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Isoprene emission from wetland sedges

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Abstract. High latitude wetlands play an important role for the surface-atmosphere exchange of carbon dioxide (CO_2) and methane (CH_4), but fluxes of biogenic volatile organic compounds (BVOC) in these ecosystems have to date not been extensively studied. This is despite BVOC representing a measurable proportion of the total gaseous C fluxes at northern locations and in the face of the high temperature sensitivity of these systems that requires a much improved process understanding to interpret and project possible changes in response to climate warming. We measured emission of isoprene and photosynthetic gas exchange over two growing seasons (2005–2006) in a subarctic wetland in northern Sweden with the objective to identify the physiological and environmental controls of these fluxes on the leaf scale. The sedge species *Eriophorum angustifolium* and *Carex rostrata* were both emitters of isoprene. Springtime emissions were first detected after an accumulated diurnal mean temperature above 0°C of about 100 degree days. Maximum measured growing season standardized (basal) emission rates (20°C, 1000 μmol m^{-2} s^{-1}) were 1075 (2005) and 1118 (2006) μg C m^{-2} (leaf area) h^{-1} in *E. angustifolium*, and 489 (2005) and 396 (2006) μg C m^{-2} h^{-1} in *C. rostrata*. Over the growing season, basal isoprene emission varied in response to the temperature history of the last 48 h. Seasonal basal isoprene emission rates decreased with leaf nitrogen (N), which may be explained by the typical growth and resource allocation pattern of clonal sedges as the leaves age. The observations were used to model emissions over the growing season, accounting for effects of temperature history, links to leaf assimilation rate and the light and temperature dependencies of the cold-adapted sedges.

1 Introduction

High-latitude wetlands are important sinks for carbon dioxide (CO_2) (Frolking and Roulet, 2007) and sources of methane (CH_4) (Christensen et al., 2004; Pelletier et al., 2007; Svensson and Rosswall, 1984), but belong to the least studied ecosystems with respect to emissions of other gaseous reduced hydrocarbons that are generally summarized as biogenic volatile organic compounds (BVOC) (Hellén et al., 2006; Janson and De Serves, 1998; Janson et al., 1999; Tiiva et al., 2007). The unsaturated BVOCs exhibit high reactivity towards the hydroxyl radical, as well as to ozone and nitrate radicals and therefore play a critical role for local tropospheric chemistry (Atkinson, 2000) as well as, for instance, having effects on the atmospheric lifetime and concentrations of CH_4 (Poisson et al., 2000). A better understanding of the amount and seasonality of northern ecosystem BVOC emissions is also necessary to quantify their role for the production and growth of secondary organic aerosols (Kulmala et al., 2004; Tunved et al., 2006) or the possible contribution of their oxidation products to atmospheric chemistry in remote regions.

Isoprene (2-methyl-1,3-butadiene) dominates global emissions of BVOC, adding an estimated 500 Tg carbon (C) annually to the atmosphere (Guenther et al., 1995). Maximum light-saturated leaf isoprene emission rates often occur at 40 to 45°C (Monson et al., 1992; Zimmer et al., 2002) and many of the identified high-emitting species are found in temperate to tropical regions. Global isoprene emissions hence are dominated by contributions from tropical regions (Guenther et al., 2006). Emissions from northern regions are expected to be relatively small, largely a result of short cool summers, but atmospheric reactions such as aerosol growth or ozone destruction/formation are regional rather than global processes (Tunved et al., 2006; Herring et al., 1997). Isoprene is

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noted as aerosol pre-cursor (Claeys et al., 2004) although a quantitative link between field observation of nordic ecosystem isoprene flux and aerosol nucleation, number concentrations or mass has not yet been attempted. Moreover, relative to total ecosystem C exchange, emissions from high-latitude ecosystems can still be substantial (Bäckstrand et al., 2008). BVOCs are thus likely to play an important, but as yet unquantified role in the complex relationship between northern ecosystem C flux, atmospheric chemistry, and climate.

It has been shown that *Eriophorum angustifolium* Honck. and *Carex rostrata* Stokes, two dominant sedges that are frequently found in temperate to subarctic wetlands, are key species influencing C cycling and CH_4 exchange in northern wetland ecosystems (Johansson et al., 2006; Öquist and Svensson, 2002; Ström et al., 2005). They are therefore relevant to study also with respect to their BVOC emissions. Enclosure studies of vegetation, mosses, and peat in boreal mire ecosystems have demonstrated that plant communities containing *Eriophorum* sp. and *Carex* sp. emit significant amounts of isoprene (Hellén et al., 2006; Rinnan et al., 2005), but very little is known about the physiological and environmental regulations of these fluxes in colder, for example subarctic environments and about the seasonal variation on leaf rather than microcosm scale. Many plant species in these ecosystems prevail at the northernmost limits of their existence and even small changes in, for example, temperature and hydrology may severely influence vegetation composition and thus biosphere-atmosphere interactions and trace gas fluxes. Our study site, Stordalen mire in northern Sweden, has over the last 30 years undergone a documented change in hydrology due to collapse of the underlying permafrost (Johansson et al., 2006; Malmer et al., 2005). This has led to an increase in the areal extent of wetter habitats dominated by tall sedge species which is estimated to have caused increased emissions of CH_4 and BVOC (Bäckstrand et al., 2008; Johansson et al., 2006) but specific information on the latter has so far not been available.

Several studies have shown that isoprene emission from woody species is linked – at least to some degree – to photosynthesis, which results from supply of substrate for isoprene synthesis (Delwiche and Sharkey, 1993; Karl et al., 2002; Kuhn et al., 2004; Sanadze et al., 1972), or supply of phosphorylation energy (ATP) and reducing power (NADPH) (Loreto and Sharkey, 1990, 1993; Possell et al., 2004). In sedges, however, we are not aware of any study that attempted to quantify the relationship between photosynthesis and isoprene emission on the leaf scale. Our objectives therefore were to (i) quantify for the first time the variation in leaf level isoprene emission from the sedges *E. angustifolium* and *C. rostrata*, as representative species in high-latidude wetlands and (ii) to investigate the seasonal variation of emissions in relation to net assimilation, photosynthetic capacity, and environmental variables. The data were also used to compare two models in terms of their capacity to reproduce the diurnal and seasonal variation of leaf isoprene emission,

and to estimate the seasonal totals. Our study was carried out in a subarctic wetland where summer daytime temperatures rarely exceed 20°C. Studies of BVOC emissions from non-woody vegetation adapted to such cold environments are scarce, and our third objective was thus to qualitatively investigate whether other volatiles (e.g., monoterpenes) would also be emitted from the studied sedges.

