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Emissions of biogenic volatile organic compounds from the boreal forest floor and understory: a study by solid-phase microextraction and portable gas chromatography-mass spectrometry

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Vegetation introduces to the atmosphere a diversity of biogenic volatile organic compounds (BVOCs) which affect atmospheric chemistry, air quality and climate. Understory emissions might contribute significantly to the total BVOCs budget. In this work, either dynamic or static solid-phase microextraction (SPME) combined with portable gas chromatography-mass spectrometry were optimised and used for the *in-situ* measurement of the most abundant BVOCs at understory level. The study was performed in summer 2015 at the SMEAR II station in Hyytiälä, Finland. The most abundant BVOCs measured in soil chambers and ambient air were α-pinene and Δ^3-carene, and their relative concentrations were similar in every chamber. These species constituted 80%–90% of the measured monoterpenes. Aliphatic aldehydes were also measured, and their amounts were lower in soil chambers than in ambient air. Air BVOC concentrations were markedly higher when the wind direction was from SE, which was associated with transportation from nearby sawmills.

Introduction

Biogenic volatile organic compounds (BVOCs) are produced in different plant tissues and physiological processes (Peñuelas and Llusià 2003). Some BVOCs are largely lipophilic, and their high vapour pressures enable them to be released into the atmosphere in significant amounts (Loreto and Schnitzler 2010). These compounds are vital for a large number of organisms, since they participate in biological processes such as plant–plant communication, protection against

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pathogens and herbivores, and wound sealing after damage (Peñuelas and Llusià 2003, Tumlinson 2014). Production of BVOCs in plant tissues has been linked with climate, as they could protect plants against high temperatures (Peñuelas and Llusià 2003). Kulmala *et al*. (2004) proposed a feedback mechanism linking forests, aerosols and climate. Accordingly, increased CO_2 concentrations increase the terrestrial temperature and vegetation productivity, which enhance emissions of a variety of BVOCs that contribute to aerosol particle formation and growth. Aerosols will then decrease temperature because of increased reflection of sunlight from low clouds back to space.

The boreal forest is a significant source of reactive organic trace gases (Rinne *et al*. 2009, Yassaa *et al*. 2012). A substantial gas-to-particle conversion of BVOCs to secondary organic aerosol (SOA) has been found over the boreal forest in northern Europe (e.g. Tunved *et al*. 2006). In the northern hemisphere, forests mainly consist of coniferous trees, and Scots pine (*Pinus sylvestris*) is the most abundant conifer in Finland (FAO 2015). Many BVOC measurements have been performed in the coniferous forest, particularly at the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II station) located in Hyytiälä, Finland. BVOC fluxes from the boreal forest canopies have been the most intensively studied quantities. However, fluxes from the forest floor and understory can also markedly contribute to the total BVOC budget (e.g. Hellén *et al*. 2006, Aaltonen *et al*. 2013, Mäki *et al*. 2017). Forest floor fluxes consist of emissions from both vegetation and soil, and are dependent on several biological processes and physical environmental factors (Aaltonen *et al*. 2013). Sampling and measurement of BVOCs from soil is challenging due to the occurrence of moist surfaces inside soil chambers and at the surface of vegetation, inherent complexity of BVOC production in the soil/understory, and considerable spatial variation of BVOC fluxes (e.g. Kolari *et al*. 2012, Aaltonen *et al*. 2013).

Scots pines have been reported to emit significant amounts of monoterpenes, of which α-pinene and Δ^3-carene are the most dominant species (e.g. Rinne *et al*. 2000). Monoterpenes are involved in plant defense, e.g. against herbivores and pathogen attack (Kesselmeier and Staudt 1999). This class of compounds is highly reactive in the atmosphere, with lifetimes on the scale of minutes to hours when reacting with hydroxyl and nitrate radicals (NO_3) and of minutes to days with respect to ozone (O_3) (Atkinson and Arey 2003). The resulting monoterpene oxidation products have a major influence on the global SOA burden (e.g. Jokinen *et al*. 2015). Monoterpene emissions are mainly dependent on temperature, but solar radiation and reaction to stress (e.g. physical damage, herbivore attack, drought and heat) can also contribute to the emissions (Nölscher *et al*. 2012). In many studies, the monoterpene fluxes are measured on-line using a proton transfer reaction quadrupole mass spectrometer (PTR-QMS), which provides the possibility for long term *in-situ* measurements with excellent time resolution (e.g. Ruuskanen *et al*. 2005, Aalto *et al*. 2014, Rantala *et al*. 2015). However, this technique cannot separate compounds with the same molecular mass, such as monoterpenes. To overcome this limitation, monoterpenes are usually sampled on cartridges filled with an adsorbent material (such as Tenax TA/Carbopack-B), and then subsequently thermally desorbed into a gas chromatograph-mass spectrometer for off-line analysis (e.g. Haapanala *et al*. 2012, Kajos *et al*. 2013).

Carbonyl compounds, such as aldehydes, are also important to atmospheric chemistry due to their participation in photochemical reactions and contribution to aerosol particle formation and growth (e.g. Kesselmeier and Staudt 1999, Han *et al*. 2016). Aldehydes can be directly emitted to the atmosphere by vegetation when exposed to stress conditions, such as ozone exposure or insect and pathogen attacks, or formed as a result of secondary reactions of biogenic hydrocarbons with radicals in the atmosphere (Kesselmeier and Staudt 1999, Wildt *et al*. 2003). Atmospheric concentrations of several different C_1–C_{12} carbonyl compounds, including aldehydes, have been reported by Hellén *et al*. (2004). These compounds were measured using 2,4-dinitrophenyl hydrazine (DNPH) coated octadecylsilica (C18)-cartridges and analysed by liquid chromatography-mass spectrometry (LC-MS).

The most common methods for sampling and analysis of BVOCs usually require long

sampling and analysis times, the need for sample preparation and storage, and infrastructure that are usually difficult to organize at the remote forest sites. To avoid some of the above mentioned limitations, solid-phase microextraction (SPME) and needle trap microextraction (NTME) based methods, combined with portable gas chromatography-mass spectrometry, can be utilized (Barreira *et al*. 2015, 2016). In this study, measurement of BVOCs from soil chambers was performed by SPME sampling and portable gas chromatography-mass spectrometry (GC-MS). Air samples were collected simultaneously by dynamic SPME to compare the type and relative amounts of BVOCs found in soil chamber samples with those measured in ambient air, and assess the influence of external sources on the performed measurements. The results obtained from the soil chambers were compared with BVOC fluxes measured by PTR-QMS and with meteorological parameters of the chambers.

Material and methods

Chemicals and materials

CALION™ PV Mix standard, containing 13 compounds adsorbed into a granular solid matrix, were used for tuning of portable GC-MS. The identification and confirmation of studied compounds with authentic standards wasn performed in our previous studies (Barreira *et al*. 2015, 2016), and obtained retention times and mass spectra were used for the same purposes in this study. For standards preparation, α-pinene (98%), (–)-β-pinene (≥ 99%), (+)-camphene (≥ 90%), (R)-(+)-limonene (≥ 99%), Δ^3-carene (≥ 98.5%), octanal (99%), nonanal (≥ 95%) and decanal (≥ 98%) from Sigma-Aldrich (St. Louis, USA) were used. Standards were prepared by evaporation of 1 μl (10 mg for camphene) of each compound in a 20-ml headspace vial, and successive transfer by gas-tight syringe to another headspace vials of same volume for dilution. CUSTODION® solid phase microextraction syringes (PDMS/DVB, 65 μm, Torion Technologies Inc., Utah, USA) were used for sampling of BVOCs at SMEAR II station, while Polyacrylate (85 μm), carboxen/polydimethylsiloxane (CAR/PDMS, 85 μm) and DVB/CAR/PDMS (50/30 μg) were also used for preliminary comparison studies. Fibres were pre-conditioned according to the manufacturer's instructions. For evaluation of fibres' extraction efficiency, standard solutions (500 μg ml^{-1}) of α-pinene and Δ^3-carene in isopropanol (99.96%, Fisher Scientific) and water were used. All headspace vials were equilibrated for 30 minutes and vigorous agitation was applied. A monotherm heatable magnetic stirrer (Variomag Electronicrührer, Labortechnik, Munich, Germany) was used for the heating and stirring of the liquid standards.

