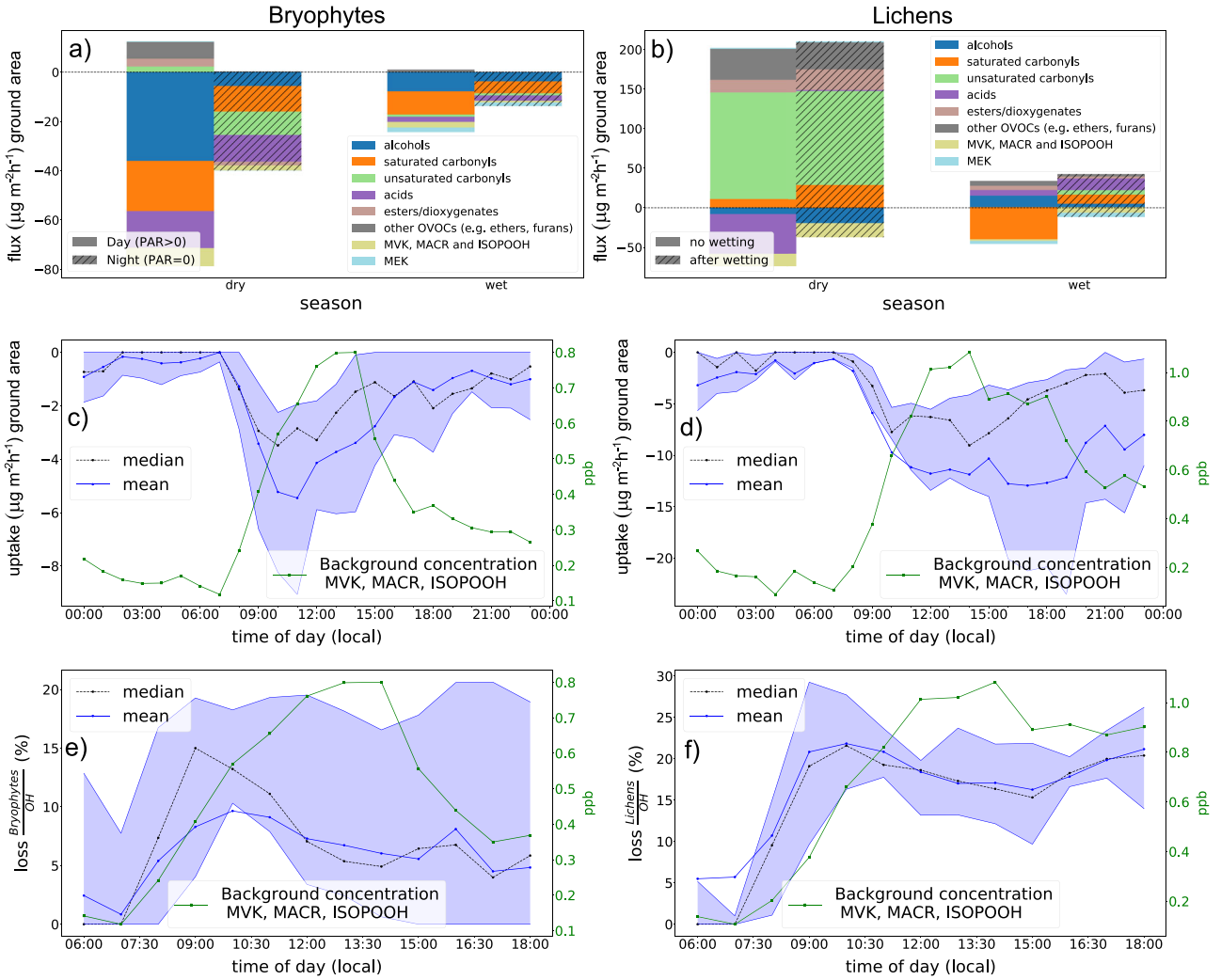

Fig. 5 Emission and uptake of oxygenated volatile organic compounds (OVOCs) and isoprene oxidation products (mass 71: MVK, MACR, ISOPOOH) from bryophytes and lichens of the Amazonian rainforest. Emission and uptake of OVOCs from **a** bryophytes and **b** lichens. Diel plots of mass 71 uptake of **c** bryophytes and **d** lichens, together with background concentrations of mass 71. Daytime diel plots of the ratio of mass 71 loss via cryptogam uptake to loss by OH oxidation for **e** bryophytes and **f** lichens, alongside with the background concentrations of mass 71. Sunrise was around 6:00 local and sunset around 18:00 local. The blue shaded area extends from the 25th to 75th percentile. Diurnal plots were calculated from all bryophyte and lichen samples. The *y*-axis for the background concentrations (MVK, MACR, ISOPOOH) in the plots **c**–**f** is on the right side.

