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Using chambers to capture biogenic volatile organic compounds (BVOCs) from trees and forest floor

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Characteristics of BVOC emissions from a Swedish boreal forest

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Using chambers to capture biogenic volatile organic compounds (BVOCs) from trees and forest floor

Min Wang

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Title and subtitle

Characteristics of BVOC emissions from a Swedish boreal forest: Using chambers to capture biogenic volatile organic colpounds (BVOCs) from trees and forest floor

Abstract

Plant-emitted biogenic volatile organic compounds (BVOCs) are a large group of hydrocarbons released by plant leaves, bark, flowers and fruits into the atmosphere and from plant roots into the soil. BVOCs have important physiological and ecological functions, such as mediating within-plant and plant-plant communication, defense against herbivores attack, protection against heat or other oxidative stress, attracting pollinators etc., and BVOCs are also important for microorganisms' communication and nutrient cycling in the soil. These emitted reactive BVOCs also have impact on atmospheric chemistry, such as affecting the oxidation rate and atmospheric concentration of other trace gases, and the oxidized BVOCs contribute to particles formation and growth. The most abundant BVOCs are terpenes, such as isoprene (C_5H_8), monoterpene (MT, $C_{10}H_{16}$) and sesquiterpene (SQT, $C_{15}H_{24}$), and woody plants tend to emit various blends of terpenes. Norway spruce and Scots pine are two dominant boreal species, which have been recognized as MT emitters, and Norway spruce is also known as a low isoprene emitter. The contribution of forest floor to the ecosystem BVOC emissions has not been thoroughly studied and evaluated.

A dynamic branch chamber system was used in this thesis to quantify the BVOC emission rates and emission spectra (composition of compounds) from 20-m and lower canopy levels of a Norway spruce and from 20-m canopy of a Scots pine from June to September of 2013 and 2014. The observed BVOC emissions from 20-m canopy of Norway spruce peaked in August 2013 and July 2014, and the minimum was found in September in both two years. The total BVOC emission rates of 2013 were significantly higher than those of 2014, and these high emissions in 2013 were likely induced by insect attack. High induced MT emissions from Scots pine were also observed in September 2014. Besides the long-term observation including seasonal variations are needed for accurately estimating or scaling up BVOC emissions, the stress-induced BVOC emissions are necessary to be incorporated into the emission models given the observed high amount of induced emissions. No clear vertical distribution pattern of BVOC emission rates was found within-canopy of the Norway spruce, and the compounds detected on different canopy levels were quite similar.

A dynamic soil chamber was used to quantify the BVOC emissions from the forest floor from June to October of 2015. The peak emission was observed in October. Litterfall might be an important source for MT emissions, especially in autumn. Air temperature inside chamber and PAR (photosynthetically active radiation) were the most influential environmental variables affecting MT and SQT emissions. The understorey vegetation coverage and composition and soil moisture also have impact on the BVOC emissions from the forest floor.

Key words: BVOCs, boreal forest, Norway spruce, forest floor, branch chamber, soil chamber

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–大学

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Contributions

Paper I: MW contributed to the study design, collected all BVOC field data, performed the data analysis and led the writing.

Paper II: MW contributed to the study design, collected all BVOC field data, performed the data analysis and led the writing.

Paper III: MW developed the study design, collected all BVOC field data, led and performed data analysis and also led the writing of the manuscript.

Paper IV: MW contributed to the study design, contributed with BVOC field data, participated in the data analysis, discussion and writing of the manuscript.

Abstract

Plant-emitted biogenic volatile organic compounds (BVOCs) are a large group of hydrocarbons released by plant leaves, bark, flowers and fruits into the atmosphere and from plant roots into the soil. BVOCs have important physiological and ecological functions, such as mediating within-plant and plant-plant communication, defense against herbivores attack, protection against heat or other oxidative stress, attracting pollinators etc., and BVOCs are also important for microorganisms' communication and nutrient cycling in the soil. These emitted reactive BVOCs also have impact on atmospheric chemistry, such as affecting the oxidation rate and atmospheric concentration of other trace gases, and the oxidized BVOCs contribute to particles formation and growth. The most abundant BVOCs are terpenes, such as isoprene (C_5H_8), monoterpene (MT, $C_{10}H_{16}$) and sesquiterpene (SQT, $C_{15}H_{24}$), and woody plants tend to emit various blends of terpenes. Norway spruce and Scots pine are two dominant boreal species, which have been recognized as MT emitters, and Norway spruce is also known as a low isoprene emitter. The contribution of forest floor to the ecosystem BVOC emissions has not been thoroughly studied and evaluated.

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A dynamic soil chamber was used to quantify the BVOC emissions from the forest floor from June to October of 2015. The peak emission was observed in October. Litterfall might be an important source for MT emissions, especially in autumn. Air temperature inside chamber and PAR (photosynthetically active radiation) were the most influential environmental variables affecting MT and SQT emissions. The understorey vegetation coverage and composition and soil moisture also have impact on the BVOC emissions from the forest floor.

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Introduction

Volatile organic compounds (VOCs) are a group of hydrocarbon trace gases other than methane in the atmosphere (Kesselmeier and Staudt, 1999). There are three main sources for VOC emissions: anthropogenic activities, biomass burning and the biosphere, in which the biosphere is the largest source of VOCs (Guenther et al., 1995, Asensio et al., 2008b). The study of biogenic VOCs (BVOCs) dated back to 1960 when the blue haze appeared in the mountain areas was investigated, and terpenes released from the plants were suggested to contributed to the development of the blue haze (Went, 1960). Since then, many studies have focused on quantification and identification of BVOC emissions from the terrestrial vegetation and investigating their physiological functions and impacts on the environment. The estimated total BVOC emissions from terrestrial ecosystem is about 760 Tg (C) $year^{-1}$ (Sindelarova et al., 2014), which is comparable to the estimated global methane emission of ~1000 Tg $year^{-1}$ (Adushkin and Kudryavtsev, 2013). The lost carbon from vegetation to atmosphere via VOC emissions accounts for 1%–2% of estimated global carbon assimilation by terrestrial ecosystems (Possell and Loreto, 2013).

Synthesis and emission of BVOCs

BVOCs are emitted from plant leaves, bark, flowers and fruits and from roots and microbial activities in the soil as well. Thousands of BVOCs have been identified from more than 90 plant families (Knudsen et al., 2006, Dudareva et al., 2013). According to their chemical structures, BVOCs could be clustered into terpenes, fatty acid derived C_6-voatiles and derivatives, phenylpropanoid aromatic compounds, and small oxygenated hydrocarbons (Maffei, 2010). Woody plants are more likely to emit various mixtures of terpenes, which are a group of hydrocarbons based on the unit of C_5H_8 (Laothawornkitkul et al., 2009). Isoprene (C_5H_8) accounts for 70% of global total BVOC emissions, monoterpene (MT, $C_{10}H_{16}$) contributes for 11%, and sesqutierpene (SQT, $C_{15}H_{24}$) contributes about 2.5% to total BVOC emissions (Sindelarova et al., 2014).

All terpenes are synthesized from the same 5-carbon precursors: isopentenyl diphosphate (IDP) and its isomer dimethylallyl diphosphate (DMADP) (Memari et al., 2013). These two precursors are synthesized either in the cytosol by mevalonate (MVA) pathway or in the plastids by 2-C-methyl-D-erythritol4-phosphate (MEP) way (Li and Sharkey, 2013). Isoprene and MT are synthesized through MEP pathway, while SQT is synthesized through MVA pathway

(Laothawornkitkul et al., 2009). Usually, terpenes are synthesized from the recent photosynthesis productions (Delwiche and Sharkey, 1993), while there are also alternative carbon sources for terpene synthesis such as starch (Schnitzler et al., 2004, Li and Sharkey, 2013) or respiratory CO_2 (Loreto et al., 2004). The availability of substrate and the synthase activities are critical factors for BVOC emissions (Fischbach et al., 2002, Laothawornkitkul et al., 2009).

