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Isoprene emission from *Sphagnum* species occupying different growth positions above the water table

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Isoprene emission from *Sphagnum* species naturally growing at different positions above the water table were measured in a subarctic peatland and at monoliths from a temperate bog. Our objectives were to investigate (1) whether emission rates were species and/or moisture dependent, and (2) whether short-term temperature history had an influence on emission capacity. We expected greater emission capacities in moist than dry growing conditions, and from species adapted to wet habitats. We also expected that higher emission capacities would be found in response to elevated temperatures. Average peak growing season isoprene emission capacities (standardized to 20 °C and PAR 1000 μmol m^{-2} s^{-1}) at the subarctic site were 106 and 74 μg C m^{-2} h^{-1} from a *S. balticum* wet lawn and a *S. balticum* dry hummock/palsa, respectively. Emission capacities correlated strongly with gross primary productivity (GPP) and the average air temperature of the 48 hours prior to measurement (T_{48}), but the effect of T_{48} seemed to be partly masked by the influence of GPP when moisture was not limiting. The laboratory experiments suggested that a typical hummock species, *S. rubellum* had higher capacity for isoprene emission than a typical lawn species *S. magellanicum*. Instantaneous emission rates increased with temperature, but no effect of temperature history was discernible. *Sphagnum* mosses are known to emit substantial amounts of isoprene, but in this study we also showed significant inter-species differences in emission capacity. The results imply that climate change induced alterations of peatland hydrology may change the total ecosystem isoprene source strength, as individual species adapt to new growth conditions or as a consequence of species succession.

Introduction

The diverse group of gaseous, non-methane hydrocarbons emitted by vegetation is generally described as biogenic volatile organic compounds (BVOC). The unsaturated nature of the BVOC molecules makes them highly reactive and, once emitted, susceptible to oxidation by hydroxyl, ozone and nitrate radicals. They, therefore, play a critical role for tropospheric chemistry (Atkinson 2000) and affect the atmospheric lifetime and concentration of, e.g., methane (CH_4) (Poisson *et al.* 2000). BVOC are also known precursors of secondary organic aerosols, with possibly large but highly uncertain effects on regional and global radiative forcing (Spracklen *et al.* 2008) and partaking in proposed vegetation–climate feedback mechanisms (Kulmala *et al.* 2004). Global BVOC emissions are dominated by isoprene (2-methyl-1,3-butadiene), which adds an estimated 500 Tg carbon (C) annually to the atmosphere (Guenther *et al.* 1995).

Isoprene emission capacity is not a general plant trait, but is highly species specific (Hewitt and Street 1992, Hanson *et al.* 1999). In boreal and subarctic peat-forming wetlands, it has been shown that key plant functional groups including sedges (*Eriophorum* sp. and *Carex* sp) and *Sphagnum* mosses can be substantial isoprene emitters (Haapanala *et al.* 2006, Hellén *et al.* 2006, Tiiva *et al.* 2007a, 2007b, 2008, Ekberg *et al.* 2009, Holst *et al.* 2010). This has not yet been considered in large scale emission models (Guenther *et al.* 2006).

In subarctic peatlands, Ekberg *et al.* (2009), and Holst *et al.* (2010) studied seasonally changing BVOC emissions and their ecophysiological controls, and Tiiva *et al.* (2007a, 2008) investigated how projected increases in UV-B radiation, temperature and litter addition influenced emissions of isoprene. But northern wetlands are also undergoing rapid changes in hydrology as a consequence of increasing mean annual temperature and changes in precipitation (Johansson *et al.* 2006). Enhanced evapotranspiration due to increasing temperatures may result in water table draw-down in boreal peatlands (Roulet *et al.* 1992). On the other hand, thawing permafrost in subarctic peatlands is currently causing a trend of increasing wetness, followed by shifts in dominating vegetation communities (Malmer *et al.* 2005). These contrasting responses stress the importance of complementing measurements of current emissions, and their short-term controls, with studies of how emissions respond to dynamic changes in ecosystem structure and function. Johansson *et al.* (2006), for instance, found that permafrost melt-related vegetation shifts seen in a subarctic peatland over the last three decades have resulted in both changes in the carbon dioxide (CO_2) and CH_4 exchange and increased net radiative forcing during that period. For the same study site, it has been suggested that enhanced emissions of total ecosystem non-methane hydrocarbons are a result of increased aerial extents of plant functional types (tall sedges) adapted to wet conditions (Bäckstrand *et al.* 2008a).

