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Biogenic volatile organic compound emissions from a boreal forest floor

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A dynamic soil chamber was used to quantify biogenic volatile organic compound (BVOC) emissions from the forest floor of a Norway spruce and Scots pine dominated boreal forest. To carry out measurements (five campaigns from June to October 2015), six plots were randomly selected. The BVOC emissions from the forest floor ranged from 0.4 to 66.6 μg m^{-2} h^{-1}, and the emission rates peaked in October with an average of 10.26 μg m^{-2} h^{-1} when the litterfall biomass was the highest and the air temperature was the lowest (< 10 °C). Monoterpene (MT) was the main group of detected BVOCs, their contribution to total BVOC emissions from the forest floor being > 80%, while the contribution of isoprene was close to zero during all campaigns and the sesquiterpene (SQT) emissions in September and October were negligible. α-pinene, Δ^3-carene and camphene were the dominant MT compounds throughout summer and autumn. The MT emission rate increased exponentially with air temperature inside the soil chamber from June to September. Variations among the frames and in time indicate that needle litter may be an important source of BVOC emissions.

Introduction

Biogenic volatile organic compounds (BVOCs) are a diverse group of hydrocarbons (excluding methane) emitted by natural sources, such as terrestrial vegetation, soils and sediments, marine and freshwater systems, and geological hydrocarbon reservoirs (Guenther 1995, Kesselmeier and Staudt 1999). Terrestrial vegetation has been considered as the largest source of BVOC, with an estimated total annual emission of 760 Tg C y^{-1} (Sindelarova *et al*. 2014). BVOCs are important reactive trace gases in the troposphere that can affect air chemistry by reacting with OH, NO_3 and O_3 or contribute to O_3 and aerosol formation (Fuentes *et al*. 2000, Atkinson and Arey 2003). The most abundant BVOCs are terpenes, such as isoprene (C_5H_8), monoterpene (MT, $C_{10}H_{16}$) and sesquiterpene (SQT, $C_{15}H_{24}$), mainly released from plant foliage (Guenther 1995, Sindelarova *et al*. 2014).

Many studies have focused on the BVOC emissions from plants, and the important biotic and abiotic drivers for these emissions (Fuentes

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et al. 2000, Laothawornkitkul *et al*. 2009). In contrast, studies on BVOC emissions from forest floor or soil are much scarcer. A study by Janson (1993) reported that the MT flux from a Scots pine floor was 20%–40% of the size of the flux from the forest crown and had similar variation during summer as that of the crown. In another study of a boreal Scots pine forest, the MT emissions from the forest floor accounted for 10% of total monoterpene emissions from the ecosystem in spring and autumn (Aaltonen *et al*. 2011).

BVOC emissions from the forest floor are coming from litter, understorey vegetation (Hayward *et al*. 2001, Aaltonen *et al*. 2011), the processes of microbiological decomposition activities at the soil surface (Hellén *et al*. 2006, Greenberg *et al*. 2012) and in the soil (Schöller *et al*. 2002, Kai *et al*. 2010), and from the root system (Janson 1993, Lin *et al*. 2007). Litter has been recognized as the main source of BVOC emissions from the forest floor (Hayward *et al*. 2001, Hellén *et al*. 2006). The roles of BVOCs in soil ecology and nutrient cycling are not fully understood, but recent studies have revealed that BVOCs could act as info-chemicals for the inter- and intra-organismic communication and function as bioactive growth-promoting or growth-inhibiting agents (Peñuelas *et al*. 2014). For instance, endophytic bacteria-produced volatiles can increase maize plants' pathogen resistance and increase parasitoid attraction in the soil (D'Alessandro *et al*. 2014), and certain MTs can inhibit net mineralization of nitrogen and net nitrification in forest soil (White 1991, 1994). Some volatiles can serve as potential carbon and energy source for soil microbes (Smolander *et al*. 2006, Owen *et al*. 2007) and promote the growth of fungi in poor natural soils (Gramss and Bergmann 2008).

Boreal forests are one of the major vegetation zones in the world, covering around 16% of the land surface on earth (Bonn *et al*. 2007). The contribution of boreal forest floor vegetation to ecosystem gross photosynthetic production is significant (Goulden and Crill 1997, Kolari *et al*. 2006), and a study in a forest stand close to the present study site showed that ground vegetation had adopted to the low light conditions and began photosynthesis already at photosynthetically active radiation (PAR) in the range of 3–30 μmol m^{-2} s^{-1} (Morén and Lindroth 2000). Therefore, the BVOC emission from boreal forest floor is an important component for the global BVOC emission budget. The objectives of this study are to quantify BVOC emissions from the floor of a mixed Scots pine and Norway spruce forest during summer and autumn, and to identify the environmental variables controlling these forest floor BVOC emission rates.

Methods

Study site

The forest site of this study is Norunda research station in central Sweden (60°05´N, 17°29´E; www.icos-sweden.se/station_norunda.html), which is also part of the atmospheric and ecosystem networks within the Integrated Carbon Observation System (ICOS), a European infrastructure for measuring greenhouse gas concentrations and fluxes. The study site is dominated by Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). The leaf area index (LAI) is in the range of 3 to 6 m^2 m^{-2}, and it can be as high as 7 m^2 m^{-2} (http://www.icos-sweden.se/station_norunda.html). The soil is sandy-loamy tills with a high content of stones, which is characterized as podzolised dystric regosols (Lundin *et al*. 1999).

Measurement design

The study was done in a 120-year-old mixed Scots pine (80% of basal area) and Norway spruce (20%) stand with a dominant height of 28 m, located about 75 m north-west from the central ICOS-tower. Bilberry (*Vaccinuim myrtillus*) was the dominant species in the field layer, but there were also other dwarf shrubs, grasses and ferns. A rather thick layer of boreal feather mosses covered most of the bottom layer. Within a 25 × 25 m area, aluminum frames (inner dimension 18.8 × 18.8 cm, outer dimension 19.2 × 19.2 cm) were inserted into the ground to a depth of 10 cm in April 2015 at six random locations (Appendix 1). The frames included channels at the surface that allowed for sealing the chamber with water during the sampling. The

plots differed in vegetation composition, litter covered area and humus layer depth (Appendix 2). Plots 1, 3 and 5 had high humus layer and high content of mosses. Plots 2 and 6 had large proportion of needle litter and other dead organic material covered area. Plot 4 had a tall grass growing inside the frame.