Measurement site

BVOC sampling was performed at the SMEAR II station (Station For Measuring Ecosystem–Atmosphere Relations, 61°50.845´N, 24°17.686´E, 179 m a.s.l.) at Hyytiälä, in southern Finland (Hari and Kulmala 2005). The station is situated in an approximately 55-year-old Scots pine stand, of about 21-m canopy height and 1170 ha^{-1} average tree density (Ilvesniemi *et al*. 2009). Tampere, a city with around half a million inhabitants, is located 60 km southwest from the SMEAR II station. Samples were collected from three different soil chambers (Fig. A1_1), each of 80 cm × 40 cm × 25 cm and made of an aluminium frame with a transparent fluorinated ethylene-propylene (FEP) film (0.05 mm) covering the top and sides of the chamber (Kolari *et al*. 2012, Aaltonen *et al*. 2013). Air inside the chambers was continuously mixed using small fans. The soil chambers were installed atop of collars located at the forest floor, and placed 10 to 30 m apart from each other. The soil is Haplic podzol, formed in a glacial till, with an average depth of 0.5–0.7 m above the bedrock (Aaltonen *et al*. 2013). The forest floor flora inside the soil chambers is a mixture of herbaceous species, mostly small-sized grasses, and dwarf shrubs such as lingonberry (*Vaccinium vitis-idaea*) and bilberry (*Vaccinium myrtillus*); the soil is also fully covered by a mixture of moss species. The dominant forest floor vascular plant species in chambers 13 and 15 are lingonberry and bilberry, whereas in chamber 10 the dominant vascular plant is twinflower (*Linnaea borealis*) and the

vascular plant coverage was clearly lower than with the other two (Aaltonen *et al*. 2013). The forest cover over the chambers is rather homogeneous with almost closed canopy layer. A dynamic SPME sampling system for collection of ambient air samples, developed in a previous study (Barreira *et al*. 2015), was installed approximately 5 metres away from chamber 10 at 30 cm height above the ground vegetation.

Sampling and analysis

Gas chromatography-mass spectrometry measurements

Samples were collected and analysed in summer 2015. The first part of the campaign was between 23 and 28 June for testing and optimization of the method, including the sampling time inside the chambers, ambient air sampling time, and comparison of the method with conventional GC-MS. During the second part of the campaign, between 5 and 27 August, natural samples were analysed by the developed methods. Sampling was performed with CUSTODION® solid phase microextraction syringes (DVB/PDMS, film thickness 65 μm). These syringes contain a push-button trigger mechanism and a screw on/off cap, which enable the protection of the SPME fibre between sampling and analysis. For the sampling, chambers were closed for 5 minutes, then the SPME fibres were inserted in the soil chambers, and samples were collected for 40 minutes. During the closure, air flow through the chambers was stopped in order to allow semi-quantitative evaluation of how gas fluxes from soil and forest floor vegetation are affecting the gas concentrations inside the chambers. Gas concentrations are then increasing throughout the sampling period, assuming that emissions are higher than sinks. Thus, they differed already to a great extent from the ambient concentrations after the referred 5 minutes of closure. For evaluation of the reproducibility, three different SPME fibres were exposed simultaneously to the ambient air for 60 minutes and amounts of BVOCs were compared. Ambient samples were collected during 60 minutes, by two homemade SPME dynamic sampling systems with flow rates of 11 l min^{-1} (Barreira *et al*. 2015). Dynamic collection was preferred for ambient sampling, since VOC mass loading on the fibre increases with an increase in wind velocity from 0 to 5 cm s^{-1} (Pawliszyn 2009). A comparison between portable and conventional GC-MS analysis was performed with two syringes by sampling passively from the same chamber and analysis with both techniques.

BVOCs were measured by a portable GC-MS (TRIDION™ -9 Torion Technologies Inc., Utah, USA), which consist of a low thermal mass injector, a low thermal mass capillary gas chromatograph (MXT-5 column, 5 m × 0.1 mm, film thickness 0.4 μm) and a miniature toroidal ion trap mass analyser. Air samples were analysed by our previously developed method (Barreira *et al*. 2015). Briefly, the SPME syringe was placed into the injection port of the portable GC-MS and exposed during 10 seconds for thermal desorption. Injector and transfer line temperatures were set to 270 °C and ion trap temperature to 150 °C. A 10:1 split ratio was applied 5 seconds after injection, and then was increased to 50:1 from 10 to 30 seconds. The temperature program started from an initial temperature of 50 °C (10 seconds), which was increased to 270 °C at 2 °C s^{-1}, and maintained at that temperature until the end of the run. Analytes were ionized by electron ionization (70 eV) and the scan range was from 43 to 500 amu (atomic mass units) The total run time was 180 seconds. The carrier gas was helium of 99.996% purity (AGA, Espoo, Finland). For semi-quantitation, total ion chromatograms (TIC) were used.

An Agilent 6890 N gas chromatograph equipped with an Agilent 5973 mass selective detector (Agilent Technologies, Palo Alto, USA) was used for comparison with the portable GC-MS. The analytical column was an Inert-Cap for Amines (30 m × 0.25 mm inner diameter., GL Sciences, Tokyo, Japan), which was connected to a deactivated fused silica retention gap (1.5 m × 0.53 mm (inner diameter), Agilent Technologies, Palo Alto, USA) with a press-fit connector (BGB Analytik, Böckten, Switzerland). The initial oven temperature was 50 °C (held for 2 min), then raised to 250 °C at 20 °C min^{-1} and held for 4 min. The total run time was 16 min. Helium (99.996%, AGA, Espoo, Finland) was

used as carrier gas in a constant pressure mode (90 kPa). Analites collected on the SPME fibres were desorbed in a splitless mode (2 min) by using a 0.75-mm (inner diameter) splitless inlet liner. The injector temperature was 250 °C. A 23-gauge Merlin Microseal septum and a Merlin nut (Merlin Instrument Company, Half Moon Bay, USA) were used in the injection port. The temperature of GC-MS transfer line was 250 °C, while the ion source and quadrupole temperatures were kept at 230 °C and 150 °C, respectively. Electron ionization (70 eV) was used and the scan range was 40–300 amu. For semi-quantitation, total ion chromatograms (TIC) were used. The same method was employed for laboratory tests, although the analytical column used was a ZB-5MS (30 m × 0.25 mm × 0.25 m, Phenomenex, Torrance, USA) with a 5% diphenyl, 95% dimethylpolysiloxane stationary phase, and the scan range was 27–100 amu. For semi-quantitation, extracted ion chromatograms with base ions were used (*m*/*z* 93 for Δ^3-carene and α-pinene). Wind speed and wind direction (33.6-m height) (available at http://avaa.tdata.fi/web/smart and provided by Junninen *et al*. 2009) were compared with ambient air results, and averaged for the period of sampling.

Proton transfer reaction-quadrupole mass spectrometery measurements

Results were compared with data from continuous PTR-QMS (proton transfer reaction – quadrupole mass spectrometer, Ionicon Analytik, Innsbruck, Austria) measurements. The on-line VOC flux measurements were conducted following the scheme explained by Aaltonen *et al*. (2013). The automatic, dynamic gas-exchange measurement system consisted of sampling tubing, analysers and different types of enclosures, including the three box-type soil chambers (volume 80 l dm^3) used in this study. The enclosure remained mostly open and only closed intermittently for 450 seconds every third hour. When the enclosures were open, the interior of the enclosures was in contact with ambient unfiltered air. During closure episodes, sample air was drawn from the enclosure into the gas analysers along the sample tubes. To avoid a vacuum from being created inside the chamber, the sample flow taken from the soil sampling chambers was compensated for by pumping ambient air into the chamber at a flow rate that was slightly higher than the sample flow rate. The air temperature inside the enclosure was measured before and during the closure and the values recorded at 5-s intervals. The VOC sub-sample (0.1 l min^{-1}) for PTR-QMS was taken from a sample tube that used flow rate 1.1 l min^{-1}. A heated FEP-tubing of 64 m length (inner diameter of 4 mm) was used as a high flow sample tube. The sub-sample for a high sensitivity PTR-QMS was drawn from the high flow sample tube through a polytetrafluoroethylene (PTFE) tube (inner diameter of 1.57 mm and length of about 5 m). Briefly, PTR-QMS measures the total concentration of all compounds that have equal atomic mass with a resolution of 1 amu and adequate proton affinity. The ionization protonates the target compound to allow mass spectrometric selection and counting. Background signals were corrected by subtracting the measured instrumental background (air purified using a Parker ChromGas Zero Air Generator, model 3501, Parker Hannifin, Ohio, Cleveland, USA) from the measured volume mixing ratios. In order to correct the changes in the sensitivity over the mass range, calibration of the PTR-QMS was conducted two to three times per month. The standard gases contained ca. 1 ppmv of methanol, acetaldehyde, acetone, isoprene, α-pinene and several other compounds (Apel-Riemer Environmental Inc., USA). The zero air generator was used for diluting the standard gas close to the atmospheric concentrations, about 5 ppbv. Volume mixing calculation method and the basis for calibration were according to Taipale *et al*. (2008). Flux rate calculation method and evaluation of chamber method for VOC measurements are described in Kolari *et al*. (2012), while soil chamber measurement method in Aaltonen *et al*. (2013). Description of the current practical operation of the measurement system is given elsewhere (Aalto *et al*. 2014).

Results and discussion

In this study, static and dynamic SPME sampling and portable GC-MS were employed for

the characterization of BVOCs emitted from soil chambers and ambient air at understory level. Static SPME was used to collect air samples from soil chambers. The relative abundance of measured BVOCs was then compared with understory ambient air measurements performed with dynamic SPME sampling. Total monoterpene fluxes measured from the same soil chambers by PTR-MS were also used for comparison with obtained results. The influence of meteorological parameters on the measured BVOC amounts was evaluated. The results reported hereby include the method optimization and main findings obtained during whole campaign period. Our discussions will focus predominantly on monoterpenes, due to their high abundance and recognized importance to atmospheric chemistry.

