BOREAL ENVIRONMENT RESEARCH 22: 353–367 © 2017
ISSN 1797-2469 (online) Helsinki 11 September 2017

Seasonal variation in biogenic volatile organic compound (BVOC) emissions from Norway spruce in a Swedish boreal forest

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Received 31 Mar. 2017, final version received 23 Aug. 2017, accepted 23 Aug. 2017

Wang M., Schurgers G., Arneth A., Ekberg A. & Holst T. 2017: Seasonal variation in biogenic volatile organic compound (BVOC) emissions from Norway spruce in a Swedish boreal forest. *Boreal Env. Res.* 22: 353–367.

Terpene emissions from the top-canopy layer (at 20 m) of one 118-year-old Norway spruce tree were measured between June and September 2013 using a branch chamber. Total terpene emissions varied from 0.05 to 332.5 $\mu g\ g_{dw}^{-1}\ h^{-1}$ with a peak in August. Monoterpenes dominated throughout the summer and on average accounted for 65% of the total terpene mass, followed by sesquiterpenes (29%) and isoprene (6%). The values obtained with an optimized hybrid model, assuming the partitioning of monoterpene emissions from both *de novo* synthesis and storage structures, were in good agreement with the observed emissions (Pearson's $r = 0.94$) at the branch level. *De novo* monoterpene emissions were found to dominate in all campaigns (> 50%) with almost 100% in June. The highest standardized (30 °C, 1000 μmol photons $m^{-2}\ s^{-1}$) monoterpene emission rate was 210.3 $\mu g\ g_{dw}^{-1}\ h^{-1}$ in August, followed by that in June (68.8 $\mu g\ g_{dw}^{-1}\ h^{-1}$). Therefore, both *de-novo*-synthesis and long-term observations that include seasonal variations are needed for accurately upscaling terpene emissions.

Introduction

Biogenic volatile organic compounds (BVOCs) are hydrocarbons known to be produced by at least 90 plant families, and are involved in plant physiological processes, reproduction and self-defense (Laothawornkitkul *et al*. 2009, Peñuelas and Staudt 2009, Loreto and Schnitzler 2010, Holopainen 2011). While the term BVOC includes hundreds of chemicals, the most important compounds are grouped into isoprene (C_5H_8), monoterpenes (MT, $C_{10}H_{16}$) and sesquiterpenes (SQT, $C_{15}H_{24}$) (Laothawornkitkul *et al*. 2009).

BVOCs are chemically very reactive with atmospheric lifetimes ranging from minutes to days (Kesselmeier and Staudt 1999) under ambient conditions, and thus are important for atmo-

Editor in charge of this article: Veli-Matti Kerminen

spheric chemistry, leading to e.g. changes in the ozone cycle and increase in the lifetime of methane (Laothawornkitkul *et al.* 2009, Arneth *et al.* 2010). BVOCs can also act as precursors for secondary organic aerosol (SOA) and that way contribute to important global and regional climate change feedback mechanisms (Charlson *et al.* 1987, Arneth *et al.* 2010, Paasonen *et al.* 2013).

Temperature and light (photosynthetically active radiation, PAR) have been shown to be key environmental controls for the synthesis and emissions of BVOCs on the short term: temperature regulates the isoprene and monoterpene (MT) synthase activities (Monson *et al.* 1992), affects availability of substrates for BVOC synthesis (Laothawornkitkul *et al.* 2009), and controls the volatility and diffusion rates of BVOC compounds (Llusià *et al.* 2006), whereas PAR determines the availability of the terpene precursor glyceraldehyde-3-phosphate and the energy requirements of ATP and NADPH (Niinemets *et al.* 1999, Niinemets and Reichstein 2003). While isoprene is emitted directly after the synthesis, MTs can be either emitted directly or stored in specific organs of the plant, e.g. in resin ducts in conifer needles (Staudt *et al.* 1997, Niinemets and Reichstein 2003, Tarvainen *et al.* 2005). The emission of terpenes from a storage pool increases exponentially with temperature (Guenther *et al.* 1993, Hakola *et al.* 2006), and emission rates for terpenes stored inside the tissue are also regulated by pool size and internal or external glands (Lerdau 1991, Kesselmeier *et al.* 1997). Terpenes not stored in any pool after synthesis are expected to have a faster and stronger short-term response to ambient conditions as compared with that of stored compounds, so that their emissions are related to PAR and photosynthetic rates and do not depend on temperature only (Staudt and Seufert 1995, Llusià and Peñuelas 2000). In addition, while most compounds are primarily emitted through stomata, emissions of some non-oxygenated terpenes and isoprene are nonetheless considered insensitive to a stomatal closure due to their low solubility with water, which rapidly increases terpene partial pressure within the leaf after the stomatal closure (Niinemets *et al.* 2002, 2004).

Besides the short-term effects of temperature and radiation on BVOC emissions, mechanical disturbance, drought stress, excessive heat or herbivore attacks can alter the diurnal and seasonal patterns and total amount of terpene emissions, and even change the spectra of emitted chemical compounds (Loreto *et al.* 2000, Loreto and Schnitzler 2010, Holopainen 2011). Furthermore, the dynamics of foliage development over a growing season (leaf unfolding, senescence) and the development of the photosynthetic capacity (Chandler and Dale 1993, Räim *et al.* 2012, Kolari *et al.* 2014) are expected to vary the regulation of BVOC emissions with temperature and PAR. For instance, Aalto *et al.* (2015) reported that the onset of photosynthesis during spring time promoted MT synthesis and led to an emission burst of MT.

Today, there is still a lack of long-term observational data on BVOC emissions covering seasonal effects, specifically for evaluating emission models. The unknown variability of species- or biome-specific emission capacities throughout the seasons causes large uncertainties in emission models (Arneth *et al.* 2008), as short-term measurements are unable to indicate the seasonality and cause great discrepancy between the measured emission rates and modeled result on longer time scales (Holzinger *et al.* 2006, Holzke *et al.* 2006).