BVOC sampling and measurements of temperature, PAR, CO_2 flux and moisture

Five campaigns were carried out between June and October 2015 with three days of measurement per campaign (Table 1). The September campaign was done in two periods one week apart. From each plot, two or three samples were collected during a period of 30 minutes between 09:00 and 18:00 during the individual campaigns, and 95 samples were collected in total during the five campaigns. The chamber used for sampling in this study was the same as in Ekberg *et al*. (2011), made of a stainless-steel frame covered with 0.05 mm FEP (fluorinated ethylene propylene) film (Flurotek AB, Knivsta Sweden). The volume of the chamber ($20.0 \times 20.0 \times 28.5$ cm) was 11.4 l and the measured soil area was 0.035 m^2 (calculated from the inner length of the frames). The chamber was placed on the frames that were pre-installed in April, and the channel was filled with water to make the frames airtight. The chamber was equipped with a temperature and humidity sensor (Tinytag view 2, Gemini Data Loggers, UK) to measure the air temperature and relative humidity inside the chamber. The measured air temperature inside the chamber represents the near-surface air conditions that are expected to drive emissions from the forest floor in natural conditions. Ambient air was pushed by two micro pumps and controlled by potentiometers, with the inlet flow rate displayed by a gas flow indicator (Key Instruments, US). Air entering the soil chamber was filtered through a hydrocarbon trap (Alltech Associates Inc., USA) containing also an MnO_2 coated copper mesh to remove ozone, and a flush time of 30 min (1 h in June) at a flow rate of 0.55 l min^{-1} (0.3 l min^{-1} in June) was applied before measurements started. Air samples from the chamber were taken via adsorbent tubes filled with Tenax-TA and carbongraph 1 TD (Markes International Limited, UK) using a pocket pump (SKC, USA) with flow rate of 0.2 l min^{-1} for 30 minutes (6 l sample volume per sample). Two blank samples were taken in each campaign to account for any instrumental background emission. The adsorbent tubes were stored at 5 °C before being analyzed in the laboratory in Finland using a thermal desorption instrument (Perkin-Elmer TurboMatrixTM 650, Waltham, USA) connected to a gas chromatograph (Perkin-Elmer Clarus 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 μm) column and a mass selective detector (Perkin-Elmer Clarus 600T, Waltham, USA).

The CO_2 concentration inside the chamber was also monitored (LI-840A, LI-COR, USA) with a measurement frequency of 30 seconds. The flow rate to the CO_2 analyzer was 0.2 l min^{-1} during the pre-measurement flushing and 0.12 l min^{-1} during sampling. PAR was measured with a quantum sensor (LI-190, LI-COR, USA) at about 30 cm above the ground next to the chamber. The data of PAR and CO_2 concentration were recorded with a datalogger (LI-1400, LI-COR, USA). Soil temperature and soil moisture were measured outside of the frame after sampling with the soil chamber.

Table 1. Timetable of the five campaigns and the number of collected samples during each campaign.

Campaigns	Number of collected samples						
	plot 1	plot 2	plot 3	plot 4	plot 5	plot 6	total
1. 15–18 Jun	3	3	2	3	3	2	16
2. 14–17 Jul	3	3	3	3	3	3	18
3. 14–17 Aug	3	3	3	4	3	3	19
4. 15–16 Sep	2	2	3	2	2	2	13
23–24 Sep	2	2	2	2	2	2	12
5. 26–28 Oct	3	2	3	3	3	3	17

Soil temperature was measured at a depth of 5 cm with three replicates for each plot, and soil moisture (volumetric soil water content) averaged over the top 5 cm of soil was measured using a portable ThetaKit (Delta-T Devices, Cambridge, UK) with three replicates for each plot as well. We expect the temperature at this depth to be representative for the main processes (litter decomposition and plant root metabolism) that would drive BVOC emissions from the soil.

Fifteen litter traps were randomly distributed on the ground with a mean height of 88.3 cm above the ground and a mean diameter of 56.4 cm. The traps were closed on 21 May, and litterfall from these 15 traps was collected later on 16 June, 16 July, 16 August, 15 September and 26 October. The collected litter was weighted after drying at 60 °C for around 48 hours.

Data analysis

CO_2 flux

The CO_2 flux was calculated as:

$$F_c = \frac{K_c P}{K_g \left(T + 273.15\right)} \times \frac{V}{A}, \quad (1)$$

where F_c is the CO_2 flux (μmol m^{-2} s^{-1}), K_c is the slope coefficient (μmol s^{-1}), which is calculated by applying a linear regression on the continuously increasing CO_2 concentration as a function of time (six continuous measurements of CO_2 concentration within three minutes), K_g is the gas constant with the value of 8.31 J mol^{-1} K^{-1}, V is the volume of the chamber (m^3), and A is the area of the frame (m^2). P is the air pressure (101 325 Pa), T is the measured air temperature inside the chamber (°C).

Emission rate

The BVOC emission rate E (μg m^{-2} h^{-1}) from each frame was calculated as the mass of each compound per m^2 and time (Aaltonen *et al*. 2011):

$$E = \frac{F\left(C_2 - C_1\right)}{A}, \quad (2)$$

where F is the air flow rate through the chamber (l h^{-1}), A is the area of frame (m^2), C_2 is the concentration of each terpene in the air leaving the soil chamber (μg l^{-1}) and C_1 is the terpene concentration of air entering the chamber (μg l^{-1}, blank samples).

Vegetation coverage

The condition of vegetation growth on each plot was manually documented by three images per plot taken with a RGB camera (Pentax K-30) during each campaign. Pentax K-30 is a single-lens reflex (SLR) camera with a 16 megapixels CMOS sensor and was equipped with a 18–55 mm lens. Viewing angle of each shot was downward-facing to the ground from a height of ~70 cm. Based on the photos, species of the field and bottom layer were identified and the coverage was estimated. The coverage was summarized into four main classes: feather mosses, dwarf shrubs, grasses and lichens.

Variable importance analysis

The relative importance of environmental variables on BVOC emissions was estimated using quantile regression forests (QRF) (Meinshausen 2006), which is a type of random forests (RF) (Breiman 2001). RF has been used in ecological studies (Prasad *et al*. 2006), and is able to describe the importance of variables based on small sample size (Díaz-Uriarte and Alvarez de Andrés 2006). Here, QRF was run 22 times for simulating each single BVOC (18 compounds), total MT, total SQT, total other BVOCs and total BVOCs based on six environmental variables (air temperature, PAR, CO_2 flux, soil temperature, soil moisture, and vegetation coverage) by using 92 samples. Only two randomly selected variables were used to build each single regression tree in the forest of 500 regression trees. The importance of any environmental variable (IV) was calculated by

$$\mathrm{IV} = \frac{\frac{1}{n}\left(\sum_{i=1}^{n} x_i\right)}{\sigma\left(x\right)}, \quad (3)$$

where x is a measure of importance for each

variable in each tree based on the changes in the mean squared error due to splits on every variable (https://se.mathworks.com/help/stats/compactregressiontree.predictorimportance.html), n is the number of trees, and $\sigma(x)$ is the standard deviation of all x. A higher value of IV obtained from the QRF analysis indicated that the variable was more important for BVOC emissions. If IV of an environmental variable was close to zero or negative, it implied that this variable is unimportant in QRF to predict BVOC emissions respectively.

Standardization of MT emissions

The measured MT emission rate E was standardized to a temperature of 303.15 K (30 °C) and PAR of 1000 μmol photons m^{-2} s^{-1} based on the temperature-dependent algorithm of Guenther *et al*. (1993):

$$E = E_S \exp\left[\beta\left(T - T_s\right)\right], \quad (4)$$

where E_S is the standardized emission rate (μg m^{-2} h^{-1}), T is the leaf temperature (K), which is estimated with the air temperature inside the chamber, T_S is the standard temperature of 303.15 K, and β is the temperature sensitivity (K^{-1}) of emissions. We used all the measured data together (with and without October data) to optimize parameters E_S and β.

The QRF analysis and the optimization of E_S and β were run with MATLAB (The MathWorks, Inc., Natick, Massachusetts, USA).