2 Materials and methods

2.1 Study site

Stordalen mire is situated 10 km east of the village of Abisko in northern Sweden (68° 20′ N, 19° 03′ E) at 351 m above sea level. The climate is subarctic with a long-term annual mean temperature of −0.6°C and 300 mm accumulated precipitation (period 1913 to 2000, data from Abisko Scientific Research Station, www.ans.kiruna.se). January and February are the coldest months (mean temperature −10.9°C) and July the warmest (mean temperature +11.6°C). The four-months growing season of most vascular plants in the area (May to September), approximately corresponds to the time period when diurnal mean temperatures are above 0°C and the soil is mostly snow-free. Stordalen mire is underlain by discontinuous permafrost which shapes its microtopography, vegetation communities, moisture, and nutrient regimes. Areas underlain by permafrost are generally elevated and therefore ombrotrophic and dominated by dwarf shrubs, *Eriophorum vaginatum*, mosses, and lichens. The remaining parts of the mire are typically wetter depressions that lack permafrost and, to variable extents, receive a flow of water from the surrounding drainage area in addition to the input from precipitation. The vegetation in these minerotrophic areas with frequently standing water is dominated by tall graminoids (*Eriophorum* sp. and *Carex* sp.) (Malmer et al., 2005).

2.2 Photosynthetic gas exchange

During three field campaigns each from early June to early September in 2005 and 2006, respectively, measurements of leaf net C assimilation (*A*) and sampling for isoprene emission from *E. angustifolium* and *C. rostrata*, which dominate the wetter parts of Stordalen mire were conducted approximately fortnightly. Photosynthesis measurements were made with a portable, infra-red gas analyzer, open gas exchange system equipped with a CO_2 injector and a red-blue LED light source (LI-6400, LI-COR, Lincoln, NE, USA). A part of a randomly selected leaf (leaf length <50 cm) was enclosed in the 6 cm^2 leaf chamber at a distance of 20–30 cm below the leaf tip at chamber conditions of 380 ppm CO_2 (C_a) and photosynthetically active radiation (PAR) 1000 μmol m^{-2} s^{-1}. Leaf temperatures were held constant at the estimated mean ambient temperature over the duration of each photosynthesis measurement/isoprene sampling period (see below). Because of total enclosure times in the order of

5–6 h, during which time ambient temperature could change substantially (± 5–$10°C$), we considered it more reliable to keep the temperature inside the leaf cuvette constant instead of continuously changing it according to ambient conditions. A flow rate of $500 \, \mu mol \, s^{-1}$ was applied. Measurements of the relationship between A and intercellular CO_2 concentration (C_i) followed directly after each isoprene sampling occasion. Leaf temperatures were maintained as described above and chamber relative humidity was controlled at ambient levels by using a set point achieved from an external logger. A-C_i responses were measured at saturating PAR (A_{sat} is photosynthesis rate at $1000 \, \mu mol \, m^{-2} \, s^{-1}$) and at reference C_a values ranging from 50 to 1800 ppm CO_2, performed at 10 to 12 steps within that interval (Ainsworth et al., 2002; Long and Bernacchi, 2003) . Throughout all field campaigns, the slope of measured A-Q curves (measured at every sampling occasion) was approaching 0 at PAR 600–$800 \, \mu mol \, m^{-2} \, s^{-1}$. Each stepwise recording was carried out at stable A (standard deviation $<0.5 \, \mu mol \, m^{-2} \, s^{-1}$) and was completed within two to three minutes.

2.3 Leaf isoprene emission

Sampling of chamber air for subsequent analysis of isoprene concentration was done in conjunction with the photosynthesis measurements. Air samples were taken following a leaf acclimation period of one hour post-enclosure to avoid sampling of any stress-related VOC emissions. Chamber conditions were maintained as described above. Chamber inlet air was filtered through a hydrocarbon trap equipped with MnO_2-coated copper nets to remove contaminants and ozone from the sample stream. The inlet flow ($500 \, \mu mol \, s^{-1}$) was controlled by the photosynthesis system. A subflow of the air exiting the leaf chamber was trapped onto dual bed stainless steel cartridges, quarter inch o.d. $\times 90$ mm length, (Markes International Limited, Pontyclun, UK) packed with the adsorbents Tenax TA (porous organic polymer) and Carbograph 1TD (graphitized carbon black). Graphitized carbon black adsorbents have been shown to enable quantitative sampling of isoprene (Brancaleoni et al., 1999; Dettmer et al., 2000; Dettmer and Engewald, 2002; Komenda et al., 2003). Two to three duplicate samples from one leaf were collected between 11:00 and 14:00 using flow-controlled sampling pumps. Due to logistical limitations, daily isoprene sampling combined with measurements of photosynthetic capacity (A-C_i and A-Q curves) could be conducted on one leaf in the sedge clone per day. Flow rates were $220 \, ml \, min^{-1}$ and sample volumes varied between 9 and 13 litres. Empty chamber blanks (incoming air circulated through the LI-6400 system) were sampled under the same environmental conditions to account for background contamination. Adsorbent cartridges were sealed with quarter inch brass long-term storage caps with PTFE ferrules and stored at $4°C$ until analysis within four weeks.

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 min. 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 ($40°C \, s^{-1}$) to $300°C$, which was maintained for 6 min. 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 $\times 0.32$ 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 $3°C \, min^{-1}$, 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 (1 ppm, Linde Gas, AGA Gas AB, Malmö, Sweden).

In order to facilitate identification of compounds other than isoprene, selected samples collected throughout the growing seasons were analysed using a HP 5890 GC equipped with a HP-1 column (60 m $\times 0.25$ mm i.d.) and a mass selective (MS) detector (HP-5972, Hewlett-Packard, USA). Peak quantification were performed using liquid standards in methanol solutions.

To test the effect of temperature history on basal isoprene emission rates, emissions from both *E. angustifolium* and *C. rostrata* were correlated with average ambient air temperature for the previous 0–96 h. Exponential regressions (fitted lines were $f = ae^{bx}$) and correlation coefficients were calculated using SigmaPlot 9.0 (Systat Software, Inc)

On one occasion, isoprene emission from *E. angustifolium* leaves was measured online in the field by connecting the air flow from the leaf chamber directly to a proton transfer reaction mass spectrometer (PTR-MS; Ionicon GmbH, Innsbruck, Austria). The drift tube E/N was maintained at 130 Td by keeping drift tube voltage, temperature and pressure at 600 V, $60°C$, and 2.2 mbar, respectively. The same photosynthesis system as described above was used for leaf enclosure, monitoring of A and control of chamber environmental conditions. Inlet air was filtered as above and the flow rate through the leaf chamber was $500 \, \mu mol \, s^{-1}$. Chamber CO_2 concentration was set to 380 ppm, PAR automatically tracked outside light intensity (monitored by an external quantum sensor; LI-COR, Lincoln, NE, USA), and chamber temperature tracked ambient conditions by continuous manual control of the IRGA sensor head block temperature. A subflow ($200 \, ml \, min^{-1}$) of the air exiting the leaf chamber was fed to the PTR-MS via a 10 m length of PFA (Per Fluoro Alkoxy) tubing (one eigth inch o.d.). Isoprene was detected as mass 69. After the field season, the PTR-MS was calibrated in the laboratory 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 could likely be derived from the standard deviation (1 sigma) of single calibrations, the certified concentration of the gas standard (5%) and performance variations of the flow controller used for dilution. For investigation of relationships between isoprene emission and leaf temperature, PAR, and A, respectively, data points from each temperature step (constant IRGA block temperature) were pooled and averaged. During the first 90 min of the experiment, temperature control was carried out by changing leaf temperature instead of block temperature, leading to slow stabilization of chamber conditions. These data points have been excluded from the reported results. Technical difficulties with the PTR-MS, unfortunately prevented the continuation of the experiment beyond one afternoon.