Norway spruce (*Picea abies*) is one of the dominant conifer species in northern and central Europe (Grabmer *et al.* 2006, Kivimaenpaa *et al.* 2013). However, compared with studies of Scots pine (Bäck *et al.* 2005, 2012, Tarvainen *et al.* 2005, Hakola *et al.* 2006, Rinne *et al.* 2007), there are only few studies about seasonal variations of BVOC emissions from Norway spruce, leaving large gaps in the emission inventory for MT and SQT in boreal forests. In short-term measurements, spruce has been reported to emit mainly MT compounds, but also to produce and release other terpenes, such as isoprene and SQT (Janson 1993, Janson *et al.* 1999, Hakola *et al.* 2000, Grabmer *et al.* 2006). The emission rates of BVOCs from boreal species and their temperature sensitivity have been observed to vary depending on provenience and stand location (Komenda and Koppmann 2002, Tarvainen *et al.* 2005, van Meeningen *et al.* 2016), and with the time of the year (Hakola *et al.* 2001, 2006, Ruuskanen *et al.* 2007). Janson (1993) and Bourtsoukidis *et al.* (2013) found maximum

MT emissions from Norway spruce during early summer (June–July), whereas SQT emissions peaked already in spring (April).

The aim of this study was to characterize the spruce BVOC emissions at a branch level in a typical spruce- and pine-dominated forest in central Sweden, with a specific focus on the temporal development of compound spectrum and terpene emission rates during a growing season (June to September). We analyzed more than 200 individual 30-min emission samples and determined their dependences on light and temperature. The effect of seasonal variations was addressed with model approaches using either a constant standardized emission rate (E_S) or a temporally varying E_S to estimate BVOC emissions over the whole growing season. Our results provide a robust understanding of emission characteristics for Norway spruce forest for the modeling community.

Methods

Study site

The study site is a boreal forest dominated by Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) located in central Sweden, about 30 km north of Uppsala. The Norunda research station (60°05´N, 17°29´E) has been used since 1994 as a flux station equipped with a 102-m-tall tower (Lindroth *et al*. 1998, Lundin *et al*. 1999), and is now included in the ICOS (Integrated Carbon Observation System, http://www.icos-sweden.se/) network. The managed stand is between 80 and 120 years old (Lundin *et al*. 1999, Lagergren *et al*. 2005), with a canopy height of around 25 m and leaf area index (LAI) of 3–6, and with higher values for these quantities in the spruce-dominated parts of the stand (Lagergren *et al*. 2005). The forest is standing on a sandy-till soil with mainly mosses and dwarf shrubs at ground level. The annual average air temperature is 5.4 °C and the annual precipitation is 520 mm (Aubinet *et al*. 2010). The growing season extends from about mid-April to mid-October based on a 5 °C threshold (Lindroth *et al*. 1998). More details about the site, plant species and soil properties can be found in Lundin *et al*. (1999).

The BVOC measurements reported here were made using a 20-m-tall scaffolding tower system located about 100 m NW of the flux tower. This allows for canopy access to a Norway spruce tree for e.g. chamber measurements.

BVOC measurements

Five campaigns of five–six days each were carried out between early June and late September 2013 (6–11 June, 3–7 July, 25–31 July, 10–16 August, 21–25 September), in which the amount and composition of BVOC emissions from Norway spruce were measured during daytime using a dynamic chamber system. The cylinder-shaped transparent PTFE chamber with a volume of 13 liters (diameter 19 cm, length 46 cm) was placed on a 26-m-tall Norway spruce tree (118 years old) with a trunk diameter of 32.5 cm (at 1.3 m above ground) on a branch in the upper part of the canopy (ca. 20 m above ground) within the reach from the scaffolding tower. For each of the five campaigns, the chamber was carefully placed on one branch and given at least one night to settle (with a ventilation lid opened) before the measurements started, in order to avoid induced emissions due to rough handling. Every morning before the measurements started, the chamber was flushed for at least one hour with a VOC-free air after the ventilation lid had been closed. When measurements stopped in the evening, the lid was opened again to vent the chamber and to keep the branch at ambient conditions during night.

A data logger (CR1000, Campbell Sci, USA) recorded measurements from two temperature and relative humidity (RH) probes (CS215, Campbell Sci., USA) placed within and next to the chamber at the same height, respectively. PAR was measured by a quantum sensor (LI-190, LI-COR, USA) fixed on the tower close to the chamber, and connected to a data logger. Ambient air was pumped through a hydrocarbon trap (Alltech Associates Inc., USA) containing MnO_2-coated copper nets to remove ozone. This air then entered the chamber with a flow rate of 6.7 $l\ min^{-1}$, so the residence time of ozone- and VOC-free air in the chamber was about two minutes. Air samples were then collected using adsorbent tubes filled with Tenax-TA and carbongraph 1 TD (Markes International Limited, UK) every hour between 08:00 and 17:00 local time (some samples were missing due to poor weather conditions or instrument failure) with a sampling time of 30 min each at a flow rate of 0.2 l min^{-1} using a PocketPump (SKC, USA). Two blank samples were taken from the VOC-free airflow before entering the chamber in each campaign to account for any instrumental background emission. No terpenes could be detected in any of the blank samples.

The adsorbent tubes were sealed with long-term storage caps immediately after use, and stored at 5 °C for a maximum of five weeks before being analyzed in the laboratory in Lund. Analysis of samples was done by automatic thermodesorption (Turbomatrix ATD, PerkinElmer, Waltham, MA, USA) and gas chromatography (GC-2010, SHIMADZU, Japan) using a 30-m column (internal diam. 0.25 mm, Varian, The Netherlands) and a mass-selective detector (GCMS-QP2010 Plus, Shimadzu, Japan) similar as Ekberg *et al.* (2011). The Tenax tubes were initially heated to 280 °C in a flow of purified helium for ten minutes. A Tenax TA cold trap maintained at –30 °C cryo-focused the volatilized VOCs downstream. Then the cold trap was flash heated to 300 °C (40 °C s^{-1}) and desorption time was maintained for six minutes. The volatilized compounds passed through a heated transfer line (200 °C) to the gas-chromatography equipped with a flame ionization detector (FID). Detected compounds were identified by comparing the measured mass spectrum with the spectra in the NIST mass spectra library. Peak quantification was done using solutions of liquid standards (α-pinene, β-pinene, 3-carene, limonene, eucalyptol, and caryophyllene) and methanol. For the compounds for which standards were not available, we used an averaged correlation equation between known masses of standard compounds and their corresponding integrated peak area.

