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Scots pine provenance affects the emission rate and chemical composition of volatile organic compounds of forest floor

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Scots pine (*Pinus sylvestris* L.) is an important source of biogenic volatile organic compounds (BVOCs) in the boreal zone. BVOC emission rate and profile affect air quality, climate forcing, plant stress tolerance, and thus the growing conditions of forests. BVOC emission profile of shoots and forest floor, and emission rates from forest floor, were studied in a latitudinal provenance experiment with 19-year-old Scots pine common garden in Central Finland. The provenances studied were Saaremaa (SAA 58°22´), Korpilahti (KOR 62°0´), Suomussalmi (SUO 65°10´) and Muonio (MUO 67°56´). A chemotype with high proportion of Δ-3-carene, terpinolene, sabinene, γ-terpinene and α-terpinene was significantly more common for the southern SAA than the northern SUO and MUO provenances. A chemotype with high proportion of α-pinene, β-pinene, limonene and myrcene was more common in the three northernmost provenances. The main compounds emitted by forest floor were α-pinene, Δ-3-carene and camphene. Similarly to shoot emissions, forest floor emissions from SAA had highest proportion of Δ-3-carene. Average total VOC emission rate from forest floor was 50 µg m^{-2} h^{-1} at the end of August. Total emission rates were 65 % higher in KOR than in MUO. High emission rates were explained by the high amount of decomposing needle litter and low moss coverage.

Keywords: tree provenance, BVOCs, forest floor, needle litter, mosses
1. Introduction

Boreal forest or taiga is the world’s largest terrestrial biome dominated by coniferous tree species and it covers one third of the total forest area of the Earth (Gauthier et al. 2015). Carbon sequestration by boreal forests is estimated to represent 20% of the annual C sink of global forests (Gauthier et al. 2015). In Finland, 86% of the land area, ca. 26 million hectares, is covered by forests, and Scots pine (*Pinus sylvestris*) occupies 65% of the forest land (Peltola 2014). Global emissions of biogenic volatile organic compounds (BVOCs), such as methanol, acetone and terpenoids isoprene, monoterpenes and sesquiterpenes, from vegetation were modelled to be 659.5 Tg C yr\(^{-1}\) and boreal forests area has a considerable contribution to monoterpane emission during summer (Messina et al. 2016). Terpenoids are components of resin, synthesized, stored and transported in the resin canals of coniferous trees (Trapp and Croteau 2001). Emissions of volatile terpenoids of Scots pine needles originate both from storage and *de novo* synthetis (Ghirardo et al. 2010). In addition, stems (Heijari et al. 2011) and roots (Lin et al. 2007) emit BVOCs. Monoterpenes 3-carene and α-pinene are the two terpenoids with the highest emission rates from Scots pines. Terpene profile of Scots pine is under genetic control, and the division of Scots pines to chemotypes of ‘low’ or ‘high proportion of 3-carene’ is well known (Baradat and Yazdani 1988). Scots pine trees growing in Northern Finland have lower proportion of high-carene chemotypes than those in Southern Finland (Muona et al. 1986) and similar latitudinal difference was observed between Scots pine provenances in a multi-site common garden experiment established in three locations in Finland (Nerg et al. 1994). Nerg et al. (1994) also reported that opposite to 3-carene, shoot α-pinene concentration increased from southern to northern provenances. Relatively similar terpene profiles have been reported for pine shoot (needles+stems) (Nerg et al. 1994), needle and wood terpene concentrations (Manninen et al. 2002) and stump BVOC emissions (Kivimäenpää et al. 2012) in the same common garden. Chemotypes characterized by α-
pinene and 3-carene were also found from Scots pine shoot BVOC emissions in a pine-
dominated mixed forest stand in southern Finland (Bäck et al. 2012).

Plants use terpenoids for defense against biotic stresses, such as pathogens and herbivores
(Trapp and Croteau 2001). They can be toxic or repellent for herbivores, or attract natural
enemies of herbivores or their egg parasitoids (Mumm and Hilker 2006). BVOC profile is
important as it is used as chemical cue both for location of herbivores and for their enemies
(Mumm and Hilker 2006). BVOCs also increase plant resistance against abiotic stress, e.g.
heat and ozone, a phytotoxic air pollutant (Loreto and Schnitzler 2010).

In the atmosphere, BVOCs affect air quality, temperature and PAR (photosynthetically
active radiation), and thus forest productivity (Holopainen 2011). Namely, BVOCs
contribute to both formation and breakdown of ozone (Lerdau and Slobodkin 2002) that
with prevailing concentrations can have adverse effects on Scots pine (Huttunen and
Manninen 2013). In addition, BVOCs reduce oxidation of greenhouse gas methane, and
thus, have a warming effect on the climate (Peñuelas and Staudt 2010). Moreover, in
reactions with atmospheric oxidants, Scots pine BVOCs contribute to the formation of
secondary organic aerosols (SOA) and via increase of cloud condensation nuclei promote
cloudiness (Kulmala et al. 2013). SOA and cloud formation can increase tree photosynthesis
and primary production in diffuse light (Holopainen 2011) and cool the climate (Scott et al.
2018). Reactivity of VOCs with various tropospheric oxidants such as ozone and OH and
NO3 radicals (Atkinson and Arey 2003) and consequent SOA mass yields (Lee et al. 2006)
differs between individual compounds. Larger BVOC emissions of stressed Scots pine
seedlings led to larger SOA formation (Joutsensaari et al. 2015). Therefore, both emission
rates and profile, especially from dominant forest species, are important in considering
significance of BVOCs on climate.
Forest floor can be a considerable source of BVOCs, because understory plant species, such as *Calluna vulgaris* (Tiiva et al. 2017) or *Rhododendron tomentosum* (Himanen et al. 2010) shrubs, conifer needle litter (Isidorov et al. 2010), litter decomposers (Isidorov et al. 2016), roots (Lin et al. 2007), rhizosphere (Rasheed et al. 2017), ectomycorrhizal fungi and endophytes (Bäck et al. 2010) emit BVOCs. BVOC emissions from Scots pine-dominated forest floor have been mainly measured in one location in Southern Finland, and estimations of emissions rates have high variation, ranging from 0-373 µg m⁻² h⁻¹ (summarized in Mäki et al. 2017). Common garden experiments where Scots pines from different provenances grow in the same location, provide a way to estimate forest floor emission rates from a wider latitudinal range. Provenance experiments also enable to study if shoot and forest floor VOC emission profiles differs between latitudes, similarly as latitude affected terpene concentration profiles of pine shoot (Nerg et al. 1994), needle and wood (Manninen et al. 2002) and stump BVOC emission profiles (Kivimäenpää et al. 2012). We can hypothesize that the influence of tree chemotype is observable in the forest floor emissions via emissions from roots and needle litter.