Method optimization

Extraction efficiency of different SPME fibre materials

The extraction efficiency of different SPME fibre materials was studied in order to choose the most suitable one for the collection of target compounds. Two replicates were performed for each type of SPME fibre used. A particular emphasis was given to monoterpenes, due to their high contribution to atmospheric composition and their relevance to atmospheric physics and chemistry. PDMS/DVB/CAR gave the highest extraction efficiencies, followed by PDMS/DVB, PDMS/CAR and PA (Fig. A1_2). This is in agreement with the study of Yassaa *et al*. (2010), where quantitative and enantioselective analysis of monoterpenes from plant chambers and ambient air was performed. However, in the referred study, PDMS/DVB was chosen for the extraction of isoprenoids, due to a reduced effect of competitive adsorption. DVB phase is mainly mesoporous, and more suitable for trapping C_6–C_{15} analytes, while the microporous nature of CAR favours the efficient trapping of C_2–C_6 analytes (Pawliszyn and Mani 1999, Yassaa *et al*. 2010). Thus, PDMS/DVB was selected as the extraction material also for our study.

Evaluation of the reproducibility of SPME fibres

The reproducibility of commercial SPME fibres was evaluated for α-pinene and Δ^3-carene. Three PDMS/DVB coated fibres were exposed simultaneously to the ambient air for 60 minutes. The experiment was repeated two times. The coefficients of variations of 9% and 12% for α-pinene, and of 26% and 15% for Δ^3-carene were found to be reasonable. The reproducibility of different fibres was considered satisfactory for the semi quantitative analysis, allowing the comparison between chambers even when different fibres were used. By collecting two SPME samples simultaneously, a satisfactory reproducibility was obtained during the whole sampling period for both soil chambers (Fig. A1_3) and ambient air samples (Figs. A1_4 and A1_5), demonstrating the successful applicability of the method for the field studies. However, occasionally, the reproducibility was higher than the values determined in the previous experiment. A possible reason for these deviations is the fact that sampling and analysis was performed manually. Even though the obtained reproducibility was considered acceptable for semi-quantitative purposes, improvements are still required for quantitative analysis.

Optimization of the extraction time

The extraction time was optimied to improve pre-concentration of the studied compounds during the sampling. The extraction times were 30 and 45 minutes and the experiment was performed two times. The peak areas obtained for monoterpenes increased with the increasing sampling time (Fig. A1_6). Due to practical reasons, related with the availability of the soil chambers and the schedule of the campaign, a collection time of 40 minutes was chosen.

The sampling time of the dynamic SPME was also optimised. Three different fibres were inserted simultaneously in previously developed dynamic sampling systems (Barreira *et al*. 2015), the flow rates of the different systems were measured, and ambient samples were simultaneously collected for 20, 40 and 60 minutes. The

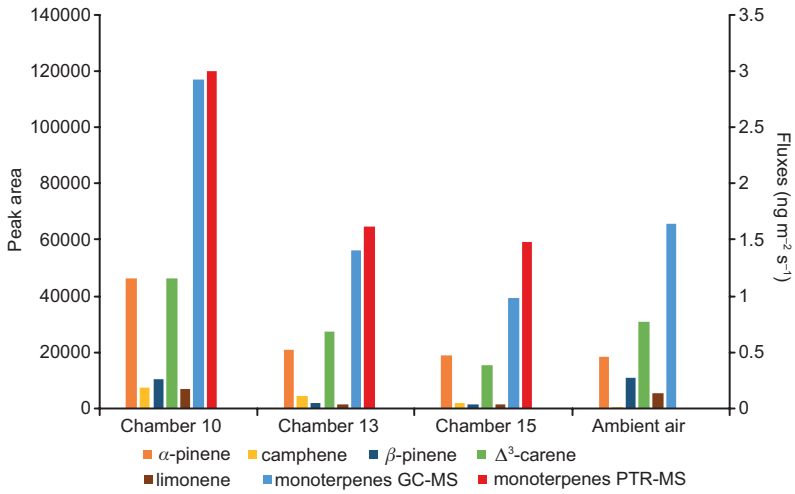

Fig. 1. Average amounts (peak area, primary axis) of monoterpenes measured during the sampling campaign by portable GC-MS. Samples were collected by static SPME from soil chambers and by dynamic SPME from ambient air. Monoterpene fluxes measured in the soil chambers by PTR-QMS are shown for comparison.

experiment was also done two times. The effect of the flow rate was neglected, since the deviation between different sampling systems was less than 5% (11.1, 10.6 and 10.4 l min^{-1}). A longer sampling time resulted in higher amounts of α-pinene and Δ^3-carene (Fig. A1_7). Thus, 60 minutes was chosen to ensure the sampling of sufficient amount of target compounds. However, in Experiment B, the Δ^3-carene signal decreases when going from 20 to 40 min. Most likely, the reason might be associated to some error during the sampling/measurement that was not noticed (for example, some change in the speed of dynamic sampling fan due to lowered charge state of the battery compared to other two similar sampling units), since the decrease in signal did not happen in the Experiment A.

Comparison of the method with the conventional GC-MS

The method was validated by simultaneous analysis of chamber samples with two instruments, conventional and portable GC-MS. Two SPME fibres were inserted simultaneously in the soil chamber and analysed by the two GC-MS systems. All three chambers were tested sequentially. The results were in good agreement (Fig. A1_8) and higher BVOCs concentrations in the chamber 10 were verified by both instruments, while lower concentrations were seen in the chambers 13 and 15. The results demonstrate the reliability of the portable GC-MS for the analysis of BVOCs.

Characterization of understory and ambient air emissions

BVOC emissions from understory vegetation play a significant role in the total ecosystem BVOC fluxes (Aaltonen *et al*. 2013) and can be influenced by the abiotic processes and biotic interactions (Peñuelas *et al*. 2014). The synthesis pathways of main BVOCs in plants are well known, but emission sources and purpose of these compounds for plants have remained somewhat uncertain (Aaltonen *et al*. 2011). In this study, a characterization of the most abundant BVOCs emitted in soil chambers was performed. α-Pinene and Δ^3-carene were the dominant species emitted at the understory level (Fig. 1). Similar results were observed in other studies performed at the same site by using different chambers, Tenax-Carbopack-B adsorbent tubes and TD-GC-MS (Aaltonen *et al*. 2011, Mäki *et al*. 2017). Soil emissions of camphene, β-pinene and limonene were also observed, but their contributions to the total VOCs were much smaller.

The amounts of monoterpenes, expressed as peak areas, were summed for comparison with total monoterpene emissions measured by PTR-QMS (Fig. 1 and Tables A2_1). The results are clearly similar, which shows the good per-

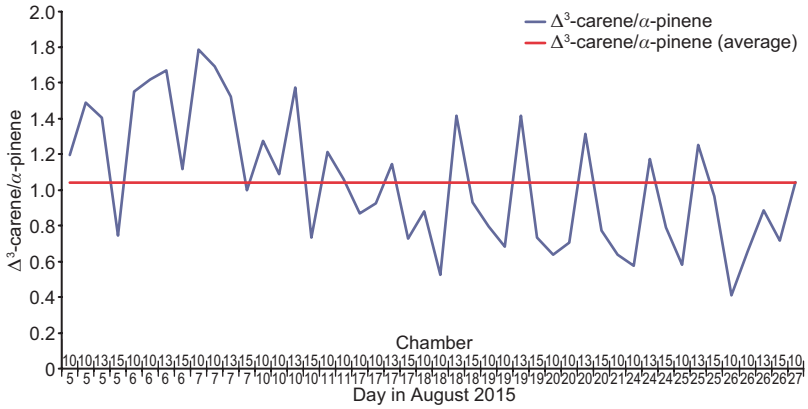

Fig. 2. Ratios between Δ^3-carene and α-pinene amounts measured during the sampling campaign by portable GC-MS (chamber numbers were included in the *x*-axis) after collection by SPME.

formance of our method for semi-quantitative measurement of monoterpenes from soil chambers. Emissions were higher in chamber number 10 with the lowest vegetation coverage, while low emissions were recorded for chambers 13 and 15. The results are also in agreement with another study performed at the same location with PTR-QMS (Aaltonen *et al*. 2013) (note that chambers 1, 2, and 3 correspond to chambers 10, 13 and 15, respectively in the referred study). This finding can be explained by the heterogeneity of the understory in the chambers. Chamber 10, characterized under drier conditions, led to less evapotranspiration, which is partially explained by the differences in vegetation type and cover, soil properties and micrometeorological conditions. This chamber has also higher photosynthetically active radiation (PAR) when compared to the other chambers, and a more pronounced variation in soil water content that is particularly prominent during rainless periods. The higher humidities of chambers 13 and 15 might also increase the surface losses of terpenes as has been described elsewhere (Kolari *et al*. 2012, Aaltonen *et al*. 2013). Differences in the humidity can result in different adsorption efficiencies of the SPME fibres (e.g. Grote and Pawliszyn 1997, Namieśnik *et al*. 2003), though the contribution of this factor is expected to be relatively small due to the hydrophobic character of the fibres used. Similar trends were observed when the amounts of monoterpenes determined by SPME-GC-MS were compared with the fluxes measured by PTR-QMS during the whole campaign period (Fig. A1_9). However, an exception was observed in the last two days of sampling (26 and 27 August) for chambers 10 and 15, which was probably caused by the high humidity during these days (Fig. A1_10). Because of the high humidity levels on these days, surface losses of terpenes may increase in the sampling tubes, which will affect the PTR-QMS measurements but not the SPME sampling.