Data analysis

Calculation of the emission rate *E*

The calculation of the BVOC emission rate, *E*, from a branch was based on the BVOC concentration of the air that was sampled with the adsorbent tubes, the flow rate through the chamber system, and the biomass that was present within the enclosure (Hakola *et al.* 2003, Ortega and Helmig 2008). *E* is defined as follows:

$$E = (C_2 - C_1)Fm^{-1},$$

where C_2 is the concentration of BVOC within the enclosure air, C_1 is the BVOC concentration of air entering the chamber, F is the flow rate through the chamber and m is the dry weight of biomass of the branch in the enclosure. Here, the air entering the chamber was filtered through activated carbon, and according to the blank samples taken $C_1 = 0$. At the end of each campaign, the branch in the enclosure was cut and dried at 75 °C until the biomass weight was constant.

For monoterpenes that are emitted either directly after synthesis or from a storage pool, the emission rate *E* can be calculated with the following hybrid model (Ghirardo *et al.* 2010):

$$E = E_{\mathrm{S}}[f_{\mathrm{denovo}} C_{\mathrm{T}} C_{\mathrm{PAR}} + (1 - f_{\mathrm{denovo}})\gamma], \qquad (1)$$

where

$$C_{\mathrm{PAR}} = \frac{\alpha C_{\mathrm{L1}}\mathrm{PAR}}{\sqrt{1+\alpha^2\mathrm{PAR}^2}},$$

$$C_{\mathrm{T}} = \frac{\exp\left[\dfrac{C_{\mathrm{T1}}(T-T_{\mathrm{S}})}{RT_{\mathrm{S}}T}\right]}{1+\exp\left[\dfrac{C_{\mathrm{T2}}(T-T_{\mathrm{M}})}{RT_{\mathrm{S}}T}\right]}, \text{ and}$$

$$\gamma = \exp[\beta(T - T_{\mathrm{S}})],$$

where E_{S} is the standardized emission rate (μg g$_{\mathrm{dw}}^{-1}$ h^{-1}) at the standard temperature T_{S} of 303.15 K and PAR of 1000 μmol m^{-2} s^{-1}, f_{denovo} is the fraction of the standardized emissions originating directly from synthesis, C_{PAR} describes the variation caused by light, and C_{T} is the temperature-dependent part, both of which were defined by Guenther *et al.* (1993). The parameters of α, C_{L1}, C_{T1}, C_{T2}, R, T_{M} were the same as in Guenther *et al.* (1993). T is the leaf temperature (K) that was approximated by the air temperature inside the chamber, PAR is the measured light condition (μmol m^{-2} s^{-1}) close to the chamber, γ is the temperature activity factor for vaporizing from the pool, and β is a parameter to account for the temperature sensitivity (K^{-1}) of emissions which was kept at 0.09 K^{-1} (Guenther *et al*. 1993).

The hybrid model was first optimized based on all the data from the five campaigns, resulting in one value for f_{denovo} and E_{S} for the entire season, which we call here hybrid_const. In the second approach, this model was optimized for each campaign separately, resulting in f_{denovo} and E_{S} varying from campaign to campaign, which we call here hybrid_adj. Pearson's correlation was used to test the level of agreement between the measured terpene emissions and terpene emissions modeled using hybrid_const and hybrid_adj approaches.

Gap filling

From the 227 individual samples, 23 samples from late July and August campaigns showed saturation of one or a few compounds during the GC-MS analysis. This concerned mainly α-pinene (22 samples) and isoprene (nine samples), but to some extent also β-pinene (four samples), myrcene (three samples) and limonene (four samples). We assumed that all the compounds released from the same branch during the period of one campaign responded to the environmental drivers in the same way, and therefore these few saturated samples were gap filled by using linear functions found between the saturated compound and other unsaturated compounds in the same sample (Table 1).

Results

Five one-week campaigns separated by 3–5 weeks were carried out from early June to the end of September 2013. Weather conditions during those campaigns were representative for the growing season of 2013. The precipitation from May to September 2013 was 258 mm, which is 207 mm less than the average for the same period during the previous three years. The average temperature at the site in May–September 2013 was similar to that in 2010 and 2011 during the same period, while it was 1.3 °C higher than in 2012. During the whole measurement period in 2013, the temperatures inside the chamber were between 5 and 40 °C with an average of 22 °C. The highest temperature in the chamber was recorded at the end of July and the lowest at the end of September (Fig. 1a). The greatest temperature difference between the inside and outside of the chamber was 12 °C when the chamber was exposed to sunlight at noon. Variations of vapor pressure deficit (VPD) followed strongly the temperature, and the discrepancy in VPD between inside and outside of the chamber was the greatest at noon (Fig. 1b). Light and temperature co-varied during most of daytime. PAR measured above the canopy (at the site's main tower at a height of 32 m) was considerably higher than inside the upper canopy level where the chamber was located, and it reached its maximum earlier than the PAR measured inside the canopy. There were generally more fluctuations in PAR and lower average values inside the canopy (Fig. 1a) due to shading by other tree tops and branches. The forest stand was already productive when BVOC measurements started in early June. Gross pri-

Table 1. The linear regressions used to fill data gaps.