2.4 Leaf nitrogen analysis

Total N contents (mg g^{-1}) of dried (70°C, 24 h) leaves were determined by elemental analysis (Elemental Combustion System 4010, Costech Instruments, Cernusco, Italy) and expressed on leaf dry weight biomass basis.

2.5 Calculation of leaf photosynthesis parameters $V_{\max 20}$, $J_{\max 20}$ and R_{d20}

Data from the A-C_i curves were used to estimate the maximum rate of ribulose-1,5-biphosphate (RuBP)-saturated carboxylation ($V_{\max 20}$), the maximum rate of electron transport contributing to RuBP regeneration at saturating PAR ($J_{\max 20}$), and the daytime leaf respiration rate resulting from processes other than photorespiration (R$_{d20}$), all expressed to a standard temperature of 20°C with:

$$A = \min\{A_c A_q\} - R_d \qquad (1)$$

A_c and A_q are the gross rates of CO_2 assimilation limited by Rubisco activity and RuBP regeneration, respectively (Farquhar et al., 1980). Values were determined by fitting (SigmaPlot 9.0, Systat Software, Inc) the model of Farquhar et al. (1980) to the data, using temperature dependencies of $V_{\max}$, $J_{\max}$, and R_d as described in Leuning (1995). Published values of parameters describing the temperature dependencies of $V_{\max}$ and $J_{\max}$ were used (Wohlfahrt et al., 1999).

2.6 Isoprene modeling

The algorithms presented by Guenther et al. (1993, 1995) (Eq. 2) and by Niinemets et al. (1999) (Eq. 3) were used to analyse the measured leaf isoprene emissions. Briefly,

in the former, emissions are characterized by the standardized basal rates (I_s, given here for a standard temperature (T_S) of 20°C and an incident photon flux density (L) of 1000 μmol m^{-2} s^{-1}) and variation e.g., over the course of a day, introduced by a hyperbolic response to light (C_L), and in a modified Arrhenius relationship with temperature (C_T) such that

$$I = I_S C_L C_T, \text{ where } C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}}, \text{ and } C_T = \frac{\exp \frac{C_{T1}(T - T_s)}{R T_S T}}{1 + \exp \frac{C_{T2}(T - T_M)}{R T_S T}} \qquad (2)$$

Basal rates were derived from the leaf measurements (see below). T is measured leaf temperature, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and α (0.0027), C_{L1} (1.066), C_{T1} (95 000 J mol^{-1}), C_{T2} (230 000 J mol^{-1}), and T_M (314 K) are empirical coefficients. Niinemets et al. (1999) simulated isoprene as a function of electron transport rate (J), supplying ATP and NADPH for its synthesis:

$$I = \varepsilon J a \tau, \text{ where } a = \frac{(C_i - \Gamma^*)}{6(4.67 C_i - 9.33 \Gamma^*)}, \text{ and } \tau = [a_x(T - T_{ref})] \qquad (3)$$

In Eq. (3), the basal rate is expressed as a fraction of electrons (ε) used for isoprene synthesis, a is a parameter that converts from photon flux into isoprene units. Arneth et al. (2007) adopted the model to be used in a dynamic global vegetation model framework, including τ to account for the difference in temperature optimum between electron transport and isoprene synthase. C_i is the leaf internal CO_2 concentration, Γ^* is the hypothetical CO_2 compensation point in the absence of non-photorespiratory respiration, a_x is a scaling parameter (0.1, see Arneth et al. (2007)), and T_{ref} is 30°C. The value of ε (0.005) was determined for 20°C and light saturation such that $I = I_s$ under these conditions. The short-term response of emissions to temperature and light has been shown in a simple model exercise to be very similar for both algorithms (Arneth et al., 2007). The hyperbolic light-response in the Guenther et al. algorithms (1993) mimics the hyperbolic light response of electron flow (the basis of the Niinemets et al. (1999) calculation) and both are based on a modified Arrhenius-type temperature-response to describes the increase of isoprene synthase activity to a maximum and decline of emissions thereafter. Here we investigate whether this similarity holds also under field conditions when compared to actual observations.

3 Results

3.1 Measurements

Analysis by GC-MS showed that isoprene was the only detected VOC emitted in significant amounts from *E. angustifolium* and *C. rostrata* leaves in this study. Traces of monoterpenes (α-pinene, 3-carene, limonene) were found, but sample concentrations were not significantly different

Table 1. Average (standard deviation) basal isoprene emission (I_{s20}, 20°C, PAR 1000 µmol m^{-2} s^{-1}, Guenther et al. (1993)), light-saturated net CO_2 assimilation, leaf N, specific leaf area (SLA), $J_{max\,20}$, $V_{max\,20}$ and R_{d20} of *Eriophorum angustifolium* and *Carex rostrata* in the three field campaigns in 2005 and 2006, respectively.