The relative abundance of individual monoterpenes was also studied, since it has been hypothesized that induced monoterpene production could result in different monoterpene composition (Thoss and Byers 2006). Interestingly the monoterpenes distribution in any chamber did not change markedly, although chambers were located 10 to 30 meters away from each other and the plant coverage was different (Table A2_2). Similar diurnal variations and responses to environmental factors have been described previously using the same soil chambers as in our study (Aaltonen *et al*. 2013). In addition, emission patterns of terpenoid fluxes have remained unchanged in that study performed between April and November, suggesting that the main process behind BVOC emissions remain relatively the same (Aaltonen *et al*. 2011). The relative abundance of monoterpenes in chamber 10 did not change markedly during the day. The average abundance of Δ^3-carene and α-pinene was also similar, with an Δ^3-carene/α-pinene ratio of 1.04, even though their relative amounts alternated during the sampling period (Fig. 2).

Among aldehydes, octanal, nonanal and decanal were found in chambers in relatively low

amounts (Fig. 3). These carbonyl compounds have been recognized to have an important contribution to atmosphere physics and chemistry, e.g. by participating in aerosol growth (Matsunaga *et al*. 2004). Clearly, nonanal was the dominant aldehyde emitted in all the chambers. Similarly to monoterpenes, aldehyde amounts were higher in chamber 10, possibly indicating similar sources. Slight changes in the aldehyde proportions were seen between soil chambers (Table A2_2), most presumably caused by low aldehyde amounts that were close to the limit of detection, where deviation is the highest. Fractions from chamber 10 were however similar in the mornings and afternoons.

The results obtained from the soil chambers were compared with those from ambient air. A similar trend in different monoterpene amounts was observed during the whole sampling period (Fig. 4A). The distribution of studied monoterpenes in ambient air was also comparable to the soil chambers (Table A2_2), suggesting that the same factors (e.g. temperature) influence the BVOCs emissions from the higher plants and understory. Apparently, the chamber 10 seems to act as a source of these compounds, since higher amounts of monoterpenes were measured. On the other hand, the relatively lower amounts measured in chamber 13 and 15 suggest that there is a possible sink under the experimental conditions of this study. An exception was observed for camphene whose measured amounts in all the chambers were relatively high when compared to the amounts measured in ambient air, demonstrating that all the chambers acted as source of these terpenoids. However, in order to make any further conclusions, additional studies are required.

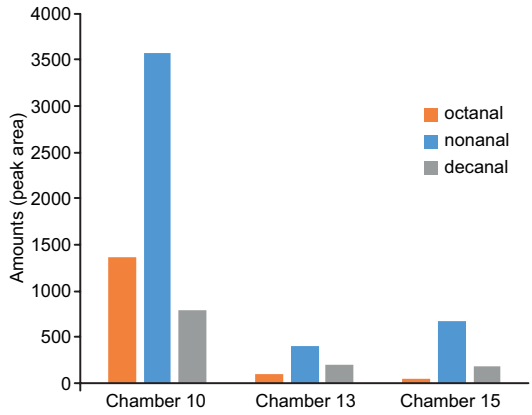

Fig. 3. Amounts (peak area) of aldehydes measured by portable GC-MS. Samples were collected by static SPME from soil chambers.

In contrast to monoterpenes, ambient air seemed to contain much higher amounts of aldehydes than observed in any soil chamber. This result suggests that their main source is not the soil or understory vegetation, or that soil/understory are acting as a sink of these carbonyl compounds. However, the role of microbial activity is largely unknown. The aldehyde distribution also changed markedly from the chambers to ambient air (Table A2_2). The nonanal concentration was the highest in the soil chambers, while decanal was the most abundant in the ambient air samples. These compounds are often reported as major C_4–C_{11} carbonyl compounds in the atmosphere (e.g. Possanzini *et al*. 2000, Cecinato *et al*. 2001), but more measurements are still required. A slightly different pattern was as well observed between the soil and ambient air aldehyde amounts during the whole campaign period (Fig. 4B).

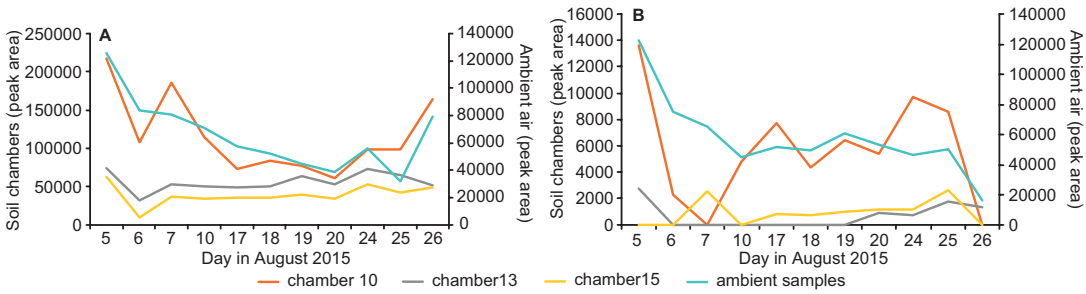

Fig. 4. Amounts of (**A**) monoterpenes and (**B**) aldehydes measured in soil chambers and in ambient air by SPME-GC-MS.

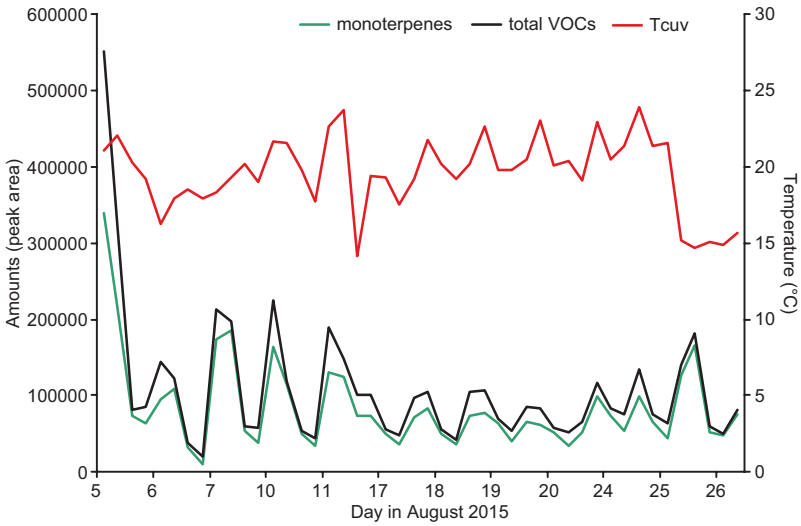

Fig. 5. Temporal variation of monoterpenes and total VOCs sampled from soil chambers by static SPME and the effect of temperature on the measured amounts.

Influence of meteorological parameters on the measured understory amounts of monoterpenes

In this study, the effects of temperature, photosynthetic active radiation (PAR) and relative humidity on the amounts of BVOCs measured from soil chambers were also evaluated. Temperature and light dependence of BVOC emissions has been described elsewhere (e.g. Tarvainen *et al*. 2005, Staudt and Lhoutellier 2011). The amount of monoterpenes followed the temporal evolution of temperature (Fig. 5). However, when these amounts are compared with PAR, the lowest peak areas coincided with the highest PAR (Fig. A1_11). This is expected, since under non-stress conditions emission of the monoterpenes measured in this study is mainly a result of their temperature-dependent residence in specific storage organs such as resin ducts or glands (e.g. Kesselmeier and Staudt 1999, Tarvainen *et al*. 2005). Understory vegetation seems then to be the main source of these compounds at the understory level, even though the role of microbial activity is still very much unknown (*see* also Mäki *et al*. 2017). However, this trend was not observed on 6 August and on the last two days of the campaign, which can be explained by the very high relative humidity and rain observed in these days (Fig. A1_10). As already mentioned, a high relative humidity increases the losses on the chamber walls, but previous studies have shown as well an increase in monoterpene emission rates at high humidity levels, during and after rain, and after re-watering treatments (e.g. Llusià and Peñuelas 1999, Schade *et al*. 1999, Peñuelas *et al*. 2009). Apparently, in our study, the strength of these source effects overcame the sink effect related to wall losses.

