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On-line field measurements of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry

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We measured the daily patterns of monoterpene emissions from Scots pine (*Pinus sylvestris*) trees in a boreal coniferous forest in August and September 2004, using an on-line chamber method combined with a proton-transfer-reaction mass spectrometry (PTR-MS) analyzer. The on-line measurements were made in two chambers with a one-year old shoot inside. Simultaneous measurements were performed for carbon dioxide (CO_2) exchange, transpiration (H_2O), exchange of trace gases (NO_x, O_3), photosynthetic photon flux density (PPFD), air temperature and relative humidity (RH). The composition of the monoterpene emission did not change during the measurement period, with Δ^3-carene and α-pinene being the dominant species. The total monoterpene emission rate (per needle area) was on average 0.5 ng m^{-2} s^{-1}, varied from non detectable to 2.1 ng m^{-2} s^{-1}, and showed a typical diurnal pattern with afternoon maximum and nighttime minimum. The emission rates determined with this on-line chamber method were in agreement with results from a simultaneously used established adsorbent sampling technique with offline GC-MS analysis. The monoterpene emissions from the chamber walls were correlated with the chamber temperature and this measurement artifact was dominating at night. Emission rates normalized to 30 °C, using temperature regression coefficient of 0.09 $°C^{-1}$, ranged from 2.1 μg $g(dw)^{-1}$ h^{-1} to 4.4 μg $g(dw)^{-1}$ h^{-1}. Measurements of emission dynamics of biogenic volatile organic compounds (BVOCs) together with plant physiological activity are urgently needed for the development of mechanistic BVOC emission models in order to assess their regional and global influence.

Introduction

The boreal zone is one of the largest forested vegetation zones in the world and produces biogenic volatile organic compounds (BVOCs) that affect air chemistry and climate in several ways. Emitted BVOCs may undergo oxidation and form less volatile organic compounds that

participate in secondary organic aerosol (SOA) production (Kulmala *et al*. 2004). One group of these BVOCs is the monoterpene family which consists of a wide range of different $C_{10}H_{16}$ substances that are secondary products emitted by a wide range of plants. Biogenic monoterpenes belong to the group of non-methane hydrocarbons that are involved in the tropospheric ozone chemistry and regulation of the oxidative capacity of the atmosphere (Chameides *et al*. 1992, Fehsenfeld *et al*. 1992). BVOC emissions may have a considerable effect on the ecosystem carbon balance, amounting up to 0.2%–10% of the assimilated carbon being re-emitted to the atmosphere, depending on for example the time of year, temperature or water availability (e.g. Sharkey *et al*. 1996, Guenther 2002, Kesselmeier *et al*. 2002).

The BVOC emissions of European boreal ecosystems have been characterized by e.g. Isidorov *et al*. (1985), Janson (1993), Rinne *et al*. (1999, 2000), and Janson and de Serves (2001). Temporal patterns in BVOC emission dynamics have generally been described using empirical algorithms based on leaf temperature and photosynthetic photon flux density (PPFD) normalized with a basal emission rate specific for a given vegetation type and a set of environmental conditions (Tingey *et al*. 1980, Guenther *et al*. 1993, Schuh *et al*. 1997). Temperature strongly controls the monoterpene emissions by influencing their volatility whereas the light dependence of emissions from certain tree species suggests a further relationship between monoterpene synthesis and photosynthesis (e.g. Niinemets *et al*. 2002). Detailed mechanistic analyses have revealed a complex mixture of triggering and controlling factors, such as water availability (Bertin and Staudt 1996), plant developmental status and leaf maturation (Hakola *et al*. 2001, Staudt *et al*. 2003), and mesophyll CO_2 concentration (Loreto *et al*. 1996), among others. In many cases the plant metabolic activity seems to impose a significant regulation on monoterpene emission quantity and quality (Staudt *et al*. 2000, 2003, Hakola *et al*. 2003, Bäck *et al*. 2005), which is not captured in the normally employed emission rate measurements. Thus, studies of changes in emission rates at different temporal scales related to changes in environmental variables as well as plant physiology are needed.

Measurement of BVOCs emitted at relatively low emission rates sets a challenge to the analysis and measurement techniques. With many techniques it is impossible to obtain both good temporal resolution and high measurement accuracy simultaneously. Canister or adsorbent tube sampling with subsequent off-line analysis by gas chromatography can offer high accuracy and low detection limit but lacks good time resolution and is time consuming and laborious. Instead, proton-transfer-reaction mass spectrometry (PTR-MS) is a method that allows fast time response on-line monitoring of VOCs at ambient, sub-ppb_v concentrations (Lindinger *et al*. 1998). Previously the PTR-MS has been used to study canopy scale biogenic emissions using the eddy covariance (EC) techniques (e.g. Karl *et al*. 2001, Rinne *et al*. 2001, Warneke *et al*. 2002, Grabmer *et al*. 2004, Lee *et al*. 2005, Spirig *et al*. 2005). Leaf or shoot level analysis of gas exchange with shoot chamber measurements can give more detailed information on the dynamics of VOC emissions than EC method. So far, to the best of our knowledge, emission rate studies combining the PTR-MS and shoot chambers have only been used in laboratory experiments under controlled environmental conditions (e.g. Hayward *et al*. 2004). We present a novel field chamber measurement system that combines fast time response PTR-MS measurements of monoterpene emissions with measurements of exchange of other trace gases and environmental variables that contribute to the gas exchange dynamics. Analysing the links between monoterpene emissions, photosynthetic processes and environmental variables allows the development of mechanistic models that include both plant physiological and physicochemical parameters, enabling better estimates of BVOC emissions.

Experimental methods

A detailed description of the measuring station has been given by Vesala *et al*. (1998) and by Hari and Kulmala (2005). Hari *et al*. (1999) describe the gas exchange measurement set-up. Consequently, we will only present them briefly here.

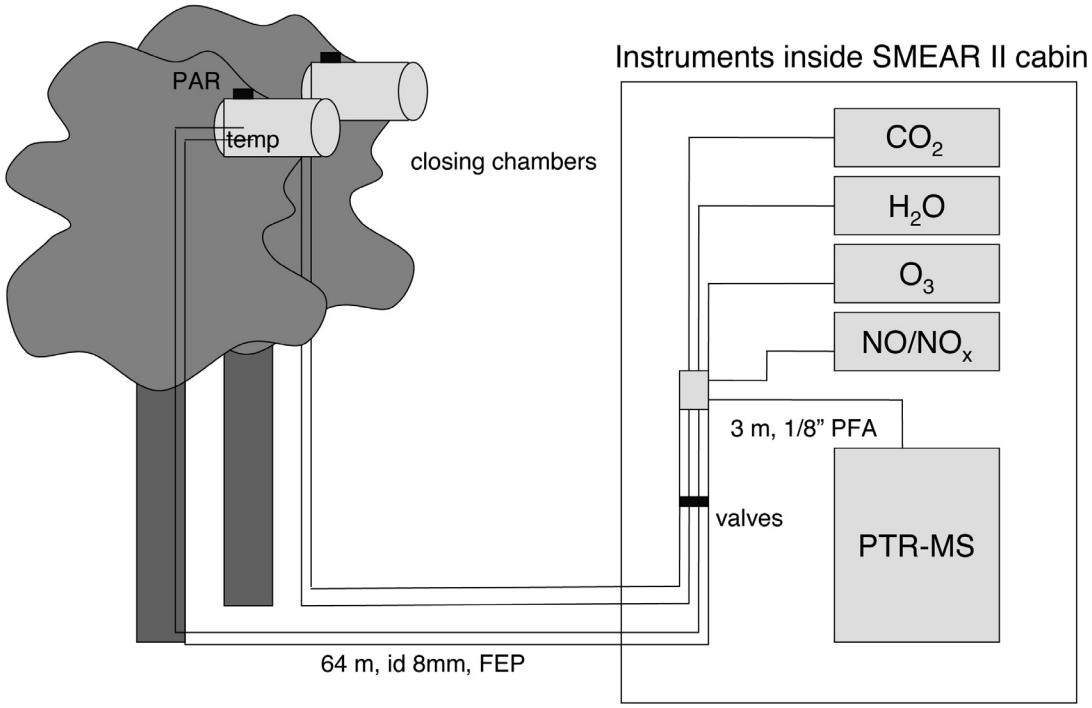

Fig. 1. Schematic picture of on-line chamber measurement set-up used for emission measurements of Scots pine (in more detail by Altimir *et al.* (2002)).