Sphagnum mosses are key components of peat-forming ecosystems and are extremely sensitive to the hydrological growth conditions. Typically, different species grow along distinct microtopographical moisture gradients (Clymo and Hayward 1982, Rydin 1993), which makes them vulnerable to changes in water table depth below the surface. Since roots, vascular tissue and stomata are lacking, water transport from the water table to the apical parts (capitula) takes place via capillary forces along the shoot. Densely growing hummock species are thus able to transport water more efficiently than species growing with a less compact carpet structure closer to the water table. There are few studies in the current literature reporting *Sphagnum* isoprene emissions from different microtopographical features, but Janson and De Serves (1998) and Janson *et al.* (1999) found higher emissions from wet flarks than from drier hummocks in a boreal peatland. Robroek *et al.* (2009) showed that the CO_2 assimilation of all investigated *Sphagnum* species occurring along a natural moisture gradient increased with capitula water content. In view of the climate change induced transitions in northern wetland hydrology, the main objective of this study was to investigate isoprene emission from *Sphagnum* species occupying different growth niches with respect to moisture. Two questions were posed: (1) How do different moisture levels (distance from moss surface to the water table) affect isoprene emission capacity from a common species, *S. balticum*, in its natural environment (field experiment)? (2) Does isoprene emission capacity from species adapted to growth at different levels above the water table (*S. magellanicum* and *S. rubellum*) differ when measured under similar, controlled moisture conditions (laboratory experiment)? In our field experiment 1, we expected that isoprene emissions would increase with moister growth conditions, particularly since *S. balticum* is considered to be a typical lawn species. In the laboratory experiment 2, the water table was held relatively close to the surface and we thus expected higher emissions from the species best adapted to moist growth conditions (*S. magellanicum*). A second objective of the study was to examine how short-term (i.e. 48 hours) temperature history affects isoprene emission from *Sphagnum* mosses. The average temperature of the days prior to measurement has been shown to influence isoprene emission from different vascular plants (Sharkey *et al*. 1999, Geron *et al*. 2000, Pétron *et al*. 2001, Ekberg *et al*. 2009), but has to our knowledge not been investigated for *Sphagnum*. In accordance with the previous findings for vascular plants, we expected generally higher instantaneous emission rates at higher temperatures. We also expected that the recent temperature history would be of importance, with emission capacities being larger when moving the experimental treatment from warm to cool conditions than from cool to warm.

Material and methods

Field experiments

Study site

The field experiments were carried out at Stordalen mire, 10 km east of the village of Abisko in northern Sweden (68°20´N, 19°03´E, 351 m above sea level; Ekberg *et al*. 2009). The region has a subarctic climate. Long-term annual mean temperature of –0.6 °C and 300 mm annual precipitation (period 1913 to 2000) were measured at the Abisko Scientific Research Station, www.ans.kiruna.se). With a mean temperature of –10.9 °C, January and February are the coldest months, and summer temperatures are modest with average maxima in July (mean temperature +11.6 °C). The growing season extends approximately from May to September. The microtopography, vegetation, moisture, and nutrient regimes on the mire reflect small-scale variation in the underlying discontinuous permafrost. So-called palsas (areas underlain by permafrost) are generally elevated, and therefore ombrotrophic and dominated by dwarf shrubs, *Eriophorum vaginatum*, *Sphagnum* sp. and other mosses and lichens. Flarks, wetter depressions on the mire, represent those areas that typically lack permafrost and, to variable extents, receive (sub-)surface water inflow from the surrounding mountains in addition to input from precipitation. These flarks are thus minerotrophic, and frequently have standing water. Their vegetation is dominated by tall graminoids (*Eriophorum* sp. and *Carex* sp.). Transitional microsites, intermediate between palsas and wet depressions occur where both water table and permafrost active layer thickness are highly variable. The vegetation in these locations mainly consists of *Sphagnum* sp., *Eriophorum* sp. and lower *Carex* sp. sedges (Malmer *et al*. 2005).

Experimental design

Six plots, each in two different subhabitats on the mire, were established in spring 2005. The plots consisted of 20 × 20 cm aluminium frames permanently inserted into the ground to a depth of 20 cm. The frames were equipped with water seal channels at the surface and were installed so that the vegetation on the ground covered was dominated by *Sphagnum balticum*. One subhabitat was located atop a hummock/palsa with some dwarf shrubs, *Eriophorum vaginatum* and lichens also present (Fig. 1). The second subhabitat was located in a lower lawn community where the only species present were *S. balticum* and scattered specimens of *Eriophorum angustifolium* (Fig. 1). The same *Sphagnum* species, *S. balticum*, grew in both habitats. Dorrepaal *et al*. (2003) found that changes in water supply to the capitula of *S. fuscum* can lead to changes in carpet bulk density, which implies that *Sphagnum* is able to adapt its morphology in the long term if exposed to altered moisture conditions. It has also been reported that precipitation alone may provide sufficient access of water to sustain growth of hollow species on hummocks (Robroek *et al*. 2007). Plant species cover in each individual plot was determined in the peak season in 2007 by a modified point intercept technique (Jonasson 1988) (Fig. 1). Contacts between plants and the tip of a narrow pin inserted into the vegetation were registered in an 81-point grid pattern of a 16 × 16 cm square (two cm between each point). 24-h accumulated precipitation was measured with a rain gauge

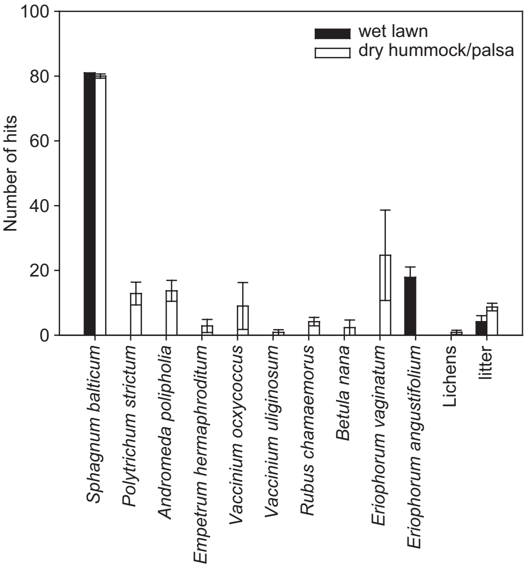

Fig. 1. Plant species composition in the wet lawn (black bars) and dry hummock/palsa (white bars) habitats. Number of hits represents the number of contacts between a species and the tip of a narrow pin inserted into the vegetation, from the top canopy down to the moss surface, in an 81-point grid pattern of a 16 × 16 cm square (two cm between each point). The measurements were carried out at a subarctic peatland (Stordalen) in northern Sweden. Error bars indicate standard errors.

at the meteorological station at Stordalen mire (Jackowicz-Korczyński *et al.* 2010). Perforated plastic tubes situated adjacent to each plot were used for manual measurements of water table depth relative to the moss surface. Active layer thickness was measured adjacent to each plot by inserting a steel rod into the ground to the depth of resistance. Precipitation, depth of the water table and active layer thickness were measured in 2007 only.