Results

The environmental conditions

Based on the continuous observation between May and October 2015 from Norunda research station, the daily averaged ambient air temperature varied between 1.9 and 24.0 °C, the soil temperature at a depth of 5 cm varied between 5.7 and 15.0 °C, the soil moisture (volumetric water content) of the top 6 cm soil layer was in the range of 9% to 33%, and the PAR measured below canopy (around 1 m above ground) was about 14% of the PAR measured above canopy on average (Fig. 1). The measured air temperature inside the soil chamber during sampling varied from 0.4 to 26.3 °C and the soil temperature at a depth of 5 cm varied between 5.0 and 13.6 °C during daytime measurements from June to October. The highest air temperature inside of chamber and soil temperature were observed in August, and the lowest values were observed in October. The measured air temperature inside the chamber was always 3–8 °C higher than soil temperature except in October when soil temperature was 1.4 °C higher than air temperature during daytime. In our measurement, the highest soil moisture averaged over the top 5 cm soil layer was observed in July with an average of 26% in the six plots, and the lowest was observed with an average of 13% in the six plots in October. The measured soil temperature of the six plots was very similar within each campaign, while the soil moisture varied between plots with differences as high as 13%.

Vegetation coverage

Plant species produce and emit different amounts and combinations of BVOCs (Laothawornkitkul *et al*. 2009), therefore, the coverage and composition of vegetation inside of the six plots could influence the BVOC emissions from each plot. Based on the analysis of images of each plot, feather mosses were determined to be the major vegetation in the plots, particularly in plots 1, 3, and 5 (Table 2). In plot 3, about 70% of the plot area was covered by *Hylocomium splendens* (Hedw.) Schimp. and in plot 1, 55% of the plot area was covered by *Ptilium crista-castrensis*, while *Hylocomium splendens* and *Ptilium crista-castrensis* occupied 45% and 40%, respectively, of the plot area in plot 5. Grasses (*Poaceae*) were only present in plot 4 and lichens only in plots 2 and 6 (Table 2). There was one mushroom growing in plot 5 on 23 and 24 September, the fruit body of which covered 4% of the plot area. Plots 3 and 5 had the highest total vegetation coverage (over 90%), while plots 2 and 4 had the lowest coverage with values below 30% (Fig. 2). The total vegetation coverage was relatively stable in plot 1 (~73%), plot 2 (~20%) and

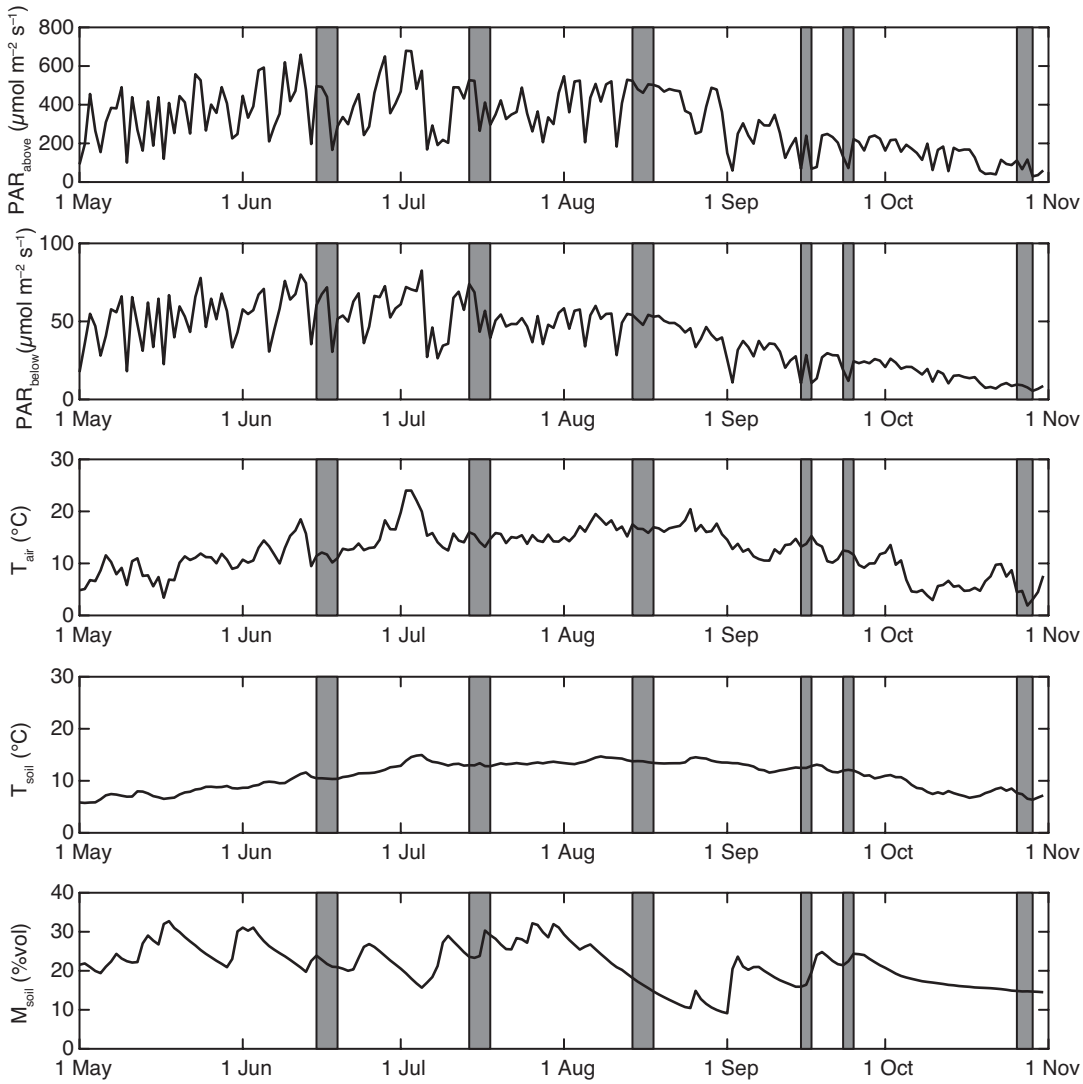

Fig. 1. Overview of climate conditions from 1 May to 30 October 2015 with daily averaged PAR above canopy (PAR_{above}, at 55 m), PAR below canopy (PAR_{below}, at about 1 meter above ground) air temperature (T_{air}, at 28 m), soil temperature (T_{soil}, at a depth of 5 cm), and soil moisture (M_{soil}, the mean of top 6 cm layer of the soil). The campaign days were marked by shading. Data from ICOS Carbon Portal (https://data.icos-cp.eu/portal/#search).

Table 2. Average coverage (%) by different classes of vegetation.

Vegetation	plot 1	plot 2	plot 3	plot 4	plot 5[d]	plot 6
Feather mosses[a]	71	17	92	8	87	36
Dwarf shrubs[b]	2	0	2	0	3	2
Grass	0	0	0	15	0	0
Lichens[c]	0	3	0	0	0	6

[a] Mainly *Hylocomium splendens*, *Pleurozium schreberi*, *Ptilium crista-castrensis* and *Dicranum scoparium.*
[b] *Vaccinium myrtillus, Vaccinium vitis-idaea* and *Linnaea borealis.*
[c] *Platismatia glauca* and *Hypogymnia physodes.*
[d] A mushroom was present in plot 5 during measurements on 23–24 September whose fruit body covered 4% of the plot area.