Measurement site

The measurements were carried out at the SMEAR II measurement station (Station for Measuring Forest Ecosystem–Atmosphere Relations) in Hyytiälä, southern Finland (61°N, 24°E, 180 m a.s.l.) between 25 August and 22 September 2004. The forest around the station is dominated by 40-year-old Scots pine (*Pinus sylvestris*) with some Norway spruce (*Picea abies*), aspen (*Populus tremula*) and birch (*Betula* sp.). In 2004, the canopy reached a height of about 16 m. A scaffolding tower permits access to the crown of some pines.

Chamber setup

The automatic gas-exchange system consisted of two shoot chambers and one empty reference chamber, sampling tubing, and analyzers (Fig. 1). The box-shaped chambers were 1-l rectangular boxes built from metacrylat except for a quartz glass cover wall. The acrylic plastic parts were coated in spring with fresh Teflon® (Fluoro Ethylene Propylene (FEP)) film. The chambers remained open most of the time and were closed intermittently three times per hour for less than two minute periods. During closure, air was drawn from the chambers to the gas analyzers along the sampling lines and the under-pressure was avoided with replacement by ambient air at equal flow rate. These measurements with the two identical chambers were conducted one after the other and the time between the consecutive measurements was five minutes. The sample lines were 64-meter long heated Teflon (FEP), tubes. One of the sampling lines led towards the CO_2 and H_2O analyzers at 1 LPM flow rate trough id of 4 mm. The second reached the O_3 and NO_X analysers at 3 LPM flow rate trough id of 6 mm (for the connection of the PTR-MS and changes resulting from it *see* next section). The timing and the flow rates were controlled via magnetic valves and flow rate controllers. The air was finally exhausted after passing the pumps that drew the air through the analyzers, thus with regard to the gas circulation this was a

linear open gas-exchange system. An in-line particulate filter (F series SS-316 sintered element, mesh size 7 μm, Nupro Company, Willoughby, OH, USA) was placed in front of the gas analyzers. Ambient atmospheric concentrations of CO_2, H_2O, O_3, NO_x and monoterpenes were measured when the chamber was open. The gas concentrations (CO_2, H_2O, O_3 and NO_x), air temperature, and PPFD were recorded at 5-second intervals and monoterpenes every 12 sec. During the chamber closure, concentration of a gas inside the chamber may change indicating a net source or sink of that particular gas in the chamber. The changes in concentration during the closure were used to determine the gas fluxes. Detailed technical descriptions as well as the methods of flux calculation and corrections for the different gases have been previously presented for CO_2 (Hari *et al*. 1999), O_3 (Altimir *et al*. 2002), NO_x (Raivonen *et al*. 2003) and water vapour (Kolari *et al*. 2004). We assumed that during a closure the monoterpene concentration reaches a steady state in the chamber. The flux of monoterpene was determined using initial and final concentrations by the mass balance equation

$$F = \frac{q\left(C\left(t\right) - C_a\right)}{A}, \qquad (1)$$

where F is the net monoterpene flux per leaf area (g m^{-2} s^{-1}), and the right-hand term is the mass flux produced by the monoterpene concentration difference in the ambient air and the air in the chamber. q is the flow rate through the chamber (m^3 s^{-1}), C_a is ambient (initial) concentration, and $C(t)$ is final inside-chamber concentration (g m^{-3}), which was determined at the end of the measurement period and considered constant. A is the shoot needle area (all sides, m^2).

The shoot gas exchange was measured about 70 times per day. The two measurement chambers were placed in the uppermost part of the canopy, on one-year-old shoots of two individuals of Scots pine. The shoots had been installed inside the chambers several months before the VOC measurement campaign started, and the chambers were gently fastened to the trunk in order to avoid mechanical damage to the shoot. The needles were gently bent to form a plane in the same angle as the sensor measuring photosynthetic photon flux density (PPFD). The pine shoots were also debudded at the moment of installation to prevent new growth inside the chambers. The total leaf areas of the experimental shoots were estimated to be 0.03 m^2, with uncertainty of about 10%, based on earlier measurements of corresponding shoots of the same trees. We used specific needle masses of the corresponding shoots measured in previous years that were about 130 g m^{-2}.

Monoterpene emission measurements

Monoterpene emissions rates were measured using a proton-transfer-reaction mass-spectrometer (PTR-MS, Ionicon GmbH, Innsbruck, Austria) which is a fast response, on-line trace gas analyzer. The sample air intake of the PTR-MS, connected to the O_3/NO_x sampling tube, was about 0.1 l min^{-1}. Monoterpene concentrations in the sample line were recorded continuously at 12-second intervals.

The PTR-MS analyzer has been described in detail by Hansel *et al*. (1998) and Lindinger *et al*. (1998). The instrument comprises four main components: an ion source, a drift tube, a quadrupole mass filter and an ion detector/amplifier. The primary ions, used for ionization of studied compounds, are H_3O^+ ions that are produced from pure water vapor in the hollow cathode ion source and pass into the drift tube. The sampled air was introduced into the drift tube at a flow rate of ~10 ml min^{-1} which was maintained at a pressure of 1.8 mbar.

In the PTR-MS, the compounds which have higher proton affinity than water (700 kJ mol^{-1}) undergo a proton-transfer reaction:

$$H_3O^+ + R \rightarrow RH^+ + H_2O. \qquad (2)$$

While the reactive compound R is present in trace quantities, the concentration of H_3O^+ remains effectively constant as $[H_3O^+] >> [RH^+]$ and concentration of product ions is given by:

$$\left[R\right] = \frac{1}{kT_r mf} \times \frac{\left[RH^+\right]}{\left[H_3O^+\right]_0} \qquad (3)$$

where $[H_3O^+]_0$ is the concentration of the primary ion in the absence of reactive compounds R, k (2.44×10^{-9} cm^3 s^{-1}) is the proton-transfer-

reaction rate (specific for each monoterpene in question, e.g. Tani *et al*. 2003) and T_r (105 μs) is the average time the ions spend in the drift tube. Experimentally determined factors were used for detection efficiency of the mass (m) and fragmentation (f) of the measured molecule. The largest inaccuracy in determined concentration and emission rates arises from the use of reaction rate k which has an uncertainty in the order of 50%. Ions are selected according to their mass in the quadrupole mass spectrometer and measured as counts per second (cps) by an electron multiplier detector. A detection limit of 2 to 5 ppt has been reported by Hansel *et al*. (1998) when the PTR-MS was tuned up for measurement of small concentrations. A typical detection limit for an integration time of ten seconds is 50 ppt.

The PTR-MS technique gives information on the mass of the measured species, thus only the sum of all species with the given molecular mass was measured. Consequently we could not distinguish between different monoterpenes. The ratios of different monoterpenes emitted were obtained by collecting air samples into Tenax-TA and Carbopack-B absorbent tubes, and later analyzing them with a gas-chromatograph mass-spectrometer (GC-MS). These measurements were performed during one hour at midday with a separate manual Teflon film chamber from an adjacent shoot in the same tree, and a detailed description of the measurement system is given in Hakola *et al*. (2003).