Isoprene sampling and analysis

One sampling campaign was carried out during the peak season (mid-June to early August) in 2006. In 2007, sampling took place early in the growing season (early to mid-June), during the peak season (mid-June to early August) and late in the season (mid-August to mid-September). Air sampling for the subsequent analysis of isoprene concentration was carried out using an 11-l (20 × 20 × 28 cm) chamber made of a stainless steel frame covered with 0.05 mm FEP (fluorinated ethylene propylene) film (Flurotek AB, Knivsta Sweden). The chamber was placed in the water-filled seal channel of the pre-installed frames during sampling. Air samples were collected following a 5-min flush period with inlet air provided by an oil-free compressor (Gardner Denver Sweden AB, Bandhagen, Sweden) filtered through a hydrocarbon trap equipped with MnO_2-coated copper nets to remove contaminants and ozone from the sample stream. The inlet flow rate was 5 l min^{-1}, giving an air residence time in the chamber of about 2 min. Subflows of air entering and exiting the chamber were collected onto preconditioned (280 °C, 15 min) dual bed stainless steel cartridges, 1/4 inch o.d. × 90 mm length, (Markes International Limited, Pontyclun, UK) packed with the adsorbents Tenax TA (porous organic polymer) and Carbograph 1TD (graphitized carbon black) using flow-controlled sampling pumps (Pocket Pump, SKC Ltd., Dorset, UK). The sampling flow rate was 220 ml min^{-1} and sample volumes varied between two and 4 l. Only PFA (per fluoro alkoxy) tubing (Swagelok, Solon, OH, USA) and PTFE (polytetrafluoroethylene) connectors and valves (Bohlender GmbH, Grünsfeld, Germany) were included in the sampling setup. Adsorbent cartridges were sealed with 1/4 inch brass long-term storage caps with PTFE ferrules and refrigerated until analysis within four weeks. Emission rates were determined as mass of emitted isoprene-C per ground surface area and time by taking all flow rates, sampling times and the difference in isoprene-C concentration between inlet and outlet samples into account. Chamber temperature and PAR (photosynthetically active radiation) were recorded by loggers (TinyView Plus, Gemini Data Loggers Ltd., Chichester, UK and LI-6400, LI-COR, Lincoln, NE, USA, respectively). For calculation of temperature history effects on emission rates measured, ambient temperatures from 2.5 m above ground, recorded at the mire's meteorological station, were used.

In the laboratory, sample cartridges underwent two stage automated thermal desorption (Turbomatrix ATD, PerkinElmer, Waltham, MA, USA). Cartridges were initially heated to 280 °C in a flow of purified helium for 10 minutes. Volatilised VOCs were cryo-focused downstream on a Tenax TA cold trap maintained at –30 °C. Secondary desorption took place as the cold trap was flash heated (40 °C sec^{-1}) to 300 °C, which was maintained for 6 minutes. Volatilised VOCs passed via a heated transfer line (200 °C) to a gas chromatograph (GC, Clarus 500, PerkinElmer, Waltham, MA, USA) equipped with a Al_2O_3/KCl PLOT column (25 m × 0.32 mm i.d., Varian, Middelburg, The Netherlands) and a flame ionisation detector (FID). An initial column temperature of 120 °C was maintained for 1 min before being increased to 165 °C at three °C min^{-1}, followed by an increase to 200 °C at 45 °C min^{-1}. This temperature was maintained for 10 min. Peak identification and quantification were achieved by comparison of GC-FID retention times and peak areas obtained from sample analysis, with those from a gaseous isoprene standard (one ppm, Linde Gas, AGA Gas AB, Malmö, Sweden).

It has been shown that temperature and PAR at the time of measurement are important determining factors for instantaneous isoprene emission from *Sphagnum* and that the frequently applied "G93" algorithm (Guenther *et al*. 1993, 1995) is well suited for calculation of emission capacities at standard conditions (Janson and De Serves 1998). Applying G93, isoprene emission rates were standardized ("basal rates") to a temperature of 20 °C and a PAR of 1000 μmol m^{-2} s^{-1} (I_{S20}), and expressed on ground surface area basis. We chose 20 °C as the reference temperature, as this is a typically-observed maximum air temperature during the summer months in the study area. Basal rates were also recalculated to 30 °C for reference to published literature that frequently uses this higher value. This is a purely numerical exercise for easier comparison between studies, but must be regarded with caution since we apply for this calculation the G93 temperature response well outside the range of the investigated *Sphagnum* species' growth environment. No measurements of actual leaf temperatures were conducted and chamber air temperature was used as an approximation of leaf temperature.

CO_2 exchange measurements

Each isoprene sampling occasion in 2007 was preceded by CO_2 exchange measurements. A closed static chamber technique was applied using an infrared gas analyzer (LI-6400, LI-COR, Lincoln, NE, USA) attached to a custom built transparent 9-l (21.5 × 21.5 × 20 cm) Lexan® chamber. The chamber was equipped with a fan in order to achieve mixing of the air during measurements, and with a 1-m pressure release tube to avoid over or under pressurization inside the chamber. The chamber was installed on the aluminium frames described above and recordings of NEE (net ecosystem CO_2 exchange) took place by logging the change in CO_2 concentration within the chamber every five seconds over a period of 3 min. Total ecosystem dark respiration was measured by the same procedure after darkening of the chamber. GPP (gross primary production) was calculated based on the difference between NEE and dark respiration. Chamber temperature and PAR were recorded as described above.