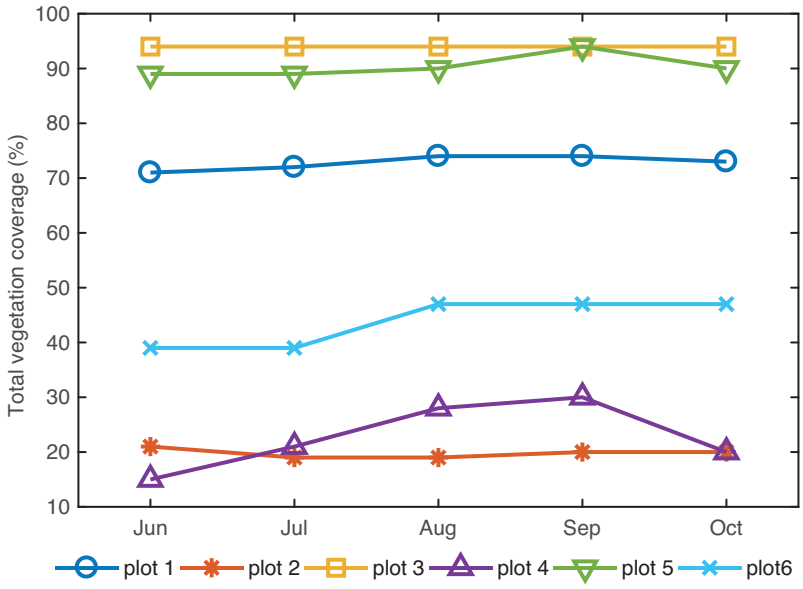

Fig. 2. Total vegetation coverage (%) in six plots for individual campaign.

plot 3 (~94%) throughout all campaigns (Table 2 and Fig. 2). Plots 4 and 5 had the peak vegetation coverage in September and a decrease of vegetation coverage occurred in October. The total vegetation coverage in plot 6 increased from 39% in July campaign to 47% in August.

Biomass of the litterfall

We assume that litter was homogeneously distributed in the forest, and the averaged dry biomass of collected litterfall from 15 traps was 1.3 g m^{-2} day^{-1} in June, 1.1 g m^{-2} day^{-1} July and 0.9 g m^{-2} day^{-1} in September. The minimum litterfall biomass was found in August (0.6 g m^{-2} day^{-1}) while the maximum litterfall biomass was observed in October with an average of 1.8 g m^{-2} day^{-1} from 15 traps (Fig. 3).

BVOC emission rate and emission spectrum

Among 95 collected samples, there were three samples with exceptionally high emission rates and emission spectra (the contribution of individual compounds to total BVOC emissions) diverting from the other samples of the same plot during the same campaign, which were excluded. 18 volatile compounds were detected in the remaining 92 samples, including isoprene, seven MTs, five SQTs, four oxidized terpenes and one aromatic ρ-cymene (Table 3). The total emission rates of all detected BVOCs were in the range of 0.4–66.6 µg m^{-2} h^{-1} during all campaigns from June to October 2015. The highest emission rate of 66.6 µg m^{-2} h^{-1} was observed in June in plot 4 when the measured PAR next to the soil chamber reached the highest record among the five campaigns (577 µmol m^{-2} s^{-1}), the second highest emission rate of 36.1 µg m^{-2} h^{-1} was in July in plot 3, which also had the second highest PAR value of 238 µmol m^{-2} s^{-1}. Largest BVOC emission rates were found in October (10.26 µg m^{-2} h^{-1} as average for the six plots), followed by June (10.15 µg m^{-2} h^{-1}), August (8.96 µg m^{-2} h^{-1}) and July (6.88 µg m^{-2} h^{-1}), while the lowest emission rate was in September with the value of 3.29 µg m^{-2} h^{-1} (Table 3). MTs were the dominant BVOCs from June to October with the mass fraction of total BVOC emission > 80%, and with the highest emission rate of 64.1 µg m^{-2} h^{-1} in June and the lowest of 0.32 µg m^{-2} h^{-1} in September. Mean MT emissions were highest in October (Table 3) and the highest mean SQT emissions were observed in August (0.21 µg m^{-2} h^{-1}). In general, isoprene

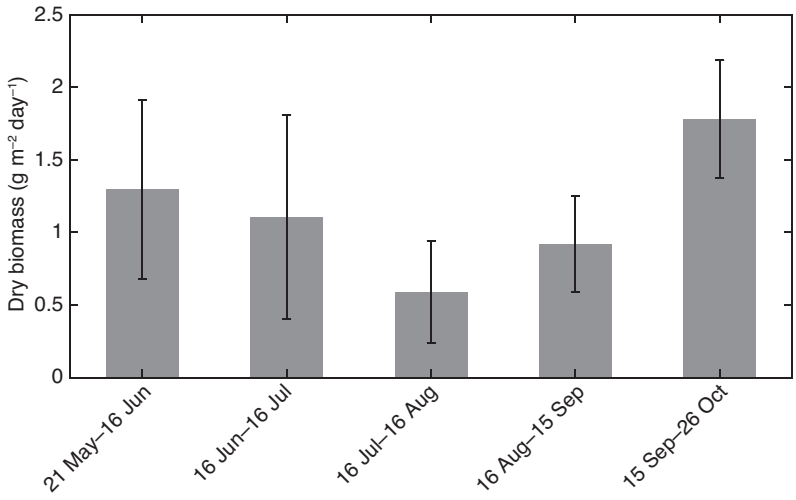

Fig. 3. Average ± SD dry biomass of litterfall per m^2 per day collected from 15 traps.

emissions were negligible from June to October. The oxidized terpenes (mainly MBO) and aromatic compound (ρ-cymene) peaked in July and became negligible after the August campaign (Table 3).

The compound composition detected from the forest floor remained almost unchanged from June to September, but the mass contribution of different compounds varied throughout the summer (Fig. 4). This stability in the composition of the spectra was also found within campaigns and appears to be independent of time of day and air temperature, except the result of plot 3 in June. The emission rate of MT from plot 3 decreased from 24.7 μg m^{-2} h^{-1} on 15 June to 3.9 μg m^{-2} h^{-1} on 17 June, and the con-

Table 3. Average (± SD for some compunds) emission rates (μg m^{-2} h^{-1}) of detected BVOC for each campaign.