The ionization method used in PTR-MS can be regarded as soft and non-destructive and usually the measured species can be detected as their molecular mass plus one. Some compounds have been observed to undergo some degree of fragmentation within the instrument. According to Tani *et al*. (2003) the monoterpenes fragment yielding up to 60% of positive ions with mass 81. In this study, monoterpene emissions were calculated from measurements of mass 81, which is the major monoterpene fragment. Also other compounds emitted by Scots pine may also appear on mass 81 (Karl *et al*. 2001) and thus the emissions were verified as monoterpene in origin with the adsorbent method as described above. The fragmentation pattern is dependent on the drift tube conditions and on the monoterpene in question (e.g. Tani *et al*. 2003). The emission spectrum (Table 1), measured with the adsorbent sampling technique, remained constant within the measurement period and was dominated by Δ^3-carene and α-pinene. Since 85% of the emitted monoterpenes consisted of these two species (Table 1), the fragmentation of emitted mixture was calculated based on their measured abundances. The fragmentation patterns of Δ^3-carene and α-pinene were determined in a laboratory experiment. Liquid monoterpenes (98.5% pure Δ^3-carene and 99.5% pure α-pinene, Sigma-Aldrich, Fluka Chemie GmbH) were evaporated alternately and the ratios of fragment mass 81 and protonated monoterpene mass 137 were determined (Table 2). The monoterpene emission spectrum was determined with the adsorbent samples and a fragmentation factor of 60% was calculated for the emitted monoterpene emission.

Table 1. Monoterpene emissions from one Scots pine shoot in Hyytiälä during 14 days (at midday) between 25 August and 20 September 2004. Emissions were measured with a GC-MS from Tenax-TA and Carbopack-B adsorbent tubes.

	Average (ng m^{-2} s^{-1})	S.D. (ng m^{-2} s^{-1})	Range (ng m^{-2} s^{-1})	Percentage of monoterpenes (range)
α-Pinene	0.04	0.05	0–0.15	13.70 (0–39)
Camphene	0.01	0.01	0–0.03	5.44 (0–19)
Sabinene	0.02	0.02	0–0.06	3.83 (0–7)
β-Pinene	0.01	0.01	0–0.06	2.92 (0–5)
Δ^3-Carene	0.24	0.30	0.04–0.92	71.39 (50–97)
1,8-Cineol	0.01	0.01	0–0.03	1.10 (0–7)
Trans-ocimene	0.00	0.00	0–0.01	0.10 (0–1)
Terpinolene	0.01	0.01	0–0.05	1.53 (0–0.5)
All monoterpenes	**0.34**	**0.40**	**0.06–1.27**	

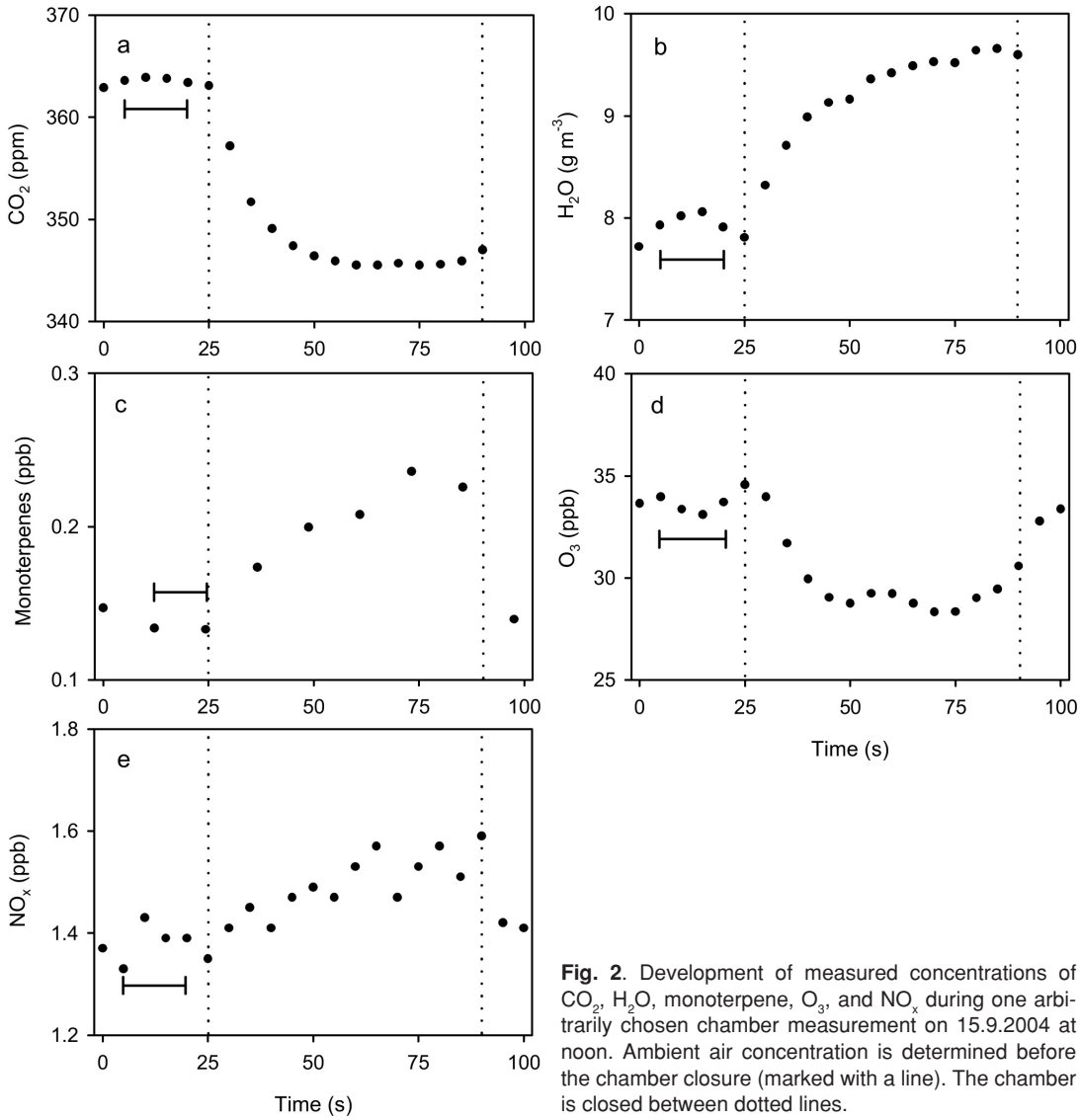

Fig. 2. Development of measured concentrations of CO_2, H_2O, monoterpene, O_3, and NO_x during one arbitrarily chosen chamber measurement on 15.9.2004 at noon. Ambient air concentration is determined before the chamber closure (marked with a line). The chamber is closed between dotted lines.

Thus, the mass 81 emission was divided by 0.60 to obtain the total monoterpene emission.

Table 2. Fragmentation patterns of Δ^3-carene and α-pinene, measured percentages of monoterpene M137 and major fragment M81 and calculated for measured monoterpene mixture, 71% Δ^3-carene and 14% α-pinene, emitted by studied Scots pine.

	Δ^3-carene (%)	α-pinene (%)	Emitted monoterpene mixture (%)
M81	54	59	60
M137	46	41	40

Results and discussion

Dynamics of CO_2, H_2O, monoterpene, O_3 and NO_x during chamber closure

As an example, measured concentrations of all species are presented during one arbitrary daytime chamber closure (Fig. 2). When the chamber closed CO_2 was taken up and H_2O was transpired by the shoot. CO_2 decreased from the ambient concentration by 4% in less than 30 seconds from the closure of the chamber. Water vapour concentration reached a steady level more

than 20% higher than the ambient concentration. Monoterpene concentration increased from ambient concentration by over 80% during the chamber closure. Ozone concentration decreased 20% during the closure mostly due to stomatal uptake with an additional contribution by non-stomatal sinks (Altimir *et al*. 2004). NO_x concentration increased by 12% from ambient level. Nitrogen oxides are emitted due to plant metabolism (Wildt *et al*. 1997) and from plant and chamber surfaces by ultraviolet light in an unknown reaction (Hari *et al*. 2003). Presumably the latter process was more important here.