Laboratory experiments

Monolith collection and experimental setup

Seven peat monoliths were collected in aluminium containers (10.5 cm diameter and 40 cm deep) at Fäjemyr, a temperate ombrotrophic peat bog in southern Sweden (56°15´N, 13°3´E, 140 m above sea level) in October 2006. The long-term (1961–1990) annual mean temperature is 6.2 °C and annual precipitation is 700 mm. The mire's surface microtopography is characterized by hummock–lawn–hollow moisture gradients. The herbaceous vegetation on the drier parts consists of dwarf shrubs (*Calluna vulgaris*, *Erica tetralix*, *Vaccinium oxycoccus*, *Andromeda polifolia*, *Empetrum nigrum*), while the moss layer is dominated by *Sphagnum* mosses (*S. magellanicum*, *S. rubellum*, *S. tenellum*, *S. cuspidatum* and *S. fuscum*). Sedges (mainly *Eriophorum vaginatum*) are common, and there are scattered occurrences of small Scots pine trees (*Pinus sylvestris*). The ground was snow covered at the monolith sampling occasion which made identification of similar sample spots difficult. As a result, five of the monoliths represented *S. magellanicum* lawn communities and only two were taken from *S. rubellum*/*S. magellanicum* lawn–hummock communities. *S. rubellum* had a cover of at least 80% in the mixed monoliths. No vascular plants were present in the monoliths. The monoliths were transported to the laboratory in Lund within six hours and incubated in darkness at 5 °C for a period of 4 months. It has earlier been shown that such a period of vegetation dormancy is crucial for monoliths collected late in the growing season, or in winter, to reach a state similar to field peak-season conditions after acclimation to experimental conditions (Ström *et al.* 2003). The water table level was maintained at five cm below the moss surface in all monoliths throughout the experiment by adding deionized water when needed. At the end of January 2007, the monoliths were transferred to a controlled environment growth chamber (light, air temperature, relative humidity and temperature of the lowest 10 cm of the monoliths were controlled) (Controlled Environments Limited, Manitoba, Canada). A 14/10 hour light/dark cycle was applied where PAR was 55 μmol m^{-2} h^{-1} during both the initial and final two hours, and 1300 μmol m^{-2} h^{-1} during the rest of the light period. Over a two-month acclimation period, a time sufficient for the monolith vegetation to mature, air temperature was controlled at 15 °C and the air relative humidity at 60%. The lowest 10 cm of the monoliths were cooled by maintaining the media surrounding the aluminium containers (glycol) at a temperature of 5 °C.

Temperature treatment and isoprene emission measurements

From the initial 15 °C, growth chamber temperature was increased in steps of 5 °C to a maximum temperature of 30 °C, and thereafter decreased in two steps, from 30 to 20 °C and from 20 to 15 °C. Measurements of isoprene emission from the *Sphagnum* monoliths were conducted 48 h after the respective temperature changes, before the next temperature change was initiated. Enclosures for air sampling and analysis consisted of 3-l Teflon bags attached to the monolith aluminium containers. Isoprene emissions were measured online by connecting the air flow from the enclosures to a proton transfer reaction mass spectrometer (PTR-MS; Ionicon GmbH, Innsbruck, Austria). The drift tube E/N (electric field within the drift tube/number of molecules per volume) was maintained at 130 Td (Townsend) by keeping drift tube voltage, temperature and pressure at 600 V, 60 °C, and 2.2 mbar, respectively. Inlet air was filtered through a hydrocarbon trap equipped with MnO_2-coated copper nets to remove contaminants and ozone from the sample stream and the flow rate through the enclosure was 460 ml min^{-1}. A subflow (200 ml min^{-1}) of the air exiting the enclosure was fed to the PTR-MS via a 3-m-long PFA tubing (1/8 inch o.d.). Isoprene was detected as mass 69. After the experiment, the PTR-MS was calibrated against a diluted gas standard mixture (Ionimed, Innsbruck, Austria) under the same drift tube settings as above. Based on repeated calibrations, transmission coefficients were recalculated. When applying the new transmission coefficients, the uncertainty of measured concentrations, compared with the concentration of the gas standard, was about 14% for isoprene. This uncertainty was derived from the standard deviation (1 σ) of single calibrations, and reflected the certified concentration of the gas standard (5% uncertainty) and performance variations of the flow controller used for dilution.

Statistical analyses

Statistical analyses were performed using SPSS 12.0.1 for Windows (SPSS Inc., Chicago, IL, USA). P values smaller than 0.05 were considered statistically significant. Habitat differences in I_{S20} and GPP measured in the field were tested using a Mann-Whitney U-test. Multiple linear regression was used to analyse the relationship between I_{S20}, temperature history of the previous 48 hours (T_{48}) and GPP. Data were log-transformed where appropriate to achieve a normal distribution. In the laboratory monolith experiments, tests for differences in emissions at different temperatures were performed for *S.*

magellanicum monoliths only. Multiple measurements were performed at 15 °C and 20 °C and, to be able to pool data, potential differences in emission within these temperature steps were analysed by a Wilcoxon signed rank test and a Friedman test, respectively. Overall temperature effects were then analysed by a Friedman test on the data pooled to represent the four temperature steps (15, 20, 25 and 30 °C) followed by a post-hoc Wilcoxon signed rank test with a Bonferroni significance correction to compensate for multiple comparisons ($p < 0.008$ were considered statistically significant). Species differences in emission were tested with a Mann-Whitney *U*-test using pooled data from measurements performed at 15 °C and 20 °C.