Statured terpene	Regression function	r^2	n	$p <$	Campaign
Isoprene	$C_{\text{isoprene}} = 1.28C_{\text{camphene}} + 2.80$	0.67	44	0.001	25–31 July
Myrcene	$C_{\text{myrcene}} = 0.24C_{\text{camphene}} - 0.26$	0.87	45	0.001	10–16 August
α-pinene	$C_{\alpha\text{-pinene}} = 1.07C_{\text{camphene}} + 3.75$	0.72	38	0.001	25–31 July
α-pinene	$C_{\alpha\text{-pinene}} = 1.74C_{\text{camphene}} + 3.89$	0.95	41	0.001	10–16 August
β-pinene	$C_{\beta\text{-pinene}} = 0.16C_{\text{limonene}} - 0.68$	0.71	48	0.001	25–31 July
β-pinene	$C_{\beta\text{-pinene}} = 0.95C_{\text{limonene}} + 0.89$	0.92	45	0.001	10–16 August
limonene	$C_{\text{limonene}} = 1.46C_{\text{camphene}} + 3.89$	0.86	49	0.001	25–31 July

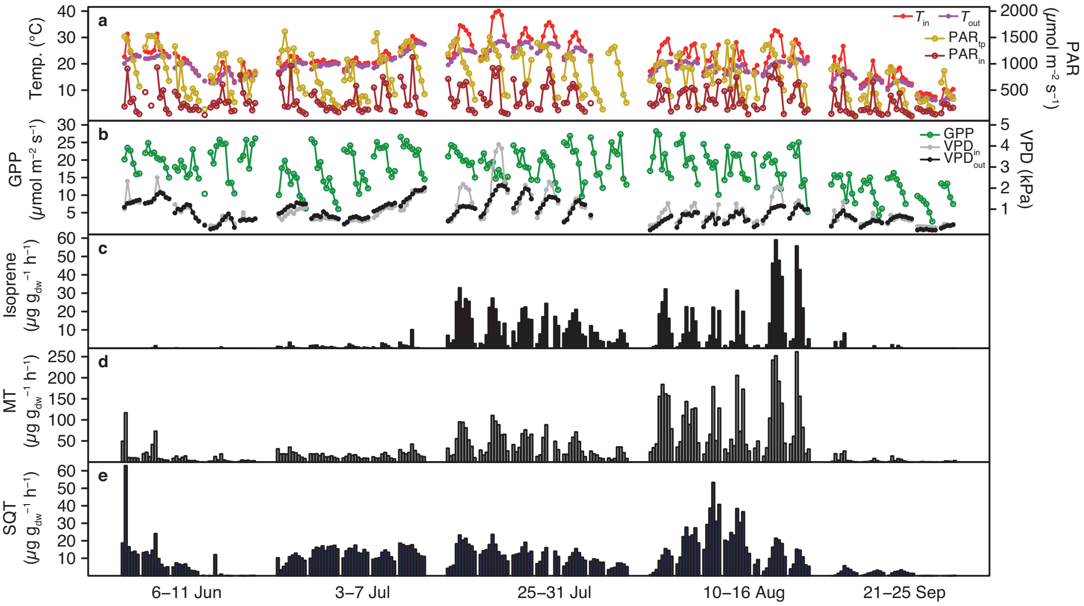

Fig. 1. Overview of the 2013 growing season conditions and measured BVOC emission rates. (**a**) temperatures inside (T_{in}) and outside the chamber (T_{out}), PAR measured inside the canopy next to the branch chamber (PAR_{in}) and from the top of the canopy from the ICOS tower (PAR_{tp}), (**b**) calculated GPP from ICOS CO_2 flux measurements, calculated VPD inside (VPD_{in}) and outside the chamber (VPD_{out}), and measured emission rates of (**c**) isoprene, (**d**) MT and (**e**) SQT.

mary production (GPP), estimated using the CO_2 flux, temperature and incoming radiation from the main tower at 32 m height with a flux-partitioning tool (Reichstein *et al.* 2005; http://www.bgc-jena.mpg.de/~MDIwork/eddyproc/index.php), remained stable from June to August with maximum values exceeding 25 μmol m^{-2} s^{-1} during daytime. During the final campaign in September, GPP was much lower (below 16 μmol m^{-2} s^{-1}; Fig. 1b).

Seasonal distribution of BVOCs emissions

Total terpene emissions measured between June and September 2013 varied between 0.05 and 332.5 μg g_{dw}^{-1} h^{-1} (0.04–293.4 μgC g_{dw}^{-1} h^{-1}). Peak emissions of isoprene, MT and SQT were in August, and the peak MT emissions were three times higher than the peak isoprene or SQT emissions (Fig. 1c–e). High isoprene emissions (average 13.3 μg g_{dw}^{-1} h^{-1} or 11.7 μgC g_{dw}^{-1} h^{-1}) were measured during two campaigns at the end of July and in August. They showed distinct diurnal patterns with increasing values in the morning, and highest emissions at noon followed by a decrease (Fig. 1c). MT emissions varied from < 0.05 μg g_{dw}^{-1} h^{-1} (0.04 μgC g_{dw}^{-1} h^{-1}) when the temperature inside the chamber was < 8 °C in September to 261 μg g_{dw}^{-1} h^{-1} (230.8 μgC g_{dw}^{-1} h^{-1}) when the temperature was about 30 °C (Fig. 1d). The highest MT emission was measured in August. It was approximately five times greater than the values measured in June and the beginning of July, and 20 times greater than emissions in September (Fig. 1d). SQT emissions were in the range of 0–62.9 μg g_{dw}^{-1} h^{-1} (0–55.5 μgC g_{dw}^{-1} h^{-1}) from June to September with the highest value measured on 6 June when the temperature inside the chamber was 31 °C (Fig. 1e). Emissions of SQT in September were below 5.8 μg g_{dw}^{-1} h^{-1} (5.1 μgC g_{dw}^{-1} h^{-1}), approximately 8% of the amount that was measured in August. When the air temperature was < 10 °C during the last two days of the measurements in September, SQT emissions became negligible (Fig. 1e). SQT emissions were much higher in early June when isoprene was not detected in most of samples, whereas the emission rates