The sum of all chromatographic peaks obtained with the method was also used for the comparison with meteorological parameters and monoterpene emissions. Clearly, total VOCs that can be sampled with the used SPME fibre and analysed by GC-MS followed the evolution of monoterpene amounts during the sampling period. However, most of the VOCs other than identified monoterpenes were close to the limit of detection, thus improvements in the extraction efficiency is needed in order to make any further conclusions. The extraction time is critical for SPME measurements, and some compounds should be extracted longer for their detection. Also, fast oxidation of some terpenes in the atmosphere and during sampling is an artefact, which can affect their determination despite possible high emissions.

Effect of wind speed and wind direction on the amount of monoterpenes

The effect of wind speed on the amounts of monoterpenes measured in ambient air was esti-

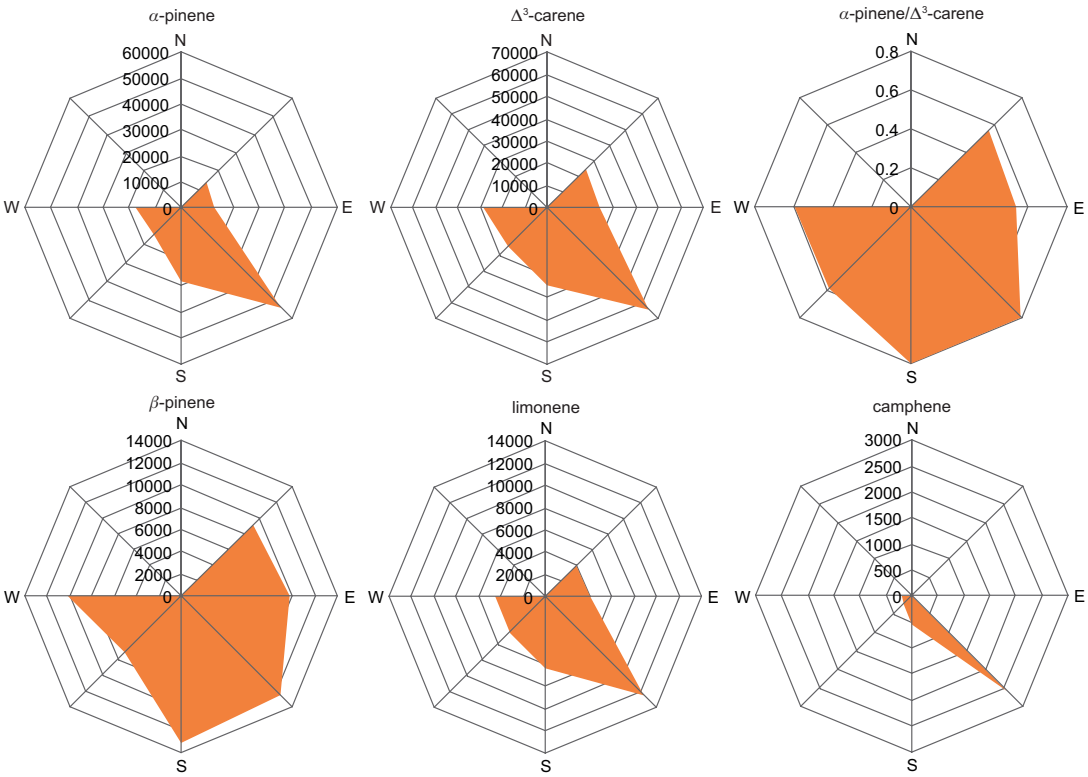

Fig. 6. Effect of the wind direction (measured at 33.6-m height) on the observed amounts (peak area) of α-pinene and Δ3-carene.

mated in this study. A negative correlation was observed between wind speed and monoterpene amounts (Fig. A1_12), explained by the fact that lower horizontal wind velocity can result in a local accumulation of BVOCs due to reduced mixing (Valach *et al*. 2015). However, wind speed did not varied substantially during the sampling campaign, with values ranging from 1.0 to 5.3 m s^{-1} during the sampling period.

The effect of wind direction on atmospheric amounts of monoterpenes was also studied. Although the lifetime of monoterpenes in the atmosphere is relatively short (Atkinson and Arey 2003), the influence from surrounding forest on the sampling site can affect the measured amounts of these compounds (Bäck *et al*. 2012). The amounts of monoterpenes were markedly higher when wind was from southeast (Fig. 6), which cannot be explained by the effect of wind speed (Fig. A1_13). The existence of two sawmills, located 6.3 km southeast from the sampling site, is responsible for this finding as has been shown elsewhere (Eerdekens *et al*. 2009, Williams *et al*. 2011). These sawmills produce together more than 400 000 m^3 per year of sawn timber. According to our results, the influence of the sawmill emissions on the observed amounts of monoterpenes in the sampling site is substantial, and must be taken into account.

The ratio between α-pinene and Δ3-carene concentrations was greatly affected by the wind direction, resulting in an increase of α-pinene amounts relatively to Δ3-carene when wind blows from south and southeast. This change can be also explained by the presence of sawmills nearby the sampling site. If those emissions are dominantly constituted by α-pinene, they will lead to its increasing in the atmosphere. However, measurements of mill emissions are required to confirm this hypothesis. Different tree chemotypes, so called pinene or carene trees, on the surrounding forest might equally contribute to the observed differences in ambient air concentrations (Bäck *et al*. 2012). Vari-

ations in this ratio could then be used to assess an influence of external sources on the sampling site measurements.

Conclusions

In this research, measurements of BVOCs from soil chambers and understory ambient air were performed in summer 2015 at the boreal forest (SMEARII, Hyytiälä, Finland). Samples from the chambers were successfully collected by SPME and analysed *in-situ* by portable GC-MS. Air samples were collected simultaneously at understory level by dynamic SPME, and the type and relative amounts of BVOCs found in soil samples were then compared with those measured in ambient air. The sample preparation was avoided, which reduced the analysis time, sample contamination and potential compound losses during the analytical process. The most abundant BVOCs measured in soil chambers were α-pinene and Δ^3-carene, although other monoterpenes and aldehydes were also determined. The contribution of each measured compound to the understory BVOC budget was estimated, and monoterpenes contributed mostly to the understory emissions. A moderate temperature-dependence on BVOC amounts inside the chambers was observed. Ambient air amounts of studied compounds were markedly higher when the wind direction was from south-east, which is associated with the transportation of BVOCs from the nearby sawmills, and lower when wind speed increased due to tropospheric mixing. A good agreement between the results obtained by PTR-QMS (monoterpene fluxes) and GC-MS (peak areas) was observed for the samples collected by SPME in the chambers. Altogether, results demonstrated the potential and versatility of the applied method for the rapid *in-situ* measurement of organic gaseous compounds. Although the study provided additional information about the understory and ambient air composition, long-term measurements combined with laboratory studies from soil and plant emissions are still needed for better understanding the sources and sinks of BVOCs in the boreal forest. The development of a calibration method is required to provide quantitative data and correct possible errors associated with fibre coating discrimination.

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Appendix 1.

Fig. A1_1. Soil chambers (10, 13 and 15 respectively) used during the sampling campaign.

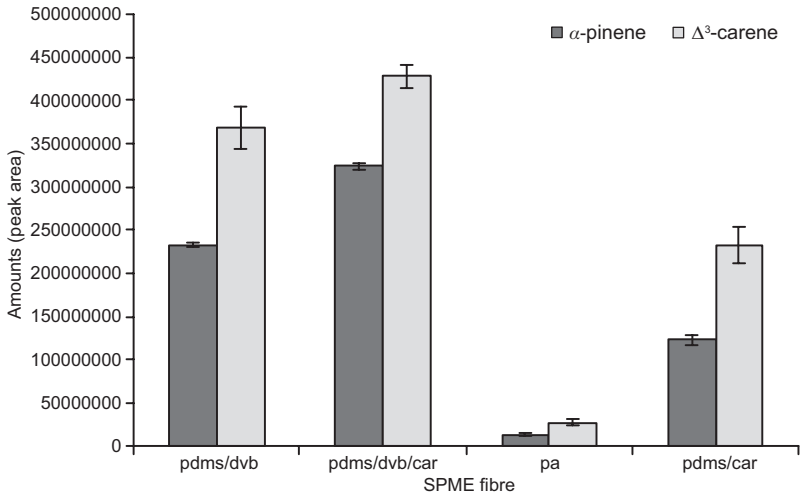

Fig. A1_2. Extraction efficiency ± SD of α-pinene and Δ3-carene using different SPME fibre materials (PDMS/DVB, PDMS/DVB/CAR, PA and PDMS/CAR).