The aims of this study were to examine if tree provenance affects 1) BVOC emission profile from the shoots, 2) BVOC emission profile from forest floor, 3) BVOC emission rates from forest floor and if 4) forest floor characteristics (needle litter, understory vegetation, temperature, moisture) influence on the emission rates.

### 2. Material and methods

#### 2.1. Experimental site and tree provenances

This study was conducted in an experimental Scots pine (*Pinus sylvestris* L.) stand with nine provenances sown in a common garden at Suonenjoki Research Unit (latitude 62°37’) of the Finnish Forest Research Institute (currently Natural Resources Institute Finland) in 1991.
Trees were grown from seeds originating from a 1200-km South-North transect from Estonia to Northern Finland. Trees of each provenance grew in five replicated 1000 m² blocks in fully replicated rows, and the area of the whole research field was 0.5 ha. More details of the site and growing conditions are described in Manninen et al. (2002). The stand has been thinned several times since its establishment, with 30-40% of the original trees left at the time of this study. The provenances selected for the present study were Saaremaa (SAA, latitude 58°22’), Korpilahti (KOR, latitude 62°0’), Suomussalmi (SUO, latitude 65°10’) and Muonio (MUO, latitude 67°56’). The Saaremaa provenance originated in Estonia, the others were from Finland. Trees were 19 years old when the sampling was conducted in 2010.

2.2. Tree selection, shoot BVOC collection and needle length measurement

Ten trees of each of the four provenances in the 0.5 ha common garden stand (Kivimäenpää et. al. 2012) were randomly selected for the study on 2 June 2010. Trees were on average 4.5 m tall. One branch per tree from the lower parts of the canopy at a height ca. 3 m was selected for BVOC collection that took place on 21 - 22 June 2010. The youngest needles were still elongating at that time. The number of needle generations was four in all SAA and KOR provenances, but there were less trees with fourth generation needles left among SUO and MUO provenances (Table 1). One shoot per tree with all existing needle generations were enclosed into a pre-cleaned (+120 °C) polyethylene terephthalate (PET) bag (Look 45x55 cm) that was tightened with a shutter around a bare stem. A hole was cut to the other corner of the bag, and ozone-free (Ozone Scrubber Cartridge, Environnement S.A., Poissy, France, to avoid degradation of VOCs in the adsorbent), charcoal-filtered air (Wilkerson F03-C2-100, Monterrey, Mexico, to remove VOCs from background air entering the collection bags) was led into the bags via Teflon-tubing at a rate of 0.6 l/min. When the
bags had expanded and the air had been replaced, the flow rate was reduced to 300 ml min⁻¹. A purified stainless steel tube (ATD sample tubes, Perkin Elmer, Norwalk, CT, USA) filled with approximately 150 mg of Tenax TA adsorbent (mesh 60/80, Supelco, Bellefonte, PA, USA) was inserted into a small hole cut in the other corner of the collection bag and fastened with a shutter. The sample was pulled through the sample tube with a vacuum pump (Thomas 5002 12 V DC, Puchheim, Germany) at a rate of 200 ml min⁻¹ for 15 minutes. The tubes were sealed with Teflon-coated brass caps and stored at +4 °C until analysis. Temperatures inside the collection bags were recorded by wireless data loggers (Hygrochron DS1923-f5 iButton, Maxim Integrated products, San Jose, CA, USA). Air temperature (sensor S-THA-M006) outside the collection bags and photosynthetically active radiation (PAR, sensor PAR S-LIA-M003) inside empty collection bag were measured and recorded (datalogger, Hobo Micro Station, Onset Computer Corporation, Bourne, MA, USA) next to shoots used for VOC-collection. Air samples from empty collection bags (blank samples) in the forest site were also collected to confirm the purity of the background air entering the collection bags. PAR in the collection bags varied between 140 and 580 µmol m⁻² s⁻¹ and temperature between 14 and 26 °C. Bag enclosure increased the temperature on average by 1.4 °C.

Needle lengths from all existing needle generations were measured first on 29 June (Table 1). Elongating current year needles from SUO were longer than from SAA, and oldest generation needles were shortest in MUO provenance (Table 1). On 21 July, current year needle lengths were measured again, and no provenance differences were observed any longer when their growth had ended (Table 1). Oldest needle generation had dropped from all studied shoots by 21 July.