Compound	Jun	Jul	Aug	Sep	Oct
Isoprene (C_5H_8)	0.004 ± 0.003	0.03 ± 0.05	0.01 ± 0.01	0.05 ± 0.12	0.003 ± 0.01
Total MT ($C_{10}H_{16}$)	9.75 ± 15.56	6.44 ± 7.54	8.55 ± 5.78	3.18 ± 3.11	10.17 ± 4.48
α-pinene	6.75	3.53	5.30	2.15	6.90
Δ^3-carene	1.63	1.78	1.84	0.71	2.28
Camphene	0.56	0.63	0.73	0.19	0.61
Limonene	0.50	0.28	0.28	0.06	0.10
β-pinene	0.20	0.15	0.33	0.03	0.17
Terpinolene	0.03	0.03	0.02	0.01	0.05
Myrcene	0.08	0.04	0.05	0.02	0.07
Total SQT ($C_{15}H_{24}$)	0.15 ± 0.17	0.15 ± 0.29	0.21 ± 0.18	0.01 ± 0.03	0.004 ± 0.04
β-caryophyllene	0.10	0.11	0.17	0.01	0.004
Aromadendrene	0.02	0.02	0.02	0.00	0.00
α-humulene	0.01	0.01	0.01	0.00	0.00
Longicyclene	0.01	0.003	0.01	0.00	0.00
Iso-longifolene	0.001	0.00	0.00	0.00	0.00
Total others	0.24 ± 0.43	0.27 ± 0.31	0.19 ± 0.21	0.05 ± 0.05	0.08 ± 0.07
MBO ($C_5H_{10}O$)	0.02	0.02	0.01	0.01	0.01
ρ-cymene ($C_{10}H_{14}$)	0.14	0.23	0.16	0.03	0.06
1,8-cineol ($C_{10}H_{18}O$)	0.03	0.004	0.01	0.001	0.002
Linalool ($C_{10}H_{18}O$)	0.01	0.01	0.004	0.002	0.00
Bornylacetate ($C_{12}H_{20}O_2$)	0.04	0.01	0.005	0.004	0.004
Sum	10.15 ± 16.11	6.88 ± 8.09	8.96 ± 6.05	3.29 ± 3.25	10.26 ± 4.51

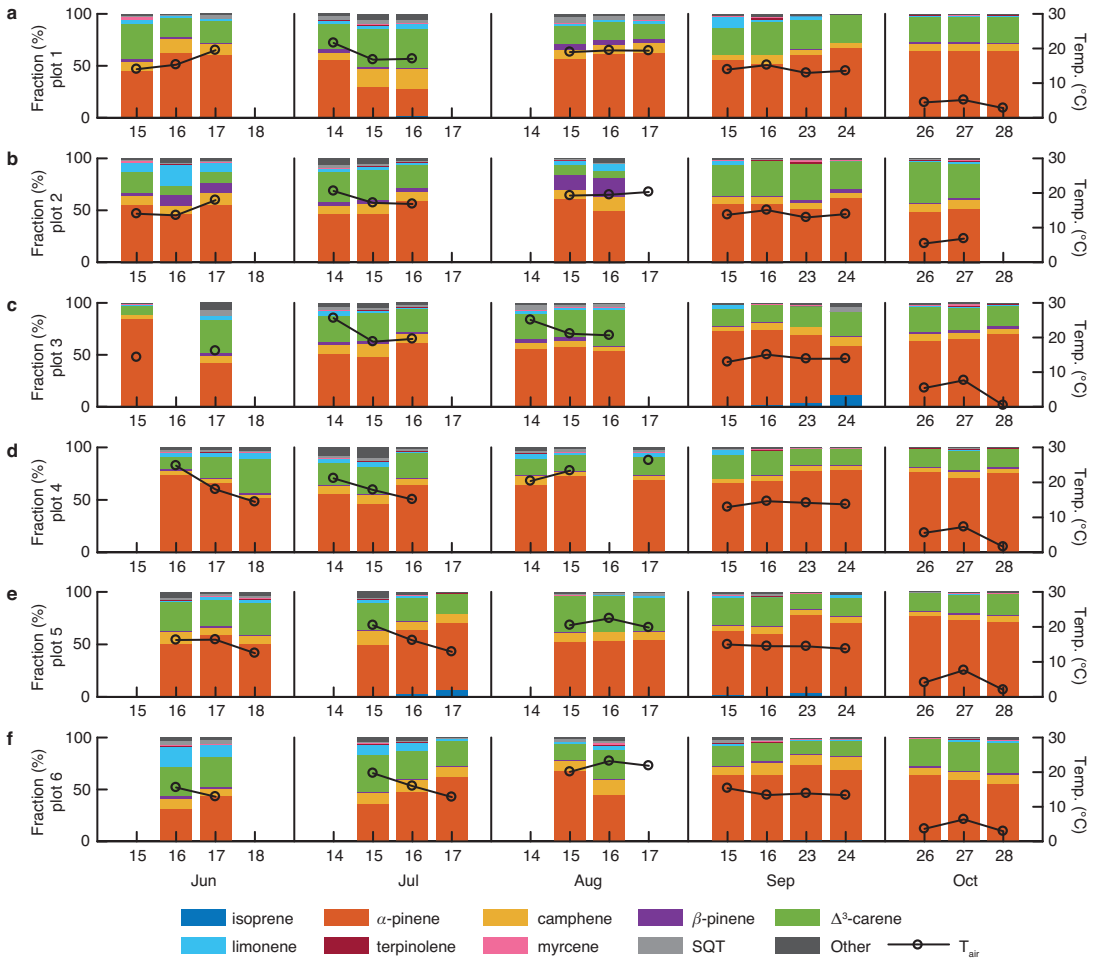

Fig. 4 The mass fraction of isoprene, all seven MT compounds, total SQT (SQT) and the other BVOCs (Other) to the total BVOCs in individual sample of all six plots collected at random time of the day. The measured air temperature inside the chamber (T_{air}) is indicated with black solid line.

tribution of α-pinene to the total BVOC emissions went down from 85% on 15 June to 42% on 17 June (Fig. 4c). α-pinene, Δ^3-carene and camphene were the dominant compounds from June to October in all plots, which collectively contributed more than 90% of the total BVOC emissions in September and October when the fractions of the remaining compounds were negligible (Fig. 4). However, not all the MT compounds peaked at the same time. α-pinene, Δ^3-carene, and terpinolene peaked in October, while β-pinene and camphene had the maximum emissions in August (Table 3). The maximum limonene emission rate was detected in June, and its mass fraction to the total BVOC emissions was highest in the samples collected from plot 2 (20%) and plot 6 (19%) in June (Fig. 4b and f). β-caryophyllene was the dominant detected SQT with a contribution to total SQT emissions from 53% in June to almost 100% in October. The second most abundant SQT was aromadendrene, followed by α-humulene. Neither longicyclene nor iso-longifolene were detected from plot 5 during whole measurement period, and iso-longifolene was not detected from plot 6 either. In September and October, both longicyclene and iso-longifolene disappeared from all plots. Especially in August when SQT emissions were highest, also some additional SQTs were detected, but these were not quantified or identified due to

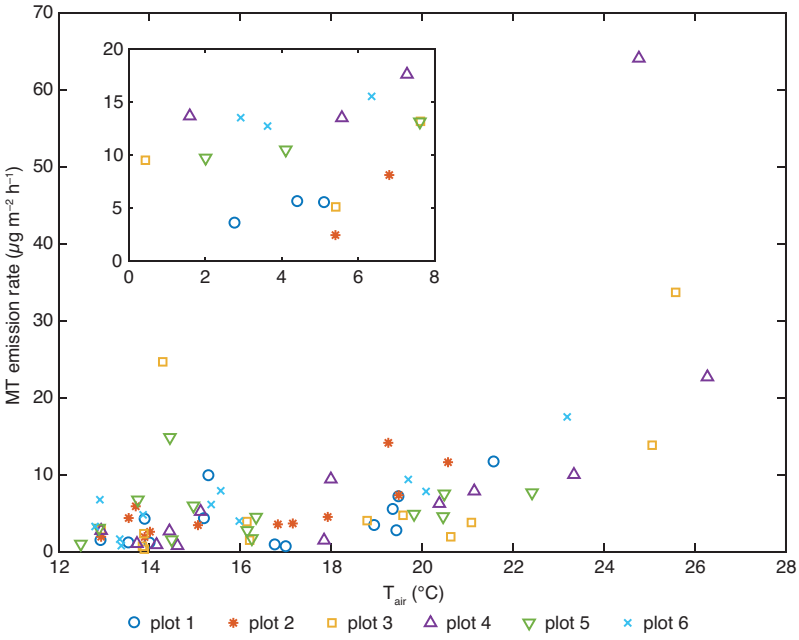

Fig. 5 MT emission rates as a function of air temperature inside the soil chamber (T_{air}) for samples collected from June to September and samples collected in October (subplot).