Isoprene and some MTs are emitted directly after *de novo* synthesis, while some MTs and SQTs can be stored in specialized structures such as resin ducts, trichoma, and glands in leaf tissue (Kesselmeier and Staudt, 1999) and being later released from there. Non-stored BVOCs are almost entirely released through leaf stomata into atmosphere, but the diffusion through cuticle also occurs (Harley, 2013).

Physiological and Ecological functions of BVOCs

Plants produce different amounts and combinations of VOCs over time, and these VOCs have important physiological and ecological functions (Schuman et al., 2016). BVOCs are signaling compounds (info chemicals) mediating within-plant and plant-plant communications (Heil and Silva Bueno, 2007, Holopainen, 2011). BVOCs directly deter herbivores from feeding (direct defense), but can also attract parasitoids or predators to defend against herbivores (indirect defense) (Fineschi and Loreto, 2012). Some herbivore-induced VOCs can elicit a defensive response in undamaged plants (or parts of plants) by reducing their attractiveness and suitability for herbivore attack (Heil and Silva Bueno, 2007). Plants can also increase their resistance against herbivore attack by absorbing the repellent volatiles released from the neighbouring plants (Himanen et al., 2010). BVOCs are also important for attracting pollinators (Kessler et al., 2008), seed dispersal (Klee and Giovannoni, 2011), and strengthening the tolerance of abiotic stresses (Loreto and Schnitzler, 2010). Some plant species can protect themselves against heat stress by synthesizing isoprene (Sharkey et al., 2008). The oxidative stress could be relieved by producing terpenes to scavenge excess reactive oxygen species (ROS) within plant (Loreto and Schnitzler, 2010).

Plant roots contain and produce similar volatiles as aboveground organs, and these volatiles are emitted in the rhizosphere (van Dam et al., 2016). Rhizosphere contains numerous microbial organisms, and many of these microorganisms such as bacteria and fungi can produce volatiles as well. The roles of BVOCs in soil ecology and nutrient cycling are not fully understood. Still, recent studies have revealed that BVOCs are important communication media for the microorganisms and they also act as bioactive growth-promoting or growth-inhibiting agents (Peñuelas et al., 2014). For instance, some bacteria produced volatiles can increase

the resistance of maize plants against pathogen 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 root exudates can affect the roots placement away from competitors or kin. (Semchenko et al., 2014, van Dam et al., 2016).

Impacts of BVOCs in the atmosphere

Many BVOCs such as terpenes are very reactive, with a life time of seconds to minutes, while some can stay in the atmosphere for hours to days and weeks (Kesselmeier and Staudt, 1999). Reactive BVOCs decrease the oxidation capacity of lower troposphere because of their reactivity with hydroxyl radical (OH), nitrogen oxides (NO_x) and ozone (O_3) in the atmosphere, and consequently affect oxidation rate and atmospheric concentration of other trace gases (Atkinson and Arey, 2003, Laothawornkitkul et al., 2009). Consumption of OH by BVOCs indirectly prolongs the lifetime of the greenhouse gas methane (CH_4) in the atmosphere (Kaplan et al., 2006). BVOCs also participates in photochemical reactions lead to the formation of O_3 in the troposphere under high atmospheric concentration of NO_x (Atkinson, 2000).

BVOCs are precursors for secondary organic aerosols (SOA) formation because their oxidation products possess low volatility to undertake gas-to-particle conversion and condense on the pre-existing particles (Di Carlo et al., 2004, Rinne et al., 2009). Terpene emissions and their oxidation products are the largest global source of SOA (Arneth et al., 2010), and SQTs have higher SOA yields than isoprene and MTs (Lee et al., 2006). The aerosol particles are known to alter the Earth's radiation balance directly by scattering solar radiation and indirectly by acting as cloud condensation nuclei (CCN), changing the cloud coverage and albedo (Kulmala et al., 2004, Laothawornkitkul et al., 2009).

Abiotic and biotic drivers for BVOC emissions

Emissions of BVOCs consist of constitutive emissions and induced emissions. Compounds of constitutive emissions can be detected throughout the plant's lifecycle or at specific plant developmental stages, while induced emissions of specific compounds are caused by mechanical damage (wind, harvesting and herbivory) or abiotic stresses such as heat, drought and air pollution etc. (Possell and Loreto, 2013 and references therein).

Temperature is one of the key environmental controls for the synthesis and emissions of BVOCs on the short term: temperature regulates the isoprene and MT

synthase activities (Monson et al., 1992), affects availability of substrates for BVOCs synthesis (Laothawornkitkul et al., 2009), and controls the volatility and diffusion rates of BVOC compounds (Llusià et al., 2006). Both BVOCs synthesis rates and emission rates respond to temperature in similar way, exhibiting an Arrhenius type function with a maximum at a temperature optimum (Possell and Loreto, 2013). Higher temperature increases the vapour pressures of volatile compounds and increase their cellular diffusion rates (Laothawornkitkul et al., 2009). The emissions of BVOCs from specific storage pool increase exponentially with temperature (Guenther et al., 1993). For compounds released directly after *de novo* synthesis, temperature has strong and fast effect on their emission rates, and their emissions are related to light (photosynthetically active radiation, PAR) and photosynthetic rates (Llusià and Peñuelas, 2000). PAR determines the availability of the terpene precursor glyceraldehyde-3-phosphate and the energy requirements of ATP and NADPH (Niinemets et al., 1999). Many constitutive BVOCs emissions displayed diurnal cycles, increasing rapidly in the morning with increasing temperature and PAR, peaking around noon, and decreasing during the afternoon and evening (Grabmer et al., 2006, Trowbridge and Stoy, 2013).

Plants are frequently exposed to single or multiple stresses, and these stresses can change constitutive emissions and induce emissions of new compounds. Expose to transiently high-temperature and light levels can induce large emissions of VOCs, especially C_6-compounds and acetaldehyde (Loreto et al., 2006). Wounding can induce large amount of MT emissions from conifers (Litvak and Monson, 1998). Heat stress causes increase of isoprene and MT emissions initially, but the emissions decline with continuous stress (Possell and Loreto, 2013). Moderate drought can decrease, enhance or have no effect on isoprene and MT emissions, but long-term water stress can significantly reduce BVOC emissions (Laothawornkitkul et al., 2009). Herbivory and pathogen attacks normally trigger rapid emissions of green leaf volatiles (GLVs) and further lead to emission of complex blend of volatiles, including methyl salicylate, indole MTs and SQTs (Niinemets et al., 2013).

Boreal forest BVOC emissions

Boreal forests are one of the major vegetation zones in the world, covering around 16% of the land surface on earth across Eurasia and Northern America (FAO, 2001), and are composed of mixed tree types such as evergreen species (pine, spruce), deciduous species (larch, birch, willow, alder, aspen), as well as various understorey vegetation (Rinne et al., 2009). These tree species are significant MT emitters (Rinne et al., 2009), but there are also high SQT emitters found in both deciduous and coniferous families based on available data (Helmig et al., 2007). In

comparison with BVOCs emissions from temperate and tropical forests, boreal forests emit less BVOCs, but they are important contributors to the regional BVOC emission budgets (van Meeningen et al., 2017).

Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) are the dominant evergreen tree species in the boreal zone, and 83% of the forests in Sweden consists of these two species (Alin and Sundberg, 2003, Petterson, 2007). MTs are the major compounds emitted from these two conifers, and Norway spruce is also recognized as a low isoprene emitter (Gramber et al., 2006). Most of the BOVC emissions from conifers were measured on branch scale by enclosure techniques, and a few studies were performed on ecosystem scale (Rinne et al., 2007, Ruuskanen et al., 2011, Schallhart et al., 2017). Compared with extensive studies of Scots pine (Bäck et al., 2005, 2012, Tarvainen et al., 2005, Hakola et al., 2006), there are few studies about the BVOC emissions from Norway spruce, which leaves large gaps in the emission inventory in boreal forests.

Some studies about BVOC emissions from boreal forest floor have shown that MT emissions from Scots pine forest floor account for 20%–40% of the flux from the forest crown during summer (Janson, 1993) or account for about 10% of total MT emissions from the ecosystem in spring and autumn (Aaltonen et al., 2011). Litter has been recognized as the main source of BVOC emissions from conifer forest floor (Hayward et al., 2001, Hellén et al., 2006). While understorey vegetation, root system and microbiological activities also contribute to the BVOC emissions from forest floor (Janson, 1993, Hayward et al., 2001, Lin et al., 2007, Kai et al., 2010).