2.3. Forest floor characteristics and BVOC collection
Soil cylinders (height 12 cm) made of polyethene and covering 68 cm² of forest floor were installed on 2 June 2010 under the foliage of the same trees as used for shoot BVOC collection \((n=10\) for KOR, \(n=9\) for other provenances) at the distance of 0.5 m (between trunk base and cylinder margin). One end of the cylinder was made narrow and sharp and was pressed to the soil. Cylinders were left open so that needle litter accumulated on soil surface inside the cylinder. BVOC emissions from forest floor were collected between 10 am – 3 pm on 23 August 2010. Pre-cleaned PET bag (25 x 55 cm) was tightly tied around the soil cylinder with rubber bands. BVOC collection time was 30 min. Otherwise, BVOC collection was done as described in section 2.2. In addition, blank samples using empty bags or soil cylinder in the bag were separately collected to take into account compounds originating from the collection system. Sensors (S-THA-M006 for temperature; S-LIA-M003 for PAR) of data loggers (Hobo Micro Station, Onset Computer Corporation, Bourne, MA, USA) measured and recorded air temperature on the soil surface and PAR-level during the collection. Temperature varied between 15-19 °C and PAR-level was < 100 µmol m⁻² s⁻¹. Soil moisture at the depth of 5 cm was measured by soil moisture sensor (Theta Probe, type ML2, Delta-T devices, Cambridge, UK) after BVOC collection. Temperature and soil moisture was not statistically different between provenances (data not shown.) The coverage (%) of mosses (mainly *Polytrichum commune* and *Pleurozium schreberi*), graminoids (mainly dried), lichens (mainly *Cladonia rangiferina*) and Scots pine bark or cones in the cylinders (Table 2) were estimated visually. The needle litter from the cylinders were collected and its dry weight was determined after drying to constant weight at +60 °C. Forest floor under trees from KOR provenance had the significantly higher amount of needle litter than trees from SUO and MUO provenances (Table 2). Coverage of mosses was significantly higher under trees from MUO than SAA and KOR (Table 2).
BVOC samples were analyzed by gas chromatography-mass spectrometry (GC-MS, Hewlett Packard type 6890, Waldbronn, Germany; MSD 5973, Beaconsfield, UK). Compounds trapped in the adsorbent were desorbed (Perkin Elmer ATD400 Automatic Thermal Desorption System, Wellesley, MA, USA) at 250 °C for 10 min, cryofocused in a cold trap at -30°C and subsequently injected onto an HP-5 capillary column (50 m x 0.2 mm id. x 0.33 µm film thickness, J&W Scientific, Folsom, CA, USA). The temperature program was 40 °C for 1 min, followed by increases of 5 °C min⁻¹ to 250 °C. The carrier gas was helium. The standards were self-made mixtures of commercial standards for monoterpenes (18 compounds), homoterpenes (1), sesquiterpenes (4), green leaf volatiles (8) and other plant volatile compounds (3) dissolved in methanol. Volumes of 2 µl standard mixtures were injected into the adsorbent tubes. The compounds were identified by comparing their mass spectra to the using commercial standards and the Wiley library. Compound quantification was based on TIC (total ion counts). Compounds for which commercial standard was not available were quantified using α-pinene (for non-oxygenated monoterpenes), 1,8-cineole (oxygenated monoterpenes) and longifolene (sesquiterpenes) as reference compounds. Emission profiles of shoots and forest floor were presented as a proportion of a compound from total emissions. Shoot emissions were measured as a part of continuing experiment, and shoots could not be interfered for needle area or biomass measurements. Therefore, shoot emissions rates (including needle and bark emissions) were calculated per shoot length as done by Ghimire et al. (2013) (Table S1). The shoot BVOC emission rates were not suitable for provenance comparison, because the needle volume per shoot length was visibly different. Emission rates of BVOCs from forest floor were calculated per forest floor area using a unit µg m⁻² h⁻¹. Forest floor emission rates were calculated also as carbon (C).

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¹ Supplementary data are available with the article through the journal Web site
emissions, as well as standardized to +20 °C, which is a typical summer temperature in boreal forests, using the algorithm by Guenther et al. (1993).

2.5. Statistics

Differences between the provenances were tested by one-way ANOVA with Tukey test for pairwise comparisons. Before that, the data were logarithm transformed to fulfill the assumptions of ANOVA (data normality and homogeneity of variances) when needed. In case the ANOVA assumptions were not met, provenance differences were tested by Kruskal-Wallis test with pairwise multiple comparison test. Differences in the proportion of individual compounds from total emissions between shoots and forest floor were tested by T-test for pairwise comparisons or Wilcoxon Signed Ranks test, when data were not normally distributed. Statistical analyses were performed by IBM SPSS 21.0.

Proportions of shoot BVOCs were subjected to a principal component analysis (PCA). The data were mean-centered and standardized to unit-variance. Compounds found in < 10 % of the samples were left out from the analysis. Partial least squares regression (PLSR) was used to analyze the influence of the dry weight of needle litter, soil moisture, air temperature and the cover of vegetation groups on individual BVOCs. One component PLSR models, that were cross-validated using seven cross-validation groups, were extracted separately for each BVOC. The PCA and PLSR analyses were conducted using Simca 14 (Umetrics, Umeå, Sweden).

3. Results

3.1. Shoot emissions profile

As an average over all the provenances, the majority of the shoot BVOC emissions consisted of monoterpenes (97.4 % ± 0.5) and the major compounds were α-pinene, Δ-3-carene,
limonene, myrcene, β-pinene, camphene (Table 3), β-phellandrene (3 %), terpinolene (2 %),
1,8-cineole (2 %), (E)-β-ocimene (1 %) and sabinene (1 %). In total, pines emitted 27
different monoterpenoids (Table S12). An average percentage for sesquiterpenes was 2.4 ±
0.5 of total emissions and the major compounds of 19 observed sesquiterpenes (Table S12)
were (E)-β-farnesene (0.7 %) and longifolene (0.5 %). The proportion of GLVs and
methylsalicylate was low (0.1 %).

PCA and PC1 revealed BVOC profiles that differed between the provenances (Fig. 1).
The trees that had a high proportion of Δ-3-carene in the emission blend also had a high
proportion of sabinene, α-terpinene, γ-terpinene and terpinolene, but a low proportion of α-
pinene, β-pinene, limonene and myrcene (Fig. 1b). There were more trees with this type
('high carene but low pinenes') among the SAA provenance compared to SUO and MUO
(Fig. 1a). Four to five of ten trees among KOR, SUO, and MUO provenances had an
opposite profile, i.e., a high proportion of pinenes but low Δ-3-carene, and there were also
intermediate profile trees. The difference in the profiles characterized by PC1 was
significant between SAA and the northernmost provenances SUO and MUO (Fig. 1a). PC2
was characterized by trees with high emissions of oxygenated monoterpenes camphor, 1,8-
cineole and sesquiterpenes cis-α-bisabolene, δ-cadinene, (E,E)-α-farnesene and an unknown
sesquiterpene (Fig. 1b), but this profile was not significantly more common in any of the
provenances. Proportions of the two most dominant compounds, α-pinene, and Δ-3-carene,
are also shown in Fig. 2. The proportion of Δ-3-carene was highest in SAA provenance and
significantly different to MUO provenance.