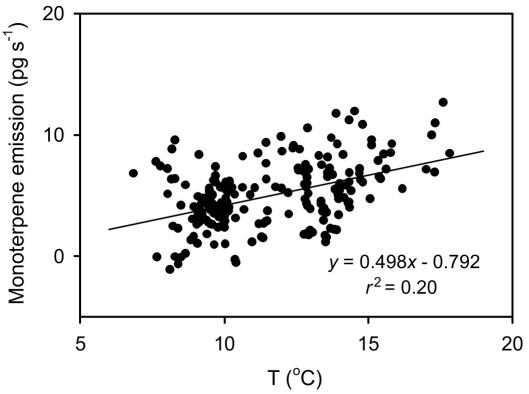

Fig. 3. Monoterpene emission from an empty chamber as a function of temperature measured between 25 August and 15 September 2004.

Artifacts in chamber flux measurements

We explored the contribution of the re-emission of the monoterpenes absorbed onto the chamber walls on the determination of the shoot emission. An empty chamber was regularly measured in between the shoot chamber measurements and its emissions were determined in the same way as for the shoot chambers, with the same presumed leaf area. The emission from the empty chamber correlated with temperature (Fig. 3). A simple method for removing the chamber artifact would be to use a linear regression of the empty chamber flux with temperature in order to subtract it from the observed monoterpene emission. However, this only accounts for a lower estimate of the chamber contribution, since it can be expected that the re-emission of monoterpene from the shoot chamber will generally be higher than from the empty chamber due to the higher monoterpene concentrations in the shoot chamber. Also, we estimated the loss of monoterpenes in the sampling tube due to ozonolysis. The estimation was based on: the reaction rate between main emitted monoterpene Δ^3-carene and ozone ($k = 37 \times 10^{-18}$ cm^3 molecules^{-1} s^{-1} in 20 °C (Atkinson 1994)), 36-second retention time, which was the calculated travel time of gas in sampling tubing, and measured ozone and monoterpene concentrations. The chemical loss was between 0.002 and 0.03 ppt depending on the monoterpene concentration. More importantly, the relative loss of monoterpene in the sampling tube was smaller than 0.005% and thus it could be neglected.

We determined the noise in the monoterpene concentration measurements using 50-second periods between two consecutive chamber closure cycles, i.e. when PTR-MS essentially measured concentration of the ambient air. Standard deviation of the 12-second concentration measurements within each 50-second period was on average 9.5 ppt. Considering that a difference greater than the error (≈ S.D.) is required between initial (ambient) and final concentration to detect the difference, then the detection limit for monoterpene emission rate was about 0.15 ng m^{-2} s^{-1}.

The emission from the empty chamber displayed a diurnal behavior with local maximum after midday and lowest values during night (Fig. 4), similar to the chambers with a shoot inside. Monoterpene emissions of trees are also caused by stress; rough handling of pine has been reported to result in 10–50-fold increase in the emission rates (Juuti *et al*. 1990). We tested the potential contribution of the chamber wall materials by inserting a branch, cut from a separate Scots pine tree, into a chamber for two days. A dramatically high emission was immediately detected (Fig. 4). When a shoot is inserted and removed from the chamber some of the needles are inevitably bent and this damage of the shoot increases the monoterpene emission. Monoterpene emissions of the cut shoot were high and the measured emission remained high even after the shoot was removed and the chamber was again empty. It took several days for the emission

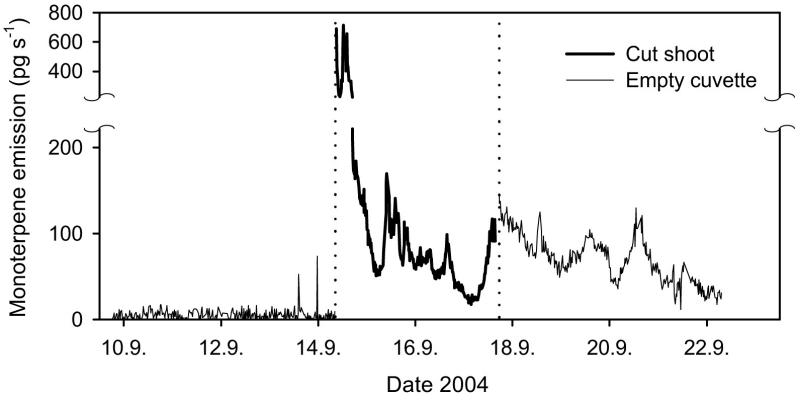

Fig. 4. Monoterpene emission from reference chamber. A branch, cut from a separate Scots pine tree, was situated in the chamber during a time period indicated with the dotted lines.

measured from this empty chamber to gradually decrease, as the monoterpenes were gradually released from the contaminated chamber walls.

The simplest interpretation resulting from this experiment was that the inner chamber materials are adsorbing the terpenoids emitted by the shoots and re-emitting them later to the air. The re-emission continued for several days, which implies a slow desorption rate. This suggests that monoterpenes were adsorbed on surfaces, most likely the internal Teflon coating. Teflon has indeed been reported to display such a memory effect in its interaction with terpenoids (Helmig *et al*. 2003) as well as with NO_x (Raivonen *et al*. 2003). Thus the level of emission from the chamber material might be related not only to the temperature but also to the previously existing monoterpene concentration. The chamber material could generate a bi-directional flux which, when not taken into account, leads to underestimation of the shoot emissions when the chamber is clean and overestimation of the shoot emissions when the chamber is dirty.

Steady state in monoterpene concentration during the chamber closure appeared to be reached later than in CO_2 concentration. This further suggests that there were reactions of the monoterpenes with the inner surfaces of the chamber and the tubing which were damping the concentration change signal and resulted in underestimation in the measured emissions. The exact magnitude of the error could not be determined due to the short chamber closure time but we estimated the underestimation introduced by the steady-state assumption to be in the order of 10%.

Since monoterpenes adsorb and desorb on chamber materials, correcting for this artifact would enable more accurate on-line measurements. However, accounting for the measurement artifacts is not an easy task and it is not sufficient to simply measure flux of the empty chamber and subtract it from the shoot chamber measurements. Also, a correction based on the observed correlation between the empty chamber emission and ambient temperature is not sufficient, even though a similar correction method can be used for the fluxes of other trace gases measured with the same system. The behavior of terpenoids in a chamber, however, is more complicated and may also be related to monoterpene concentration or vapor pressure deficit inside the chamber, as the measurements on the cut branch suggest. In theory it is possible to describe the behavior of all components and their various interactions, but considering the huge amount of compounds involved, an all-inclusive correction remains elusive in practice. Therefore, at this point the monoterpene emission was not corrected for any measurement artifacts.