Research Objectives

The emission rates and emission spectra (composition of compounds) of emitted BVOCs from trees and forest floor vary with the time of the year and differ between stand locations. Leaves or needles within the canopy are exposed to varying light and temperature conditions at different height levels, therefore, the emission rates and emission spectra of different canopy levels are expected to be different. The aim of this thesis is to characterize the conifer BVOC emissions on branch level at the upper and lower canopies during growing season with focus on Norway spruce, and to detect the BVOC emissions from forest floor during summer and autumn.

The specific objectives were:

- To quantify BVOC emission rates from top sunlit canopy of Norway spruce and study the seasonal variation of emissions and the emission dependence on temperature and light (Paper I).
- To quantify BVOC emission rates and emission spectra on four different canopy heights of Norway spruce and to investigate the vertical distribution of BVOC emissions within the canopy (Paper II).
- To quantify BVOC emissions from the forest floor during summer and autumn, and to identify the environmental variables controlling forest BVOC emissions (Paper III).
- To compare the BVOC emissions from the measured Norway spruce stand at Norunda with other Norway spruce trees growing at different locations (Paper IV).

Material and Methods

Study site

All the field campaigns were carried out at Norunda research station (60°05'N, 17°29'E, elevation 69 m), which is located in central Sweden (Fig. 1) and is part of the Integrated Carbon Observation System (ICOS) network in Sweden (*http://www.icos-sweden.se/station_norunda.html*). It is a managed boreal forest dominated by 80-120 years old Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* (L.) Karst) with tree heights of 25–28 m. 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). Bilberry (*Vaccinuim myrtillus* L) is the dominant ground vegetation, and there are also other dwarf-shrubs, grasses and ferns. A rather thick layer of boreal feather mosses (*Hylocomium splendens* and *Pleurozium Schreberi*) constitutes most of the bottom layer vegetation. The mean annual air temperature was 6.5°C and the mean annual precipitation was 576 mm for the period of 1980–2010 measured 30 km south of Norunda (Sundqvist et al., 2014).

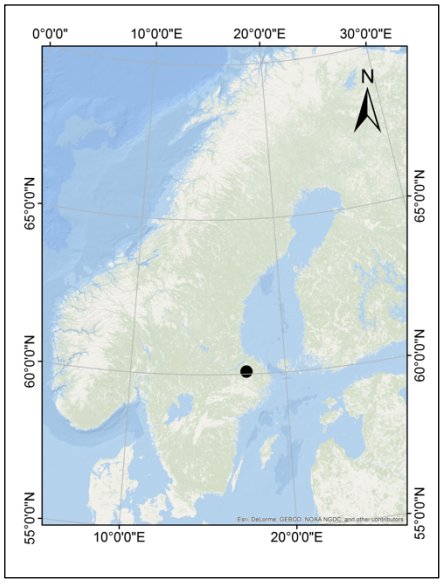

Figure 1. The location of Norunda research station, marked with black dot.

Branch chamber measurements (Paper I, II & IV)

Field measurements

A branch chamber was used for measuring BVOC emissions at 20-m height of one 118-year-old Norway spruce from June to September 2013 (Table 1). The volume of this cylinder-shaped transparent PTFE (polytetrafluoroethylene) chamber was 11.3 liters (diameter 19 cm, length 46 cm), and it was equipped with a temperature

and relative humidity (RH) probe (Fig. 2a). Ambient air was pumped through a hydrocarbon trap containing MnO_2-coated copper nets to remove all VOCs and O_3, this VOC-free air then entered the chamber. Air samples were collected from the chamber using adsorbent tubes filled with Tenax-TA and carbongraph 1 TD (Markes International Limited, UK) once every hour between 8:00 and 17:00 with a sampling time of 30 min. Two blank samples were taken from the air inlet after the hydrocarbon trap in each campaign to account for any instrumental background emission. At the end of each campaign, after all samples were collected, the branch inside the chamber was cut, needles and twigs were separated and dried at 75°C until the biomass weight was constant. The dry weight of needles was later used for the emission calculation. Ambient air temperature, RH and PAR close to the branch chamber were also measured.

Table 1. The detailed information of field campaigns between 2013 and 2015.

Year	Study species	Canopy height	Date of campaign	Paper
2013	Norway spruce	20 m	6th–11th Jun 3rd–7th Jul 25th–31st Jul 10th–16th Aug 21st–25th Sep	I
2014	Norway spruce	20 m & 3 m	12th–17th Jun	II, IV
		20 m & 11 m	20th–24th Jul	
		20 m & 15 m	14th–20th Aug	
		20 m & 20 m	13th–17th Sep	
2014	Scots pine	20 m	20th–22nd Jun 15th–17th Jul 9th–12th Aug 30th Sep–2nd Oct	
2015	forest floor		15th–18th Jun 14th–17th Jul 14th–17th Aug 15th–16th & 23rd–24th Sep 26th–28th Oct	III

During the growing season of 2014, two of these branch chambers were used to measure the BVOC emissions from the same Norway spruce stand, one branch chamber was set at 20 m height with the same branch growing inside all the time from June to September as a reference, the other one was set at 3 m (June), 11 m (July), 15 m (August), and at 20 m (September) respectively for each campaign (Table 1, Fig. 2b). The lid of the reference chamber was open when no campaign was carried out. The sampling method was the same as the campaigns in 2013. Scots pine was also sampled during four campaigns from June to the beginning of October in 2014 with 3-days sampling per campaign (Table 1).

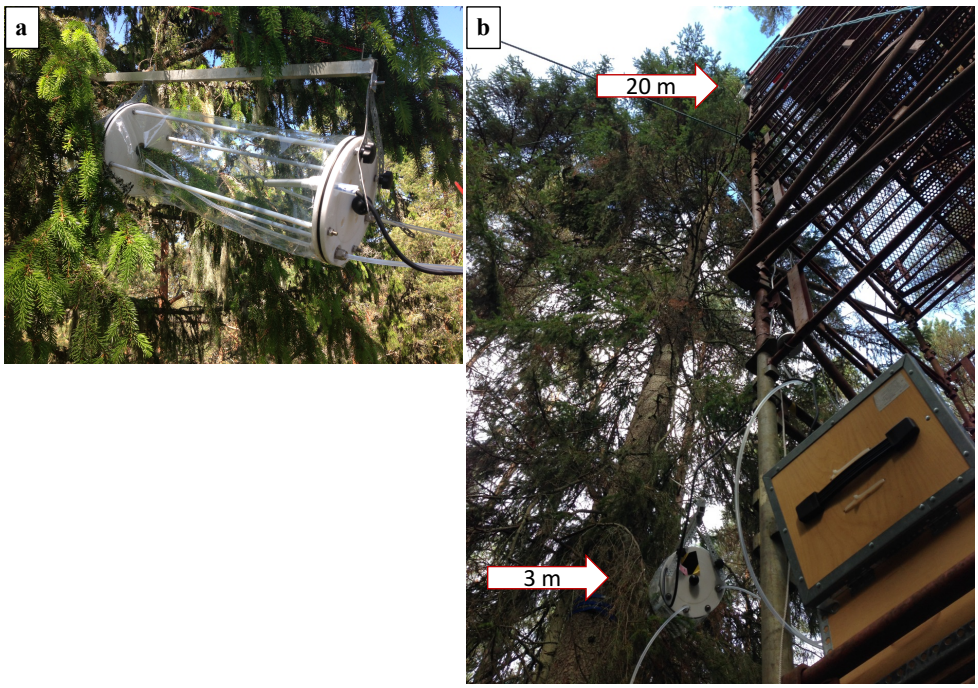

Figure 2. A branch chamber was set on 20 m canopy of a Norway spruce in June 2013 (**a**) and the two branch chambers were set at 3 m and 20 m of the same Norway spruce stand in June 2014 (**b**).