Table 3 Summary of general linear mixed model (LLM). Summary of general linear mixed model (LLM) for SQTs emissions and isoprene oxidation products (mass 71) uptake, as a function of PAR, T and RH and the interaction between these factors and with the season (Season x PAR, Season x RH and Season x T). Bryophytes: $n = 426$ and lichens: $n = 448$.

		Bryophytes				Lichens			
		***F*-value**	***p*-value**			***F*-value**	***p*-value**		
SQTs	PAR	13.9	0.0001			1.71	0.1919		
	RH	11.26	0.0009	r^2	0.68	5.11	0.0242		0.58
	T	31.51	0.0001	Fixed	0.16	2.83	0.0933	Fixed	0.29
	Season	0.09	0.77	Random	0.52	6.88	0.0305	Random	0.29
	Season x PAR	5.27	0.0222			5.33	0.0214		
	Season x RH	1.42	0.2347			7.03	0.0083		
	Season x T	2.53	0.1123			3.74	0.0536		
mass 71	PAR	240.916	0.0001			13.65718	0.0002		
	RH	362.2176	0.0001	r^2	0.73	216.5351	0.0001	r^2	0.46
	T	1.4456	0.2299	Fixed	0.65	71.78071	0.0001	Fixed	0.43
	Season	16.1304	0.0051	Random	0.08	3.6172	0.0937	Random	0.03
	Season x PAR	38.4377	0.0001			5.482	0.0197		
	Season x RH	69.7594	0.0001			4.93052	0.0269		
	Season x T	0.2424	0.6227			0.876	0.3498		