Results

Moisture effects on isoprene emission from the same species (field experiment)

The water-table depth below the moss surface increased with active layer thickness in both the wet and dry habitats until late July 2007 (Fig. 2). In response to a period of frequent rain, the water table rose gradually thereafter towards the surface in the wet habitat, but continued to decrease to lower levels in the dry habitat (Fig. 2). Maximum water table depths below the moss surface were 16.4 ± 1.7 (SE) cm in the wet habitat and 19.4 ± 0.7 cm in the dry habitat. However, the actual moss moisture contents at the two study sites are not adequately reflected solely by the water table depths. The *Sphagnum* shoot length in the wet habitat was approximately 30 cm (top 8–10 cm were green), while the shoot length in the dry habitat was 5–10 cm (top 2–4 cm were green). Since *Sphagnum* mosses supply the photosynthesizing top parts (capitula) of the shoots with water via capillary forces along the full length of the shoots, there was a continuously available water supply in the wet habitat, while the moss carpet in the dry habitat lost contact with the water table once it fell below 10 cm.

The observed peak-season wet and dry habitat basal isoprene emissions (I_{S20}, emissions standardized to 20 °C and PAR 1000 μmol m^{-2} s^{-1}) differed significantly in 2006 (Table 1 and Fig. 3). In 2007, habitat emission capacities were significantly different in the early season only (Table 1 and Fig. 3). A statistically significant difference in microsite GPP was found for the 2007 peak season only (Table 1 and Fig. 3). Temperature history of the previous 48 h (T_{48}) and GPP together explained 78.0% (r^2 = 78.0, p = 0.001) of the I_{S20} variation in the wet habitat and 80.0% ($r^2 = 0.80$, $p = 0.001$) of the variation in the dry habitat (Fig. 4 and Table 2).

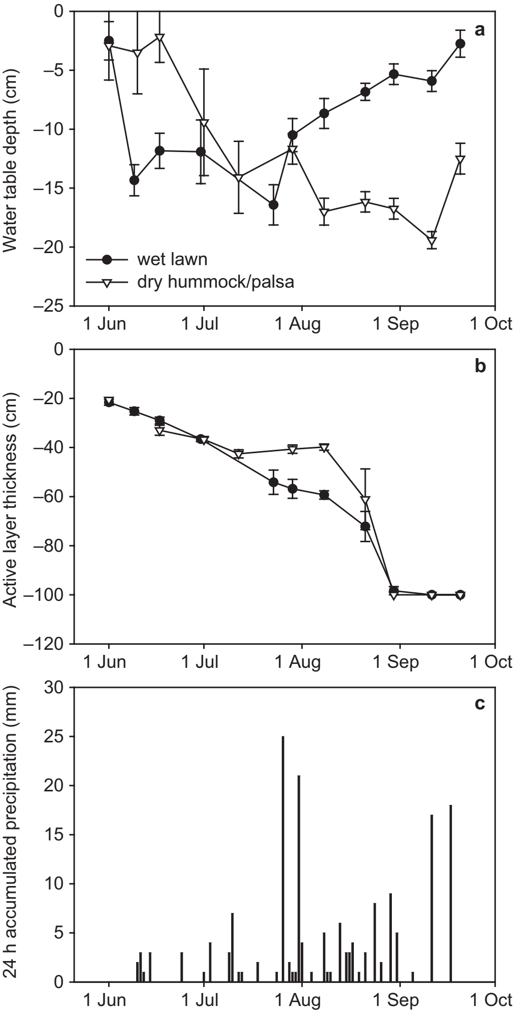

Fig. 2. (**a**) Water table depth below the moss surface, (**b**) active layer thickness, and (**c**) 24-hour accumulated precipitation in 2007. Closed circles represent the wet lawn habitat and open triangles the dry hummock/palsa habitat. The measurements were carried out at a subarctic peatland (Stordalen) in northern Sweden. Error bars indicate standard errors.

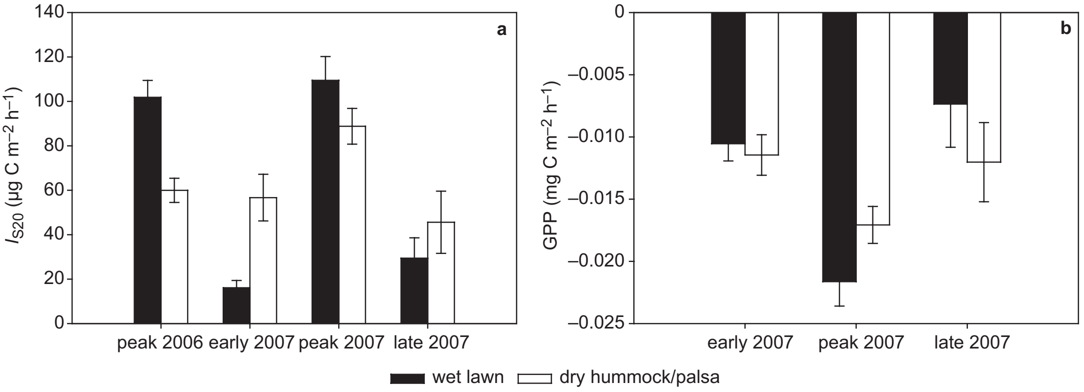

Fig. 3. (**a**) Isoprene emission capacity (I_{S20}, emissions standardized to common temperature 20 °C and PAR 1000 µmol m^{-2} s^{-1}, Guenther *et al.* 1993) from the wet lawn habitat (black bars) and dry hummock/palsa habitat (white bars) in the peak season in 2006 and in the early, peak and late seasons in 2007. (**b**) Gross primary production (GPP) in the wet lawn habitat (black bars) and dry hummock/palsa habitat (white bars) in the early, peak and late seasons in 2007. The measurements were carried out at a subarctic peatland (Stordalen) in northern Sweden. Error bars indicate standard errors.