Sample analysis

All the collected samples from branch chambers were analyzed with a gas chromatography-mass spectrometer (GC-MS) to identify and quantify the trapped BVOCs in the adsorbent tubes. The compounds are volatilized and separated in the GC bypassing through one column, and then enter the MS where the compounds molecules are ionized and split into charged fragments, and detected according to the mass to charge ratio of each fragment. The detected compound is identified by comparing the measured mass spectrum with the spectra in the NIST mass spectra library. The samples collected in 2013 were analyzed in the laboratory in Lund Sweden. Analysis was done by automatic thermal desorption instrument (PerkinElmer TurboMatrixTM 650, Waltham, USA) connected to a gas chromatography (GC-2010, Shimadzu, Japan) using a 30-m column and a mass-selective detector (GCMS-QP2010 Plus, Shimadzu, Japan). The samples collected in 2014 were analyzed in the laboratory in Helsinki Finland. Analysis was done by the same automatic thermal desorption instrument connected to a gas chromatography (Perkin-Elmer Clarus 600, Waltham, USA) with a 60-m column and a mass selective detector (Perkin-Elmer Clarus 600T, Waltham, USA).

Emission rate calculation

The BVOC emission rate E (μg g_{dw}^{-1} h^{-1}) from the branch is defined by the mass of each compound per dry biomass weight and time (Hakola et al., 2003):

$$E = \frac{F(C_2 - C_1)}{m} \quad (1)$$

where C_2 is the concentration of BVOC within branch chamber and C_1 is the BVOC concentration of air entering the branch chamber (calculated from the collected blank samples in each campaign). F is the air flow rate through the branch chamber, and m is the dry weight of needles on the branch in the chamber.

Soil chamber measurements (Paper III)

Field measurements and sample analysis

BVOC emissions from six plots on the forest floor were measured with a soil chamber during June to October of 2015 (Table 1). Six aluminum frames (inner dimension 18.8 x 18.8 cm, outer dimension 19.2 x 19.2 cm) were inserted into the ground to a depth of 10 cm at six random locations in April 2015 (Fig. 3). The soil chamber was made of a stainless-steel frame covered with 0.05 mm PEP (fluorinated ethylene propylene) film (Fig. 4), with a volume of 11.4 L (20.0 × 20.0 × 28.5 cm), and the measured soil area was 0.035 m^2 based on the calculation of inner length of the frame. Air entering the soil chamber was filtered by a hydrocarbon trap containing MnO_2 coated copper mesh to remove VOCs and ozone. Air samples were taken from the soil chamber with adsorbent tubes filled with Tenax-TA and carbongraph 1 TD (Markes International Limited, UK). Two or three samples were collected at random time of the day from each plot during the individual campaigns. Two blank samples were taken in each campaign to account for any instrumental background emission. All collected samples were analyzed in the laboratory in Helsinki (Finland) using the same analysis method for the samples collected from branch chambers in 2014.

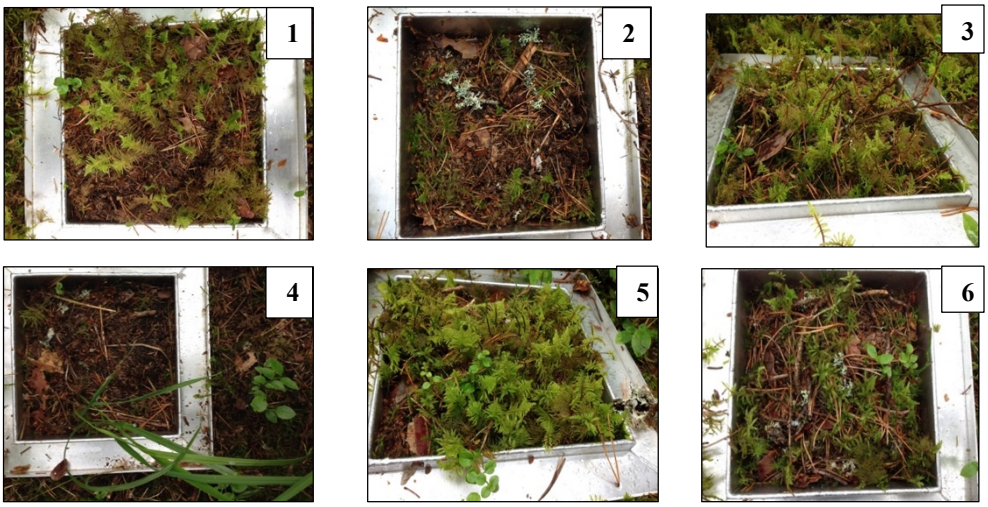

Figure 3. Six random plots were selected on the forest floor in 2015.

The soil 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. CO_2 concentration inside chamber, PAR next to the chamber (at ~30 cm above ground), soil temperature at depth of 5 cm, soil moisture (volumetric soil water content %vol) of top 5 cm soil layer were also measured. Litterfall from 15 traps randomly set on the ground was collected. The bottoms of the traps were closed on 21st of May, and litterfall was collected on 16th June, 16th July, 16th August, 15th September, and 26th October respectively. The collected litter was dried at 60°C for around 48 hours and weighted afterward.

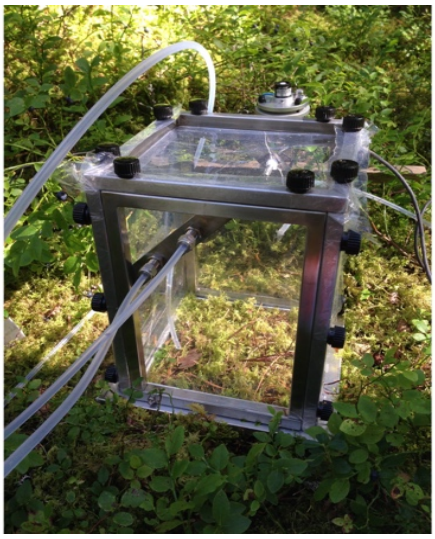

Figure 4. A soil chamber was placed on the frame with tap water filled in the channel to make the frame airtight.

Emission rate calculation

The BVOC emission rate E (μg m^{-2} h^{-1}) from each plot on the forest floor was calculated as the mass of each compound per square meter and time (Aaltonen et al., 2011):

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

where C_2 is the concentration of each BVOC within soil chamber and C_1 is the BVOC concentration of the air entering the soil chamber (blank samples). F is the air flow rate through the soil chamber, and A is the area of frame.

Standardization of BVOC emission rates

Measured MT emissions from branches of Norway spruce were standardized to a temperature of 303.15 K (30°C) and PAR of 1000 μmol photons m^{-2} s^{-1} based on a hybrid model of Ghirardo *et al*. (2010) which partitions the MT emissions from both *de novo* synthesis and storage pool in Paper I and II:

$$E = E_S \times [f_{denovo} \times C_T \times C_L + (1 - f_{denovo}) \times \gamma] \quad (3)$$

$$\gamma = e^{\beta (T - T_S)} \quad (4)$$

where E is the measured MT emission rate with branch chamber (μg g_{dw}^{-1} h^{-1}), E_S is the standardized emission rate (μg g_{dw}^{-1} h^{-1}) at the standard temperature T_S of 303.15 K and PAR of 1000 μmol photons m^{-2} s^{-1}, f_{denovo} is the fraction of the emissions originating directly from synthesis, γ is the temperature activity factor for vaporizing from the pool. T is the leaf temperature (K), which was approximated by the air temperature inside the chamber. β is a parameter to account for the temperature sensitivity (K^{-1}) of emissions, which was set as 0.09 K^{-1} in Paper I and II. C_T describes the temperature dependence and C_L describes the variation caused by light conditions, and both are defined by Guenther *et al*. (1993):

$$C_T = \frac{\exp\left(\frac{C_{T1}(T - T_S)}{RT_S T}\right)}{1 + \exp\left(\frac{C_{T2}(T - T_M)}{RT_S T}\right)} \quad (5)$$

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1+\alpha^2 L^2}} \quad (6)$$

where T_S is 303.15 K, T is the measured air temperature (K) inside the chamber in this study, L is the measured PAR (μmol photons m^{-2} s^{-1}) next to the chamber. All the other parameters were kept the same as the reported by Guenther *et al*. (1993).