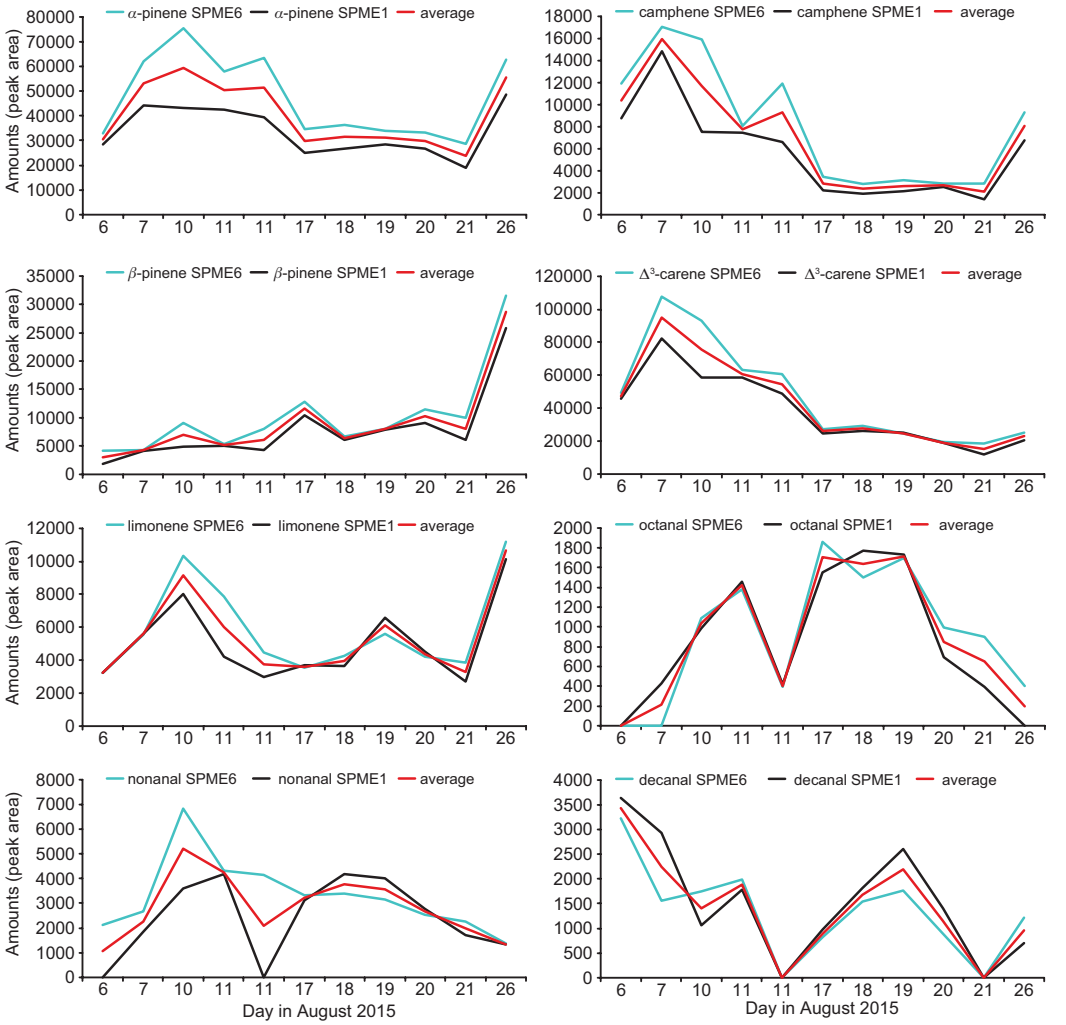

Fig. A1_3. Extraction of monoterpenes and aldehydes from soil chambers on two different SPME fibres during the whole campaign period. Samples were analysed by portable GC-MS.

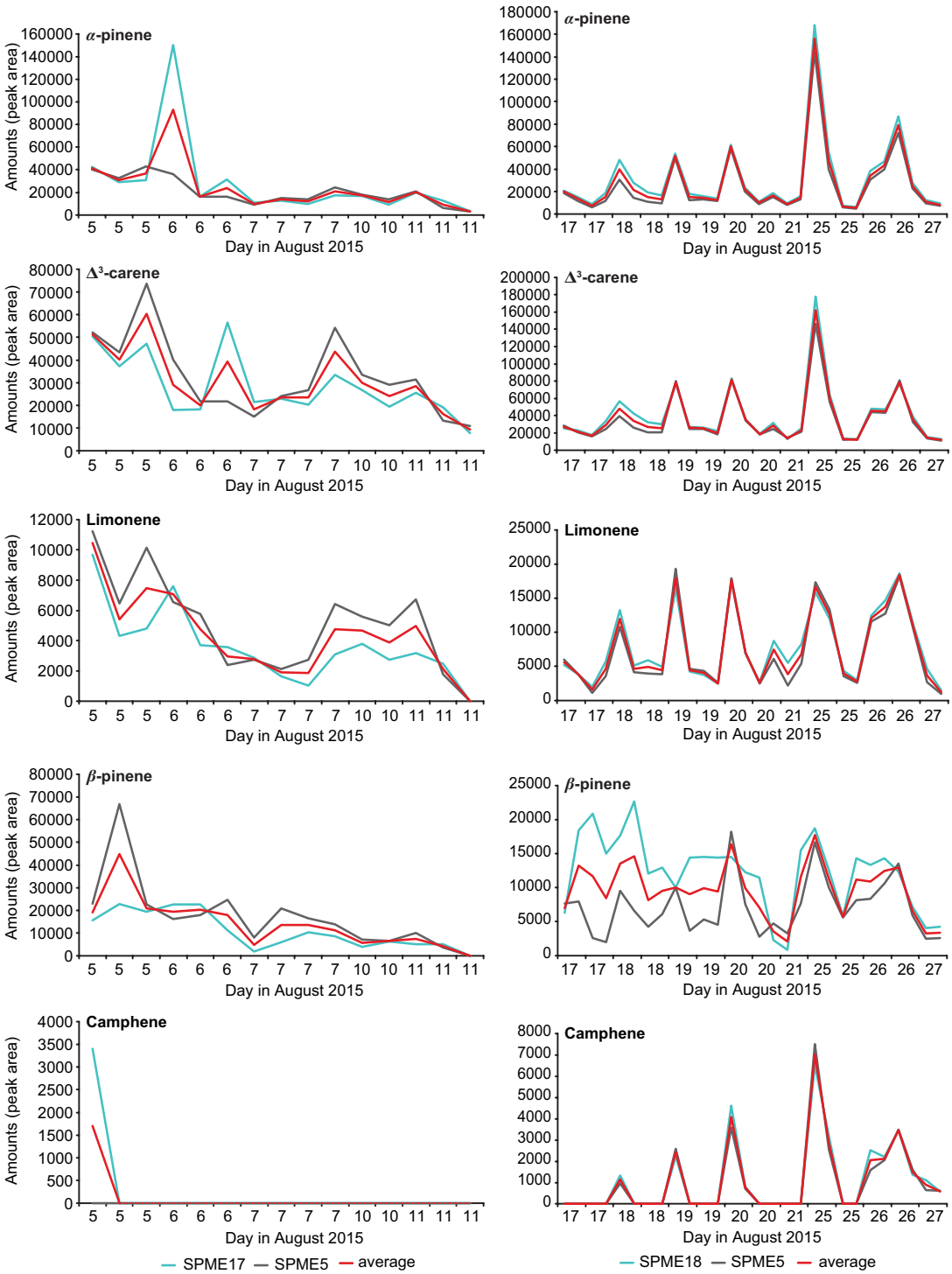

Fig. A1_4. Dynamic extraction of monoterpenes from ambient air on two different SPME fibres during the whole campaign period. Samples were analysed by portable GC-MS.