3.2. Emission rates and profile from forest floor

2 Supplementary data are available with the article through the journal Web site
Unstandardized BVOC emission rates from the forest floor were 50 ± 7 µg m⁻² h⁻¹ when averaged over all the provenances. Respective emission rate standardized to +20 °C was 67 ± 8 µg m⁻² h⁻¹. Emission rate calculated as C at 20 °C was 59 ± 7 µg m⁻² h⁻¹. Temperature-standardized total emission rates were significantly higher in KOR than other provenances (Table 4). The difference between the provenances with the highest and lowest emission rates was 65 %. Compounds α-pinene and Δ-3-carene contributed a major fraction of the emissions from the forest floor (Table 3). Tricyclene, α-pinene, and camphene contributed higher fraction and limonene and myrcene lower fraction in the forest floor emissions than in the shoot emissions (Table 3). The proportion of Δ-3-carene was the highest in SAA provenance and significantly different from KOR and SUO (Fig. 2). Emission rates of Δ-3-carene, on the other hand, were significantly higher in KOR provenance than MUO and SUO (Table 4). Emission rates of α-pinene were significantly higher in KOR than MUO and marginally significantly (p<0.1) between KOR and other provenances (Table 4). Similar differences between KOR and other provenances were also observed for minor compounds, limonene, bornyl acetate and γ-cadinene (Table 4). Unstandardized and temperature-standardized emission rates of individual compounds showed similar differences between the provenances (data not shown).

The PLSR analysis showed that emission rates of α-pinene, Δ-3-carene, myrcene, tricyclene, p-cymene, camphor and bornyl acetate were positively related to the dry mass of the needle litter and emission rates of myrcene and bornyl acetate negatively related to the coverage of mosses (Fig. 3, Fig. S1³).

4. Discussion

³ Supplementary data are available with the article through the journal Web site
This study showed that Scots pine provenance affected BVOC emissions profile of the
shoots and forest floor, and high carene and high pinene chemotypes similar to previous
studies were found. Highest proportion of Δ-3-carene both in the shoots and forest floor
emissions in the southernmost provenance SAA agree with the previously reported
differences in Δ-3-carene concentrations in pine shoot (needles+stems) (Nerg et al. 1994),
needle and wood concentrations (Manninen et al. 2002) and stump emissions (Kivimäenpää
et al. 2012) between the same provenances. Moreover, these studies showed a similar
increase in the proportion of α-pinene with latitude, and decreases in sabinene, terpinolene
and γ-terpinene with latitude, as reported here for shoot emission profile. Thus, terpene
profile is very similar for concentrations and volatile fraction of different plant parts.
Positive correlation between Δ-3-carene and terpinolene, as well as between limonene and
α-pinene and β-pinene emissions, observed in shoots of this study, are in line with results by
Bäck et al. (2012) of Scots pine shoots in a natural forest stand in southern Finland. Positive
correlation between 3-carene and terpinolene also in Scots pine oleoresin composition has
been reported (Baradat and Yazdani 1988). These observations might be related to the
differences in carbon sources in synthesis and emission of these “groups” of monoterpenes.
CO₂ labeling experiment by Lüpke et al. (2017) showed that α-pinene, β-pinene, limonene
and myrcene in Scots pine monoterpene emissions were rapidly labeled with \(^{13}\text{C}\) indicating
de novo synthesis while Δ-3-carene was almost non-labeled indicating carbon source from a
storage pool.

Forest floor emitted mainly monoterpenes, α-pinene, Δ-3-carene and camphene being
the main compounds, similarly as reported by Aaltonen et al. (2011) from Scots pine-
dominated forest in southern Finland. PLSR analysis showed that emission rates from forest
floor were largely explained by the amount of needle litter. Thus, needle litter likely
explained some of the differences in the emission profile of the forest floor between the
provenances. Highest proportion of Δ-3-carene from forest floor under the trees of the
southernmost provenance SAA is in accordance with the shoot emission profile and needle
concentrations (Manninen et al. 2002), but the similar latitudinal difference in forest floor
emission profile between the other provenances was not observed. One reason may be that
both Δ-3-carene and α-pinene dominate emissions from fungal species that decompose pine
litter (Isidorov et al. 2016), and potentially different amounts of fungal hyphae and activity
of these decomposers between the provenances may mask the emissions from decaying
litter. On the other hand, emissions of ectomycorrhiza species occurring in Scots pine forest
were dominated by linalool and limonene and those of endophyte species by sesquiterpenes
(Bäck et al. 2010). In a study by Ditengou et al. (2015) sesquiterpenes were the main
compounds emitted by ectomycorrhizal fungi species typical of Scots pine. Thus, the
influence of ectomycorrhiza on forest floor emissions and profiles may have been of minor
importance in this study. The difference in terpene profile between forest floor and shoot
emissions supports the role of litter as a major emission source of forest floor and that the
majority of the litter was decomposing, not fresh. Specifically, the higher proportion of
tricyclene, camphene and α-pinene but lower proportion of limonene in the forest floor
emission compared to the shoot emissions are consistent with results by Kainulainen and
Holopainen (2002) who followed monoterpane concentrations in decomposing Scots pine
needles for 19 months and compared the concentration to the freshly cut and the living
needles in Central Finland. Isidorov et al. (2010) reported similar terpene profile changes in
pine litter concentration and BVOC emissions in Poland, Central Europe. Kainulainen and
Holopainen (2002) also reported increase in concentrations of oxygenated monoterpenes,
such as verbenol and verbenone, in decomposing needle litter, but these compounds were
not observed in forest floor BVOC emissions in this study. The reason may be the lower
volatility of oxygenated monoterpenes and their hydrophilicity and their consequent
dissolution to moist forest floor. Litter from forest floor emits also other volatile compounds, such as C$_1$ – C$_2$ compounds methanol, acetone, and acetaldehyde (Greenberg et al. 2012) that could not be measured by the technique used in our study.

The emission rates of monoterpenes from forest floor were highest in the KOR provenance and lowest in the two northernmost provenances, SUO and MUO, and the differences were explained by the amount of needle litter. Lowest amount of litter leading to lowest terpenoid emission rates in the northern provenances is in accordance with previously reported shorter shoots with lower biomass in the northern than southern provenances (Manninen et al. 1998), as well as with the shortest needle lengths in some years in the northernmost MUO provenance, observed in this study. Moreover, at the age of seven years, KOR was the best growing provenance (Manninen et al. 2002). Terpene concentration of the needle litter hardly explains differences in the emission rates, because the needle terpene concentrations increased with latitude towards the North (Manninen et al. 1998). Scots pine roots are also a source of BVOC emissions (Lin et al. 2007), but their contribution to emissions could not be measured in this study. However, if the growth responses in the roots are the same as in the shoots (Manninen et al. 1998), smaller root volume and root BVOC emission could be expected from the northern provenances.