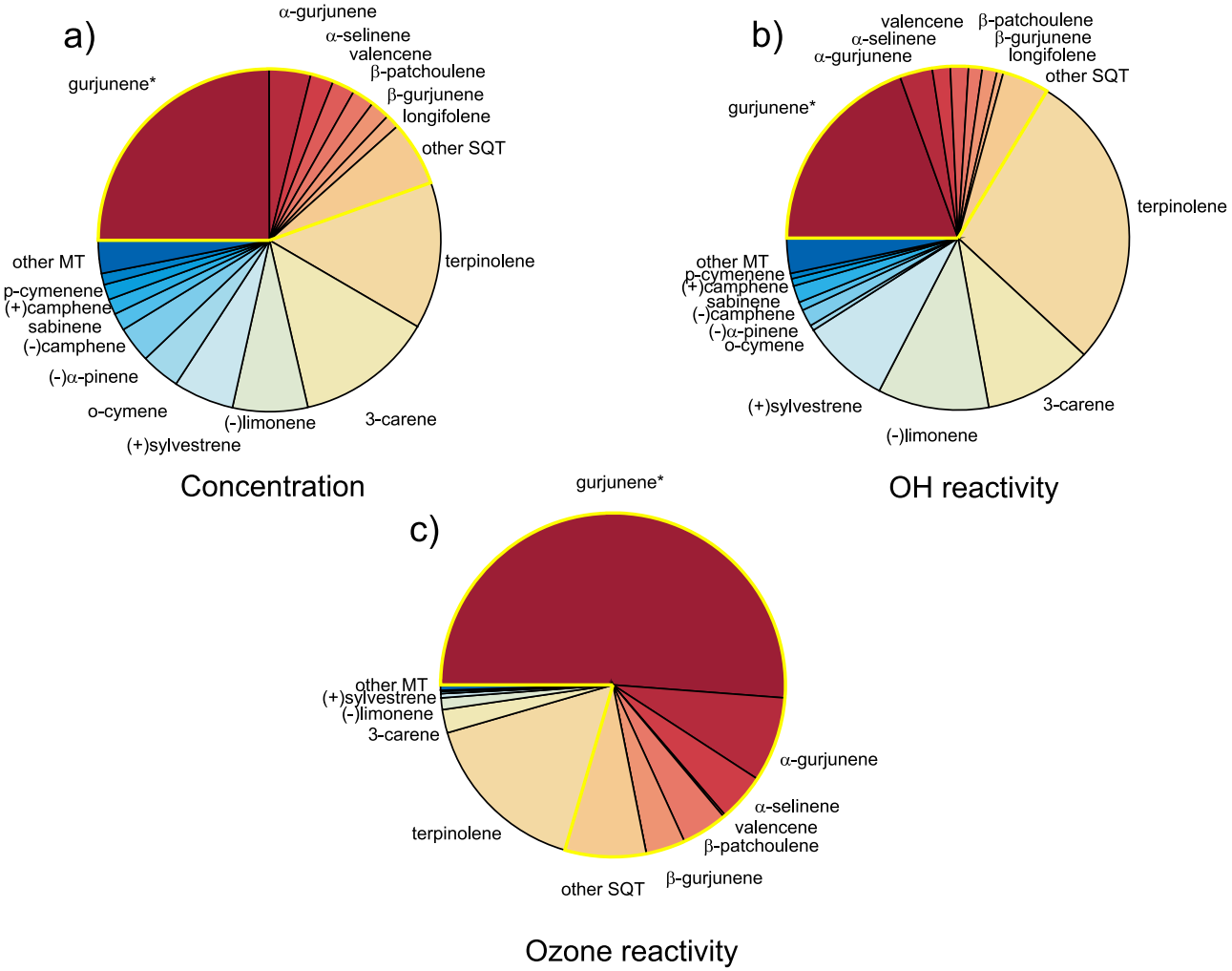

Fig. 6 Contributions of sesquiterpenes and monoterpenes to molar concentration, OH reactivity and ozone reactivity of bryophyte emissions. Speciated contribution of terpenes to **a** molar emissions, **b** OH reactivity emissions, and **c** ozone reactivity emissions (average of two typical bryophyte samples). The yellow outline denotes sesquiterpenes, the remaining substances are monoterpenes (MT). *This compound was tentatively identified as α-gurjunene (MS matching factor with NIST library > 850, considered a "good match", see methods).

SQT emissions was dominated by ozone (SQT lifetime towards ozone: $\tau_{SQT,O3} = 0.91$ h and towards OH: $\tau_{SQT,OH} = 1.66$ h), while the main sink of the bryophyte-derived monoterpenes was the OH radical ($\tau_{MT,O3} = 4.20$ h, $\tau_{MT,OH} = 0.99$ h; assuming $[O_3] = 5$ ppb and $[OH] = 2*10^6$ molecules cm^{-3} in the tropical forest[44]).

Bryophyte and lichen samples collected in the field may harbor a variety of different bacteria and fungi[45–47]. We cannot rule out that the fluxes from our bryophytes and lichens are partly a product of the associated microbes living on them. Therefore, the measured fluxes presented must be understood as being from bryophyte and lichen communities. Furthermore, bryophytes and lichens growing on the foliage might reduce foliar emissions of the vascular plants. However, as the coverage on leaves only accounts for 17% (16–24%) of the total cover on trees, this potential modulating effect does not influence the conclusion that bryophytes and lichens are important contributors to BVOC fluxes.

Discussion: implications for global biogenic VOC budgets and atmospheric chemistry

The sesquiterpenoid emissions from bryophytes and lichens reported here (SQT, SQT2, OSQT and DT emissions added together) amount to 279 (115–384) $\mu g\, m^{-2} h^{-1}$ per ground area.

If these values, obtained from samples within the *terra firme* rainforest at the ATTO site, are considered as representative for all *terra firme* rainforests of the Amazon (4.66 million square kilometers), one obtains an annual emission of sesquiterpenoids of 11.4 (4.7–15.7) Tg yr^{-1}, and for global tropical rainforests (7.1 million square kilometers) 17.5 (7.2–24) Tg yr^{-1}. A recent global annual sesquiterpenoid emissions estimate (calculated with MEGAN)[2] suggested a value of 29 Tg yr^{-1}. It should be noted that MEGAN only considers SQT and OSQT emissions from tropical trees[2], whereas we included SQT2s and DTs in this analysis of lichen and bryophyte emissions. It is therefore possible that an extended speciation for tropical tree species may reveal higher total emissions. Nevertheless, SQT and OSQT emissions contribute 87% to our total sesquiterpenoid emissions, with SQTs alone contributing almost 80%. SQTs can be therefore considered the dominant chemical family of these emissions. The emission algorithm of sesquiterpenoids in MEGAN[2] is based on SQT measurements summarized in a review by Duhl et al[29]. These include measurements of plants in controlled laboratory settings as well as branch enclosure measurements, but no above canopy flux measurements. None of these measurements reported cryptogamic covers on their plants. Therefore, it has to be noted that sesquiterpenoid emissions from bryophytes and lichens are not currently included in these emission inventories. This means that

emissions from bryophytes and lichens in the Amazon rainforest alone potentially add 39% (16–54%) to previously modeled annual global sesquiterpenoid emissions. Assuming similar emissions for the global tropical rainforests, the overall global emissions would be 60% (25–83%) higher.