lack of authentic standards. SQT had the highest contribution in plot 1 (6.3%) and plot 3 (5.6%) during the August campaign (Fig. 4a and c). The oxidized terpenes and aromatic BVOC (Other) had the highest contribution in July (Fig. 4) when the total emission rate of these compounds was highest among five campaigns (Table 3), and the highest mass fraction to total BVOC emissions occurred in plot 4 with an average of 9.0% in July (Fig. 4d). *ρ*-cymene dominated the group of oxidized and aromatic BVOCs and MBO was the second most abundant compound of this group. Linalool was only found during June to September when it was present in all plots except plot 1.

Importance of air temperature and standardization of MT emissions

We used the QRF approach to rank the relative importance of five measured environmental variables (air temperature inside chamber (T_{air}), PAR, CO_2 flux, soil temperature (T_{soil}) and soil moisture (M_{soil})) and the vegetation coverage within the six plots for the forest floor BVOC emissions. Results for isoprene, iso-longifolene, MBO and bornylacetate were not conclusive since all the values of importance were close to zero (Appendix 3). In general, the air temperature inside the chamber was the most important variable for determining emissions of most BVOCs (Appendix 3), except for *β*-pinene and linalool for which vegetation coverage was the most important driver. Measured MT emission rates from June to September increased exponentially with increasing air temperature inside the soil chamber (Fig. 5). The MT emission rates in October did not show a noticeable temperature dependence based on the scatterplot (Fig. 5 inset) and linear regression (p = 0.44) of these two variables. MT emissions from June to September/October were standardized based on the algorithm describing BVOC temperature dependence (Eq. 4).

Equation 4 was used to obtain the optimized standardized emission rate E_S and the temperature sensitivity β based on the data of individual samples. Because of the remarkably high emissions in October, we performed the analysis for two periods: June to October and June to September. The obtained E_S (76.0 μg m^{-2} h^{-1}) and β (0.22 K^{-1}) based on June-to-September data had higher value of correlation coefficient R and lower value of root-mean-square error (RMSE) in comparison with the result obtained from data

set including all campaigns (Appendix 4). The obtained E_S of 76.0 μg m^{-2} h^{-1} and β of 0.22 K^{-1} were used to calculate MT emissions (Eq. 4) in October, the modelled MT emissions were only 4% of measured MT emissions, on average.

In addition, we applied the temperature sensitivity β from the June–September analysis (0.22 K^{-1}) in Eq. 4 to obtain the optimized E_S for each plot based on the data set of June to October (Jun–Oct) and June to September (Jun–Sep) respectively (Table 4). The calculated E_S of MT for plots 2, 3 and 4 did not vary much whether or not October was included in the analysis, but the E_S optimization for plot 5 failed when the October data were included (Table 4). Still, the E_S optimization for all plots except for plot 5 resulted in higher correlation coefficients when excluding October. The result from the E_S optimization based on the June-to-September data revealed that the MT E_S from five plots (plot 5 was excluded) were in the range of 60.9 to 94.6 μg m^{-2} h^{-1} and that plot 2 had the highest E_S followed by plot 4 and plot 6, while the vegetation coverage of plots 2, 4 and 6 were the lowest of all six plots (Fig. 2).

Discussion

BVOC emissions and the sources

The emission spectra of detected BVOCs were constant from June to September, which may indicate that the main sources for BVOC emissions did not vary greatly throughout the growing season. The observed composition of terpenes released from the forest floor were quite similar to the measured BVOCs emitted from the canopy of Scots pine at the same site, of which MT contributed to about 90% of total terpene emissions from June to September 2014. The contribution of isoprene to the total BVOC emissions (< 1%) was much lower from the forest floor than from the canopy of the Norway spruce at the same site, but close to that from the Scots pine canopy (2%). The dominant MTs emitted from the forest floor (α-pinene, Δ^3-carene and camphene) differed slightly from leaf-level emissions from Norway spruce (dominated by α-pinene, limonene and camphene) and Scots pine (dominated by Δ^3-carene, α-pinene and myrcene) at the study site. This implies that the combination of spruce and pine needles litter might be an important source for ground terpene emissions. The root system of conifers has been considered as a strong MT source as well (Janson 1993, Lin *et al*. 2007), which we were not able to separate from other forest floor emission in this study. The vegetation coverage of plots 2 and 4 were the lowest of all six plots (Fig. 2), while the optimized MT E_S of these two plots were the highest (Table 4). This suggested that the high MT E_S was determined by other sources than vegetation, such as needle litter in the plot. Similar to the temperature dependence of leaf emissions (Guenther *et al*. 1993), BVOC emissions from litter was also found to depend exponentially on temperature because the emissions mainly originate from the evaporation of stored BVOC pools in litter (Greenberg *et al*. 2012).

Emissions from mosses have been mainly studied in moss ecosystems, e.g. as found in wetlands. A study of BVOC emissions from a fen showed that mosses (*Sphagnum* species) were the main source for isoprene emission (Hellén *et al*. 2006). In our study, the isoprene emissions from plot 3 and plot 5 were higher than that from the remaining plots, and these two plots have the highest coverage of mosses and dwarf shrubs among the 6 plots. Therefore, we suggest that the

Table 4. Results of E_S optimization (Eq. 4, β = 0.22 K^{-1}) with two different data sets. Values in boldface are inconclusive ($p > 0.05$). E_S is the standardized emission rate (μg m^{-2} h^{-1}), R is the correlation coefficient and RMSE is the root-mean-square error.

Data set	Plot	E_S	R	p	RMSE
Jun–Oct	1	**61.5**	**0.43**	**0.097**	**3.24**
	2	95.6	0.67	0.009	2.91
	3	63.7	0.57	0.020	7.97
	4	89.9	0.61	0.012	12.27
	5	**56.5**	**–0.12**	**0.657**	**6.09**
	6	**86.5**	**0.37**	**0.194**	**6.68**
Jun–Sep	1	60.9	0.59	0.033	2.78
	2	94.6	0.81	0.002	2.19
	3	63.3	0.66	0.015	7.56
	4	89.4	0.71	0.006	11.65
	5	**54.9**	**0.22**	**0.472**	**4.24**
	6	84.6	0.90	0.000	2.42

detected isoprene emissions were mainly from the ground vegetation, even though isoprene emissions have also been found from root-associated fungi (Bäck *et al*. 2010) and from needle litter (Gray *et al*. 2010). The heavier BVOCs, such as SQT, can be emitted by ground vegetation (Rinnan *et al*. 2013) or needle litter (Greenberg *et al*. 2012). The microbial processes in soil have been reported to release mainly low molecular weight and oxygenated compounds (Bäck *et al*. 2010). The random forests analysis showed that the vegetation coverage was not related to SQT emissions but that the air temperature and PAR were the most influential variables for SQT emissions. *β*-carophyllene was found as the dominant SQT in the forest floor emission spectra, which has also been found for the canopy of Norway spruce and Scots pine at the same site. *β*-carophyllene was also found as the dominant SQT released from litter in a Scots pine forest floor (Asensio *et al*. 2008a). Therefore, we speculate that both ground vegetation and the needle litter were dominant SQT sources in this study.