Our results about the needle litter as a major emission source from forest floor emissions supports the previous study conducted in pine-dominated forests (Mäki et al. 2017). Mäki et al. (2017) also showed that litterfall and the fraction of needles in the litter explained the autumnal peak monoterpane emissions from forest floor in Scots pine dominated forests in southern Finland. Autumnal litterfall did not take place before the BVOC sampling from the forest floor in Suonenjoki in the study year. The oldest needle generation (fourth in the study region) senesces, i.e., rapidly turns yellow, at the end of August – beginning of September, and drops later in Suonenjoki region (Kivimäänpää and
Sutinen 2007). However, some needles from the lower parts of the canopy can drop earlier during the growing season, which was observed in all provenances here. The BVOC composition of the forest floor supports the role of decomposing and not freshly fallen litter as an emission source (Kainulainen and Holopainen 2002), as discussed above. Volatile emissions from forest floor peaks also in spring or beginning of growing season, and are influenced e.g. by growth state of the vegetation and air temperature (Aaltonen et al. 2011).

Thus, emission rates of this study should be compared to the other measurements conducted in the middle or end of the growing season before litter fall. The average unstandardized emission rate of BVOCs, 50 µg m⁻² h⁻¹, consisting primarily of monoterpenes in our study, is similar to emission rate of total monoterpenes, 49 µg m⁻² h⁻¹, reported from the floor of a forest stand dominated by 55-year old Scots pines in southern Finland also at the end of the growing season (Mäki et al. 2017). Forest floor of mixed Scots pine and Norway spruce forest in the southern Sweden also emitted monoterpenes up to 50 µg C m⁻² h⁻¹ during the growing season (June-September) (Janson et al. 1999). Mäki et al. (2017) summarized the previous estimations of boreal forest floor emissions, which showed high variation, ranging from 0-373 µg m⁻² h⁻¹. Our study showed that tree provenance is an additional source of variation, as it caused 65 % differences to forest floor emissions rates.

Negative relationship between myrcene and bornyl acetate emissions with moss coverage in our study may be because mosses have acted as sinks of monoterpenes (Mäki et al. 2017). Adhesion of myrcene on mosses and decomposition by ozone may be another explanation to negative relationship between myrcene emission rates and moss coverage. Myrcene was shown to adhere on plant surfaces from a surrounding source and being a compound sensitive to oxidation by slightly elevated, on average 42 ppb, ozone concentrations (Mofikoya et al. 2017). In Kuopio, 40 km NE from the study area, monthly means for ozone concentration were 29 ppb in June, 30 ppb in July and 26 ppb in August.
(Kivimäenpää et al. 2017), and in Ähtäri EMEP station (62 °33’) 27, 31 and 24 ppb, respectively (Hjellbrekke et al. 2012) during the study year. Higher coverage of soil mosses in the two northernmost provenances is likely a consequence of lower amount of litter, which have allelopathic influence on understory vegetation growth (Reigosa and González 2006). For example, monoterpane-rich conifer needle litter may reduce N mineralization of forest soil (Paavolainen et al. 1998) and thus, may have reduced N availability of mosses for growth under trees of provenances KOR and SAA. Higher moss coverages in MUO and SUO may also have physically restricted potential BVOC emissions from roots and soil microbiota.

Scots pine is one of the species that will benefit from climate change in northern Europe (Reich and Oleksyn 2008). Shoot biomass of Scots pine will increase in a warmer climate (Rasheed et al. 2017), and thus the amount of litter and forest floor BVOC emissions will increase. Moreover, warming increases BVOC emissions from pine foliage (Kivimäenpää et al. 2016). Therefore, BVOC emission rates are expected to increase at the forest level. Plant VOCs have a cooling net effect on climate (Unger 2014), thus Scots pine and boreal forests can provide valuable ecosystem services against climate change. Warming affects also the BVOC composition. For example, Kivimäenpää et al. (2016) showed that 3-carene emissions from Scots pine shoots were not affected by long-term warming, while α-pinene emissions were increased by a factor of 1.5-2. Such changes, as well as Scots pine chemotypes, can affect oxidative properties of the atmosphere under climate change because α-pinene is more reactive. For example, lifetime of α-pinene with O₃ is only 4.6 h while that of Δ-3-carene is 11 h in similar atmospheric conditions (Atkinson and Arey 2003). Our sampling method may underestimate the emission rates of highly reactive sesquiterpenes (Atkinson and Arey 2003) and cause variation in BVOC profile because sesquiterpenes can adhere to enclosure surfaces particularly at low temperatures.
Global BVOC emissions are quantified using models such as MEGAN or ORCHIDEE, which take into account emission profiles from different plant functional types (Messina et al. 2016). The proportions of the two major monoterpenes $\alpha$-pinene and $\Delta$-3-carene in our study (28 and 26%, respectively) and in the ORCHIDEE model for the plant functional type ‘boreal needleleaf evergreen tree’ (35 and 18%, respectively) (Messina et al. 2016) agrees well with that Scots pine is the major evergreen tree species in the boreal region.

Estimations of the contribution of forest floor on forest stand emissions are variable. For example, Räisänen et al. (2009) calculated that one-quarter of emissions from the period June-September could originate from forest floor of mature Scots pine forest, whereas according to Janson et al. (1999) forest floor emissions were a few percents of emissions of mixed Norway spruce and Scots pine forest. This study suggests that the chemotype-related effects of Scots pine provenances on the atmosphere may differ over a 1000 km South-North transect in northern Europe. Emissions from forest floor will have an additive effect on forest scale BVOC profile. The influence of tree chemotypes and litter should be considered in modeling BVOC emissions and their impact on atmospheric quality and climate parameters.

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Figure captions

Fig. 1. a) Score and b) loading plots of Principal Component Analysis (PCA) on the proportions of shoot BVOCs from mature Scots pine trees of four provenances Saaremaa (SAA), Korpilahti (KOR), Suomussalmi (SUO) and Muonio (MUO). The variance explained by two first principal components (PC) are shown in parentheses. In a) average scores with SE of PC1 and PC2 of ten trees are shown. Different letters below the bars indicate statistical difference ($P < 0.05$, pairwise multiple comparison of Kruskal-Wallis test) in the average PC1 score between the provenances. In b) monoterpenoids are shown with normal font, sesquiterpenes in cursive and GLVs emboldened, st1 and st2 refer to unidentified sesquiterpenes.