Species and temperature effects on isoprene emission (laboratory experiment).

Emission rates at 15 °C and 20 °C were measured during the temperature increase phase of the experiment (going from 15 °C to 30 °C) as well as during the temperature decrease phase (going from 30 °C to 15 °C) and the measurements were repeated two and three times, respectively. No statistically significant differences in emissions between those temperature steps were detected, therefore the emission rates were subsequently pooled to represent each individual temperature level. The isoprene emission rates (expressed on *Sphagnum* dry-weight basis; average shoot densities were 37.5 mg cm^{-2} and 23.1 mg cm^{-2} for *S. magellanicum* and *S. rubellum*, respectively) at each investigated temperature were for *S. magellanicum* 2.0 ± 0.15 (15 °C), 1.9 ± 0.11 (20 °C), 2.3 ± 0.18 (25 °C) and 2.9 ± 0.27 (30 °C) ng C g^{-1} h^{-1}, and for *S. rubellum* 10.8 ± 2.0 (15 °C), 16.3 ± 3.0 (20 °C), 12.3 ± 0.37 (25 °C) and 60.2 ± 18.0 (30 °C) ng C g^{-1} h^{-1} (Fig. 5). Species differences in the isoprene emission were tested by using the

Table 1. Average seasonal isoprene emissions (µg C m^{-2} h^{-1} ± SE) standardized to PAR 1000 µmol m^{-2} s^{-1} and 20 °C (I_{S20}) and 30 °C (I_{S30}), and gross primary production (GPP) (mg C m^{-2} h^{-1} ± SE) in 2006 and 2007. The statistics show the results of a Mann-Whitney *U*-test for differences between the wet and dry habitats. n.s. = non significant.

Year season	I_{S20}		I_{S30}		Statistics for I_{S20}	GPP		Statistics for GPP
	wet	dry	wet	dry		wet	dry	
2006								
peak	101.8 ± 7.6	60.0 ± 5.4	365.4 ± 22.1	203.4 ± 14.3	$Z = -5.6$			
	$n = 74$	$n = 72$	$n = 74$	$n = 72$	$p < 0.001$			
2007								
early	16.1 ± 3.3	55.3 ± 10.0	58.3 ± 11.8	210.8 ± 36.3	$Z = -3.2$	–126.6 ± 11.2	–132.0 ± 13.4	n.s.
	$n = 18$	$n = 19$	$n = 18$	$n = 19$	$p = 0.001$			
peak	109.4 ± 10.7	88.8 ± 8.0	396.9 ± 38.9	321.6 ± 29.1	n.s.	–257.0 ± 14.2	–204.9 ± 15.5	$Z = -2.4$
	$n = 23$	$n = 24$	$n = 23$	$n = 24$				$p = 0.015$
late	29.4 ± 9.2	45.6 ± 14.0	95.8 ± 33.2	170.3 ± 50.6	n.s.	–139.3 ± 16.8	–144.7 ± 18.1	n.s.
	$n = 21$	$n = 22$	$n = 21$	$n = 22$				

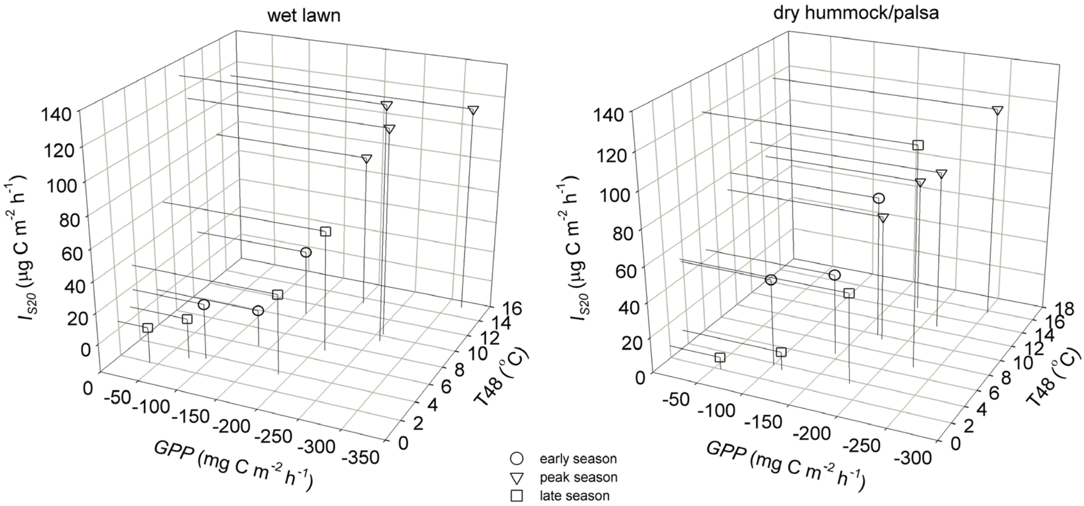

Fig. 4. Isoprene emission capacity (I_{S20}, emissions standardized to common temperature 20 °C and PAR 1000 µmol m^{-2} s^{-1}, Guenther *et al.* 1993) (**a**) plotted against gross primary production (GPP) and average temperature of the 48 hours prior to the measurements in the wet lawn habitat, and (**b**) in the dry hummock/palsa habitat in the early (circles), peak (triangles) and late (squares) seasons in 2007. The measurements were carried out at a subarctic peatland (Stordalen) in northern Sweden.