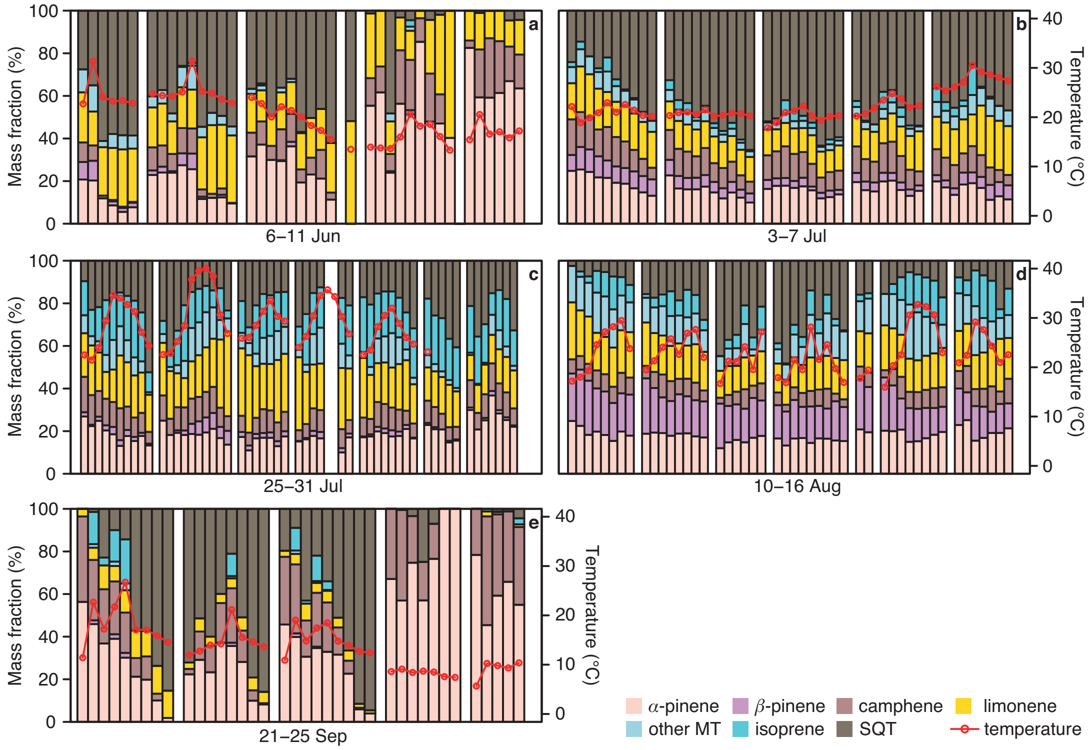

Fig 2. Daily distributions of isoprene, dominant monoterpenes (α-pinene, β-pinene, limonene, camphene), other monoterpenes (other MT), and sesquiterpene (SQT) as fractions of the total terpene emissions. Temperatures inside the chamber during each campaign are also shown.

of isoprene and SQT became comparable in late July (~11 μg g_{dw}^{-1} h^{-1} or ~9.7 μgC g_{dw}^{-1} h^{-1}; Fig. 1c and e). During the August campaign, the highest SQT emissions were recorded on 12 August and the highest MT emissions on 16 August (Fig. 1d and e).

Chemical composition of emission spectrum

The composition of detected terpenes varied among the individual campaigns and even during the course of the day. Isoprene was detected in most of the samples in July and August, SQTs were present in most of the June–September samples, and MT compounds appeared in all the samples. The most complex chemical composition with 13 different MT species (tricyclene, α-pinene, camphene, thujene, β-pinene, myrcene, α-phellandrene, 3-carene, 2-carene, limonene, sabinene, terpinene, and terpinolene) in some of the samples was recorded in late July, while eight different SQT species (α-farnesene, β-farnesene, longifolene, caryophyllene, bergamotene, α-bisabolene, humulene, α-longipinene) were detected in some of the samples collected in August. However, the August data contained the highest average fraction (73% by mass) of MTs as compared with that measured during the other campaigns, and at the same time the proportion of SQTs was the lowest fraction (15%) of all campaigns (Fig. 2d). 3-carene, 2-carene, thujene, terpinene and bergamotene appeared only in July and August, and α-phellandrene was only present in the middle of the day during July and August. The isoprene fraction of the total terpene mass was close to 0% in June, increased to 4% in the beginning of July and exceeded 10% during the last three campaigns (Fig. 2a–e).

The dominant MTs were α-pinene, limonene, camphene, β-pinene, which collectively contributed 48%–59% of the total terpene emissions during summer time in 2013. α-pinene, camphene and limonene were continuously present in all samples (Fig. 2). The fraction of α-pinene in June and September varied from nearly 0% to almost 100% of total terpenes, but was rather stable in July (17% ± 3.7%) and August (18% ± 2.7%) (Fig. 2a and e). The mass fraction of β-pinene in August was higher in comparison with other months (18% ± 3.9%), and roughly the same as the fraction of limonene and α-pinene at the same time (Fig. 2d). Limonene accounted for about 15% ± 3.7% of the total terpene mass in the beginning of July with a relatively stable distribution throughout these five days (Fig. 2b). When the temperature was below 10 °C, the dominant MTs were α-pinene and camphene, which contributed to almost 100% of total terpenes, and the mass fractions of α-pinene and camphene varied in June and September (Fig. 2a and e). The fractions of both α-pinene and camphene were low at high temperatures when isoprene emissions increased, but went up with the decreasing temperature. The emission of myrcene was almost zero in September when it appeared only in the samples taken at noon time. The ratio of camphene/α-pinene was varying from 0.4 to 0.7 among different campaigns, with the lowest ratios in June. The fraction of β-pinene and myrcene was in the range of 0%–5% in most of campaigns except in August, and the temperature sensitivities of myrcene and β-pinene were similar in all the months. The highest myrcene/β-pinene ratio was 1.1 in late July and the lowest (0.1) in August due to the high emissions of β-pinene in the August campaign. The limonene/camphene ratio for each campaign was within a range of 0.3 to 1.8.