Fig. 2. Average proportion (+ SE) of emissions $\alpha$-pinene and $\Delta$-3-carene from total BVOC emissions in shoots of Scots pine trees of four provenances Saaremaa (SAA), Korpilahti (KOR), Suomussalmi (SUO) and Muonio (MUO) and forest floor under the same trees, $n=10$ for shoots, $n=9$ for forest floor (expect $n=10$ for KOR). Different letters above the bars show significant differences between the provenances ($P < 0.05$ pairwise multiple comparisons from Kruskal-Wallis test for shoots, Tukey test from ANOVA for forest floor).

Fig. 3. Regression coefficients of partial least squares regression (PLSR) models for the covariance between coverage of vegetation groups, needle litter, bark and cones, air temperature, soil moisture and the emissions of $\alpha$-pinene (a), myrcene (b) and $\Delta$-3-carene (c). Positive regression coefficients indicate positive relationship and negative ones negative relationship. Error bars show confidence intervals of the regression coefficients. Significant factors (error bars not crossing zero) are shown in black.
Table 1. Average (SE) length (cm) of current (2010) and previous years (2009, 2008, 2007) needles of Scots pines from four provenances SAA=Saaremaa, KOR=Korpilahti, SUO=Suomussalmi, MUO=Muonio.

<table>
<thead>
<tr>
<th>Date</th>
<th>Needle generation</th>
<th>SAA 58°22´</th>
<th>KOR 62°0´</th>
<th>SUO 65°10´</th>
<th>MUO 67°56´</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>29 June 2010</td>
<td>1.4 (0.1) a</td>
<td>1.7 (0.1) ab</td>
<td>1.8 (0.1) b</td>
<td>1.6 (0.1) ab</td>
<td>0.022*</td>
<td></td>
</tr>
<tr>
<td>21 July 2010</td>
<td>2.2 (0.2)</td>
<td>2.2 (0.2)</td>
<td>2.4 (0.2)</td>
<td>2.1 (0.1)</td>
<td>0.747†</td>
<td></td>
</tr>
<tr>
<td>29 June 2009</td>
<td>2.5 (0.2)</td>
<td>2.2 (0.2)</td>
<td>2.3 (0.2)</td>
<td>2.3 (0.3)</td>
<td>0.649‡</td>
<td></td>
</tr>
<tr>
<td>29 June 2008</td>
<td>3.2 (0.2) a</td>
<td>3.1 (0.2)</td>
<td>3.2 (0.2)</td>
<td>2.6 (0.2)</td>
<td>0.173*</td>
<td></td>
</tr>
<tr>
<td>29 June 2007</td>
<td>3.4 (0.2) a</td>
<td>3.3 (0.2) a</td>
<td>3.3 (0.3) a</td>
<td>2.3 (0.2) b</td>
<td>0.011*</td>
<td></td>
</tr>
</tbody>
</table>

Note: Different letters between the provenances show statistical difference at $P < 0.05$ level, $n=10$.

*ANOVA
† Kruskal-Wallis test
‡ needles left in six of ten trees
Table 2. Average (SE) needle litter (g DW) and coverage (%) (min, max) of vegetation and bark and cones on VOC collection cylinders under Scots pines from four provenances SAA=Saaremaa, KOR=Korpilahti, SUO=Suomussalmi, MUO=Muonio.

<table>
<thead>
<tr>
<th></th>
<th>SAA 58°22'</th>
<th>KOR 62°0'</th>
<th>SUO 65°10'</th>
<th>MUO 67°56'</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Needle litter</td>
<td>4.7 (0.7)</td>
<td>6.6 (0.6)</td>
<td>3.9 (0.5)</td>
<td>2.7 (0.7)</td>
<td>0.001*</td>
</tr>
<tr>
<td>Mosses</td>
<td>0 (0, 5)</td>
<td>5 (0, 50)</td>
<td>30 (0, 100)</td>
<td>40 (0, 100)</td>
<td>0.001†</td>
</tr>
<tr>
<td>Lichens</td>
<td>0 (0, 5)</td>
<td>0 (0, &lt;5)</td>
<td>0 (0, &lt;5)</td>
<td>10 (0, 45)</td>
<td>0.520†</td>
</tr>
<tr>
<td>Graminoids</td>
<td>5 (0, 40)</td>
<td>0 (0, &lt;5)</td>
<td>0 (0, &lt;5)</td>
<td>0 (0, &lt;5)</td>
<td>0.506†</td>
</tr>
<tr>
<td>Bark and cones</td>
<td>0 (0, 0)</td>
<td>0 (0, &lt;5)</td>
<td>0 (0, &lt;5)</td>
<td>0 (0, &lt;5)</td>
<td>0.507†</td>
</tr>
</tbody>
</table>

Note: Different letters between the provenances show statistical difference at P < 0.05 level, n=10 for KOR, n=9 for SAA, SUO, MUO.

*ANOVA
†Kruskal-Wallis test
Table 3. Proportions (%) of key compounds found from both shoot and forest floor emissions as an average (SE) of all Scots pine provenances, $n=35$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Shoot</th>
<th>Forest floor</th>
<th>$P$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricyclene</td>
<td>&lt;0.1 (&lt;0.1)</td>
<td>0.6 (0.2)</td>
<td>0.011†</td>
</tr>
<tr>
<td>$\alpha$-Pinene</td>
<td>27.9 (2.7)</td>
<td>52.8 (2.0)</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Camphene</td>
<td>2.6 (0.5)</td>
<td>10.5 (1.3)</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>$\beta$-Pinene</td>
<td>5.0 (1.1)</td>
<td>3.7 (0.7)</td>
<td>0.276*</td>
</tr>
<tr>
<td>Myrcene</td>
<td>8.7 (1.5)</td>
<td>0.7 (0.2)</td>
<td>0.011†</td>
</tr>
<tr>
<td>$\Delta$-3-Carene</td>
<td>25.8 (4.3)</td>
<td>28.9 (1.2)</td>
<td>0.437*</td>
</tr>
<tr>
<td>p-Cymene</td>
<td>0.4 (0.1)</td>
<td>0.4 (0.1)</td>
<td>0.185†</td>
</tr>
<tr>
<td>Limonene</td>
<td>11.3 (2.5)</td>
<td>1.4 (0.4)</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Camphor</td>
<td>0.2 (0.1)</td>
<td>0.6 (0.2)</td>
<td>1.000†</td>
</tr>
</tbody>
</table>