OH reactivity measurements in tropical rainforest uncovered significant missing OH reactivity, which can be an indicator for unknown or underestimated emissions[36,48]. The missing OH reactivity was originally attributed to unmeasured oxygenated intermediates[36] or to a mix of OVOCs and various primary BVOCs[48]. Recently, closure of the OH reactivity budget was achieved at the ATTO site by measuring an extended range of VOCs, including SQTs. However, the lowest measurement point of this study was at 80 meters above ground and it was shown that most SQTs were at that height already lost due to oxidation[38]. Therefore, the large previously observed missing reactivity within the canopy and understory[48] could be, at least partly, due to the emission of sesquiterpenoids from cryptogams.

Even though our understanding of SOA formation is still far from complete, owing to the inherent chemical complexity[49,50], oxidation of BVOCs is considered to be the dominant source of SOA[51]. Oxidation of BVOC by OH, ozone and NO_3 leads to a large number of low volatility oxygenated organic compounds that contribute to SOA formation and growth[49,52]. Due to the chemical complexity, most BVOCs and SQTs are not included in global models, and these models tend to underestimate SOA abundance compared to measurement. Sesquiterpenoids react rapidly with ozone to produce SOA with a yield of 20–70%[53,54]. Khan et al. added an oxidation mechanism for SQTs into a global chemistry model (based on β-caryophyllene and 29 Tg/yr) to account for SQT oxidation[55]. This yielded an increase in SOA of 48%, but compared with measured values still underpredicted SOA[55]. SOA is important for global climate predictions because it can scatter or absorb radiation and increase concentrations of cloud condensation nuclei (CCN)[52,56]. Multigeneration oxidation products from sesquiterpenoids can be transported above the boundary layer and thus impact SOA on large spatial and temporal scales[55]. This newly found large emission of sesquiterpenoids from cryptogams is therefore important for radiative forcing, cloud formation and atmospheric chemistry over tropical rainforests and beyond.

It should be noted that the current SQT emissions calculated from MEGAN are associated with a high uncertainty (higher than a factor of three)[2], since it is based on enclosure studies that can easily generate disturbed fluxes. It would therefore not be appropriate to directly add these newfound SQT emissions from bryophytes and lichens to the inventory without further constraining measurements such as direct fluxes, as they may lie within existing uncertainties. Although current model underestimates of SOA would support additional SQT emissions to be added to the emissions inventory, constraints such as specific tracers of SQT oxidation in aerosol should be sought to ensure accurate attribution of the effect.

With the strong ozone reactivity of the bryophyte and lichen emissions, a previously unknown ozone sink in the rainforest canopy has been discovered. Bryophytes by far dominate sesquiterpenoid emissions in comparison to the lichens. As bryophyte biomass is largest in the canopy, this may be a missing sink that potentially explains why the canopy is the largest ozone sink in the Amazon rainforest[57]. Additionally, reactions of sesquiterpenoids with ozone lead to the formation of OH[58] and therefore accelerate BVOC oxidation. The significant OH reactivity emissions showed that cryptogam-derived BVOCs can also impact atmospheric oxidation capacity in Amazonia.

Recently, bidirectional fluxes of VOCs have been reported for some ecosystems[59,60]. Uptake by vegetation can be the dominating atmospheric removal process[59] for some VOCs, and in some cases a compensation point can exist so that the plant will emit or uptake depending on the ambient air concentration[61]. As is evident from Fig. 5a, bryophytes act as a sink for most OVOCs. Plants can rapidly metabolize OVOCs enzymatically and integrate them into their carbon and energy processing pathways[61]. MVK, MACR and ISOPOOH, acids, saturated carbonyls and alcohols were continuously taken up by bryophytes in our experiments. For lichens, permanent uptake of only mass 71 (MVK, MACR and ISOPOOH) was observed. An anticorrelation with NO_x indicates that mass 71 uptake is due to uptake of ISOPOOH. It has been shown that ISOPOOH, which is toxic to plants, can be enzymatically decomposed within plants[41].

The ratio of mass 71/isoprene[62] has been used previously to determine photochemical oxidation times in forest environments, with mass 71 assumed to be MVK and MACR. More recent studies have shown that PTR-MS measurements made under standard conditions also detect ISOPOOH on the exact same mass[39,40]. Since ISOPOOH is also an oxidation product of isoprene, the ratio of mass 71/isoprene appears to be a good indicator of the degree of isoprene oxidation in an airmass, allowing ambient OH levels to be calculated, provided that reaction times can be estimated. Our measurements demonstrate that mass 71, most likely ISOPOOH, is taken up by bryophytes and lichens in the same order of magnitude as OH loss for mass 71, thus invalidating this approach. The biogenic uptake of an oxidized product of isoprene also has implications for assessment of OH recycling rates when based on data collected in low NO_x environments[37].