SQTs comprised 42% of the total terpene mass in the beginning of July and the mass fraction of MT was 54% during the same period (Fig. 2b). The fraction of SQT seemed to decrease when the temperature was high at noon (Fig. 2c and d), while it was fairly stable from 3 to 7 July (Fig. 2b) when the temperatures were relatively stable (17.8–30.5 °C) as compared with those during the other campaigns. β-farnesene was the main SQT compound recorded in June–August, and its mass fraction decreased with time from 25% in June to 10% in August even though its emission rate increased from 5.3 μg g_{dw}^{-1} h^{-1} (4.7 μgC g_{dw}^{-1} h^{-1}) in June to 12.1 μg g_{dw}^{-1} h^{-1} (10.7 μgC g_{dw}^{-1} h^{-1}) in August. In September, α-farnesene became the dominant compound with a mass fraction of 13% of total emitted terpenes.

Separation of MT emissions using a hybrid model

To analyze the importance of *de novo* synthesis and emissions from storage for the observed MT compounds, a hybrid model (Ghirardo *et al.* 2010; Eq. 1) was applied to the measured data. The approach of hybrid_const, which optimized the hybrid model based on all the campaign data together, resulted in f_{denovo} of 83.6% and E_S of 99.4 μg g_{dw}^{-1} h^{-1}. In the second approach of hybrid_adj, this hybrid model was optimized for each campaign separately. In all the campaigns, MT emissions were mostly attributed to *de novo* synthesis as f_{denovo} was above 50% throughout all the months (Table 2). All MT emissions were considered from *de novo* synthesis in June and 86.2% of emissions in September, while around half of the MT emissions were from storage pools at the end of July (f_{denovo} = 50.7%). As for the campaign-based standardized emission rate E_S (Table 2), it was the highest in August (210.3 μg g_{dw}^{-1} h^{-1}), followed by that in June (68.8 μg g_{dw}^{-1} h^{-1}) and the one at the end of July (57.7 μg g_{dw}^{-1} h^{-1}). The lowest standardized emission rate of all campaigns was that in September (42.6 μg g_{dw}^{-1} h^{-1}).

To evaluate both approaches, MT emissions were calculated using the hybrid model with

Table 2. The optimization results of hybrid model based on each campaign presenting the fraction of MT emissions from *de novo* synthesis (f_{denovo}) and the standardized MT emission rate (E_S).

	6–11 Jun	3–7 Jul	25–31 Jul	10–16 Aug	21–25 Sep
f_{denovo} (%)	100	59.6	50.7	59.7	86.2
E_S (μg g_{dw}^{-1} h^{-1})	68.8	46.2	57.7	210.3	42.6

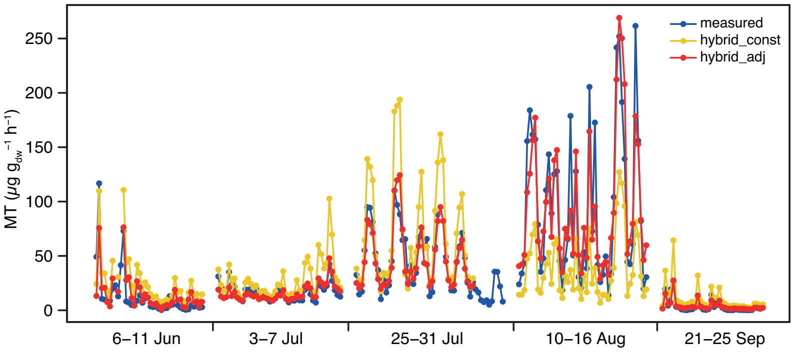

Fig. 3. The distribution of measured MT emissions and modeled emissions based on two methods of hybrid_const and hybrid_adj.

both constant and changing values of f_{denovo} and E_S, and compared with the measured emissions. Not surprisingly, the MT emissions calculated with hybrid_adj agreed with the measured emissions much better than those calculated with hybrid_const (Fig. 3). Hybrid_const overestimated the MT emissions for June, July and September, but underestimated those for August when the measured emission rates were the highest (Fig. 3). The MT emissions calculated with hybrid_adj were in the range of 0.6–269.1 μg g_{dw}^{-1} h^{-1}, which was close to the measured MT emissions (0.05–261.6 μg g_{dw}^{-1} h^{-1}). The Pearson's correlation (r_p) between the measured MT emissions and those calculated with hybrid_adj was 0.94 ($n = 213$, $p < 0.01$), and it captured the large fluctuations of the MT emissions in August (Fig. 3), while the correlation (r_p) between the measured MT emissions and those calculated with hybrid_const was only 0.64 ($n = 213$, $p < 0.01$).

Effect of seasonality on canopy MT emissions

To estimate how the variation of emission rates affects the calculation of the amount of MT emissions during the growing season on the canopy-scale, we used a simple upscaling based on the results from the previous section. For this, the hybrid model (Eq. 1) was used for computation of the seasonal emissions. The values of E_S and f_{denovo} were taken from the previous step, and E_S of MT was transformed from μg g_{dw}^{-1} h^{-1} to μg m^{-2} h^{-1} based on the measured specific leaf area 312.5 g m^{-2} and leaf area index of the Norunda forest which was 4.8 m^2 m^{-2} (Sundqvist *et al.* 2015) to result in an emission rate for the canopy of the forest, E_C. The temperature and PAR data measured from the ICOS tower at 29 m between 1 June and 30 September 2013 were used in the calculations. Method 1 represented the calculated E_C based on constant E_S or f_{denovo} for the entire growing season. In method 2, E_S and f_{denovo} from each campaign were assumed to be representative for the middle of the month, and a linear interpolation was applied for these two parameter values between campaigns. For July, E_S and f_{denovo} from the first campaign was set as that calculated for 5 July and from the second campaign was set as that calculated for 25 July.

The daily averaged canopy emission rate E_C of MT calculated using method 1 with fixed parameters was 3.9–8.7 mg m^{-2} h^{-1} (3.4–43.0 mgC m^{-2} h^{-1}) from June to September 2013 (Fig. 4). However, the E_C of MT calculated using method 2 showed substantial fluctuations in August, and the highest daily emission reached on average 71.7 mg m^{-2} h^{-1} (63.3 mgC m^{-2} h^{-1}). The discrepancy in calculated E_C of MT between methods 1 and 2 was as much as 47.2 mg m^{-2} h^{-1} (41.6 mgC m^{-2} h^{-1}) in August, when the campaign-based E_S (210.3 μg g_{dw}^{-1} h^{-1}) of MT was particularly high as compared with a constant E_S (99.4 μg g_{dw}^{-1} h^{-1}). In June, in the beginning of July and in September, however, method 2 showed lower canopy emission rates of MT. Generally, the adjusted model produced a stronger seasonality in the emissions. Method 1 with a constant parameter setting gave in total 48% less canopy MT emissions as compared with method 2 with varying E_S and f_{denovo} throughout the season (June–September).