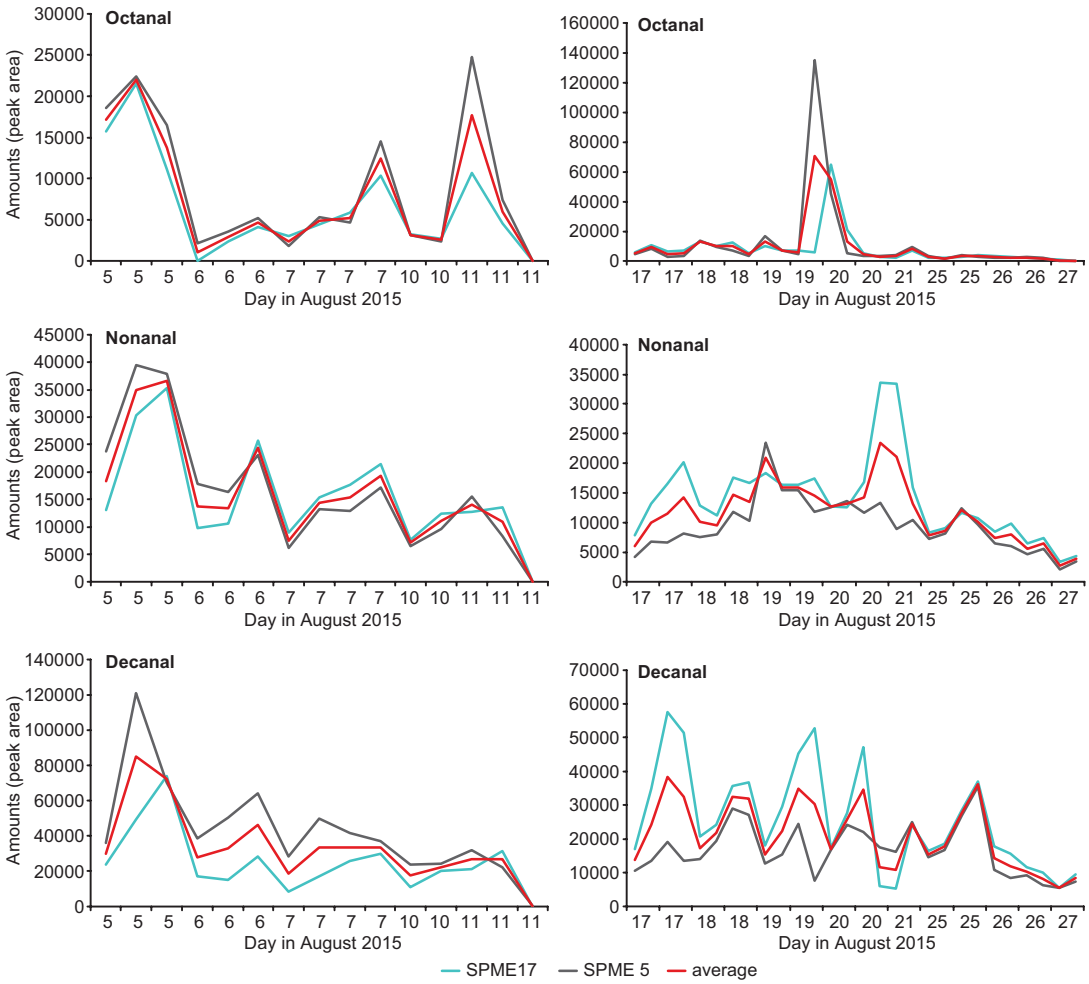

Fig. A1_5. Ddynamic extraction of aldehydes from ambient air on two different SPME fibres during the whole campaign period. Samples were analysed by portable GC-MS.

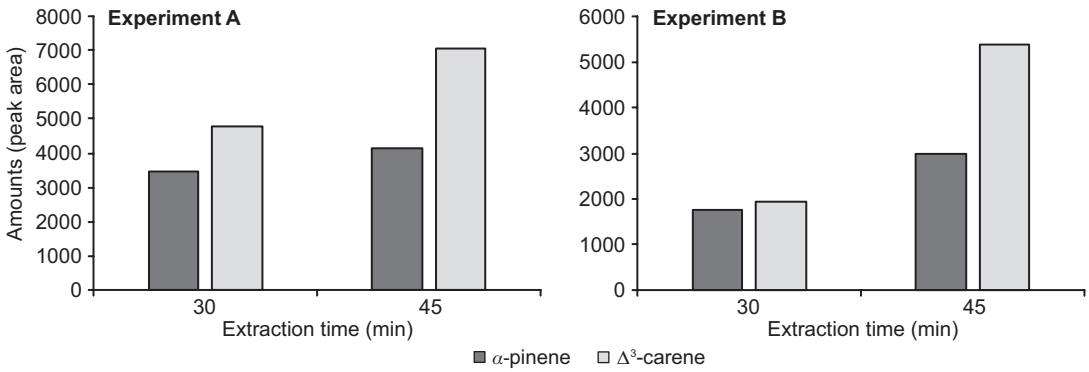

Fig. A1_6. Optimization of the extraction time for α-pinene and Δ^3-carene. A soil chamber was closed for 5 min, after which two SPME fibres were inserted for the simultaneous collection of VOCs during 30 and 45 min, respectively. The experiment was repeated two times (experiments A and B). Compounds were analysed by portable GC-MS.

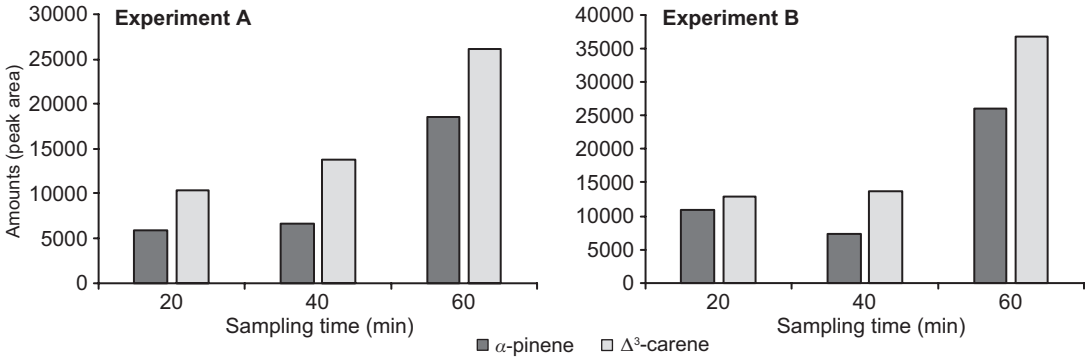

Fig. A1_7. Optimization of dynamic SPME extraction time for α-pinene and Δ^3-carene. Three dynamic sampling systems for SPME were used simultaneously for the extraction of these terpenes during 20, 40 and 60 min. Flow rate was 11 l min^{-1}. The experiment was repeated two times (experiments A and B). Compounds were subsequently analysed by portable GC-MS.

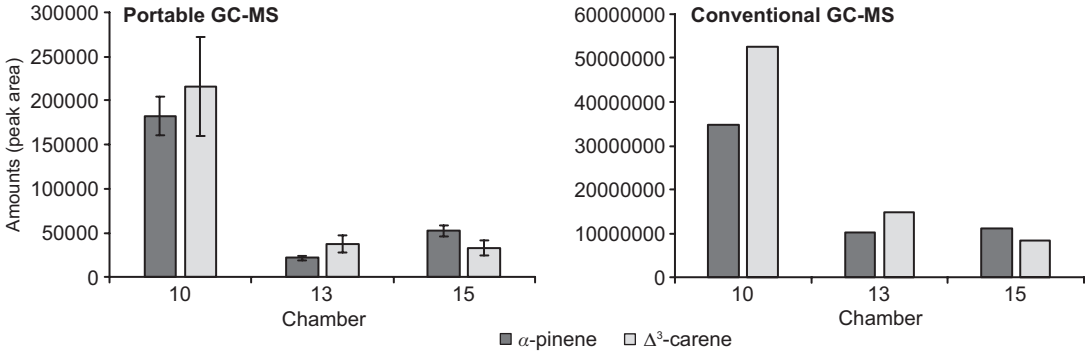

Fig. A1_8. Comparison between amounts of α-pinene and Δ^3-carene collected by SPME and measured simultaneously from three different soil chambers by portable and conventional GC-MS. Error bars are the highest standard deviations obtained in the reproducibility experiment.

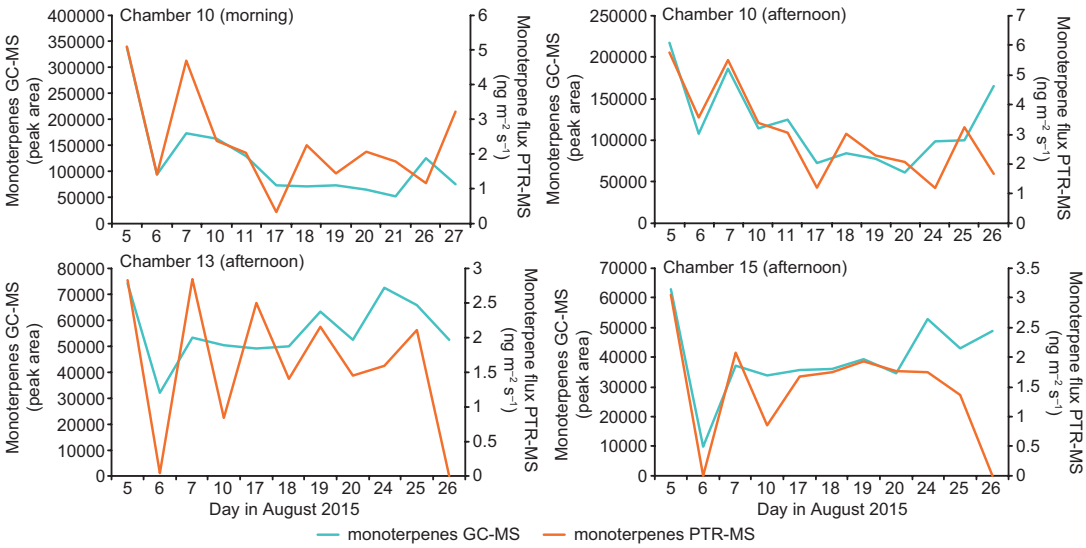

Fig. A1_9. Comparison between the total amounts (peak area) of monoterpenes collected by static SPME and analysed by GC-MS and monoterpene fluxes (ng m^{-2} s^{-1}) measured by PTR-QMS from soil chambers.