In summary, we observed that bryophytes and lichens have a major impact on the composition and quantity of BVOCs in the atmosphere of the Amazonian rainforest. The large sesquiterpenoid emissions from, and the OVOC uptakes by cryptogamic covers need to be included in atmospheric models and driven separately from those of vascular plants in order to accurately simulate current atmospheric chemistry and future climate responses. Extensive measurements of bryophytes and lichens under controlled laboratory conditions are needed to find suitable parameters for modeling their fluxes. As prodigious producers of SOA precursors, cryptogams can impact regional radiative forcing and cloud formation and by taking up photolyzable oxygenated species they can impact radical concentrations above the rainforest. Therefore, incorporation of these newly found fluxes will help to improve climate model predictions.

Methods

The Amazon Tall Tower Observatory site (ATTO). The ATTO site is located in a pristine *terra firme* (plateau) rainforest ca. 150 km northeast of Manaus (Brazil). It is equipped with several towers for atmospheric chemistry and meteorology observations. A detailed description can be found elsewhere[4]. The average rainfall at the site reaches its monthly maximum of ~335 mm in the wet (February to May) and its minimum of ~47 mm in the dry season (August to November), with transitional periods in between[63]. More than 400 tree species with a maximum canopy top height of ~35 m have been identified at the site[4,64]. For an overview of the microclimatic and ecophysiological growth conditions of bryophytes at ATTO, the reader is referred to Löbs et al[9].

Bryophytes and lichens samples. Bryophytes and lichens samples were collected in the rainforest understory at the ATTO site at ca. 1.0–1.5 m height. They were removed from tree barks incurring as little damage as possible. For transportation to the cuvettes for VOC measurement, they were stored in aluminum foil to avoid contamination. Samples were cleaned from visible impurities and remaining pieces of tree bark before measurement. Dry weight of the samples was determined when they were completely dried out. The surface area covered by each sample was measured from photos of the original growth location after sample removal (Supplementary Fig. 10). This way, the area originally covered by the sample was used to calculate emission fluxes per tree area. Identification of the bryophyte and lichen species present in the samples was done with the aid of a stereomicroscope, followed by the examination of certain features under the microscope. Specialized

taxonomic[65–67] and ecological literature[68] was used for species identification and to verify the sample representativeness of the Amazonian lichen and bryophyte flora.

Cuvette fluxes sampling setup. A cuvette system consisting of three 2.5 L glass bottles connected to rainforest air (inlet) and a valve system (outlet) was used to measure VOC exchange between samples and the forest (Supplementary Figure 1). All three cuvettes were constantly flushed with 500 mL min^{-1} of rainforest air. One of the three cuvettes served as background (no sample). The other two cuvettes contained bryophytes/lichens samples. The cuvettes were placed at a location in the shaded understory (similar to the conditions experienced by the sample organisms in the forest) next to the laboratory container. Using a valve system, air from each sample cuvette was fed into the VOC and OH reactivity measurement devices inside the laboratory container for 10 min, followed by the background cuvette. All tubing and connections were inert PTFE (polytetrafluoroethylene), insulated and heated to ca. 40 °C from the point where they entered the air-conditioned laboratory container.

PTR-MS measurements. Time-resolved composition and abundance of volatile organic compounds (VOCs) were measured using PTR-MS[26]. H_3O+ mode allows for soft chemical ionization which is highly sensitive to all those VOC compounds whose proton affinity is higher than that of water, which includes the vast majority of VOCs. In 2016 and 2017, a PTR-quadrupole mass spectrometer (PTR-QMS)[26] was employed, which required preselection of masses to be monitored (masses monitored see Supplementary Data 2). From 2018 on, a PTR-time of flight mass spectrometer (PTR-ToF-MS)[69] was used, allowing for simultaneous detection of masses up to 500 amu. The PTRs were operated under standard conditions ($E/N = 120–130$ Td). Precision of the measurements is ≤5%. Calibrations were performed with the help of a gravimetrically prepared VOC calibration gas mixture. The calibrations were performed at humidity levels comparable to ambient humidity levels encountered during the measurements. Concentrations for compounds included in the standard were calculated with the help of these calibrations with an uncertainty of ≤20%. The concentrations for compounds not included in the standard (SQT, SQT2, OSQT, and DT) were calculated using reaction rates and transmission curves[26]. Therefore, concentrations calculated for these compounds are associated with a higher uncertainty of ≤50%. At standard PTR conditions, the ionization of SQTs, SQT2s, OSQTs, and DTs results in multiple fragments. Fragmentation depends on the structure of the sesquiterpenoid. We used the parent masses (e.g., $m/z = 205$ for SQTs) for quantification. Based on published fragmentation values at similar PTR-MS operating conditions for the detected sesquiterpenes or sesquiterpenes with similar structure[70,71], we estimated and corrected for an average fragmentation loss of 50% on these masses.