Temporal fluctuations of measured variables

The measured environmental variables exhibited clear diurnal behavior (Fig. 5). Temperature range was typical for August and September in southern Finland and changes in the ambient air temperature were related to diurnal variations and larger scale weather phenomena. Relative humidity over 80% during day time was related

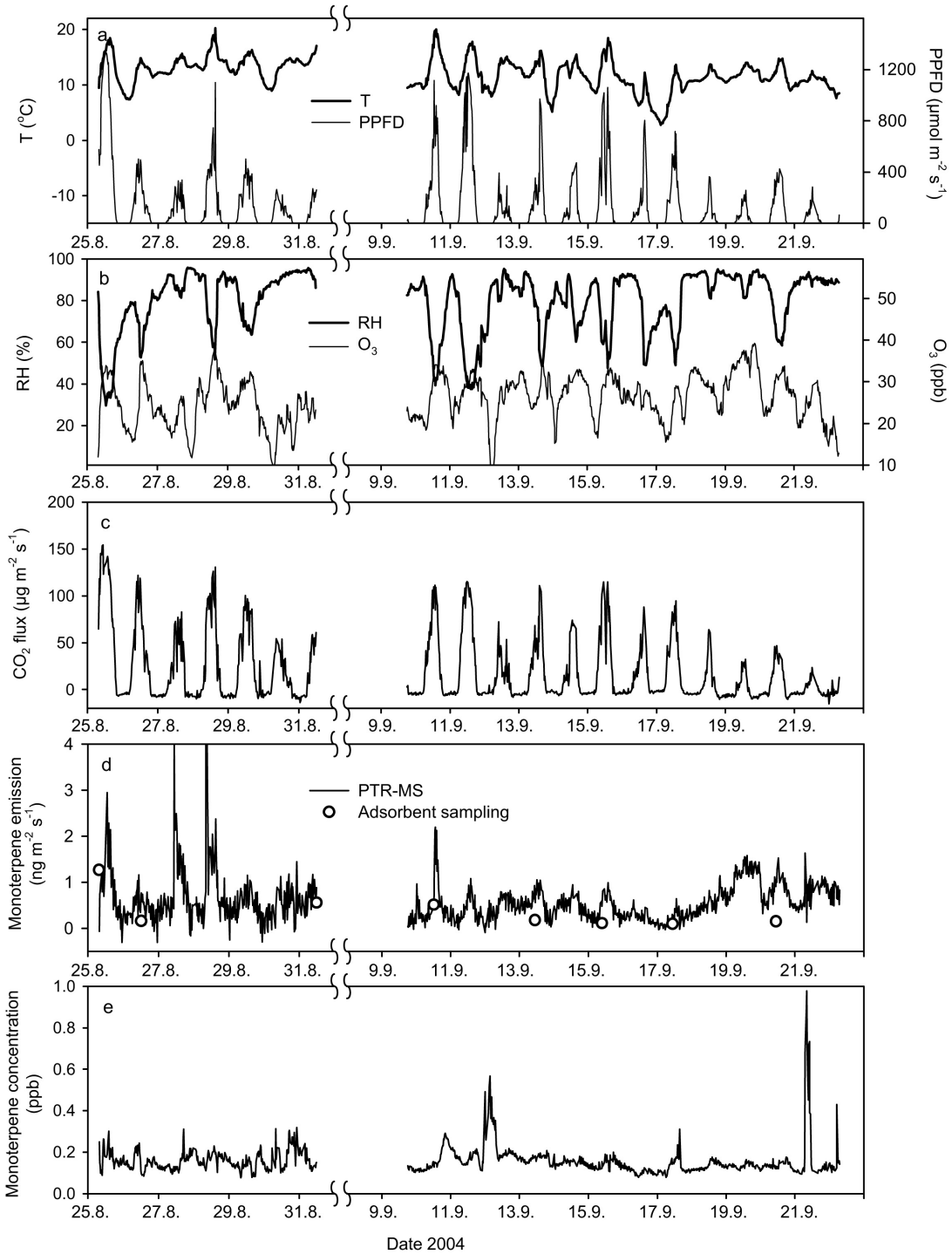

Fig. 5. (**a**) Temperature (inside chamber) and photosynthetic photon flux density (PPFD, above chamber), (**b**) relative humidity (RH, in chamber) and concentration of O_3 (in chamber), (**c**) CO_2 flux, (**d**) monoterpene emission rate from on-line PTR-MS measurements (solid line) and one hour adsorbent samples analyzed with gas-chromatograph mass-spectrometer (GC-MS) measurements dots, and (**e**) ambient air concentrations of monoterpene from PTR-MS measurements during chamber opening from 25 August to 22 September 2004. PTR-MS results are an average from measurements of two shoots.

to precipitation, as on 30 August 2004 when the total rainfall was 7.7 mm.

The diurnal pattern of carbon dioxide (CO_2) exchange and transpiration (H_2O) followed closely the changes in the temperature inside the chamber and PPFD (Fig. 5). Exchange of NO_x and O_3 had a less well defined diurnal pattern but exhibited local maximum after midday and lowest values during night, as did the monoterpene emission rates on most days. Monoterpene emissions from both shoots exhibited a similar diurnal pattern and in general the monoterpene emission was comparable between the two measured shoots. However, occasionally the difference between the two shoots was on the order of a magnitude. This variation was not systematic, and thus it was probably not due to systematic differences in e.g. meteorological variables such as temperature or inherent emission capacity between shoots, but it rather reflected some momentary differences of undetermined factors. Few nocturnal monoterpene flux measurements displayed high values which we attributed to poor nighttime mixing. During a chamber closure, the monoterpene concentration in the chamber can increase suddenly as a local eddy transports air with a high concentration into the air intake. These outliers were removed from further analysis.

The typical diurnal behavior could not be observed during two periods, first one from 30 August to 1 September and second from 17 to 20 September 2004 (Fig. 5). During these periods the monoterpene emission rates increased steadily during two or three consecutive days. Clear afternoon maximum of monoterpene emissions has been reported for coniferous forest (e.g. Spirig *et al*. 2005). The diurnal pattern of monoterpene emissions from *Pinus sylvestris* (Janson 1993, Tarvainen *et al*. 2005) and other coniferous trees (Staudt *et al*. 2000) has been observed to depend on the diurnal cycle of the temperature as well as on the season. Also, emissions of some monoterpene compounds from Scots pine have been observed to depend on irradiation (Shao *et al*. 2001).

The monoterpene emission spectrum was obtained from the measurements by the manual chamber and adsorbent sampling technique with analysis by GC-MS (Table 1). The emission spectra remained almost unchanged during the measurement period. Two thirds of the emitted monoterpenes were Δ^3-carene, and slightly less than 14% was α-pinene. The total monoterpene emission rates per needle area measured with on-line chambers and PTR-MS varied notably from non detectable to 2.1 ng m^{-2} s^{-1} (Fig. 5) with the average of 0.5 ng m^{-2} s^{-1}. Midday readings of monoterpene emissions rates measured with manual chambers with adsorbent were from 0.06 to 1.27 ng m^{-2} s^{-1} (Table 1). Emission rates determined simultaneously using the manual and on-line chambers agreed well most of the days, although on some days manual chambers resulted in slightly lower monoterpene emission rates. The small disagreement may partially be due to the error produced by the estimation of leaf area of the shoot in the on-line chambers, which influences the absolute values of the measured emission rates. Note, however, that the temporal emission rate patterns are not biased by this. The different emission rate values obtained by the two sampling methods may also result from the adsorbent samples being unable to record fast fluctuations in monoterpene emission rates (Fig. 5), and from shoot-to-shoot variability of emissions, as only one shoot was sampled using the manual chamber.

Three consecutive days (10–13 September 2004) were selected for closer investigation. The monoterpene emissions from shoot and empty chamber, chamber temperature and solar radiation are presented in Fig. 6. At night the signal appeared to be dominated by emissions from the chamber walls. However, during daytime the emission from the shoot chamber was significantly higher than that from the empty chamber. The daily maxima of the monoterpene emission were observed during the afternoon hours. However, due to the daily cycle in the turbulent mixing, the in-canopy ambient air monoterpene concentrations exhibited maxima during night (Rinne *et al*. 2005). Ambient monoterpene concentrations during these three days ranged from 0.1 to 0.7 ppb.