pooled data from measurements performed at 15 °C and 20 °C. The species-specific emissions rates were significantly different at both temperatures (Mann-Whitney *U*-test: higher emissions from *S. rubellum* monoliths, $n_{S.magellanicum} = 9$, $n_{S.rubellum} = 4$, $Z = -2.8$, $p = 0.005$ at 15 °C and $n_{S.magellanicum} = 14$, $n_{S.rubellum} = 6$, $Z = -3.5$, $p = 0.001$ at 20 °C).

Differences in the actual isoprene emission rates between applied experimental temperatures were analysed for the *S. magellanicum* monoliths only because of poor replication of the *S. rubellum* monoliths. The overall temperature effect on the emission rates from *S. magellanicum* was investigated for the temperatures 15, 20, 25 and 30 °C. A significant general temperature effect was found (Friedman test: $n = 5$, $\chi^2 = 10.2$, $p = 0.017$), but due to the conservative *p* value (0.008) applied after Bonferroni correction of the posthoc *p* values, no significant differences in the emission rates were detected between any of the analysed temperature steps.

Discussion

Moisture effects

Water availability is an important determining factor for *Sphagnum* isoprene emission capacity. But contrary to our expectations, we did not find consistently higher isoprene emissions from the wet habitat even though there was a tendency towards higher emission capacities in the peak

Table 2. Results of the regression modelling used to analyse the relationship between isoprene emissions standardized to PAR 1000 µmol m^{-2} s^{-1} and 20 °C (I_{S20}), temperature history of the previous 48 hours (T_{48}) and gross primary production (GPP) in the wet lawn and dry hummock/palsa habitats. Function: Y = constant + b_1X_1 + b_2X_2. numbers within brackets indicate standard errors.

Habitat	df	*F*	*p*	r^2	Constant	Coefficients	
						GPP	T_{48}
Wet	2	18.3	0.001	0.78	–35.5	–0.49 (0.14)	0.41 (2.75)
Dry	2	21.2	0.001	0.8	–30.1	–0.53 (0.14)	1.13 (1.68)

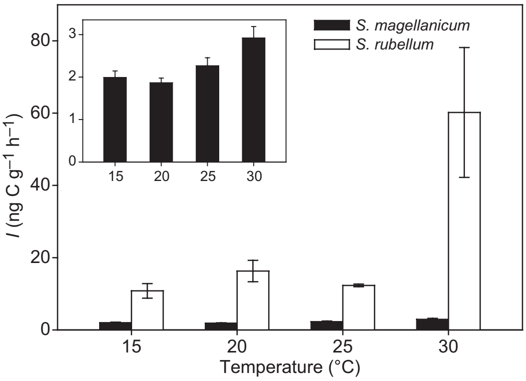

Fig. 5. Average isoprene emissions from *Sphagnum magellanicum* (black bars) and *Sphagnum rubbellum/Sphagnum magellanicum* (at least 80% cover of *S. rubellum*, open bars) monoliths in response to different temperatures. The small inset bar graph shows the enhanced emissions from the *S. magellanicum* monliths. The monoliths were collected at a temperate peat bog (Fäjemyr) in southern Sweden. Error bars indicate standard errors.

season (significant in 2006, non-significant in 2007). Early and late in the season, the trend was the opposite with higher emission capacities in the dry habitat (significant in the early season, non-significant in the late season).

Janson and De Serves (1998) reported average June–August standardized *Sphagnum* isoprene emission rates (30 °C and PAR 1000 μmol m^{-2} s^{-1}) from two southern boreal Scandinavian fens of 18 μg C m^{-2} h^{-1} (dry hummock) and 624 μg C m^{-2} h^{-1} (wet flark). The average (2006–2007) peak-season emission capacity (30 °C and PAR 1000 μmol m^{-2} s^{-1}) measured in the field in our study was about half the value in the wet habitat (381 μg C m^{-2} h^{-1}, Table 1), but an order of magnitude higher than in the dry habitat (263 μg C m^{-2} h^{-1}, Table 1). This implies that *Sphagnum* emission capacities in high-latitude regions may be comparable to those reported for warmer environments, but that emissions are strongly limited by water availability.

The substantial seasonal variation remaining after normalization of emissions to common temperature and PAR is likely due to factors like average temperature of the previous few days, variation in photosynthesis rates (Bäckstrand *et al*. 2008b) or different stages of plant development early and late in the growing season (Gaberščik and Martinčič 1987). With field measurements, it is often difficult to separate these effects from each other. For instance, to avoid confounding effects of seasonally changing developmental stages and temperature history effects, the time period for which such a temperature effect is investigated should not be too long. A 48-hour average (T_{48}) has earlier been found suitable for sedges at our subarctic study site (Ekberg *et al*. 2009), which should also implicitly include effects of varying radiation, since temperature and radiation are strongly correlated. We applied a similar averaging time period for the *Sphagnum* species in this study.