**Note:** $P$-values show differences in proportions between shoots and forest floor.

*paired samples T-test
† Wilcoxon signed ranks test
Table 4. Emission rates (µg m⁻² h⁻¹) of individual compounds and total terpenoids from forest floor under trees from four different Scots pine provenances (KOR=Korpilahti, SAA=Saaremaa, SUO=Suomussalmi, MUO=Muonio) expressed as standardized to +20 °C, total C at +20 °C and total non-standardized emissions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SAA 58°22′</th>
<th>KOR 62°0′</th>
<th>SUO 65°10′</th>
<th>MUO 67°56′</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricyclene</td>
<td>0.6 (0.5)</td>
<td>1.2 (0.7)</td>
<td>0.4 (0.2)</td>
<td>0.3 (0.3)</td>
<td>0.704†</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>31.5 (9.5) ab</td>
<td>69.4 (16.8) a</td>
<td>31.4 (8.2) ab</td>
<td>25.5 (5.0) b</td>
<td>0.024*</td>
</tr>
<tr>
<td>Camphene</td>
<td>5.0 (1.8)</td>
<td>9.9 (2.4)</td>
<td>7.7 (3.1)</td>
<td>3.9 (2.1)</td>
<td>0.231†</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>2.1 (0.7)</td>
<td>3.6 (1.3)</td>
<td>2.8 (1.1)</td>
<td>1.0 (0.5)</td>
<td>0.474†</td>
</tr>
<tr>
<td>Myrcene</td>
<td>0.4 (0.3)</td>
<td>1.6 (0.7)</td>
<td>0.2 (0.2)</td>
<td>0.2 (0.2)</td>
<td>0.229†</td>
</tr>
<tr>
<td>Δ-3-Carene</td>
<td>18.8 (4.1) ab</td>
<td>31.4 (4.14) a</td>
<td>15.2 (4.3) b</td>
<td>12.1 (2.3) b</td>
<td>0.009*</td>
</tr>
<tr>
<td>p-Cymene</td>
<td>0 (0)</td>
<td>0.7 (0.3)</td>
<td>0.5 (0.3)</td>
<td>0.1 (0.1)</td>
<td>0.134†</td>
</tr>
<tr>
<td>Limonene</td>
<td>0.4 (0.4)</td>
<td>2.5 (0.8)</td>
<td>1.2 (0.6)</td>
<td>0.2 (0.2)</td>
<td>0.040†</td>
</tr>
<tr>
<td>β-Phellandrene</td>
<td>0.1 (0.1)</td>
<td>0.2 (0.2)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0.322†</td>
</tr>
<tr>
<td>(E)-β-Ocimene</td>
<td>0 (0)</td>
<td>0.3 (0.2)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0.136†</td>
</tr>
<tr>
<td>Camphor</td>
<td>0.2 (0.2)</td>
<td>1.2 (0.7)</td>
<td>0.2 (0.2)</td>
<td>0.2 (0.2)</td>
<td>0.567†</td>
</tr>
<tr>
<td>Bornyl acetate</td>
<td>0 (0) a</td>
<td>0.7 (0.3) b</td>
<td>0 (0) a</td>
<td>0 (0) a</td>
<td>0.008†</td>
</tr>
<tr>
<td>γ-Cadinene</td>
<td>0 (0)</td>
<td>1.1 (0.6)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0.036†</td>
</tr>
<tr>
<td>δ-Cadinene</td>
<td>0 (0)</td>
<td>0.1 (0.3)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0.136†</td>
</tr>
<tr>
<td>Total +20 °C</td>
<td>59.1 (13.6) b</td>
<td>124.3 (18.7) a</td>
<td>59.5 (15.3) b</td>
<td>43.5 (8.7) b</td>
<td>0.007*</td>
</tr>
<tr>
<td>Total C +20 °C</td>
<td>47.2 (11.6) ab</td>
<td>97.9 (14.9) a</td>
<td>51.2 (14.5) b</td>
<td>34.4 (7.0) b</td>
<td>0.007*</td>
</tr>
<tr>
<td>Total unstand.</td>
<td>40.5 (11.8) ab</td>
<td>81.5 (13.3) a</td>
<td>46.3 (14.5) ab</td>
<td>28.9 (5.9) b</td>
<td>0.011*</td>
</tr>
</tbody>
</table>

Note: Different letters between the provenances show statistical difference at p < 0.05 level. n=10 for KOR, n=9 for SAA, SUO and MUO.