Measured MT emissions from Scots pine and forest floor and SQT emissions from Norway spruce and Scots pine were standardized based on the light-independent algorithm of Guenther *et al*. (1993):

$$E = E_S \times e^{\beta (T - T_S)} \quad (7)$$

where E is the measured MT or SQT emission rate (μg g_{dw}^{-1} h^{-1} for tree branches / μg m^{-2} h^{-1} for forest floor), E_S is the standardized emission rate (μg g_{dw}^{-1} h^{-1} for tree branches / μg m^{-2} h^{-1} for forest floor), T is the leaf temperature (K), which was replaced by the air temperature inside the chamber, T_S is the standard temperature of 303.15 K, β is the temperature sensitivity (K^{-1}) of emissions.

The measured isoprene emission rates from Norway spruce and Scots pine were standardized based on the temperature and light dependent algorithm of Guenther *et al.* (1993):

$$E = E_S \times C_T \times C_L \quad (8)$$

where E is the measured isoprene emission rate from tree branches (μg g_{dw}^{-1} h^{-1}), E_S is the standardized emission rate (μg g_{dw}^{-1} h^{-1}), C_T and C_L are the same as the description of eqn 5 and eqn 6.

Results and discussion

Seasonal variation of top canopy terpene emissions (Paper I and II)

BVOC emissions from the branches at 20-m height of one Norway spruce stand were measured during the summer of 2013 and 2014 in order to get a long-term measurement of the seasonal behaviors of different BVOC compounds, particularly focusing on terpene emissions in this study. Total measured terpene emission rates from Norway spruce in 2013 varied between 0.05 and 332.5 μg g_{dw}^{-1} h^{-1} with peak emissions in August even though the campaign of late July (25^{th}–31^{st} July) had the highest measured air temperature inside the chamber of all five campaigns (Fig. 5a). In 2014, the measured terpene emission rates from the branch at 20-m height of the same Norway spruce stand were in the range of 0.03 to 7.93 μg g_{dw}^{-1} h^{-1} with the peak in July and followed by August based on the averaged emission rate per campaign (Fig. 5b). The terpene emissions presented a clear diurnal pattern during campaigns of late July and August in 2013 and 2014, with increasing values in the morning and highest emissions at noon followed by a decrease. The composition of MT compounds was stable from June to September, but more SQT compounds were detected in some samples collected in August 2013. MT was the dominant group of terpenes emitted from the 20-m canopy level of Norway spruce in 2013 accounting for 65% of total terpene emissions, followed by SQT (29%) and isoprene (6%). α-pinene, limonene, camphene were the dominant MTs, and β-farnesene and α-farnesene were the main SQTs during all campaigns in 2013. While in 2014, isoprene was the dominant compound from July to September, and MT was the major group of emitted terpenes in June. The dominant MTs in 2014 were the same as the result of 2013, while β-caryophyllene and α-humulene were the main SQTs in the campaigns of 2014. The partitioning of MT emissions from *de novo* synthesis and storage pool were analyzed by the hybrid model (eqn 3, Ghirardo et al., 2010) using data of each campaign, which exhibited that the fraction of *de novo* MT emissions (f_{denovo}) was varying throughout campaigns, but it was always the major contribution to MT emissions with values of f_{denovo} almost 100% in June 2013 and 96% in June 2014.

Compared with previous studies (Janson et al., 1999, Yassaa et al., 2012) of Norway spruce terpene emissions, the actual emission rates of 2013 were exceptionally high while the results in 2014 were similar as the reported. This observed high MT emissions were probably caused by beetle attacks, which could induce the emissions of α-pinene, camphene and limonene were 39-, 55- and 15-

fold higher than emissions before the attack according to the study by Ghimire *et al.* (2016). The observed dominant SQTs α-farnesene and β-farnesene in 2013 were commonly induced compounds for the self-defense against insect attacks (Blande et al., 2009). Although we were not able to detect any visible signs of insect attacks, we cannot exclude that such attack induced high terpene emissions as we measured in campaigns of 2013. The induced BVOC emissions by herbivore attack are a challenge for modelling emissions at the moment (Arneth and Niinemets, 2010). The high SQT emissions from Norway spruce in 2013 would have an impact on atmospheric aerosol formations since oxidized SQT resulted in higher aerosol yields in comparison with isoprene and MT (Hemig et al., 2007).

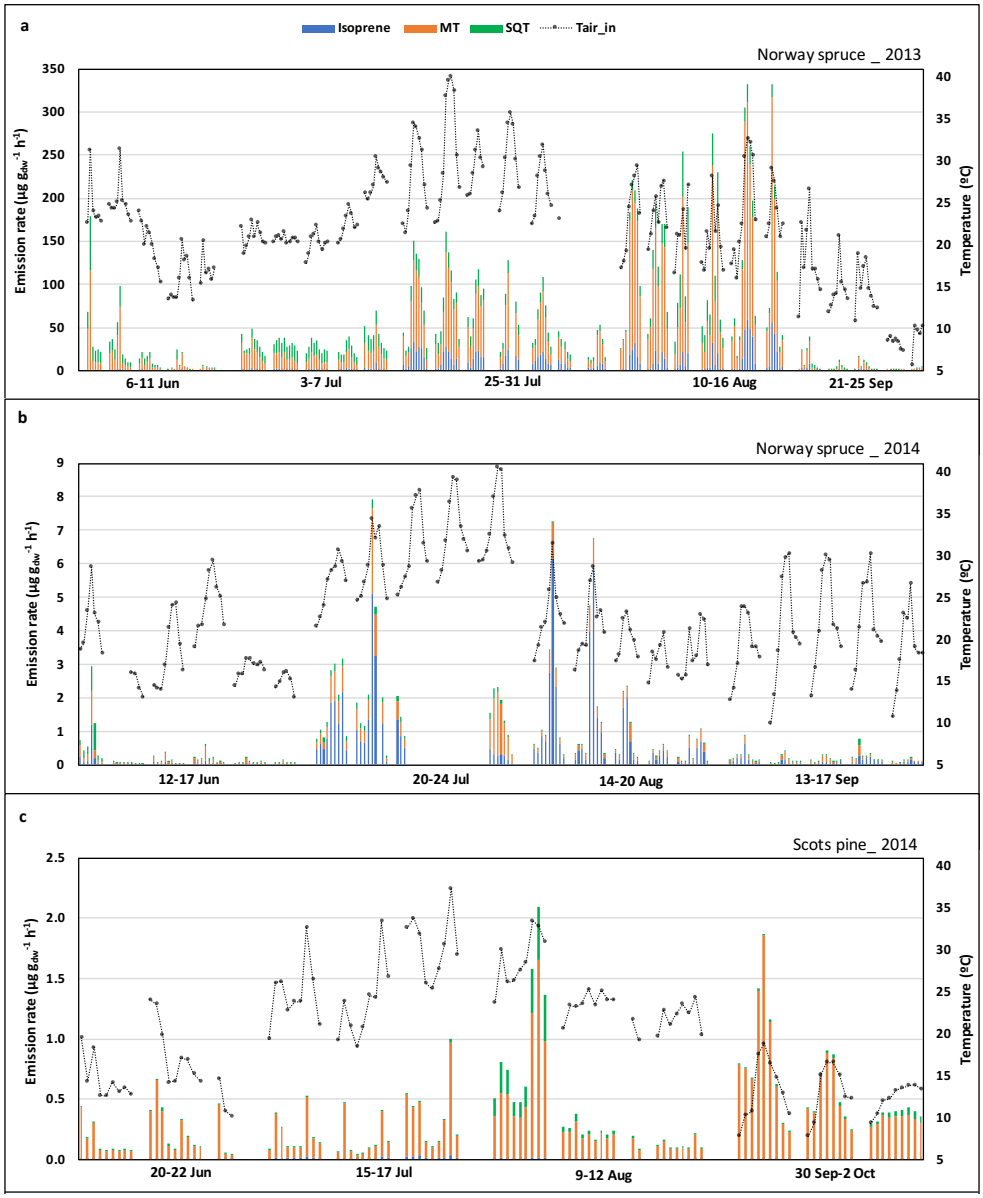

Figure 5. Measured terpene emission rates of Norway spruce at 20-m canopy in 2013 (**a**) and 2014 (**b**) and Scots pine at 20-m canopy in 2014 (**c**) during growing season. The measured temperature inside the branch chamber (Tair_in) is indicated in black dash line. There were 18 samples were missing due to GC-MS instrument failure between 22nd and 24th of July (**b**).