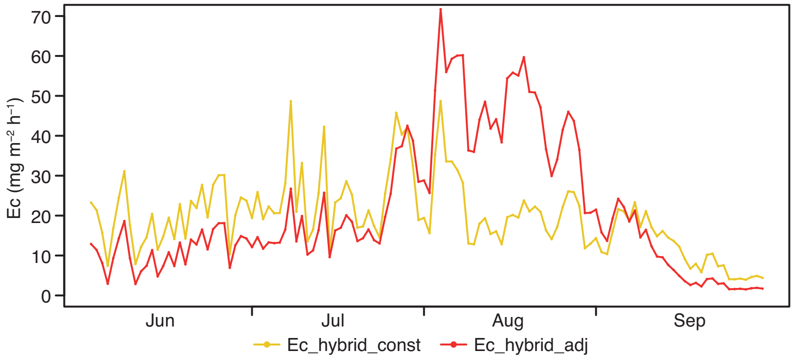

Fig. 4. Daily averaged emission rates (E_C, mg m^{-2} h^{-1}) of MT at the canopy scale based on Eq. 1 between 1 June and 30 September 2013. Ec_hybrid_const uses a seasonal average E_S and f_{denovo} to calculate E_C, Ec_hybrid_adj has a campaign-wise optimized E_S and f_{denovo} to calculate E_C. A linear interpolation was used for E_S and f_{denovo} between campaigns.

Discussion

The emission rate and emission spectra of BVOCs

Compared with the previous studies, the total amount of MT emitted from the measured Norway spruce was high. For instance, a 50-year-old Norway spruce growing in the vicinity of our current site emitted MT in the range of 0.1 to 5.7 μg g_{dw}^{-1} h^{-1} from May to September (no August data reported), which was only 3%–4% of our measurements (Janson *et al*. 1999). Yassaa *et al*. (2012) observed total MT emissions from a 50-year-old Norway spruce in the range of 0.55 to 12.2 μg g_{dw}^{-1} h^{-1} during July and August, which was much lower compared with our measured range of 5.1 to 261.6 μg g_{dw}^{-1} h^{-1} during the same period. However, differences in the measurement height and techniques could possibly contribute to the variability in the results. Janson *et al*. (1999) used a PTFE bag tied around a branch at a height of 15 m, and Yassaa *et al*. (2012) used a smaller chamber in the middle part of the canopy together with a solid-phase microextraction (SMPE) technique to quantify terpenes, while this study used a dynamic chamber in the upper part of the canopy at 20 m. The measured Norway spruce in our study is around 118 years old, which is much older than most of the spruces used in previous studies. However, we are not aware of any study that reports a variation in the BVOC emission capacity with age for spruce. Large variability in BVOC emission patterns exist among individual trees of the same species under natural growing conditions (Lindfors and Laurila 2000, Bäck *et al*. 2012), and therefore we cannot say that the high terpene emission from the measured tree represents the whole forest at Norunda given that our study was based on only one tree.

High MT emissions could possibly be a result of mechanical stress, but had such high emissions been induced they would have decreased quite rapidly (Litvak and Monson 1998, Bourtsoukidis *et al*. 2013). In our case, MT emissions in August indicated a clear diurnal pattern without any decline during six days of continuous daytime measurements, which would make mechanical stress to cause these high emissions rather unlikely. However, the specific leaf area (SLA, cm^2 g^{-1}) varies with age, such that a current-year foliage has a much higher SLA than older needles (Hager and Sterba 1985), and growing Scots pine needles have been reported to emit more MT than mature needles (Aalto *et al*. 2014). The biomass enclosed in the chamber was at the tip of the branches, which always includes new needles. This could have contributed to the measured high emission rates of MT from the spruce tree. Another possible cause of the high MT emissions could be beetle attacks: Ghimire *et al*. (2016) reported that the bark emission rates of α-pinene, camphene and limonene were 39-, 55- and 15-fold higher, respectively, in beetle-attacked Norway spruce trees than in control trees. However, we cannot provide any evidence to support this assumption since no visible signs of attacks were found during the measurement campaigns.

SQT emissions in the boreal zone are 5%–15% of the total MT emissions (Hakola *et al*. 2003, 2006, Rinne *et al*. 2009), although studies of SQT emissions from Norway spruce are very limited. A recent study showed that SQT emission from spruce peaked in April (Bourtsoukidis *et al.* 2013), and Holzke *et al.* (2006) reported that for pine the SQT contribution to the total BVOCs was as high as 70% in March and fell to 1%–2% in August and September. However, the contribution of SQT to total terpenes in our study was in a wide range of 0% to 65% from June to August, and there was an even higher percentage in the September samples (Figs. 1 and 2e). The dominant SQTs were α-farnesene and β-farnesene, which are commonly induced compounds for the self-defense against insect attacks, e.g. as emission after the attack by beetles (Blande *et al.* 2009). Methyl-jasmonate (MeJA, not measured in this study), together with MT and SQT accumulation in needles, is an indicator of plant defense in Norway spruce (Martin *et al.* 2003). The SQT compounds reported by Martin *et al.* (2003) (α-farnesene, β-farnesene and α-bisabolene) were identical to the compounds found in our samples. Another study, examining mite-infestation-induced terpene emissions from Norway spruce, confirmed that β-farnesene and α-farnesene were the main volatiles emitted from infested trees (Kannaste *et al.* 2009). Kajos *et al.* (2013) reported the emissions of terpene from herbivore-affected Siberian *Larix cajanderi* to be up to 10 times higher in June and July and almost 100 times higher in August as compared with those from unaffected trees, but wind-induced mechanical stress could also be a reason for the emission difference. Haapanala *et al.* (2009) reported that SQT emissions from a mountain birch in 2007 were less than 1% of those in 2006 due to the fading effect of an herbivory damage (Autumnal moth) which had occurred in 2004. Although we were not able to detect any visible signs of insect attacks on the tree used in this study, we cannot exclude such an attack by insects before the measurements, given the observed high amounts of SQT emissions throughout the whole growing season until September when the air temperature inside the chamber decreased to 10 °C.