The highest total BVOC emissions from the forest floor were observed in October when the measured litterfall biomass reached its peak (Table 3 and Fig. 3), whilst the air temperature, soil temperature and soil water content were low, and MTs accounted for about 99% of total BVOC emissions at the same time (Fig. 4). In contrast to the earlier campaigns, the MT emissions in October did not show any dependency on air temperature (Fig. 5), which indicates that the dominant source for MT emissions had changed in October. We could not separate the release of MTs from the storage pools in the litter needles from the microbial decomposition of litter. Still, this result indicates that the litterfall may have been the dominant source for BVOC emissions in autumn, and the needle litter may have been a significant MT reservoir. Hellén *et al.* (2006) also indicated that the forest floor was a significant source of monoterpenes by comparing the MT emission rates from both forest floor and Scots pine canopy, and pointed out that BVOC emissions from the boreal forest soil peaked in spring and autumn. Other studies have confirmed conifer needle litter as the major source of terpene emissions on the ground (Hayward *et al*. 2001, Asensio *et al*. 2008a). In August, higher air temperature was favorable for BVOC emissions from the vegetation (Monson *et al*. 1992, Llusià *et al*. 2006). Meanwhile, the low soil water content in August changed the soil physical properties, which can contribute to increased BVOC emissions (Asensio *et al*. 2008b). Unfortunately, we were not able to quantify the contribution of each single source for forest floor BVOC emissions throughout the summer and autumn. The variations of BVOC emissions together with the environmental variables implied that the contributions of individual sources of BVOC emissions were shifting with time.

BVOC emissions from the forest floor peaked in October 2015, which differed from branch-level measurements at the 20-m canopy height of a Norway spruce and a Scots pine at the same study site, which had their maximum emissions in July and August respectively based on the results of 2014 campaign. The forest floor BVOC emissions accounted for 0.6%–3.2% of upscaled BVOC emissions from branch-level measurements at 20-m canopy height of Norway spruce during June to September with 3.2% in June and 1.4% in September, and accounted for 0.9%–2.5% of upscaled BVOC emissions from branch-level measurements at the 20-m canopy height of Scots pine during the same period with 2.5% in June and 1.5% in September. There were no canopy BVOC emission data of October available to compare with the forest floor emissions, but based on the obtained emission results, we would speculate that BVOC emissions from forest floor accounted for more than 2% of canopy BVOC emissions in October.

Spatial variation of BVOC emissions and the drivers

The forest soil is heterogeneous at a scale of tens of centimeters (Pihlatie *et al*. 2007, Aaltonen *et al*. 2013), and the composition and density of ground vegetation are not homogeneous either. The six plots that were studied here had varying BVOC emission rates, and the emission spectra differed as well (Fig. 4).

Linalool was found in all the plots except plot 1 from June to September, with the highest emission from plot 4 where grass (Poaceae)

was growing inside. Linalool has been found as a major component of the essential oils of palmarosa, which is belonging to the *Poaceae* family (Lewinsohn *et al*. 2001), and has been reported in relation to stress-related emissions from Norway spruce (Pettersson 2007, Blande *et al*. 2009). The highest *β*-pinene emission was from plot 2 where lichens were found to cover 2% of ground area within the plot. This stresses the importance of vegetation composition.

Temperature and PAR are the main abiotic drivers for BVOC emissions from plant leaves or needles (Niinemets *et al*. 2004 and references therein), but there are only a limited number of studies about how temperature and PAR affect BVOC production and emission from soils. The measured air temperature inside the soil chamber and PAR were the most important variables for determining MT, SQT and other compound emissions in this study (Appendix 3). Measured MT emissions from June to September showed a dependence on the air temperature (Fig. 5), but the chamber sampling does not allow determining which BVOC source was affected most by the increasing temperature. There was a positive linear relationship between measured MT emissions and PAR at ~30 cm above the ground during June to September ($R^2 = 0.60$). The measured low PAR was not inhibiting photosynthesis since the ground vegetation has adapted to the low light conditions, but the photosynthesis rate had been low (Morén and Lindroth 2000). Therefore, the MT released from ground vegetation should increase with a rising PAR because the MT synthesis increases with an increasing photosynthesis rate (Staudt and Bertin 1998).

The variations in the soil temperature were much smaller than those in the air temperature during these five campaigns. Therefore, the soil temperature is not expected to be as important as air temperature for controlling BVOC emissions from ground in this study (Appendix 3). However, the soil temperature may have an influence on the retention of microbially-produced VOCs in the soil (Insam and Seewald 2010). Asensio *et al*. (2007) also indicated that some soil VOC emissions might be enhanced with an increasing soil temperature.

Soil moisture was not an important variable for isoprene and dominated MT emissions based on QRF analysis (Appendix 3), while the linear regression test between BVOC emission rates and soil moisture showed that isoprene emission positively correlated with soil moisture ($p = 0.006$) while MT emissions were negatively correlated with soil moisture ($p = 0.009$). A study of Mediterranean shrubland also showed that long-term drought increased soil MT emissions, but other BVOC emissions decreased with reduced soil moisture (Asensio *et al*. 2008b).

The CO_2 flux was an indicator for forest floor photosynthesis rate and respiration rate. Most of the measured CO_2 flux during sampling was positive, implying higher respiration rate than photosynthesis rate inside the soil chamber. The CO_2 flux was an important variable besides air temperature and PAR that correlated with MT emissions, particularly for Δ^3-carene emissions (Appendix 3). However, there was no unified conclusion about the relation between the CO_2 flux and BVOC fluxes in the forest floor. The CO_2 flux was found not to be correlated with BVOC fluxes in a boreal forest floor (Aaltonen *et al*. 2013), but was found to be positively correlated with BVOC fluxes in a Mediterranean shrubland (Asensio *et al*. 2008b).

Besides the above-mentioned environmental variables, the distance between the chamber and the tree trunk has also been reported to impact BVOC emissions (Asensio *et al*. 2008a), which was not considered in our study when the six frames were randomly set on the ground. A study by Asensio *et al.* (2008a) showed decreasing terpene concentration in the soil with increasing distance to the pine tree trunk. More detailed designed field and laboratory studies are needed to identify the sources of BVOC emissions and their contributions, and to study how environmental variables affect BVOC emissions from the ground vegetation, litter and soil.

Conclusion

The measured BVOC emissions from forest floor were in the range of 0.4 to 66.6 μg m^{-2} h^{-1}, with the maximum in October when there was a maximum amount of fresh litter. The BVOC emission spectra were relatively stable from June to September with MTs as the dominant compounds,

which indicates that the main sources of BVOCs were stable. Our results indicate that needle litter was an important source of BVOC emissions in October, with MT emissions contributing more than 99%. However, the method used here did not allow us to separate individual sources of BVOC emissions in the soil-litter-vegetation system. The air temperature inside the chamber and PAR were the most important variables controlling BVOC emissions. On average, BVOC emissions from the forest floor accounted for roughly 1% of Norway spruce 20-m canopy emissions, and about 1.2% of Scots pine 20-m canopy emissions from June to September, and we believe that this percentage number would be higher in October. The importance of BVOC emissions from forest floor is probably underestimated so far.