It has been observed for a range of vascular plant species that isoprene emission capacity of mature leaves correlates with the average temperature of the few preceeding days (Ekberg *et al*. 2009, Geron *et al*. 2000, Pétron *et al*. 2001, Sharkey *et al*. 1999). Temperature history effects on isoprene emission capacity from mature poplar leaves have been suggested to result from the influence on both the enzyme isoprene synthase and on substrate (DMAPP, dimethylallyl diphosphate) supply (Wiberley *et al*. 2008). Photosynthesis (measured as GPP in this study) provides precursors and energy needed for the isoprene synthesis and, together with T_{48}, explained 80% of the variation in isoprene emissions remaining after standardization to common temperature and PAR. Coinciding with the higher wet habitat isoprene emission capacities in the peak season, there was a significant difference in GPP between habitats in the 2007 peak season (not measured in 2006) (Table 1). Robroek *et al*. (2009) showed that water availability plays a vital role for CO$_2$ assimilation in all *Sphagnum* species, irrespective of the hummock–hollow moisture gradient niche separation. During the early and late parts of the season, when no habitat differences in GPP appeared, isoprene emission capacities tended to be higher in the dry habitat (Table 1). We thus suggest that the impact of temperature history on isoprene emission capacity was more pronounced in time periods, or during growth conditions, when GPP was suppressed. This underlines the important and shared roles of photosynthesis and temperature history as controlling factors for *Sphagnum* isoprene emission capacity.

Based on the chamber data, Bäckstrand *et al.* (2008a) found a general relationship between net ecosystem CO_2 exchange (NEE) and non-methane hydrocarbon emissions at Stordalen mire. Tiiva *et al.* (2007b) found that isoprene emissions from boreal peat microcosms were related to the number of *Eriophorum* leaves present. The presence of *Eriophorum* leaves in our experimental plots was similarly likely to contribute to measured isoprene emission rates as well as to GPP. With our chamber measurements, the relative contribution of sedge and moss emissions can not be separated. *Eriophorum* leaf densities, however, were similar in both habitats, and thus this species' influence on the functional relationship between I_{S20}, GPP and T_{48} likely did not differ between habitats. Our emission measurements were mostly carried out over the course of the same day in both habitats, and hence similar T_{48} history (measured at 2.5 m above ground) are inherent in the data. However, it is possible that moss surface temperatures were higher in the dry habitat due to less evaporative cooling than in the wet habitat.

Species and temperature effects

In the laboratory monolith experiment, the aim was to investigate how changes in water availability, as one plausible effect of permafrost thawing at the subarctic Stordalen peatland (Malmer *et al.* 2005), would influence species-specific *Sphagnum* isoprene emission. The water table in all monoliths was maintained at a level typical for *Sphagnum* lawn communities. We expected that the species naturally occurring in such microhabitats (*S. magellanicum*) would perform better, and have higher isoprene emissions, than the species adapted to growth in hummocks (*S. rubellum*). However, we observed the opposite, with higher isoprene emission rates from monoliths dominated by *S. rubellum* at both investigated temperatures (15 °C and 20 °C). Assuming no differences in evaporative cooling of the moss carpet surfaces, these data suggest that the hummock species *S. rubellum* has a higher potential for isoprene emission in growth environments where no moisture limitations exist, possibly due to the link between *Sphagnum* photosynthetic performance and water availability (Robroek *et al.* 2009). This implies that short-term increases in wetness of microhabitats that are dominated by *Sphagnum* hummock communities may enhance total ecosystem isoprene emissions, but this picture only holds before species better adapted to high water tables are established.

Once high-temperature induction of elevated isoprene production has occurred, emission capacity may remain high even when the plants are again exposed to lower temperatures (Wiberley *et al.* 2008). In our controlled environment experiment, the *Sphagnum* monoliths were exposed to a period of temperature increase from 15 °C to 30 °C (in steps of 5 °C), followed thereafter by a period of gradually lower temperatures from 30 °C to 15 °C. Multiple measurements from both the temperature increase and decrease phases were carried out at 15 °C and 20 °C. Contrary to our expectation, high-temperature (30 °C) induction did not lead to increased emissions at those lower temperatures during the subsequent temperature decrease phase. We can only speculate about the explanation of this result, but a possible reason may be that temperature history effects on *Sphagnum* isoprene emission is partly masked by the influence of photosynthesis when no moisture limitation exists. We did, however, find a generally positive correlation between isoprene emission and temperature in *S. magellanicum* when analysing the pooled data.

Summary

Our results indicate that the dependence on moisture was linked to photosynthetic performance of the mosses and that emission capacity was higher for the investigated hummock species than for the species typically growing in lawn communities when no moisture limitation existed. In the peak season, when hummocks were relatively dry, highest emission capacities, as well as highest photosynthetic rates, were found in the wettest habitat. In the early and late seasons, when no differences in photosynthesis were detected, a tendency towards higher emission capacity in the dry habitat was found. We can only speculate about reasons for this variation over the season, but suggest that the effect of temperature history became more pronounced in periods when the environmental conditions for photosynthesis were not optimal.

Although there was a clear positive correlation between temperature and isoprene emission in the laboratory monolith experiment, we did not find any significant effects of 48-hour temperature history when the water table was maintained at a non-limiting level. Under such environmental conditions, we suggest that the effect of the average temperature of the days prior to the measurement may be masked by the controlling influence of photosynthesis.

Peat-forming wetlands are extremely sensitive to changes in hydrology that affect ecosystem structure as well as function by its influence on microtopographical features, species composition and trace-gas exchange. In this study, we have shown that complex feedback mechanisms exist between isoprene emission capacity, *Sphagnum* species composition, water availability and temperature. In order to fully assess the consequences of this for total ecosystem isoprene emission in peatlands subjected to climate change, further studies and incorporation of results into emission models are needed.

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