	campaign	I_{s20} [µg C m^{-2} h^{-1}]	A_{sat} [µmol m^{-2} s^{-1}]	Leaf N [mg g^{-1}]	SLA [cm g^{-1}]	$J_{max\,20}$[a] [µmol m^{-2} s^{-1}]	$V_{max\,20}$[a] [µmol m^{-2} s^{-1}]	R_{d20}[a] [µmol m^{-2} s^{-1}]
2005								
E. angustifolium	17–27 Jun	578.6 (440.3)	10.4 (4.0)	27.9 (4.5)	123.5 (19.2)	124.0 (65.8)	43.2 (22.5)	2.9 (1.0)
	29 Jul–3 Aug	285.9 (2.0)	12.2 (3.2)	20.5 (1.2)	119.3 (0.3)			
	20 Aug–5 Sep	21.0 (23.7)	11.4 (1.8)	19.7 (2.1)	109.6 (9.9)			
C. rostrata	16–24 Jun	424.0 (150.2)	15.4 (4.2)	34.1[b]	206.3 (14.1)	159.9 (30.5)[c]	70.2 (5.5)[c]	1.6 (1.4)[c]
	1–6 Aug	2.3 (1.3)	17.5 (0.2)	29.0 (0.6)	157.2 (23.6)	162.8[d]	66.0[d]	1.8[d]
	29 Aug–2 Sep	7.6 (7.1)	19.3 (3.7)	25.7 (1.1)	131.7 (25.9)			
2006								
E. angustifolium	5–15 Jun	99.0 (91.1)	7.8 (2.8)	28.0 (5.7)	150.6 (38.6)	101.0 (46.8)	41.0 (10.9)	2.1 (0.7)
	30 Jun–30 Jul	782.1 (316.5)	11.8 (3.3)	22.3 (3.8)	141.0 (34.0)	132.6 (33.9)	58.3 (17.7)	1.2 (0.3)
	1–8 Aug	755.6 (249,3)	13.8 (0.7)	19.2 (1.5)	138.7 (8.7)	136.1 (10.1)	56.5 (6.8)	1.3 (0.1)
C. rostrata	6–20 Jun	48.7 (36.7)	9.7 (4.9)	30.5 (2.2)	203.3 (15.3)	104.7 (34.5)	50.5 (16.7)	1.2 (0.6)
	1–10 Jul	175.8 (65.9)	15.6 (1.9)	27.8 (3.2)	188.4 (33.1)	114.9 (67.2)	52.0 (19.3)	-2.8 (5.4)
	2–9 Aug	215.0 (198.9)	13.8 (0.7)	23.6 (1.2)	196.4 (16.4)	137.5 (22.6)	53.9 (7.3)	1.2 (0.7)

[a] Missing values were due to technical problems.
[b] *C. rostrata* Leaf N was measured once during the first field campaign.
[c] *C. rostrata* photosynthetic parameters were measured two times during the first field campaign.
[d] *C. rostrata* photosynthetic parameters were measured once during the second field campaign.

from collected blanks. Terpenoid emissions from the tall-sedge community at Stordalen has been found be dominated by isoprene also on the landscape-scale (Holst et al., 2008).

All isoprene emission rates reported here are expressed as basal rates, i.e. standardized to a temperature of 20°C and PAR 1000 µmol m^{-2} s^{-1} (I_{s20}) according to Guenther et al. (1993), and expressed on a leaf area basis; specific leaf areas are given in Table 1. The maximum emissions of *E. angustifolium* were 1075 µg C m^{-2} h^{-1} in 2005 and 1118 µg C m^{-2} h^{-1} in 2006; maximum *C. rostrata* emissions were 489 µg C m^{-2} h^{-1} in 2005 and 396 µg C m^{-2} h^{-1} in 2006 (Fig. 1). Mean specific leaf areas of the two sedges were 138.4 and 195.3 cm^2 g^{-1} (Table 1). The measurement campaign in 2006 captured the approximate onset of leaf isoprene emission in both species, which occurred after 103°D (the cumulative sum of diurnal mean temperatures above 0°C after the last spring frost; 5 June) for *E. angustifolium*, and after 108°D (6 June) for *C. rostrata*. Measurement occasions preceding 5 June when isoprene emissions were below detection limit are not included in Fig. 1. The first measurements in 2005 were carried out after approximately 700°D, which likely explains the difference in emission magnitude between the two years. In 2005, *C. rostrata* emissions were just above detection limit during the August campaign. Over the growing seasons 2005–2006, emissions from both species were correlated with average ambient temperature for the previous 48 h (T48; r^2=0.67 and r^2=0.70 for *E. angustifolium* and *C. rostrata*, respectively) (Fig. 2a) with a relationship that appeared steeper for *E. angustifolium*. However, when expressing I_{s20} in relative terms the between-species

differences in the response to T48 merged into a common, albeit scattered relationship (Fig. 2b). For normalization we chose I_{s20} when T48=12°C, the average temperature of the warmest month (570 µg C m^{-2} h^{-1} for *E. angustifolium* and 131 µg C m^{-2} h^{-1} for *C. rostrata*; Fig. 2a). Two large values measured in *C. rostrata* in July 2005 (Fig. 1c) stand out on the data in Fig. 2a and b, but we have no obvious reason to exclude these from the overall analysis. When fitting a simple exponential relationship to the data, parameter values did not change notably between fits with and without these two data points, but r^2 increased from 0.25 to 0.63 when using the latter (Fig. 2b). The slopes of linear regressions performed on semi-logged transformed data (data were normally distributed and had equal variances) were not statistically different between the *E. angustifolium* and *C. rostrata* data (Student's $t_{.05[30]}$=0.6283, p>0.05).

Leaf N in both species was at its maximum, approximately 30 mg g^{-1} (3%) of leaf dry weight, in mid June and decreased progressively thereafter (Fig. 1g, h). Light-saturated A (A_{sat}) of *E. angustifolium* and *C. rostrata* varied between approximately 5 and 20 µmol m^{-2} s^{-1} within the growing seasons. (Fig. 1e, f). No clear seasonal trends in A_{sat}, and $V_{max\,20}$ or $J_{max\,20}$ were apparent (Table 1), but in *E. angustifolium*, A_{sat} decreased with leaf N in 2006 (Table 1). Neither leaf (N), nor A correlated with ambient temperature over the season. There was also a decrease in *E. angustifolium* R_{d20} over the season 2006 (Table 1).