During the period under closer investigation the weather conditions showed some variation (Fig. 6). The first two days, 10 and 11 September 2004, were sunny with occasional local clouds. The first day, 10 September 2004, was warm

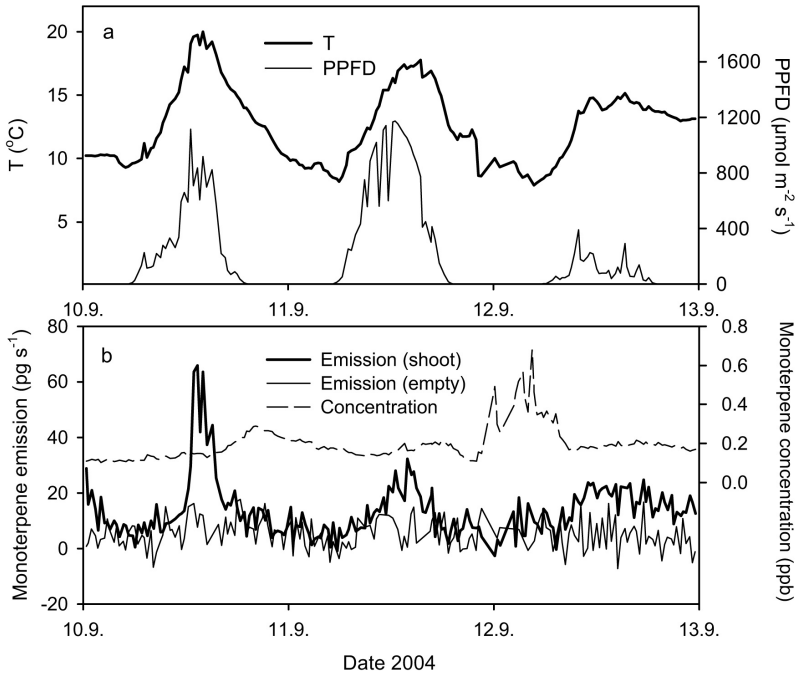

Fig. 6. (**a**) Temperature (inside chamber), and (**b**) PPFD (above chamber), monoterpene emission measured with PTR-MS from on-line shoot chambers (solid thick line), and an empty chamber (thin line) and monoterpene concentration measured during chamber opening (dashed line) between 10 and 13 September 2004.

and the chamber temperature increased from the nighttime minimum of 10 °C to early afternoon values of 20 °C. The monoterpene emissions exhibited diurnal cycle being highest, around 65 pg s^{-1}, during midday. The second day, 11 September 2004, was sunnier but a few degrees cooler. Monoterpene emissions were lower and midday maximum was around 30 pg s^{-1}. The last day, 12 September 2004, was cloudy and the chamber temperature remained below 15 °C. The monoterpene emissions from the shoot chamber were low, below 30 pg s^{-1}, and only slightly higher than that from the empty chamber. No clear midday maximum could be seen either for the chamber temperature or for the monoterpene emissions during this day.

Factors influencing the monoterpene emission rate in Scots pine

CO_2 exchange of the shoots declined slightly towards the end of the measuring period (Fig. 5) indicating a corresponding decline of biological activity in general, attributable to the beginning of the winter hardening period. Midday maximum of the chamber temperature as well as that of the monoterpene emission exhibited a generally declining trend towards the end of the measurement period. There was no notable change in the nighttime temperatures during the measurement period except on 17 September 2004 when the chamber temperature dropped to 4 °C. After the cold night the measured monoterpene emissions increased.

This clear increase in the measured monoterpene emissions may have been caused by a sudden contamination with insects, which were observed in the chambers when the ambient air temperatures near the soil surface during the cold night dropped to near zero degrees. The emissions measured with the on-line chambers were higher than those measured using the manual chamber, which was not contaminated with insects. This further suggests a potential role for the contamination in the emission increase.

On the other hand, the increase in monoterpene emission rates after the cold night in the end of the measurement period in this study may be related to changes in metabolism of pine needles occurring during autumn. Due to decrease in ambient temperatures and PPFD levels, the shoot photosynthetic capacity of the Scots pines starts to decline and their frost tolerance increases (Teskey *et al.* 1995, Hari and Mäkelä 2003, Mäkelä *et al.* 2004). The majority of the oldest

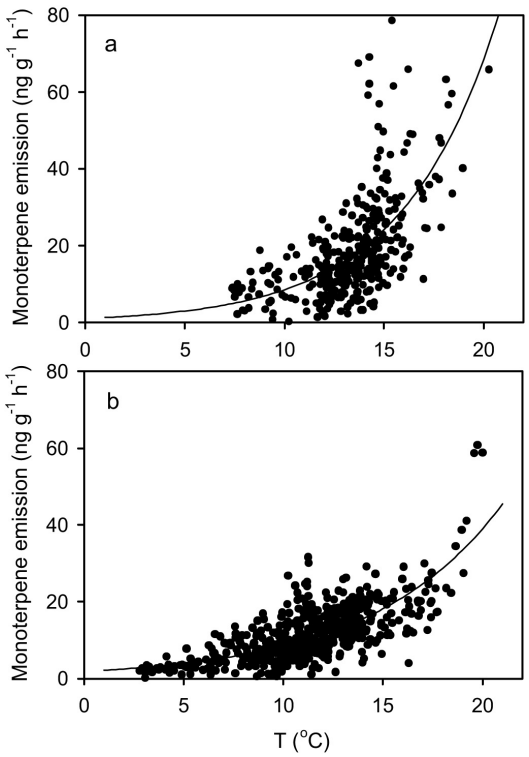

Fig. 7. Temperature regression of monoterpene emission, PTR-MS measurements from two shoot chambers, during (**a**) 25–31 August, (**b**) 10–18 September 2004. Lines indicate the exponential function fitted to the measured data, corresponding parameter values for the temperature regression were E_{30} = 548 ng g^{-1} h^{-1} and β = 0.208 °C^{-1} for 25 to 31 August, E_{30} = 181 ng g^{-1} h^{-1} and β = 0.153 °C^{-1} for 10 to 18 September 2004.

age class of needles is shed in September. These physiological changes may also involve changes in production, storage and emission of secondary compounds such as monoterpenes. Also, it has been hypothesized that during periods of low photosynthetic activity, terpenoid emissions may be related to photorespiratory processes providing substrates for their biosynthesis (Bäck *et al.* 2005).

According to Hakola *et al.* (2003) the highest total ambient air monoterpene concentrations in the boreal Scots pine stands are observed during summer. Nonetheless, the autumn concentrations of Δ^3-carene, camphene and limonene, are of the same order of magnitude than in the summer and that of α-pinene is even slightly higher (Hakola *et al.* 2003). The ambient air concentrations are not only affected by the emission rate but, also, by loss due to photochemistry and dilution by turbulent mixing. In addition to these phenomena influencing the atmospheric concentrations, the seasonal behavior of the monoterpene emission is affected by complex physicochemical controls of VOC emissions related to biological processes within needles (e.g. Niinemets *et al.* 2002). The standardized monoterpene emission potential of Scots pine has been observed to be highest during spring and early summer, and to increase again in the autumn (Tarvainen *et al.* 2005).

Monoterpene emissions from boreal conifer trees are traditionally modelled as a function of temperature (Tingey *et al.* 1980). The emission (E) can be calculated as

$$E = E_{30}\exp[\beta(T - T_{30})], \quad (4)$$

where E_{30} is the standardized emission rate at 30 °C, β is an empirical coefficient, T is the leaf temperature and T_{30} is the standardized leaf temperature (30 °C) (Guenther *et al.* 1993). The observed values for the β vary generally between 0.05 °C^{-1} and 0.2 °C^{-1} (e.g. Juuti *et al.* 1990, Guenther *et al.* 1991, Hakola *et al.* 1998, Janson and de Serves 2001, Komenda and Koppmann 2002, Tarvainen *et al.* 2005). Standardized monoterpene emission rates vary between branches of different age of the same tree (Komenda and Koppmann 2002), as well as between different seasons (Hakola *et al.* 1998, Janson and de Serves, 2001, Komenda and Koppmann 2002, Tarvainen *et al.* 2005). However, in emission models β is commonly taken to be constant with the value of 0.09 °C^{-1}.