GC-MS measurements. For chiral monoterpene and sesquiterpene speciation, air samples from the overflow of the sampling setup were collected on sorbent filled tubes using a custom-built automatic sampler. Custom-built stainless-steel cartridges (Silcosteel1 (Restek, USA) 89 mm × 5.33 mm I.D.) containing two sorbent beds composed of 130 mg of Carbograph 1 followed by 130 mg of Carbograph 5 were used to collect air samples and a quartz filter impregnated with a solution of 10% w/w sodium thiosulfate was used to scrub ozone upstream in the sampling flow. After sampling, air samples and blanks were stored at room temperature in air-conditioned containers, transported to the laboratory and analyzed within 3 months. The material was tested for sesquiterpenes sampling with a certified gas mixture (Apel Riemer, USA) containing β-caryophyllene ($C_{15}H_{24}$). Tests were conducted by actively sampling the diluted gas mixture (~200 ppt of β-caryophyllene) through the cartridge with a sampling flow of 200 ml min^{-1} for 10 min, for a total collected volume of ~2 L, as was done for the air samples of bryophytes and lichens. The cartridge material was tested for breakthrough, desorption, and storage artifacts. In all three cases the material responded well for sampling β-caryophyllene. The same gas mixture was tested with cartridges filled with Tenax (TA)/Carbograph 1 and the same peak area was found for the same sampling conditions. A Thermodesorption Gas Chromatograph system equipped with a chiral column (dimethyl TBS β-cyclodextrin-based column (0.15 µm, 0.15 mm I.D., 25 m length), MEGA, Italy) and combined with a Time of Flight Mass Spectrometer (TD-GC-TOF-MS, Bench ToF Tandem Ionization, Markes International, UK) was used to analyze the samples. Identification and quantification of the main chemical compounds was obtained by injection of a gas standard mixture (162 VOCs provided by Apel Riemer Environmental Inc., USA) and by use of liquid standards. For those compounds not available in the gas or liquid standards their identity was attributed by comparing the MS spectra with the MS library (provided by NIST) for the same ionization energy. Spectral matches were considered excellent for matching factors above 900, good for matching factors between 800 and 900 and fair for matching factors between 700 and 800 (Yee et al. and references therein)[53]. The LOD is ~1 pptv and method uncertainty is 23%. More details are available in Zannoni et al[72].

Flux calculations. Fluxes (F) were calculated using the following equation:

$$F = f * \frac{C_s - C_B}{N_{a,g}} \quad (1)$$

where f is the flow rate through the sample bottle, C_s is the concentration of the sample cuvette and C_b the concentration of the background cuvette. Concentrations were averaged over the measuring time of one cuvette excluding the first two minutes after switching to this cuvette. The background cuvette was always measured before and after the sample cuvette and the values interpolated to the times of the sample cuvette. N_a is the area of the sample in m^2 or N_g the dry weight of the sample in g. In the first case the flux is given in the unit of µg m_{tree}^{-2} h^{-1} and in the second case in ng g_{dry}^{-1} h^{-1}. Negative values for the flux indicate uptake and positive emission. The standard deviation of the background cuvette was used to determine the limit of detection (LOD) throughout the measurements for all compounds. Absolute values below the respective LOD (two times standard deviation) were set to zero. The mean/median LOD values of all samples were for SQTs: 11.1/4.6 µg m_{tree}^{-2} h^{-1} (119.2/37.6 ng g_{dry}^{-1} h^{-1}), SQT2s: 3.9/1.7 µg m_{tree}^{-2} h^{-1} (45.9/16.4 ng g_{dry}^{-1} h^{-1}), OSQTs: 2.6/1.9 µg m_{tree}^{-2} h^{-1} (22.4/15.1 ng g_{dry}^{-1} h^{-1}), DTs: 1.7/1.6 µg m_{tree}^{-2} h^{-1} (13.4/12 ng g_{dry}^{-1} h^{-1}) and MVK, MACR, ISOPOOH: 1.5/0.9 µg m_{tree}^{-2} h^{-1} (12.6/7.2 ng g_{dry}^{-1} h^{-1}). The error of the flow rate measurement is $E_f = 1\%$, the error of the area measurement $E_a \leq 10\%$ or the error for the dry weight determination $E_g \leq 5\%$ and the uncertainty for the concentration is $E_c \leq 20\%$ for compounds in the calibration gas standard and $E_c \leq 50\%$ for compounds not in the standard. Thus, the total uncertainty of the emission fluxes E is obtained via the following equation.