Scots pine was also measured at 20-m height in four campaigns during summer and early autumn of 2014. The measured total terpene emissions varied between 0.04 and 2.09 μg g_{dw}^{-1} h^{-1}, and the highest emission occurred in the end of September and beginning of October with an average of 0.6 μg g_{dw}^{-1} h^{-1} of the 3-days campaign, followed by August with an average of 0.4 μg g_{dw}^{-1} h^{-1} (Fig. 5c). The contribution of MT to total terpene emissions was highest in June and September with 96%, followed by July 92%, and it decreased to 78% in August when measured SQT emissions were at the peak and constituted 21% of total terpene emissions. SQT emissions from Scots pine were also found had the maximum in late summer (late July and beginning of August) in Hyytiälä (Tarvainen et al., 2005). The dominant MTs were Δ^3-carene, α-pinene and myrcene, and the detected SQT was mainly β-carophyllene. Isoprene also appeared in some samples in campaigns of June to August with the highest emission rate observed in July. Scots pine has been recognized as a non-isoprene emitter in some field studies (Tarvainen et al., 2005, Hakola et al., 2006), but one laboratory study of VOC emissions from Scots pine reported small amounts of isoprene emissions (Shao et al., 2001). We noticed that the needles of Scots pine trees in the forest at Norunda turned yellowish at the start of the campaign on 11th of September 2014 (Fig. 6), which might be caused by beetle attack (Giunta et al., 2016). Most of the yellow needles had dropped when the measurement carried out. Therefore, the high MT emissions in September might be a result of induction by insect attack.

Figure 6. Canopy of a Scots pine tree with yellow needles, photo was taken in September 2014.

Measured terpene emissions from 20-m Scots pine were standardized to a temperature of 30°C and PAR of 1000 μmol photons m^{-2} s^{-1}: isoprene was standardized with the temperature and light dependent algorithm (eqn 8), MT and SQT were standardized with the light independent algorithm (eqn 7) and the β value was set as 0.09 K^{-1} for MT and 0.15 K^{-1} for SQT respectively (Tarvainen et al., 2005). The measured terpene emissions from Norway spruce at 20-m height were standardized in the same way as Scots pine. Overall, total standardized terpene emissions from Norway spruce at 20-m canopy level were higher than those from Scots pine of the same height during the summer of 2014. The standardized isoprene emission rate of Norway spruce was higher than Scots pine isoprene E_S in each individual campaign. Though the selected branches in our measurements could not represent the whole 20-m canopy level, the total terpene emissions from Norway spruce are expected to be higher than the emissions from Scots pine during summer considering Norway spruce has a higher LAI and crown length in comparison with Scots pine (Majasalmi et al., 2017). Therefore, the species composition of a forest is important for estimating BVOC emissions on the ecosystem scale.

Vertical distribution of terpene emissions within canopy of Norway spruce (Paper II)

Needles are exposed to varying light and temperature conditions from top to bottom of the canopy in a dense forest like Norunda. This different microclimate within the canopy imposes influence on BVOC emissions, particularly on isoprene and other light-dependent compounds (Guenther et al., 2013). Therefore, terpene emissions from different canopy levels of the same Norway spruce stand were measured from June to September 2014 using two branch chambers. One chamber was set on 20 m enclosed the same branch from June to September as a reference and the other one was set at 3 m in June, 11 m in July, 15 m in August and 20 m in September. As presented previously, terpene emissions on 20 m varied throughout all campaigns with the highest emissions in July (Fig. 7a-d). However, there was no clear vertical distribution pattern of terpenes within the canopy based on the analysis of vertical profile measurements (Fig. 7).

The impact of seasonal changes on terpene emissions seemed to be more pronounced than the within-canopy variability of microclimate. The maximum of measured terpene emission rate was found in July at 20 m and 11 m (Fig. 7b), and the minimum occurred in September with two chambers set on different branches at 20 m (Fig. 7d). Both PAR and ambient temperature peaked in July, which could explain why the highest emissions of terpene occurred in July. And the daytime fluctuation patterns of measured total terpene emissions were similar between 20 m and lower canopy levels even though the actual total amounts were different (Fig. 7a-d). Observed isoprene emissions from 20 m was higher in comparison with 11 m and 15 m because the upper canopy was exposed to more light, but the amount of measured MT emissions from these three levels were quite close when using 20 m emission as a reference. The measured isoprene and MT emissions from 3 m were 3 and 5 times higher, respectively, than the measured emissions from 20 m. This was probably due to that the selected branch at 3 m was close to an open path, which exposed to higher light condition at certain time in comparison with other branches at the same height level. And, Rayment *et al.* (2002) reported the strongest gradient of light within the black spruce canopy occurred horizontally along the branches, from the needles at the end of branches that were nearly always sunlit to the interior parts of the crown that practically was shaded most of the time. Therefore, the inclination angle of the selected branch was not representative for the whole measured canopy level, which gives a poor coverage of the mean microclimate conditions within the canopy. And we cannot directly separate the seasonal impact from the influence of canopy heights on terpene emissions because the measurements of different heights were carried out in different months.

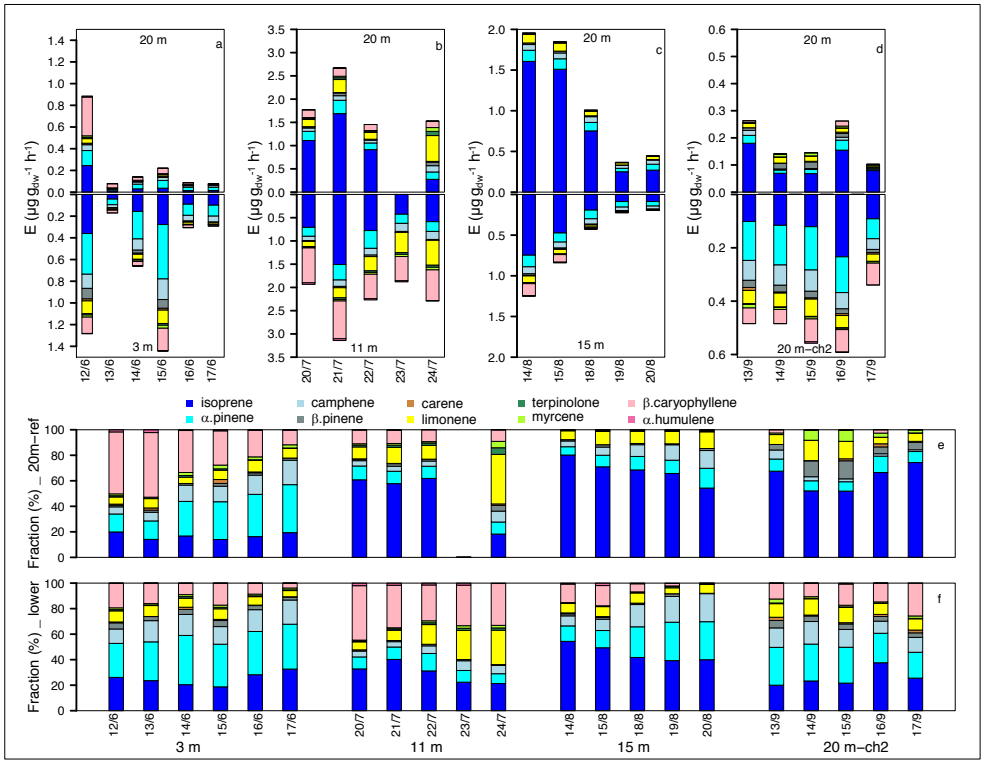

Figure 7. The daily average of measured terpene emission rates from 20-m canopy and lower levels of the canopy: 3 m (**a**)/ 11 m (**b**)/ 15 m (**c**) / 20 m (**d**), and the emission spectrum of terpenes on 20 m (**e**) and lower canopy levels of 3 m, 11 m, 15 m and 20 m (**f**). Measurements were carried out between June and September in 2014. Lower canopy levels include the second chamber set at 20-m canopy in September (20 m-ch2).