Seasonal variation of MT emissions from branches and canopy

MT emissions originate from both *de novo* synthesis and storage (Kahl *et al.* 1999), which makes it hard to separate light-dependent emissions from temperature-regulated emissions. Currently, there are no adequate studies for Norway spruce needles to demonstrate which MT compounds originate from a storage pool or are emitted directly after synthesis, or whether the MT emissions are a combination of these two factors. The hybrid model gave a better estimation of the MT emissions by including the effects of both temperature and light (Fig. 3). Ghirardo *et al.* (2010) reported that the fraction of MT emissions from *de novo* biosynthesis in mature Norway spruce needles was 33.5% by applying $^{13}CO_2$ fumigation and isotope analysis, while our optimized f_{denovo} of MT emissions was over 50% during all the campaigns (Table 2). The high f_{denovo} values in June and September were partly due to low evaporation rate of MT compounds from the storage pool when temperature inside the chamber was lower in comparison with the temperatures in July and August. A study of Mediterranean woody species by Llusià and Peñuelas (2000) showed that the stored terpenes had the lowest emissions in spring and reached the maximum emissions in autumn. The amount of MT stored inside spruce needles is probably very low in spring as well, which could explain why the optimized f_{denovo} was as high as 100% in June. The varying compound composition could be one of the reasons for the variability of f_{denovo} as well. A study from Schurmann *et al.* (1993) showed that α-pinene emissions from Norway spruce needles increased with an increasing light intensity, which indicated that α-pinene originated from *de novo* synthesis. A high fraction of α-pinene in emissions could contribute to the high values of f_{denovo} in June and September. The variation in f_{denovo} is also caused by the different activity levels of terpene synthases and other related enzymes during needle development (Ghirardo *et al.* 2010). BVOC production and emissions exhibit similar developmental profiles in all plant organs, with increasing emissions during the early development stage (when e.g. leaves are not fully expanded), and either decreasing or constant emissions afterward (Dudareva *et al.* 2013). The MT synthases' activity in holm oak leaves increased fast after leaf emergence, reaching the peak values in summer and declined in winter (Fischbach *et al*. 2002). Similarly, we assume that increased enzyme activities in the Norway spruce during the needle elongation caused high f_{denovo} of 100% in June. The concentration of MT compounds is also known to differ between the needles and bark of Norway spruce (Sallas *et al*. 2003, Ghirardo *et al*. 2010). However, we only took the needle mass enclosed in the branch chamber into account, and did not include any potential bark surface emissions. Therefore, we could not exclude the impacts that might have been caused by using different branches in these five campaigns.

There were pronounced variations in the amount and composition of terpene emissions among campaigns. Both the measured MT emission rates and the standardized emission rates E_S were at their maximums in August (Fig. 1c–e and Table 2), while the lowest emission rates were recorded in September. Staudt *et al*. (2000) reported high MT standardized emissions (E_S) from pine in summer and much lower in winter, and other studies revealed that the emission potentials of conifers were high in spring and early summer and decreased in late summer and autumn (Janson 1993, Tarvainen *et al*. 2005). The need to accurately account for seasonal variations of emission rates on a canopy scale becomes obvious from the comparison of the two simple approaches applied in our study, one with constant E_S and f_{denovo} for the entire growing season (method 1), and the second one with a campaign-based E_S and f_{denovo} (method 2). The differences in calculated MT emissions between methods 1 and 2 were more pronounced during the middle of summer when high campaign-based E_S values dominated in the estimates produced by method 2. However, neither of the calculating methods could capture extreme emission events that were observed on individual days. We are also aware of that the temperature sensitivity β was constant in our calculations, which could have caused discrepancies between the measured and calculated emissions. Also, as gradients of light, air temperature and humidity exist within the forest canopy (Schurgers *et al*. 2015), the simple approach used here to calculate E_C from measurements at the top canopy level may not be representative for the whole canopy emissions. However, this quick estimate shows that to precisely assess BVOC emissions from the whole canopy, the seasonal variations in emission rates need to be taken into account.

Conclusions

We measured emissions of BVOCs from the sun-exposed upper branch of an old spruce tree within a forest using a dynamic branch chamber throughout most of the growing season. Terpene emission rates were greater, and the compound spectrum was more complex, in July and August compared with those in early summer or autumn. Exceptionally high terpene emissions were measured in August, which were due to high temperatures, possibly combined with the accumulation of terpenes in storage pools in July. The relative contributions of the dominant MT compounds to the total BVOC emissions were fairly stable for each branch of the individual campaign, and even compounds with considerably different chemical properties showed a constant ratio of emissions. A hybrid model incorporating both *de novo* and storage pool emissions, thereby capturing the impacts of both temperature and light, was able to produce a good estimate of MT emissions (r_P = 0.94) from branches. The fraction of MT emissions from *de novo* synthesis was above 50% from our sample tree, being the highest in June and September. However, the seasonal variation in terpene emissions requires a more detailed parameterization of algorithms used to model BVOC emissions throughout the growing season, as constant parameters for E_S, f_{denovo} and β using either a growing-season or monthly fitting could not reproduce the observed variability entirely. Thus, the use of an emission algorithm that is based only on a short-term response to the temperature and light to estimate annual or seasonal BVOC emissions could bear large uncertainties.

Acknowledgements: This project was funded by the Swedish Research Council VR (2011-3190). We are very grateful to A. Båth and I. Lehner from ICOS Norunda research station for technical support during each campaign. We thank M. Mölder, F. Lagergren and P. Vestin (Lund Univ., Sweden) for sharing data from the research site and inspiring discussions.

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