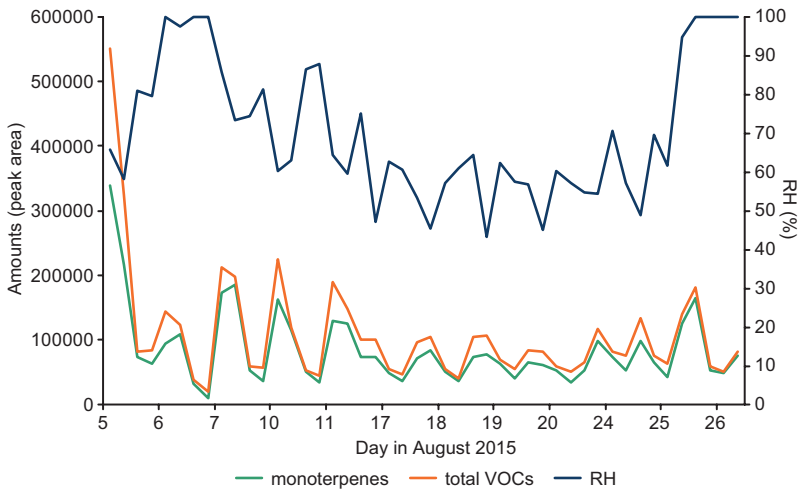

Fig. A1_10. Temporal variation in monoterpenes and total VOCs sampled from soil chambers by static SPME and the effect of relative humidity (measured inside the chambers) on the measured amounts.

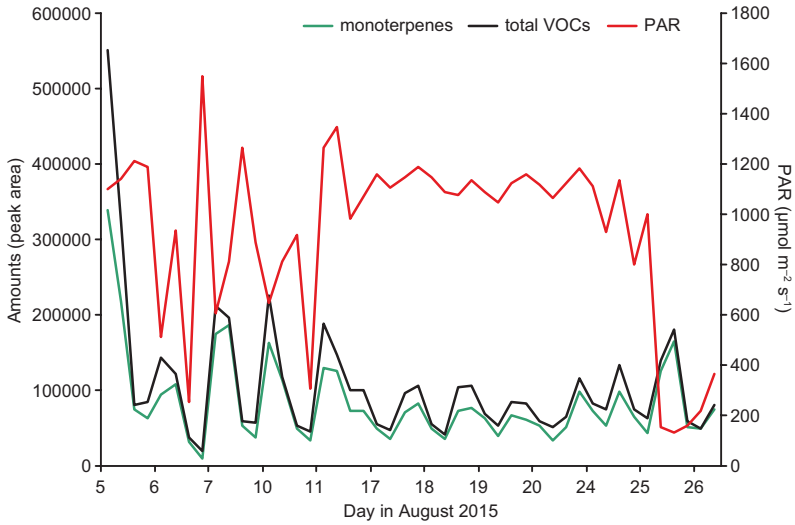

Fig. A1_11. Temporal variation in monoterpenes and total VOCs sampled from soil chambers by static SPME and the effect of photosynthetic active radiation (PAR) on the measured amounts.

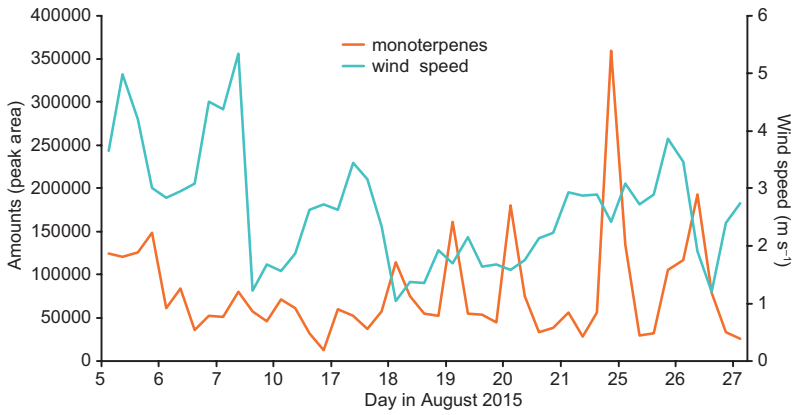

Fig. A1_12. Effect of wind speed (measured at 33.6-m height) on the monoterpene amounts in ambient air within the subcanopy space of a boreal forest.

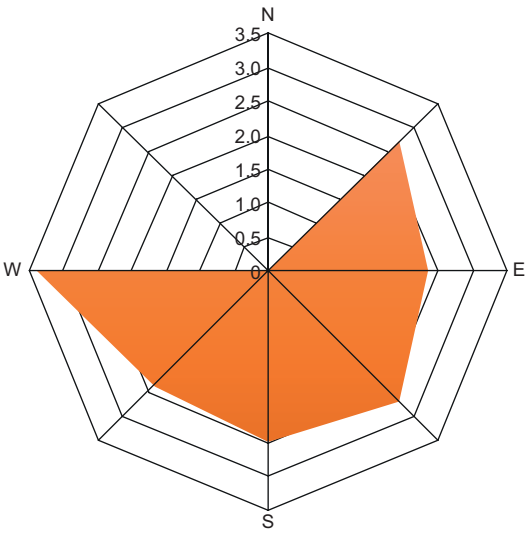

Fig. A1_13. Average wind speeds (m s^{-1}) from different geographical directions during the sampling campaign.

Appendix 2. Monoterpene fluxes measured in 2015 from soil chambers and identified monoterpenes and aldehydes.

Table A2_1. Monoterpene fluxes (ng m^{-2} s^{-1}) measured in 2015 from soil chambers by PTR-QMS and averaged during the sampling period of each SPME sample.

	Monoterpene fluxes (ng m^{-2} s^{-1})	Temperature (°C)	PAR (μmol m^{-2} s^{-1})	Relative humidity (%)
Chamber 10 (morning)				
5 Aug	5.104	21.1	1099	66
6 Aug	1.423	16.2	512	100
7 Aug	4.697	18.3	605	86
10 Aug	2.385	21.7	646	60
11 Aug	2.035	22.6	1265	64
17 Aug	0.334	14.1	981	75
18 Aug	2.250	19.2	1147	54
19 Aug	1.435	20.1	1080	64
20 Aug	2.068	20.4	1123	57
21 Aug	1.801	19.1	1123	55
26 Aug	1.174	15.2	154	95
27 Aug	3.235	15.7	368	100
Chamber 10 (afternoon)				
5 Aug	5.761	22.0	1139	58
6 Aug	3.585	17.9	935	97
7 Aug	5.515	19.3	810	73
10 Aug	3.389	21.5	813	63
11 Aug	3.057	23.7	1347	60
17 Aug	1.201	19.4	1071	47
18 Aug	3.032	21.7	1191	45
19 Aug	2.305	22.6	1136	43
20 Aug	2.064	23.0	1161	45
24 Aug	1.206	22.9	1182	54
25 Aug	3.245	23.9	1138	49
26 Aug	1.678	14.7	133	100

continued

Table A2_1. Continued.

	Monoterpene fluxes (ng $m^{-2} s^{-1}$)	Temperature (°C)	PAR (μmol $m^{-2} s^{-1}$)	Relative humidity (%)
Chamber 13				
5 Aug	2.838	20.3	1211	81
6 Aug	0.039	18.5	253	100
7 Aug	2.845	20.2	1265	74
10 Aug	0.834	19.8	917	87
17 Aug	2.505	19.3	1159	63
18 Aug	1.402	20.2	1148	57
19 Aug	2.160	19.7	1091	62
20 Aug	1.452	20.1	1121	60
24 Aug	1.596	20.5	1115	71
25 Aug	2.104	21.4	803	70
26 Aug	0	15.1	161	100
Chamber 15				
5 Aug	3.052	19.2	1190	80
6 Aug	0	17.9	1549	100
7 Aug	2.085	19.0	889	81
10 Aug	0.854	17.8	308	88
17 Aug	1.684	17.5	1107	61
18 Aug	1.756	19.2	1091	61
19 Aug	1.927	19.7	1049	57
20 Aug	1.775	20.4	1063	57
24 Aug	1.747	21.4	928	57
25 Aug	1.367	21.6	1001	62
26 Aug	0	14.9	218	100

Table A2_2. Identified monoterpenes and aldehydes (%) in the three different soil chambers and ambient air during the sampling campaign. Average peak areas were used for the comparison.

Analytes	chamber 10 (morning)	chamber 10 (afternoon)	chamber 13	chamber 15	ambient air
Monoterpenes					
α-pinene	37.8	39.6	37.1	48.2	33.2
Camphene	7.7	6.4	8.1	5.6	0.9
β-pinene	8.3	8.5	3.1	3.8	13.9
Δ^3-carene	40.9	40.0	48.6	38.9	44.0
Limonene	5.3	5.6	3.0	3.5	8.0
Aldehydes					
Octanal	15.5	23.5	14.2	5.3	18.5
Nonanal	53.6	63.1	57.5	73.8	27.8
Decanal	30.9	13.4	28.3	20.9	53.7