Soils can act as both BVOCs sources and sinks (Insam and Seewald 2010), and soil degradation and deposition of BVOCs were not considered in this study. Considering the soil heterogeneity, continuous flux measurements combing chamber measurements with more study plots to quantify BVOC emissions from forest floor could provide longer-term and larger scale data in future studies.

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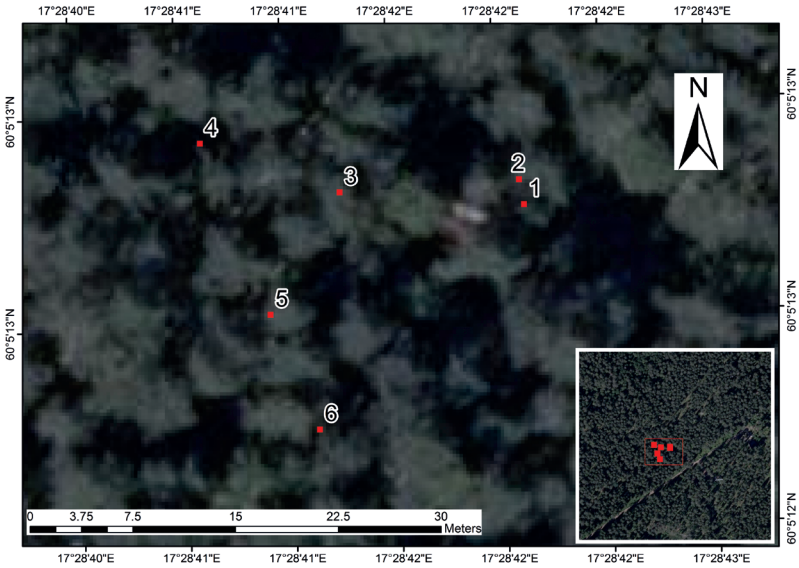
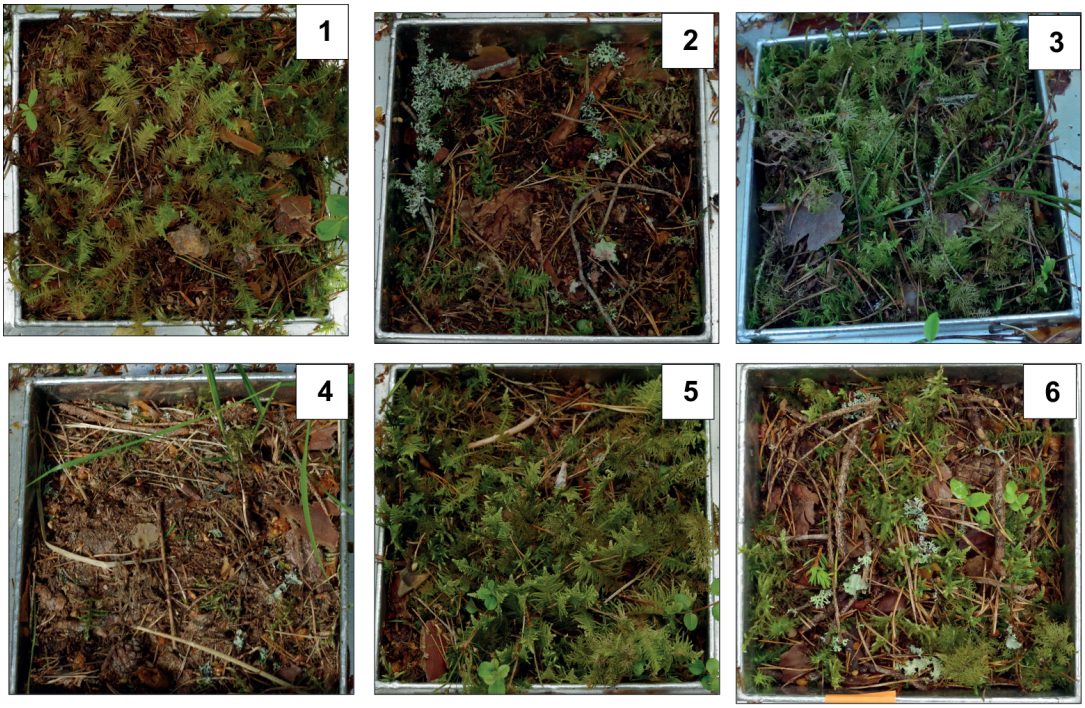


Appendix 1. Distribution of the six plots on the forest floor.



Appendix 2. Photos of the six study plots taken during the June 2015 campaign.

Appendix 3. The importance rank of environmental variables to forest floor BVOC emissions based on quantile random forests (QRF) analysis. The higher number represents the importance of the variable, a negative value indicate that the variable was irrelevant for the BVOCs emissions. Values in boldface are not conclusive.

	T_{air}	PAR	Vegetation	CO_2 flux	T_{soil}	M_{soil}
Isoprene	**0.23**	**0.15**	**0.08**	**0.24**	**0.22**	**0.00**
MT	0.75	0.39	0.03	0.34	0.23	0.30
SQT	0.90	0.50	–0.07	0.04	0.31	0.11
Other	0.76	0.50	0.33	0.05	0.06	0.01
α-pinene	0.71	0.38	0.02	0.32	0.22	0.26
Camphene	0.82	0.37	0.12	0.34	0.09	0.12
β-pinene	0.39	0.24	0.53	0.00	0.14	0.25
Δ^3-carene	0.93	0.39	0.06	0.40	0.31	0.33
Limonene	0.67	0.45	0.37	0.30	0.19	0.08
Terpinolene	0.68	0.25	0.07	0.23	0.39	0.18
Myrcene	0.66	0.23	0.12	0.19	0.16	0.11
β-caryophyllene	0.85	0.49	–0.04	0.04	0.28	0.08
Aromadendrene	0.81	0.35	–0.05	0.05	0.16	0.01
α-humulene	0.82	0.54	–0.03	0.06	0.21	0.01
Longicyclene	0.72	0.27	0.46	0.13	0.20	0.15
Iso-longifolene	**0.15**	**0.18**	**0.27**	**0.06**	**0.12**	**0.06**
MBO	**0.19**	**0.29**	**0.04**	**0.05**	**0.20**	**0.15**
p-cymene	0.81	0.43	0.31	0.07	0.05	-0.07
1,8-cineol	0.51	0.22	0.06	0.06	0.10	0.08
Linalool	0.09	0.34	0.51	0.01	0.01	0.09
Bornylacetate	**0.26**	**0.10**	**0.04**	**0.07**	**0.07**	**0.02**

Appendix 4. The result of curve fitting (Eq. 4) with two different data sets. *R* is the correlation coefficient and RMSE is the root-mean-square error.

Data set	*E* (mg m^{-2} h^{-1})	β (K^{-1})	*R*	*p*	RMSE
Jun–Oct	64.0	0.19	0.52	< 0.001	7.45
Jun–Sep	76.0	0.22	0.68	< 0.001	6.50