During this late summer measurement campaign the relation of monoterpene emissions to the measured environmental variables was rather weak (data not shown). However, the observed temperature regression of the monoterpene emission, measured using the on-line chamber, followed Eq. 4, which supports the assumption that a majority of the monoterpene emissions originated from large persistent storage pools. As the emission seemed to behave differently before and after the low temperatures on 16 September 2004, we determined the temperature regression separately for these two periods. The value of the empirical β coefficient

was practically the same during both periods, β = 0.17 °C^{-1}, and was within the range of values reported in earlier studies (Fig. 7). However, we observed the monoterpene emission rate, standardized to 30 °C by the observed temperature coefficient, to increase from 7.2 μg g(dw)$^{-1}$ h^{-1} to 19.7 μg g(dw)$^{-1}$ h^{-1} after the cold night. The commonly used temperature coefficient β = 0.09 °C^{-1} led to normalized emission rates of 2.1 μg g(dw)$^{-1}$ h^{-1} and 4.4 μg g(dw)$^{-1}$ h^{-1} before and after the cold night, respectively. These values are in agreement with the reported normalized emission rates from the same site (Tarvainen *et al*. 2005). The increase in the monoterpene emission rate could have been due to the momentary contamination of the on-line chambers, or due to the beginning of the winter hardening period, as discussed above.

Conclusions

In this paper, we described a system for fast response measurements of Scots pine shoot monoterpene emission rates, plant physiological phenomena (CO_2 exchange and transpiration), exchange of other trace gases (NO_x, O_3), and environmental variables (PPFD, temperature and RH) by an on-line chamber system. With the system described we determined the monoterpene emission rates on a time scale of minutes with detection limit of about 0.15 ng m^{-2} s^{-1}. Clear diurnal patterns were revealed in the monoterpene emission rates, with maxima in the afternoons and minima at night. Adsorbent-tube samples taken at midday from a manual chamber and the simultaneous fast response PTR-MS measurements from on-line chambers resulted in comparable shoot emission rates. Emission rates per needle area, determined by the on-line chamber method and the manual chamber ranged from non detectable to 2.1 ng m^{-2} s^{-1} and from 0.06 to 1.27 ng m^{-2} s^{-1}, respectively.

Monoterpene emissions from Scots pine are also caused by stresses; mechanical damage of the shoot was observed to lead to an orders-of-magnitude increase in the monoterpene emissions. Also, the temperature dependent measurement artifacts revealed by the use of an empty reference chamber increase the uncertainty of the measured monoterpene emissions. This calls for the development of an algorithm for the correction of the chamber artifacts, as has been done for other trace gases.

The monoterpene emission rates during the measurement period were correlated with temperature but we did not observe a clear correlation with irradiance. The temperature coefficient (β) was 0.17 °C^{-1} for the measurement period. The determined normalized monoterpene emission rates were comparable to the values of previous studies and increased from 7.2 μg g(dw)$^{-1}$ h^{-1} to 19.7 μg g(dw)$^{-1}$ h^{-1} after a cold night.

Continuous simultaneous monitoring of CO_2 exchange and monoterpene emission provides a valuable tool for linking together the factors involved in monoterpene biosynthesis and their emissions as well as possible seasonal physiological regulation of the monoterpene emissions. The on-line, simultaneous recording of concentrations of monoterpenes and other trace gases, photosynthesis, together with shoot CO_2 uptake, changes in temperature, irradiation and humidity changes, can in the future be utilized in the development of mechanistic models describing the diurnal, seasonal and annual dynamics of BVOC emissions.

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References

Altimir N., Tuovinen J.-P., Vesala T., Kulmala M. & Hari P. 2004. Measurements of ozone removal by Scots pine shoots: calibration of a stomatal uptake model including the non-stomatal component. *Atmos. Environ.* 38: 2387–2398.

Altimir N., Vesala T., Keronen P., Kulmala M. & Hari P. 2002. Methodology for direct field measurements of ozone flux to foliage with shoot chambers. *Atmos. Environ.* 36: 19–29.

Atkinson R. 1994. Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Data, Monograph* 2: 1–216.

Bäck J., Hari P., Hakola H., Juurola E. & Kulmala M. 2005. Dynamics of monoterpene emissions in *Pinus sylvestris* during early spring. *Boreal Env. Res.* 10: 409–424.

Bertin N. & Staudt M. 1996. Effect of water stress on monoterpene emissions from young potted holm oak (*Quercus ilex* L.) trees. *Oecologia* 107: 456–462.

Chameides W.L., Fehsenfeld F., Rogers M., Cardelino C., Martinez J., Parrish D., Lonneman W., Lawson D.R., Rasmussen R.A., Zimmerman P., Greenberg J., Middleton P. & Wang T. 1992. Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res.* 97: 6037–6055.

Fehsenfeld F., Calvert J., Fall R., Goldan P., Guenther A., Hewitt N., Lamb B., Liu S., Trainer M., Westberg H. & Zimmerman P. 1992. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Global Biogeochemical Cycles* 6: 389–430.

Grabmer W., Graus M., Lindinger C., Whisthaler A., Rappenglück B., Steinbrecher R. & Hansel A. 2004. Disjunct eddy covariance measurements of monoterpene fluxes from a Norway spruce forest using PTR-MS. *Int. J. Mass Spectrom.* 239: 111–115.

Guenther A. 2002. The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems. *Chemosphere* 49: 837–844.

Guenther A., Zimmerman P.R., Harley P.C., Monson R.K. & Fall R. 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *J. Geophys. Res.* 98: 12609–12617.

Guenther A.B., Monson R.K. & Fall R. 1991. Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. *J. Geophys. Res.* 96: 10799–10808.

Hakola H., Rinne J. & Laurila T. 1998. Hydrocarbon emission rates of tea-leafed willow (*Salix phylicifolia*), Silver birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmos. Environ.* 32: 1825–1833.

Hakola H., Laurila T., Lindfors V., Hellén H., Gaman A. & Rinne J. 2001. Variation of the VOC emission rates of birch species during the growing season. *Boreal Env. Res.* 6: 237–249.

Hakola H., Tarvainen V., Laurila L., Hiltunen V., Hellén H. & Keronen P. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* 37: 1623–1634.

Hansel A., Jordan A., Warnike C., Holzinger R. & Lindinger W. 1998. Improved detection limit of the proton-transfer reaction mass spectrometer: on-line monitoring of volatile organic compounds at mixing ratios of few pptv. *Rapid Commun. Mass Spectrom.* 173: 191–241.

Hari P. & Kulmala M. 2005. Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II). *Boreal Env. Res.* 10: 315–322.

Hari P. & Mäkelä A. 2003. Annual pattern of photosynthesis in Scots pine in the boreal zone. *Tree Physiol.* 23: 145–155.

Hari P., Raivonen M., Vesala T., Munger J.W., Pilegaard K. & Kulmala M. 2003. Ultraviolet light and leaf emission of NO_x. *Nature* 422: 134.

Hari P., Keronen P., Bäck J., Altimir N., Linkosalo T., Pohja T., Kulmala M. & Vesala T. 1999. An improvement of the method for calibrating measurements of photosynthetic CO_2 flux. *Plant, Cell and Environment* 22: 1297–1301.

Hayward S., Tani A., Owen S. & Hewitt N. 2004. Online analysis of volatile organic compound emissions from sitka spruce (*Picea sitchensis*). *Tree Physiology* 24: 721–728.