Generally, the composition of compounds emitted from different canopy levels did not vary much, but the contribution of individual compounds was changing with time and height (Fig. 7e-f). Isoprene was the compound with the highest observed emissions in the reference chamber from July to September, and MT was the most important compound at lower canopies and even in the second chamber set at 20 m. α-pinene, limonene, camphene were the main MTs at all different canopy levels with one exception of the reference branch measured in September, of which dominant MT compounds were α-pinene, limonene and β-pinene. β-caryophyllene was the most important SQT of all measurements. MT compounds have been recognized as the dominant terpenes emitted from Norway spruce in previous studies (Janson et al., 1999, Grabmer et al., 2006, Bourtsoukidis et al., 2014) and even in the study of the same tree at the same canopy height in 2013. SQT emissions from Norway spruce were found to increase at the end of July and August (Hakola et al., 2017). Also, the measurement in the second chamber at 20 m showed that SQT contributed to 16% of total terpene emissions in September. Therefore, the continuous decline of SQT emissions in the reference chamber from

July to September combining isoprene dominating terpene emissions was probably a sign of acclimation. The reference branch might have been adapting to the new growth condition: inside the Teflon chamber. Even though the lid of the chamber was open when no campaigns were carried out, the climate condition inside was still not the same as ambient condition.

Comparison of Norway spruce BVOC emissions among different sites (Paper IV)

The standardized terpene emissions from Norway spruce in June and July 2014 were used to compare with other measurements of Norway spruce stands growing at different latitudes across Europe, to investigate the drivers for interspecies variation of terpene emissions, e.g. local adaption, latitude and heights etc. The observed isoprene emissions were standardized using the temperature and light dependent algorithm (eqn 8), and the observed MT and SQT were standardized using light-independent algorithm (eqn 7) with β value of 0.09 for both (Table 2). Excluding the three Swedish sites (Hylte-mossa, Skogaryd and Norunda), the Norway spruce trees from the remaining sites listed in Table 2 were genetically the same, they were part of the International Phenological Garden (IPG) network in Europe. Terpene emissions from Norunda were significantly different from other sites due to its high isoprene emissions (particularly at 3 m) and different emission spectra (high contribution of isoprene, low contribution of limonene and SQT). High isoprene emission at 3 m was very likely due to high irradiation events on the selected branch, and the Norway spruce tree at Norunda was growing in a much denser forest in comparison with the other sites, which possibly lead to a difference in shade acclimation (van Meeningen et al., 2017). The difference of standardized terpene emission rates from Norway spruce growing at different sites did not show much difference across latitudes or between genetically different trees, but the emission spectra was mainly influenced by genetics as the study revealed (van Meeningen et al., 2017). The potential effect from heights, season and inter annual variations on terpene emissions were not easy to separate and investigate, and difference in terpene emissions from different sites may also be derived from different experimental setups.

Table 2. The standardized emission rate ($\mu g\ g_{dw}^{-1}\ h^{-1}$) of isoprene (IS), monoterpene (MT) and sesquiterpene (SQT) from different sites, months and heights within canopy. The standardized emission rates are averaged ($\pm$ standard deviation) and n.d. stands for no data available. This table is adapted from Table 2 in Paper IV (van Meeningen et al., 2017).

Country (Latitude)	Site	Month	Height (m)	IS ($\pm$std)	MT ($\pm$std)	SQT ($\pm$std)
SI (46º04'N)	Ljubljana*	Apr–May	1–2	0.31 ($\pm$0.29)	1.17 ($\pm$1.46)	0.50 ($\pm$1.28)
DE (48º18'N)	Grafrath*	Jun	1–2	0.64 ($\pm$0.92)	1.60 ($\pm$1.24)	0.10 ($\pm$0.29)
DK (55º40'N)	Taastrup*	Jul	1–2	0.51 ($\pm$0.78)	1.96 ($\pm$1.95)	0.33 ($\pm$0.84)
DK (55º40'N)	Taastrup*	Jul	5.5	0.06 ($\pm$0.23)	3.81 ($\pm$3.83)	0.55 ($\pm$1.18)
DK (55º40'N)	Taastrup*	Jul	12.5	0.10 ($\pm$0.31)	4.35 ($\pm$3.42)	0.09 ($\pm$0.21)
SE (56º06'N)	Hylte-mossa*	Jul	1–2	0.43 ($\pm$0.12)	1.25 ($\pm$1.14)	0.34 ($\pm$0.38)
SE (58º23'N)	Skogaryd**	Oct	2.5–3.5	0.11 ($\pm$0.61)	0.29 ($\pm$0.25)	n.d.
SE (60º05'N)	Norunda**	Jun	3	3.79 ($\pm$3.48)	1.51 ($\pm$1.19)	0.23 ($\pm$0.20)
SE (60º05'N)	Norunda**	Jul	11	2.96 ($\pm$2.65)	0.95 ($\pm$0.41)	0.73 ($\pm$0.38)
SE (60º05'N)	Norunda**	Jun–Jul	20	0.98 ($\pm$1.25)	0.59 ($\pm$0.36)	0.17 ($\pm$0.22)
FI (60º23'N)	Piikkiö*	Jul	1–2	0.10 ($\pm$0.08)	1.47 ($\pm$1.52)	0.17 ($\pm$0.19)

*The measurements were done with a volume of 270 cm^3 conifer chamber connected to a portable infra-red gas analyzer (LI-6400, LICOR, Lincoln, NE, USA).
**The measurements were done with one or two 13 L cylindrical and transparent branch chamber(s).

Forest floor BVOC emissions (Paper III)

Studies of BVOC emissions from forest floor and soil are much scarcer in comparison with studies of above ground plants BVOC emissions. However, a few studies have indicated that the forest floor is an important source of MT emissions in boreal ecosystem (Janson, 1993, Hellén et al., 2006, Aaltonen et al., 2011). We used a dynamic soil chamber to quantify BVOC emissions from six randomly located plots on the forest floor during five campaigns from June to October in 2015. There were 18 volatile compounds detected from all collected samples, including isoprene, seven MTs, five SQTs, four oxidized terpenes and one aromatic ρ-cymene (Table 3). The largest BVOC emission rates were found in October with an average of 10.26 μg m^{-2} h^{-1} of six plots when the amount of fresh litter was at its maximum of all campaigns, while the air temperature, soil temperature and soil water content were low. Isoprene emissions were almost negligible from June to September, the emissions of SQT were close to zero after August, and the emissions of the remaining compounds (mainly ρ-cymene and MBO) became minor in autumn as well. MTs were the dominant group of all detected compounds, contributing more than 80% of total BVOC emissions throughout summer and autumn. The dominant MT compounds were α-pinene, Δ^3-carene, and camphene, which seemed to be a combination of the dominated MTs emitted from the needles of Norway spruce (Wang et al., 2017) and Scots pine at the same study site.

The measured MT emissions from forest floor increased exponentially with air temperature inside the soil chamber from June to September, however the MT emissions in October were independent from air temperature inside chamber (Fig. 8), which indicated that the major source for MT emissions changed in October. In this study, we could not separate evaporation of MTs from storage pools in the litter needles from microbial decomposition of litter, but the results implied that the litter fall may have been the dominant source for BVOC emissions in autumn, and the needle litter may have been a significant MT reservoir. There are other studies also confirmed that needle litter was the major source of terpene emissions on the forest ground (Hayward et al., 2001, Asensio et al., 2008a).

Isoprene was mainly emitted from two plots with the highest coverage of mosses and dwarf shrubs, which suggested that the isoprene emissions were mostly from the ground vegetation. The SQT emission was mainly contributed by β-caryophyllene emission (Table 3), and β-caryophyllene was the observed dominant SQT from needles of Scots pine and Norway spruce in the campaigns of 2014 at the same site. This suggested that the needle litter was one important source for SQT emissions as well.