*ANOVA
† Kruskal-Wallis test
Table S1. Temperature-standardized (20 °C) emissions rates of terpenes and actual emissions of green leaf volatiles (ng h⁻¹ cm⁻² shoot length) collected from branches of Scots pine trees of four provenances (SAA=Saaremaa, KOR=Korpilahti, SUO=Suomussalmi, MUO=Muonio). Values are averages (SE) of ten trees.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SAA 58°22’</th>
<th>KOR 62°0’</th>
<th>SUO 65°10’</th>
<th>MUO 67°56’</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
<td>28.2 (12.8)</td>
<td>24.8 (8.4)</td>
<td>99.2 (43.0)</td>
<td>191.6 (83.1)</td>
</tr>
<tr>
<td>Camphene</td>
<td>1.1 (0.2)</td>
<td>1.6 (0.4)</td>
<td>2.9 (0.8)</td>
<td>4.8 (1.2)</td>
</tr>
<tr>
<td>Sabinene</td>
<td>3.4 (1.7)</td>
<td>2.4 (1.2)</td>
<td>4.5 (2.7)</td>
<td>3.4 (1.3)</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>1.4 (0.6)</td>
<td>19.3 (14.1)</td>
<td>9.8 (3.8)</td>
<td>24.8 (17.0)</td>
</tr>
<tr>
<td>Myrcene</td>
<td>21.7 (18.3)</td>
<td>12.9 (7.2)</td>
<td>27.2 (9.6)</td>
<td>137.4 (70.4)</td>
</tr>
<tr>
<td>α-Phellandrene</td>
<td>0.7 (0.4)</td>
<td>0.4 (0.2)</td>
<td>0.9 (0.5)</td>
<td>1.0 (0.4)</td>
</tr>
<tr>
<td>3-Carene</td>
<td>104.3 (54.8)</td>
<td>62.6 (35.7)</td>
<td>125.0 (77.1)</td>
<td>64.9 (41.2)</td>
</tr>
<tr>
<td>p-Cymene</td>
<td>0.8 (0.4)</td>
<td>0.6 (0.2)</td>
<td>0.9 (0.3)</td>
<td>1.1 (0.3)</td>
</tr>
<tr>
<td>Limonene</td>
<td>3.0 (1.6)</td>
<td>14.3 (11.6)</td>
<td>30.4 (17.2)</td>
<td>198.9 (85.7)</td>
</tr>
<tr>
<td>β-Phellandrene</td>
<td>1.4 (0.6)</td>
<td>7.5 (4.3)</td>
<td>10.0 (5.9)</td>
<td>36.9 (16.6)</td>
</tr>
<tr>
<td>1,8-Cineole</td>
<td>1.0 (0.2)</td>
<td>2.5 (1.9)</td>
<td>0.8 (0.3)</td>
<td>2.5 (0.6)</td>
</tr>
<tr>
<td>(E)-β-Ocimene</td>
<td>11.8 (11.4)</td>
<td>0.3 (0.1)</td>
<td>0.5 (0.2)</td>
<td>9.0 (6.2)</td>
</tr>
<tr>
<td>γ-Terpine</td>
<td>0.9 (0.6)</td>
<td>0.5 (0.3)</td>
<td>0.8 (0.4)</td>
<td>0.8 (0.3)</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>7.8 (5.2)</td>
<td>4.1 (2.4)</td>
<td>6.6 (3.4)</td>
<td>6.1 (3.4)</td>
</tr>
<tr>
<td>Camphor</td>
<td>0.1 (&lt;0.05)</td>
<td>0.1 (0.1)</td>
<td>0.1 (&lt;0.05)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>Bornyl acetate</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.3 (0.1)</td>
<td>0.3 (0.1)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>α-Terpinene</td>
<td>0.7 (0.5)</td>
<td>0.4 (0.2)</td>
<td>0.7 (0.3)</td>
<td>0.9 (0.3)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>188.9 (105.0)</strong></td>
<td><strong>155.3 (61.1)</strong></td>
<td><strong>320.5 (118.2)</strong></td>
<td><strong>685.7 (222.8)</strong></td>
</tr>
<tr>
<td>Monoterpenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Longipene</td>
<td>0 (0)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.1 (0.1)</td>
<td>&lt;0.05 (&lt;0.05)</td>
</tr>
<tr>
<td>α-Copaene</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0 (0)</td>
<td>0.1 (&lt;0.05)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>β-Bourbonene</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.1)</td>
<td>0.2 (0.1)</td>
<td>0.5 (0.2)</td>
</tr>
<tr>
<td>Longifolene</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>1.2 (1.0)</td>
<td>0.6 (0.2)</td>
<td>0.7 (0.2)</td>
</tr>
<tr>
<td>β-Caryophyllene</td>
<td>0.1 (0.1)</td>
<td>0.2 (0.1)</td>
<td>0.3 (0.2)</td>
<td>0.6 (0.3)</td>
</tr>
<tr>
<td>(E)-β-Farnesene</td>
<td>0.4 (0.2)</td>
<td>0.4 (0.1)</td>
<td>0.4 (0.2)</td>
<td>3.0 (1.2)</td>
</tr>
<tr>
<td>α-Humulene</td>
<td>0.1 (0.1)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>Unknown st c</td>
<td>0.1 (&lt;0.05)</td>
<td>0.1 (&lt;0.05)</td>
<td>0.1 (0.1)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>(E, E)-α-β-Farnesene</td>
<td>0.1 (&lt;0.05)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.2 (0.2)</td>
<td>0.1 (0.1)</td>
</tr>
<tr>
<td>Sesquiterpenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Selinene c</td>
<td>0.2 (0.1)</td>
<td>0.1 (0.1)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.5 (0.2)</td>
</tr>
<tr>
<td>α-Murolene c</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.1 (&lt;0.05)</td>
<td>0.1 (0.1)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>α-Selinene c</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.1)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>γ-Cadinene c</td>
<td>0.1 (&lt;0.05)</td>
<td>0.2 (0.1)</td>
<td>0.1 (&lt;0.05)</td>
<td>0.3 (0.1)</td>
</tr>
<tr>
<td>δ-Cadinene</td>
<td>0.1 (&lt;0.05)</td>
<td>0.3 (0.1)</td>
<td>0.1 (0.1)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>Cis-α-bisabolene c</td>
<td>0.1 (&lt;0.05)</td>
<td>&lt;0.05 (&lt;0.05)</td>
<td>0.0 (0.0)</td>
<td>0.3 (0.1)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>5.3 (4.7)</strong></td>
<td><strong>29.7 (11.8)</strong></td>
<td><strong>12.1 (5.2)</strong></td>
<td><strong>42.7 (22.5)</strong></td>
</tr>
</tbody>
</table>

**Total GLVs**

<table>
<thead>
<tr>
<th>GLVs</th>
<th>0.2 (0.1)</th>
<th>0.2 (0.2)</th>
<th>0.2 (0.1)</th>
<th>1.2 (0.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total VOCs</strong></td>
<td>190.5 (105.3)</td>
<td>158.5 (61.4)</td>
<td>323.0 (119.1)</td>
<td>694.5 (223.9)</td>
</tr>
</tbody>
</table>

Emission rates calculated using α-Pinene, 1,8-Cineole or Longifole as a reference.

Emissions rates of monoterpenes tricyclene (max. 1.2), linalool (2.7), borneol (0.4), terpinen-4-ol (<0.05), allo-ocimene (0.3), pinocarvone (0.3), verbene (0.3), eucarvone (0.6), ocimene (0.1), piperitone (0.7), sesquiterpenes α-cubebene (0.1), longicyclene (0.4), sativene (0.3), aromadendrene (0.2) emitted by 1-3 tree individuals are not shown.

GLVs consisted mainly of (Z)-3-hexenyl acetat (max. 6.9) and (Z)-3-hexen-1-ol (0.5) and methyl salicylate (0.7).
Fig. S1. Regression coefficients of partial least squares regression (PLSR) models for the covariance between coverage of vegetation groups, needle litter, bark and cones, air temperature, soil moisture and the emissions of tricyclene (a), p-cymene (b), camphor (c) and bornyl acetate (d). Positive regression coefficient indicate a positive relationship and negative ones negative relationship. Error bars show confidence intervals of the regression coefficients. Significant factors (error bars not crossing zero) are shown in black.