$$E = \sqrt{E_c^2 + E_f^2 + E_{a,g}^2} \quad (2)$$

This yields a total uncertainty of ≤23% for the gas standard calibrated compounds and ≤ 51% for compounds not included in the gas standard.

Transformation of fluxes per tree area to fluxes per ground area. In order to obtain emissions per ground area values from emissions per tree area we employ stem area index (SAI) and leaf area index (LAI), which are defined as the total stem or leaf area per unit ground area. Tropical forests have an average SAI of 1.7 $m_{tree}^2 m^{-2}$ and an average LAI of 5.4 $m_{tree}^2 m^{-2}$ (with lianas adding another 1.7 $m_{tree}^2 m^{-2}$)[10]. Elbert et al. reviewed over 200 studies for fractional coverage values on leaves and stems[10]. In studies concerning tropical trees, the fractional coverage of bryophytes and lichens, was at least 33% but often as high as 90% or more, but the results were mainly from forest understory and lower canopy. These estimates combined with our own observations during bryophyte sampling at different sites in the Amazon[68,73], including upper canopy branches, led to the following coverage estimates. We consider a coverage of 40% on stems and lianas and 5% on leaves for bryophytes and the same for lichens as a realistic working assumption. This results in a bryophyte area index (BAI) and lichen area index (LiAI) of 1.63 $m_{tree}^2 m^{-2}$. A conservative assumption of 1/6 cover on stems and lianas and 2% on leaves each, yields a BAI and LiAI of 0.67 $m_{tree}^2 m^{-2}$. We consider a coverage of 50% on stems and lianas and 10% on leaves each as an upper limit, which yields a BAI and LiAI of 2.24 $m_{tree}^2 m^{-2}$. Adding up bryophytes and lichens coverage never exceeds 100%. Multiplication of the emission per tree area by the BAI or LiAI then results in the emissions per ground area. Throughout this manuscript, all emission values per ground area are calculated with a BAI or LiAI of 1.63 $m_{tree}^2 m^{-2}$. The range obtained by using the lower (0.67 $m_{tree}^2 m^{-2}$) and upper (2.24 $m_{tree}^2 m^{-2}$) limit of the BAI or LiAI is added in parentheses.

General linear mixed models. The influence of environmental conditions on sesquiterpenoid emissions and mass 71 uptake was explored by fitting different general linear mixed models (LMMs). More precisely, we used season as fixed factor, sample as a random factor and incoming photosynthetically active radiation (PAR), temperature and relative humidity (RH) as continuous predictors. These are factors readily available for model input. PAR was measured on a tree close to the measurement cuvettes at 1.5 meters height (similar light conditions as cuvettes). Days with sensor data gaps for PAR were filled with regression data calculated from PAR values taken at the top of the canopy. This was considered appropriate as it showed good correlation with values measured in the understory. Temperature and RH of the air entering the cuvettes was measured. In order to identify differences in the response to changing environmental conditions between dry and wet season, the interactions between continuous predictors and season were also included in the model. Then five different models were separately developed for lichens and bryophytes, one for each compound (SQTs, SQT2, OSQT, DT and mass 71). p-values lower than 0.05 were interpreted as significant effects, and residuals were visually scrutinized and did not deviate substantially from normal. The analysis was based on the flux data normalized to dry weight using the Lme4 package in R (R Core Team, 2017)[74].

OH and ozone reactivity emission fluxes. Total OH reactivity was measured and analyzed using the comparative reactivity method[75] (CRM) as described elsewhere[38,76]. Briefly, the method applies the known OH reactivity of a pyrrole gas standard and compares it with the reactivity of all compounds found in the air sample by a competitive reaction for artificially produced OH radicals. CRM uses three different modes[75]: C1 (OH scavenger + pyrrole + UV light at ≈ ambient humidity), C2 (OH + pyrrole, ambient humidity), and C3 level (ambient air + pyrrole + OH). Here, we alternated between C2 and C3 modes every 5 min, so that both C2 and C3 were measured for each sample cuvette before the valve system switched to the next cuvette. C1 was determined at least weekly. The system was