Table 3. The average of measured BVOC emission rates (±standard deviation) (μg m^{-2} h^{-1}) from forest floor of each individual campaign.

Compound	Emission rate (μg m^{-2} h^{-1})				
	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	0
α-humulene	0.01	0.01	0.01	0	0
longicyclene	0.01	0.003	0.01	0	0
iso-longifolene	0.001	0	0	0	0
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
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)

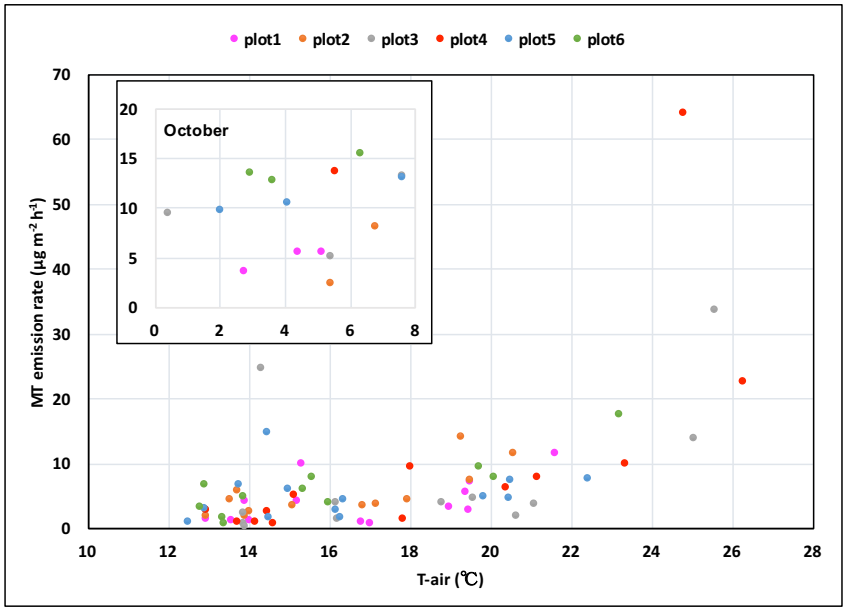

Figure 8. Measured monoterpene (MT) emission rates as a function of air temperature inside the soil chamber (T-air) for samples collected from June to September. The data in the subfigure on top left was collected in October.

The measured air temperature inside the soil chamber and PAR next to the chamber were the two most influential variables for determining MT, SQT and ρ-cymene emissions in this study. The variations of soil temperature were much smaller in comparison with the air temperature inside chamber, and it was not expected to exhibit high influence on BVOC emissions as air temperature, but it may have an influence on retention of microbially produced VOCs in the soil (Insam & Seewald, 2010). Isoprene emissions were positively correlated with soil moisture while MT emissions showed negative correlation with soil moisture. A study of shrubland also showed long-term drought increased MT emissions from soil, but reduced emissions of other BOVCs (Asensio et al., 2008b). The understorey vegetation composition also impacted certain BVOC emissions, such as β-pinene and linalool in our study. The highest β-pinene emission was found in plot 2 where lichens were present within the plot, and the highest linalool emission was observed in plot 4 where grass *Poaceae* was growing inside the plot.

Measured BVOC emissions from forest floor during June to September of 2015 were used to compare with the measured BVOC emissions from the branches of Norway spruce and Pine during June to September of 2014. First, the measured BVOC emission rates (µg g_{dw}^{-1} h^{-1}) on branch levels were needed to transform to emissions per m^2 of ground (µg m^{-2} h^{-1}) for comparison. The specific leaf area (SLA) for Norway spruce was set as 38.4 cm^2/g based on the measurement of the reference branch at 20 m, while the SLA for Scots pine was set as 43.8 cm^2/g based on the study of Xiao *et al.* (2006). LAI was set as 4.8 m^2/m^2 (Sundqvist et

al., 2014) for both Norway spruce and Scots pine. On average, the BVOC emissions from forest floor accounted for roughly 1% of BVOC emissions from Norway spruce based on the calculation from 20-m branch-level measurements, and around 1.2% of Scots pine BVOC emissions which was also estimated from 20-m branch-level measurements. The forest floor BVOC emission is an important component of the whole boreal forest BVOC budget, and the importance of this component is probably undervalued so far.

Conclusion and outlook

The main objective of this thesis was to characterize BVOC emissions from a Norway spruce and Scots pine dominated boreal forest with focus on terpene emissions from Norway spruce during summer and autumn. Using a dynamic branch or soil chamber combining cartridge sampling can capture the emitted compounds before they are oxidized in the air. The GC-MS analysis is able to identify and quantify the trapped compounds, even compounds with same molecular weights, such as different MT compounds or SQT compounds. Long-term observations of BVOC emissions from branches of top and lower tree canopies and from the forest floor are required to study the seasonal variations and for accurately upscaling BVOC emissions for the whole ecosystem.

The measured Norway spruce presented seasonal variation of BVOC emissions on branch level at 20-m canopy in 2013 and 2014, with the highest emission rates and more complex emission spectra in late July (2014) and August (2013). The fraction of MT emissions from *de novo* synthesis also varied over time. This observed seasonal variation in BVOC emissions provides an optional reference for evaluating emission models.

The observed extreme high BVOC emission rates in 2013 were likely due to insect attacks, because high MT, α-farnesene and β-farnesene emissions can be induced by such an attack, even though no visible signs of insect attacks were detected during the measurements. High MT emissions from the branch of Scots pine were observed in the end of September 2014 when the needles turned yellow and dropped off. Induced BVOC emissions can be very high and they are tricky to be estimated by the emission models. There are limited studies to quantify herbivore-induced BVOC emissions. Insect outbreaks are expected to increase under warmer climate conditions, therefore, more efforts are needed to study the biotic stress-induced BVOC emissions under natural condition. Additionally, the induced high emissions of MT and SQT in the boreal forest can have a great impact on particle formation and growth, and further have an impact on regional climate. In this study, the observed high isoprene and SQT emissions were mainly from Norway spruce canopy, while Scots pine canopy and forest floor mostly contributed to MT emissions. SQT is known to have a higher efficiency of particle formation than isoprene and MT, which implies that Norway spruce might have a greater influence on particle formation and growth in the boreal forest in comparison with Scots pine.

No vertical distribution pattern of terpene emissions was found within the canopy of Norway spruce in our study. The inclination angle of the selected branches

might not represent the light condition of whole canopy level. The reference branch enclosed in the chamber at 20-m canopy for more than three months may have acclimated to the new growth condition, which may have led to the alteration of BVOC emission rates and emission spectra, such as increasing isoprene emission rate and declining SQT emission rate. The observed terpene emissions from Norway spruce varied with sites, season, genetics, different canopy levels and different branches of the same canopy level. Therefore, more replicates of branches of different canopy heights and more replicates of Norway spruce stands are needed for the measurements to get conclusive results of within-canopy distribution of BVOC emissions.

The BVOC emissions from forest floor varied from June to October in 2015 with the campaign-averaged maximum emission in October, when the biomass of fresh litter was the highest. Variations of BVOC emissions over time indicated that needle litter might be an important source for BVOC emissions. Air temperature inside soil chamber and PAR measured at ~30 cm above ground were the most important variables influencing BVOC emissions in this study. However, soil temperature, soil moisture and understorey vegetation coverage and composition potentially also affect BVOC emission rates. BVOC emissions from forest floor are indispensable for estimating boreal forest ecosystem BOVC emissions, while BVOC emissions from this understorey vegetation-litter-soil system have not been thoroughly studied yet. More detailed designed field and laboratory studies are necessary to quantify the individual sources of BVOC emissions, and to study how the environmental variables affect BVOC emissions from ground vegetation, litter and soil. For instance, sampling vegetation, litter and soil separately for BVOC emissions in the field, using climate chamber to grow mesocosms under different environmental conditions, and using a proton-transfer-reaction mass spectrometry (PTR-MS) for real-time observation of BVOC emissions under natural and controlled growing conditions, etc. Meanwhile, longer-term observations on more plots on the ground are also needed to more precisely quantify diurnal and nighttime BVOC emissions from forest floor on annual or larger-time scale.

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