The influence of leaf N on isoprene emission differed in 2005 and 2006. In 2005, emissions were independent of the variation in leaf N over the season (Table 1), but in 2006
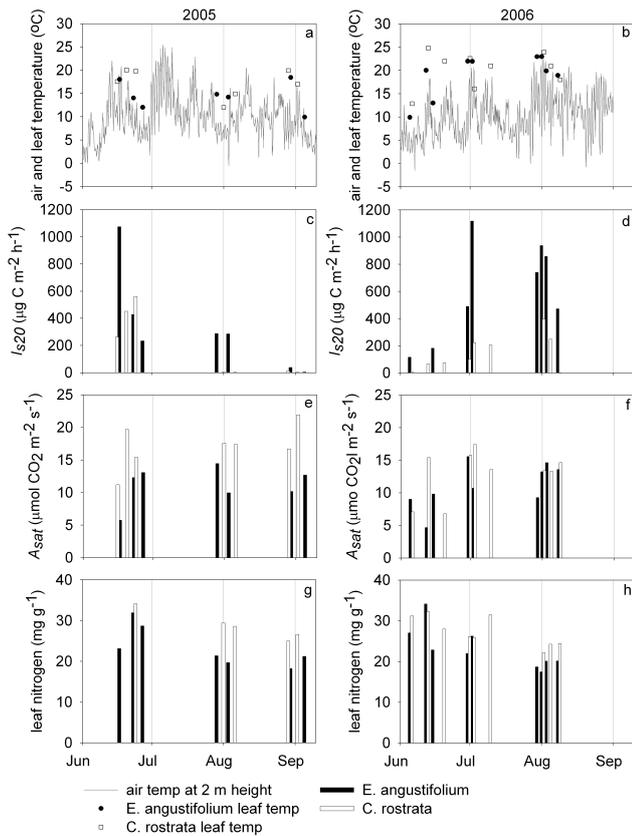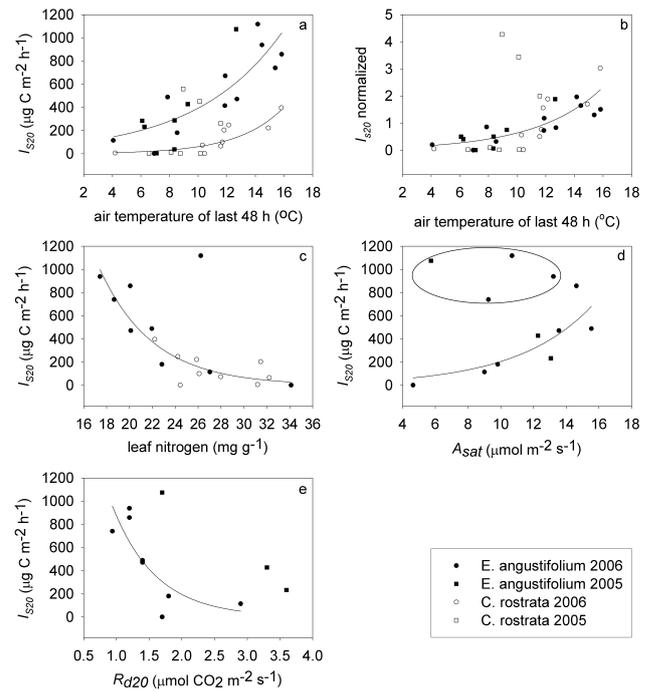
Fig. 1. (a) and **(b)**: Air (2 m height) and leaf temperature, **(c)** and **(d)**: basal leaf isoprene emission (I_{s20}, temperature 20°C, PAR 1000 μmol m^{-2} s^{-1}), **(e)** and **(f)**: light-saturated net CO_2 assimilation (A_{sat}), and **(g)** and **(h)**: leaf N in *Eriophorum angustifolium* (closed symbols) and *Carex rostrata* (open symbols) in June to September 2005 (left panel) and 2006 (right panel). Each bar represents the mean of duplicate or triplicate samples from single leaves.

Fig. 2. (a): *Eriophorum angustifolium* (closed symbols) and *Carex rostrata* (open symbols) basal leaf isoprene emissions (I_{s20}, temperature 20°C, PAR 1000 μmol m^{-2} s^{-1}) as functions of average air temperature of the previous 48 h (T48) in 2005 (squares) and 2006 (circles). Fitted lines are $f = ae^{bx}$. For *E. angustifolium* a=74.1 and b=0.17 (r^2=0.67). For *C. rostrata* a=4.61 and b=0.28 (r^2=0.70). **(b)**: Same as (a) but with emission rates normalized to be unity at T48=12°C. A single fit was determined with a=0.19 and b=0.15 (r^2=0.63). **(c)**: *E. angustifolium* (closed symbols) and *C. rostrata* (open symbols) I_{s20} as a function of leaf N in 2006. **(d)** and **(e)**: *E. angustifolium* I_{s20} in 2005 (squares) and 2006 (circles) as functions of light-saturated net CO_2 assimilation (A_{sat}) (circled points are measurements where ambient temperature exceeded 15°C) (d), and modelled daytime respiration at standard temperature 20°C (R_{d20}) (e). Curves in (c), (d) and (e) are exponential fits (outliers excluded) and for guidance of the eye. Each point represents the mean of duplicate or triplicate samples from single leaves.

there was a pronounced negative correlation (Fig. 2c). No correlation between isoprene emission and A_{sat} was found for *C. rostrata* (Table 1). In leaves of *E. angustifolium* basal emission rates tended to increase with A_{sat} (Fig. 2d) for measurements made at leaf temperatures close to the long-term July average (11.6°C), while the emissions decreased with R_{d20} (Fig. 2e). The three distinct outliers in Fig. 2e are all from 2005, but the low number of data points prevents further analysis of potential differences in correlation between I_{s20} and R_{d20}.

3.2 Modelling

Figure 3 summarises the data obtained by connecting an *E. angustifolium* leaf directly to the PTR-MS for online monitoring of isoprene emissions. As expected, emission was strongly correlated with leaf temperature on short temporal scales (minutes to hours), but relationships with PAR as well

as with A also appeared (Fig. 3). Together with the seasonal observations (Fig. 2b) the data were used for a simple model analysis to investigate whether the temperature and light response of the northern sedges would follow a similar response as found for many temperate or tropical species, and with the aim of quantifying isoprene emissions from the sedges over the entire growing season. The Guenther et al. algorithms (1993) were fitted to the data shown in Fig. 3 using the published standard values to describe temperature (C_{T1}, C_{T2}) and light (α, C_{L1}) responses. The resulting I_{s20} was 846 μg C m^{-2} h^{-1} (r^2=0.82; Fig. 4, red long dash line). In a second experiment, not only I_{s20} but also the parameters from the temperature and light responses were determined from the non-linear fitting procedure. This improved the
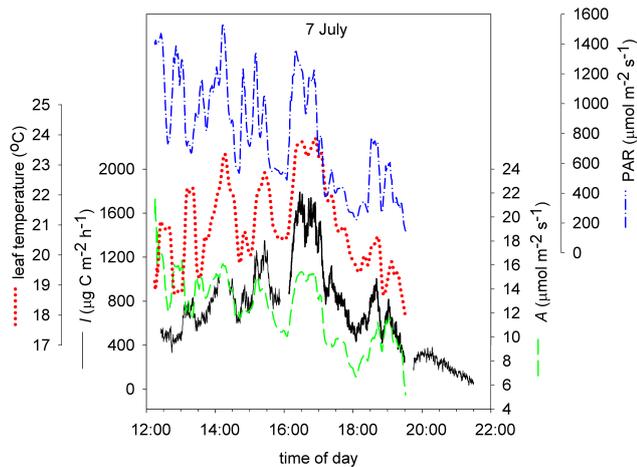
Fig. 3. *Eriophorum angustifolium* isoprene emission (I) measured online by PTR-MS (black solid line), net CO_2 assimilation (A) (green long dash line), leaf temperature (red dotted line) and photosynthetically active radiation (PAR) (blue dash-dot line) plotted against time of day on 7 July 2006. All values are 1-min running averages.