operated at pyrrole/OH ratios of 1.75 to 2.9, which deviates from pseudo-1st-order conditions, as is typical for CRM. As the dominant reactants in the bryophytes emissions were highly reactive mono- and sesquiterpenes, the correction for this deviation was based on tests with known concentrations of similarly reactive isoprene at varied humidities, resulting in a pyrrole/OH *(pyr/OH)* dependent correction factor of

$$f = a\left(\frac{pyr}{OH}\right) + b, \quad (3)$$

where a and b were experimentally derived and amounted to $a = -0.5$ and $b = 2.98$ in 2017, $a = -2.23$ and $b = 8.25$ in 03/2018, $a = -0.99$ and $b = 4.33$ in 10/2018. The 5 min detection limit was 3.4 s^{-1}.

The total OH reactivity emission flux (TOHRE) was calculated from the background cuvette reactivity R_b (s^{-1}), the sample cuvette reactivity R_s (s^{-1}), flow rate f $(m^3\ s^{-1})$ and normalized either by sample area N_a (m^2) or by sample dry weight N_g (g):

$$\mathrm{TOHRE} = (R_s - R_b) * \frac{f}{N_{a,g}} \quad (4)$$

Speciated OH and ozone reactivity from individually measured VOCs was calculated from VOC concentrations observed by the PTR-MS as described previously[76]. A list of compounds included in the calculation and the reaction rate constants used can be found in Supplementary Data 2. Calculated OH reactivity of the emissions (COHRE) was derived from speciated OH reactivity of the background and sample cuvettes according to Eq. 4.

Exclusion of stress-related emissions. In most but not all bryophyte and lichen samples, some BVOCs were emitted in high amounts only in the first ~12 h after insertion into the sampling cuvette, which was interpreted as a clear indicator for mechanical stress-related emissions due to damage related to the removal of the samples from their growth location to the cuvette. This emission pattern was also evident in green leaf volatiles (hexenal, hexanol) (Supplementary Fig. 9) known to be markers for stress in plants[77]. These first hours (9–12 h) influenced by stress emission where excluded from all analyses presented in this manuscript.

Upscaling of measured emissions. The Amazon basin covers an area of 8 million square kilometers of which more than 70% are tropical rainforests representative of the forest at the ATTO site (5.8 million square kilometers)[3,78]. The Amazon tropical rainforest can be further subdivided into different vegetation types, e.g., *terra firme, várzea, white sands, igapós* with *terra firme* constituting around 80% of the area[79]. All our samples were taken from *terra firme* forest locations and our coverage estimations are based on *terra firme* locations as well. Therefore, we only scale up to all *terra firme* type vegetations in the Amazon rainforest (4.66 million square kilometers).

The bryophytes samples represent a mix of common Amazonian species, dominated by the family of *Lejeuneaceae* by far the most speciose and abundant bryophyte family in the Amazon[73].

Samples of lichens primarily contained species of the *Ramalinaceae* and *Graphidaceae* family which are common at the ATTO site and representative for the Amazon rainforest[80].

Thus, we consider our bryophyte and lichen measurements presented here to be a good proxy for most of the Amazon basin, justifying extrapolation of the in-situ measured fluxes to the aforementioned Amazon areas (regarding limitations of this extrapolation see Supplementary Discussion).

Upscaling to global tropical rainforests. Globally tropical rainforests cover around 8.9 million square kilometers[3]. As for the Amazon rainforest, we use 80% of this area for upscaling. Our sampled species only represent the Amazon; nevertheless, we justify upscaling to global tropical forests with convergent evolution. Even if the species in different rainforests are not closely related, they occupy similar niches in a similar ecosystem resulting in similar evolutionary adaptions. Upscaling therefore can be justified but will be associated with a larger uncertainty than for the Amazon.

Data availability

Flux measurement timeseries data of bryophytes and lichens for all compounds in units of µg m_{tree}^{-2} h^{-1} and ng g_{dry}^{-1} h^{-1} available via: https://doi.org/10.17871/atto.232.15.860.

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Author contributions

A.E. and E.P. performed the VOC and OH reactivity measurements, analyzed the data, and drafted the article. A.P.F., C.G.G.B., and R.P.A. contributed to sample collection and identification. E.R.C. contributed the model (LMMs) calculations. N.Z. performed monoterpene and sesquiterpene speciation. S.W., A.T., and M.S. contributed the NOx data and the meteorological data were supplied by MOS and ACA. A.A. helped with lichen identification. S.M.O. contributed the bryophyte identification and contributed to

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The authors declare no competing interests.

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