Helmig D., Revermann T., Pollmann J., Kaltschmidt O., Hernandez A.J., Bocquet F. & David D. 2003. Calibration system and analytical considerations for quantitative sesquiterpene measurements in air. *J. Chromatogr. A* 1002(1–2): 193–211.

Isidorov V.A., Zenkevich I.G. & Ioffe B.V. 1985. Volatile organic compounds in the atmosphere of forests. *Atmos. Environ.* 19: 1–8.

Janson R.W. 1993. Monoterpene emissions from Scots pine and Norwegian spruce. *J. Geophys. Res.* 98: 2839–2850.

Janson R. & de Serves C. 2001. Acetone and monoterpene emissions from the boreal forest in northern Europe. *Atmos. Environ.* 35: 4629–4637.

Juuti S., Arey J. & Atkinson R. 1990. Monoterpene emission rate measurements from a Monterey pine. *J. Geophys. Res.* 95: 7515–7519.

Karl T., Guenther A., Lindinger C., Jordan A., Fall R. & Lindinger W. 2001. Eddy covariance measurements of oxygenated volatile organic compound fluxes from crop harvesting using a redesigned proton-transfer-reaction mass spectrometer. *J. Geophys. Res.* 106: 24157–24167.

Kesselmeier J., Ciccioli P., Kuhn U., Stefani P., Biesenthal T., Rottenberger S., Wolf A., Vitullo M., Valentini R., Nobre A., Kabat P. & Andreae M.O. 2002. Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget. *Global Biogeochemical Cycles* 16(4), 1126, doi:10.1029/2001GB001813.

Kolari P., Keronen P. & Hari P. 2004. The accuracy of transpiration measurements with a dynamic cuvette system. *Report Series in Aerosol Science* 68: 112–114.

Komenda M. & Koppmann R. 2002. Monoterpene emissions from Scots pine (*Pinus sylvestris*): field studies of emission rate variabilities. *J. Geophys. Res.* 107(D13), 4161, doi:10.1029/2001JD000691.

Kulmala M., Suni T., Lehtinen K.E.J., Dal Maso M., Boy M., Reissell A., Rannik Ü, Aalto P., Keronen P., Hakola H., Bäck J., Hoffmann T., Vesala T. & Hari H. 2004. A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.* 4: 557–562.

Lee A., Schade G.W., Holzinger R. & Goldstein A.H. 2005. A comparison of new measurements of total monoterpene flux with improved measurements of speciated monoterpene flux. *Atmos. Chem. Phys.* 5: 505–513.

Lindinger W., Hansel A. & Jordan A. 1998. On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) — medical applications, food control and environmental research. *Int. J. Mass Spectrom.* 173(3): 191–241.

Loreto F., Ciccioli P., Cecinato A., Brancaleoni E., Frattoni M. & Tricoli D. 1996. Influence of environmental factors and air composition on the emission of α-pinene from *Quercus ilex* leaves. *Plant Physiology* 110: 267–275.

Mäkelä A., Hari P., Berninger F., Hänninen H. & Nikinmaa

E. 2004. Acclimation of photosynthetic capacity in Scots pine to the annual cycle of temperature. *Tree Physiol.* 24: 369–376.

Niinemets Ü., Hauff K., Bertin N., Tenhunen J.D., Steinbrecher R. & Seufert G. 2002. Monoterpene emissions in relation to foliar photosynthetic and structural variables in Mediterranean evergreen *Quercus* species. *New Phytologist* 153: 243–256.

Raivonen M., Keronen P., Vesala T., Kulmala M. & Hari P. 2003. Measuring shoot-level NO_x flux in field conditions: the role of blank chambers. *Boreal Env. Res.* 8: 445–455.

Rinne H.J.I., Guenther A.B., Warneke C., de Gouw J.A. & Luxembourg S.L. 2001. Disjunct eddy covariance technique for trace gas flux measurements. *Geophys. Res. Lett.* 28: 3139–3142.

Rinne J., Hakola H. & Laurila T. 1999. Vertical fluxes of monoterpenes above a Scots pine stand in the boreal vegetation zone. *Phys. Chem. Earth (B)* 24: 711–715.

Rinne J., Hakola H., Laurila T. & Rannik Ü. 2000. Canopy scale monoterpene emissions of *Pinus sylvestris* dominated forests. *Atmos. Environ.* 34: 1099–1107.

Rinne J., Ruuskanen T.M., Reissell A., Taipale R., Hakola H. & Kulmala M. 2005. On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem. *Boreal Env. Res.* 10: 425–436.

Schuh G., Heiden A.C., Hoffmann T.H., Kahl J., Rockel P., Rudolph J. & Wildt J. 1997. Emissions of volatile organic compounds from sunflower and beech: dependence on temperature and light intensity. *J. Atmos. Chem.* 27: 291–318.

Shao M., Czapiewski K.V., Heiden A.C., Kobel K., Komenda M., Koppman R. & Wilt J. 2001. Volatile organic compound emissions from Scots pine: mechanism and description by algorithms. *J. Geophys Res.* 106: 20483–20491.

Sharkey T.D., Singsaas E.L., Vanderveer P.J. & Geron C.D. 1996. Field measurements of isoprene emission from trees in response to temperature and light. *Tree Physiology* 16: 649–654.

Spirig C., Neftel A., Ammann C., Dommen J., Grabmer W., Thielmann A., Schaub A., Beauchamp J., Whisthaler A. & Hansel A. 2005. Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry. *Atmos. Chem. Phys.* 5: 465–481.

Staudt M., Joffre R. & Rambal S. 2003. How growth conditions affect the capacity of *Quercus ilex* leaves to emit monoterpenes. *New Phytologist* 158: 61–73.

Staudt M., Bertin N., Frenzel B. & Seufert G. 2000. Seasonal variation in amount and composition of monoterpenes emitted by young *Pinus pinea* trees — implications for emission modeling. *J. Atmos. Chem.* 35: 77–99.

Tani A., Hayward S. & Hewitt C.N. 2003. Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS). *Int. J. Mass Spectrom.* 223: 561–578.

Tarvainen V., Hakola H., Hellén H., Bäck J., Hari P. & Kulmala M. 2005. Temperature and light dependence of the VOC emissions of Scots pine. *Atmos. Chem. Phys.* 5: 989–998.

Teskey R.O., Sheriff D.W., Hollinger D.Y. & Thomas R.B. 1995. External and internal factors regulating photosynthesis. In: Smith W.K. & Hinckley T.M. (eds.), *Resource physiology of conifers*, *Phys. Ecol. Series*, Academic Press, London, pp. 105–139.

Tingey D.T., Manning M., Grothaus L.C. & Burns W.F. 1980. Influence of light and temperature on monoterpene emission rates from slash pine. *Plant Physiology* 65: 797–801.

Vesala T., Haataja J., Aalto P., Altimir N., Buzorius G., Keronen P., Lahti T., Markkanen T., Mäkelä J.M., Nikinmaa E., Palmroth S., Palva L., Pohja T., Pumpanen J., Rannik Ü., Siivola E., Ylitalo H., Hari P. & Kulmala M. 1998. Long-term field measurements of atmosphere–surface interactions in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry. *Trends in Heat, Mass and Momentum Transfer* 4: 17–35.

Warneke C., Luxembourg S.L., de Gouw J.A., Rinne H.J.I., Guenther A.B. & Fall R. 2002. Disjunct eddy covariance measurements of oxygenated volatile organic compound fluxes from an alfalfa field before and after cutting. *J. Geophys. Res.* 107(D8), doi:10.1029/2001JD000594.

Wildt J., Kley D., Rockel P. & Segschneider H.J. 1997. Emission of NO from several higher plant species. *J. Geophys Res.* 102: 5919–5928.

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