model-data agreement slightly (r^2=0.85; Fig. 4, green dotted line), with values of: 124 154 ($J\,mol^{-1}$, C_{T1}), 1 078 228 ($J\,mol^{-1}$, C_{T2}), 0.003 (unitless, α) and 1.19 (unitless, C_{L1}) (Guenther et al., 1993). The value of I_{s20} that was determined this way was 677 $\mu g\,C\,m^{-2}\,h^{-1}$. To evaluate whether the incorporation of the additional parameters in the Guenther et al. (1993) model lead to a real model improvement or whether the increase in r^2 simply was caused by the increase in number of parameters and hence introduced over-fitting, we used a simplified version of the Bayesian Information Criterion (BIC, Schwarz, 1978). Even though the number of parameters increased from one in the standard Guenther et al. (1993) model to five in the model where all parameters were determined by non-linear curve-fit, the BIC decreased from 2703 to 2685. Hence we consider the latter model to represent a slight, but real improvement, yet we also note that a longer period of continuous on-line measurements would strengthen this analysis and prevent possible instabilities in the model. Finally, using the basal rate of 846 $\mu g\,C\,m^{-2}\,h^{-1}$ to calculate ε (cf., Eq. 4; ε=0.005), together with the photosynthetic electron flux calculated using the values of $V_{max\,20}$=52, $J_{max\,20}$=124, and R_{d20}=1.56 (all in $\mu mol\,m^{-2}\,s^{-1}$) that were determined from the photosynthesis measurements, isoprene emissions were also simulated in a forward way (Fig. 4, blue dash-dot line).

To estimate effects of different algorithms on emissions over a longer period, daily isoprene emissions of *E. angustifolium* and *C. rostrata* in the growing season 2006 were calculated using meteorological data measured at the site and applying average seasonal basal rates of 570 and
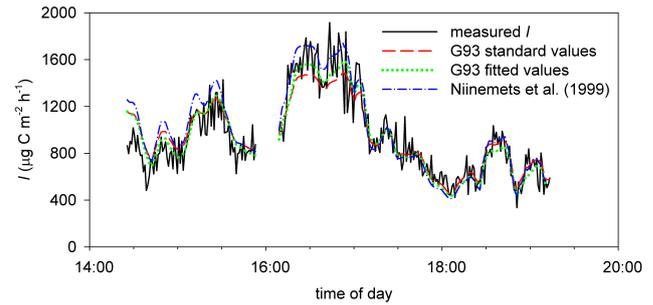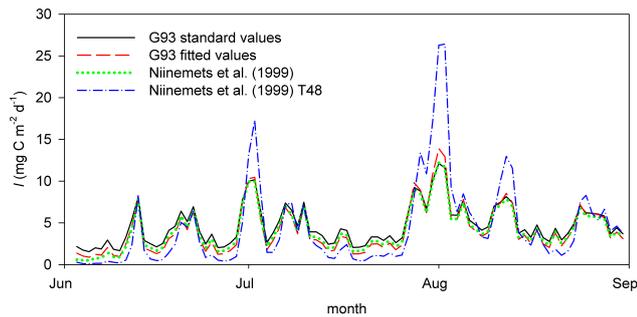

Fig. 4. Isoprene emission (black solid line) and simulated isoprene emissions using the models by Guenther et al. (1993) (G93) with standard parameter values (red long-dash line, I_{s20}=846 $\mu g\,C\,m^{-2}\,h^{-1}$), G93 with fitted parameter values (green dotted line, I_{s20}=677 $\mu g\,C\,m^{-2}\,h^{-1}$) and Niinemets et al. (1999) (blue dash-dot line, using I_{s20}=846 $\mu g\,C\,m^{-2}\,h^{-1}$).

131 $\mu g\,C\,m^{-2}\,h^{-1}$, respectively, for the two species (cf. Fig. 2a) together with the (Guenther et al., 1993, standard parameter settings and modified as above) and Niinemets et al. (1999) models (Fig. 5, black, red and green lines; for simplicity, only *E. angustifolium* is shown). Calculations were repeated with the Niinemets et al. (1999) approach with and without varying basal rates, and hence ε, in response to 48 h temperature history (Figs. 2b and 5, blue line). The annual totals calculated this way were 287, 253, 255 and 269 $mg\,C\,m^{-2}$, respectively, for the Guenther et al. (1993) standard and modified, and the Niinemets et al. (1999) and the Niinemets et al. (1999) + temperature history calculations. For *C. rostrata*, for which only standard Guenther et al. algorithm values were available, these totals were 66, 59 and 62 $mg\,C\,m^{-2}$.

4 Discussion

4.1 Measurements

Eriophorum angustifolium and *Carex rostrata* in the investigated subarctic wetland were notable isoprene emitters. The growth patterns, as well as habitiat preferences, of the two species are generally very similar (Malmer et al., 2005; Saarinen, 1998), but the more clear-cut relationships between, e.g., photosynthesis and emission rate were found for *E. angustifolium*. Herbaceous vegetation, particularly grasses and sedges, is often either low- or non-emitting, but we measured maximum basal leaf emission rates of up to 1118 $\mu g\,C\,m^{-2}\,h^{-1}$ at 20°C and 1000 $\mu mol\,m^{-2}\,s^{-1}$ in leaves of *Eriophorum*, corresponding to 4051 $\mu g\,C\,m^{-2}\,h^{-1}$ at 30°C and 1000 $\mu mol\,m^{-2}\,s^{-1}$, (Guenther et al., 1993). Expressed on dry weight basis these maximum basal rates were 12 $\mu g\,C\,g^{-1}\,h^{-1}$ at 20°C and 36 $\mu g\,C\,g^{-1}\,h^{-1}$ at 30°C. Measurement of sedge emissions at the typically used

Fig. 5. Simulated leaf isoprene emissions from *Eriophorum angustifolium* from 1 June to 31 August 2006. Four approaches are compared: (i) a simulation using the Guenther et al. (1993) algorithms (G93), (black solid line) and an average basal emission rate (at 20°C) of 570 µg m^{-2} h^{-1} (cf. Fig. 2a), (ii) a simulation using the G93 with fitted parameter values (red long-dash line), (iii) a simulation using the model by Niinemets et al. (1999) (green dotted line) with the fraction of electrons (ε) used for isoprene synthesis chosen to result in $I=I_{s20}$ (Arneth et al., 2007), and (iv) as in (iii) but varying I_{s20} (and thus ε) according to the temperature of the last 48 h (T48) as in Fig. 2b (blue dash-dot line).

reference temperature of 30°C were not considered sensible since the cold-adadpted sedges in this study likely would experience temperature stress, possibly lowering the photosynthetic capacity and thus the potential to produce isoprene. The recalculation of basal rates to 30°C was therefore performed for comparative reasons only and must be regarded with caution since we must apply for this calculation the Guenther et al. (1993) temperature-response to temperatures well outside the range of the sedge's growth environment. To our knowledge this is the first study that investigated the environmental controls of isoprene emissions on species from the *Cyperaceae* family on a leaf scale. Other (temperate to tropical) members of the monocotyledonae like *Arundo donax* or *Phragmites mauritianum* (both family *Poaceae*) are known to be substantial emitters with basal rates (at 30°C) of 34 and 31 µg C g^{-1} h^{-1}, respectively (Kesselmeier and Staudt, 1999), which is comparable to the emission capacity of the sedges in our study. Microbial production of isoprene in peat soils has not been extensively studied, but the comparison of our results with literature values indicates that it may not be a significant isoprene source.

A lag between the onset of photosynthesis and the capacity of a leaf to emit isoprene has been frequently observed, typically longer at cool growth temperatures, and is related to the expression of isoprene synthase (Wiberley et al., 2005). Cumulative temperature sums above a threshold temperature (often 0°C or 5°C) is a general measure to investigate onset of plant physiological processes in strongly seasonal environments. It allows to compare different locations based on average climate rather than by date. Particularly in northern environments that can display large interannual variation

in spring conditions, as well as rapid increase in temperatures once snow starts to melt, this is quite helpful as a measure of how plant growth conditions rather than leaf developmental stage induce isoprene emission. In a range of temperate, boreal and northern woody ecosystems, onset of isoprene emissions has been found to occur after 200 to 600°D (Geron et al., 2000; Monson et al., 1994; Pétron et al., 2001; Pressley et al., 2005). By contrast, emission induction in the subarctic sedges in this study occurred already at approximately 100°D (in 2006), two to six times earlier than what was observed previously. Non-woody vegetation in northern regions is well adapted to survival under conditions of short active seasons and can rapidly start photosynthesising early in spring at still low mean daily temperatures (Moore et al., 2006). Net ecosystem CO_2 uptake at Stordalen mire, measured by the eddy covariance technique, occurred after DOY 120 in 2006, which is 18 days before the last spring frost (M. Jackowicz-Korczynski, personal communication, 2007). This suggests that the capacity of the investigated subarctic sedges to produce isoprene develops fast once the accumulated degree days have reached a critical threshold. Wiberley et al. (2005) showed that plant growth conditions, rather than leaf developmental stage, exerted primary control of isoprene emission induction. They found that the time delay between developed photosynthetic competence of kudzu leaves and onset of isoprene emission was temperature dependent; a lag of two weeks was observed when the plants were grown at a sub-optimal temperature.

Temperature history of the previous 48 h (T48) was an important determinant of isoprene emission capacity from *E. angustifolium* and *C. rostrata*, with only a slightly higher T48 temperature sensitivity found for (normalized) I_s of *E. angustifolium* compared to *C. rostrata*. It has been observed for a range of plant species that isoprene emission capacity is strongly correlated with weather conditions, particularly average temperature, over the previous few days (Geron et al., 2000; Pétron et al., 2001; Sharkey et al., 1999; Wiberley et al., 2005). Fuentes and Wang (1999) showed that temperatures below 10°C, which is frequently encountered during the subarctic growing season, were of particular importance for the magnitude of subsequent isoprene emission rates in a temperate forest. Using a neural network analysis, Boissard et al. (2008) detected a low frequency signal of accumulated air temperatures over 21 days on measured isoprene emissions from a number of temperate and tropical species. Guenther et al. (2006) argued for an effect of leaf temperature averaged over the past 24 and 240 h to be included in emission models, in addition to short-term acclimation to changing light. The increasing evidence emerging about weather effects on basal emission rates seems to indicate that the response is not uniform in terms of the length of the averaging period as well as the form of the response function. While variability of I_s need to be accounted for in the typically used multiplicative models (Guenther et al., 2006; Arneth et al., 2007) care should be taken to

not unintentionally double account, particularly for low frequency signals. In our case we deliberately did not extend the time period beyond a few days and also excluded light effects because of the strong co-variation of light and temperature at our site. Observed variation in response to weather accumulated over periods of a number of weeks might in fact reflect a response to seasonal leaf development (age, leaf N content) (Fuentes and Wang, 1999; Holzke et al., 2006) while short-term effects (few days) are more likely to reflect a more direct response of isoprene synthase to weather.

Photosynthesis provides precursors and energy for isoprene metabolism. Hence, photosynthetic electron transport, providing ATP and NADPH for isoprene synthesis, has been shown to be an important determinant of emission rates (Lerdau and Keller, 1997; Niinemets et al., 1999; Possell et al., 2004; Sharkey and Loreto, 1993). Kuhn et al. (2004) found that isoprene emission capacity was strongly, and mostly linearly, related to gross photosynthetic capacity (defined as the sum of maximum assimilation rate observed during daytime, and maximum nighttime respiration) over the course of a season in the tropical tree *Hymenaea courbaril*. In our case, an increase of *E. angustifolium* I_{s20} with A_{sat} became apparent at temperatures above the long-term mean July temperature. Overall, the relationship was much more curvelinear although the range of calculated gross photosynthetic rates (defined as the sum of measured A_{sat} and modelled R_{d20}) was comparable to Kuhn et al. (2004). By contrast, we found no clear pattern between isoprene emission and A_{sat} in *C. rostrata*.

It has been argued that the positive seasonal correlation between isoprene emission and photosynthesis that has been observed in aspen leaves is explained by a common dependence on leaf N (Monson et al., 1994). Leaf N has further been identified as an important control of emission from oak and aspen leaves belonging to the same phenological stage, likely due to positive effects on the activity of enzymes involved in isoprene biosynthesis (Litvak et al., 1996; Possell et al., 2004). However, at our study site net assimilation and photosynthetic capacity did not show the expected positive correlation with leaf N, which may be explained by the vegetative growth pattern that is typically found in arctic and subarctic clonal sedges: large amounts of N stored in roots and rhizomes are rapidly allocated to above-ground structures early in the season to support rapid growth and photosynthesis, followed by a gradual decline in leaf N as the growing season progresses (Jonasson and Shaver, 1999). Leaf N, however, remains high enough during the entire season to sustain photosynthesis rates. Woody species and shrubs adapted to cold and nutrient deficient growth environments often have similiar, but not as pronounced, nutrient use strategies and this plant functional group commonly also display high correlation between leaf N and photosynthesis (Moore et al., 2006; Muraoka et al., 2008). Even though some arctic sedge species utilize organic N sources (Chapin et al., 1993), the sedges in this study seemed to follow this typical nutrient allocation pattern, which results in the observed negative seasonal relationship between isoprene emission and leaf N. It is not, however, possible to draw conclusions about whether this decline in emission was directly linked to decreasing N availability, or reflecting some other metabolic link coupled to isoprene biosynthesis. Monson et al. (1994) argued that a negative correlation between isoprene emission and leaf N around the time of leaf development could be explained by a dominating influence of phenology and temperature early in the season. If the same reasoning applies to our whole-season data-set, this further emphasizes the dominating influence of temperature on isoprene emission from the investigated subarctic sedges. Moreover, unlike the relationship with N, the correlation between temperature and basal isoprene emission was robust across seasons. A further possible explanation can be sought in the decrease in mitochondrial respiration that occurred in parallel with the decline in leaf N. Rosenstiel et al. (2004) suggested that a negative correlation between respiration and isoprene emission reflects competition for C substrate (phosphoenolpyruvate, PEP) between 1) cytosolic nitrate assimilation and/or mitochondrial respiration, and 2) import of PEP into chloroplasts where its dephosphorylated form (pyruvate) is one of the main precursors for isoprene biosynthesis. However, the exact mechanisms are not yet fully understood and in a subsequent study by Loreto et al. (2007) it was shown that the competing effect of growth respiration may only be significant at early phenological stages when leaf development requires high energy input.

4.2 Modelling

In some studies, isoprene and light dependent monoterpene emissions tracked diel measurements of assimilation at least as closely as the diel course of temperature and light (Kesselmeier et al., 1996; Kuhn et al., 2002). From our limited PTR-MS data set it was not possible to distinguish the separate effects of photosynthesis and temperature from the effect of correlated scaling between the two factors (Kesselmeier et al., 1996) although the relationship of isoprene emissions with temperature was somewhat clearer than the one with assimilation rate. Still, both the light and temperature driven algorithm (Guenther et al., 1993) as well as the one linked to electron flux (Niinemets et al., 1999; Arneth et al., 2007) were able to mimic the diel pattern measured the one day with the PTR-MS with coefficients of determination between 0.82 and 0.86. For the day of the PTR-MS measurements, I_{s20} could have been estimated by the relationship shown in Fig. 2b, based on the preceeding 48 h temperatures (T48). However, I_{s20} derived from the online measurements directly, exceeded this calculated value substantially by 49%. One possible reason for the discrepancy lies in the obvious scatter in the relationship of I_{s20} and T48. Being statistically significant, (linear regression of semi-logged transformed data; ANOVA, $F=8.422$, $p=0.01$) the shown

relationship is applicable over the course of the growing season, but not precisely predicting I_{s20} on day-to-day basis.

The agreement between the diurnal modeled and measured emissions was very good with little variation between the three tested algorithms. Model-data agreement improved only slightly when all parameters of the Guenther et al. (1993) algorithm were determined by non-linear curve fit. Interestingly though, the modified values suggest a higher temperature sensitivity compared to the standard values from Guenther et al. (1993). Holst et al. (2008) also found isoprene emissions on the ecosystem scale to be extremely sensitive to temperature change at Stordalen mire. Our data is too limited for a more rigorous analysis but such a modified response might nonetheless be considered a plausible adaptation to the cool growth environment with relatively low solar elevation and warrants further study. For some tropical woody species, the parameters describing light and temperature sensitivities have also been found to differ from the values that were originally determined for temperate plants in the Guenther et al. (1993) algorithm (Oku et al., 2008). It was therefore suggested that locally optimized parameter values are of importance to obtain accurate global isoprene emission estimates.

Over the course of the season the simulated totals of leaf isoprene emission were overall remarkably similar when comparing a number of algorithms. Taken together with the close agreement between the models to reproduce the diel response in Fig. 4, this confirms previous analyses that the short-term variation of isoprene emission is simulated in a very similar fashion with both approaches. But, while the seasonal totals were unaffected when I_{s20} was varied dynamically depending on weather-history, the day-to-day amplitude became notably more pronounced. Using dynamically varying values for I_s in regional or global models may therefore be important when coupling emission rates to atmospheric chemistry calculations that require high temporal resolution. Furthermore, a temperature-dependent variation in I_s similar to what was observed at our study site and elsewhere (Geron et al., 2000; Sharkey et al., 1999) could possibly also be indicative for the capacity of isoprene emissions to acclimate to higher temperatures (Guenther et al., 2006) in a warming climate. But, whether a simple relationship as shown in Fig. 2a and b is sufficient to describe such a possible temperature acclimation (which would be advantageous from a global modelling perspective), or whether more complex ones as suggested earlier (Guenther et al., 2006) are needed remains to be determined.

5 Summary and conclusions

In summary, we present here field observations on isoprene emission from the two common subarctic sedges *E. angustifolium* and *C. rostrata*. From the overall emission patterns and their environmental constraints a complex interaction

of short-medium term constraints was identified and can be summarized as: 1) isoprene emission did not show the expected positive correlation with leaf N, 2) instantaneous leaf temperature was, not surprisingly, an important factor controlling isoprene emission, but, 3) the temperature history of the previous 48 h explained most of the variation in emission capacities, 4) a positive influence of photosynthesis on emissions capacities was found for one of the investigated sedge species (*E. angustifolium*), 5) emission response to environmental factors varied strongly between the two years.

The investigated subarctic sedges were notable isoprene emitters and seasonal average emission rates were within 10% of those reported from areas with higher average growing season temperatures. Emission response to environmental factors varied considerably within, as well as between growing seasons. Since the investigated leaves probably belonged to the same clone, genetic factors were not likely to have contributed to the observed variation to a large degree. We found temperature over the last 48 h to affect basal isoprene emission rates of the investigated sedges. Large between-year, as well as within-season differences in temperature are not unusual in high-latitude ecosystems and were also a common feature at our subarctic study site. The recent day's thermal history is therefore likely to be of great importance for the regulation of emission capacity in plants adapted to this environment. Such adaptations might also include a higher sensitivity of emission to changes in temperature than what is typically found in plants adapted to warmer climates. While simulated growing season emission totals were insensitive to the leaf isoprene model used, a considerable day-to-day uncertainty may be introduced depending on whether or not these processes are included in models.

We are aware of the limits of our analysis that arise from the relatively small number of samples and further studies will be required to substantiate (or refute) our observations. Nonetheless, the number of studies on leaf emissions under field conditions over two consecutive growing seasons is limited, as is data on isoprene emissions from remote subarctic locations. This is a region that currently undergoes rapid changes in response to warming, but has not yet been characterised in terms of its BVOC emission patterns. The correlations identified from the field observations are at the same time of possible general value to refine BVOC emission models (e.g., response to short-term weather history, response to changes in leaf N). It is clear that better mechanistic understanding of relevant processes is required to ensure the applicability of simulations in future or past environments that lie outside of the range of conditions for which semi-empirical models have been developed.

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