

On-line field measurements of BVOC emissions from Norway spruce (*Picea abies*) at the hemiboreal SMEAR-Estonia site under autumn conditions

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We investigated biogenic volatile organic compound (BVOC) emissions from a Norway spruce (*Picea abies*) in a hemiboreal mixed forest in autumn. Measurements were performed at the SMEAR-Estonia forest station, using PTR-MS techniques and a dynamic branch enclosure system. Parallel to BVOC measurements, atmospheric (CO₂, CH₄, H₂O, CO) and meteorological (temperature, relative humidity, global radiation, wind speed, precipitation) parameters were monitored in the ambient atmosphere and inside the enclosure (temperature, relative humidity, ozone). Prior to the measuring period, a new inlet line consisting of 19.4 m of heated and isolated glass tube was constructed. The new inlet system allowed the on-line detection and calculation of sesquiterpene (SQT) emission rates for the first time for a hemiboreal forest site. In total, 12 atmospherically relevant BVOCs were continuously monitored during the measurement campaign and the emission rates of terpenoid species and predominant oxygenated VOCs were estimated, with monoterpenes to be emitted the most, followed by acetone, acetaldehyde and sesquiterpenes.

Introduction

Plants emit a variety of different volatile organic compounds (VOCs) into the atmosphere, which comprise a substantial fraction of assimilated carbon released as VOCs (Peñuelas and Llusà 2003). Comparing biogenic and anthropogenic contributions, the natural emissions from vegetation is by far the largest source of VOCs exceeding the anthropogenic ones by almost an order of magnitude (Guenther *et al.* 1995, Goldstein and

Galbally 2007). Biogenic VOCs that are emitted by plants are involved in processes associated with life, such as plant growth, development, reproduction and defense (Kesselmeier and Staudt 1999, Peñuelas and Staudt 2010). They also function as communication signals among plants and plant communities as well as between plants and insects (Engelberth *et al.* 2004, Gershenson 2007, Laothawornkitkul *et al.* 2008).

The boreal and hemiboreal regions are covered by a large amount of conifers, which are

expected to contribute substantially to the global budget of biogenic VOC release. Most of biogenic emission studies are focusing on terpenoids, which comprise a large and diverse class of naturally emitted VOCs, derived from five-carbon isoprene units assembled and modified in thousands of different ways (Lichtenthaler *et al.* 1997). Because of their volatility and faster productivity, isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) are the major terpenoids emitted from the biosphere. These compounds play a vital role in tropospheric chemistry by affecting its oxidative capacity (Fuentes *et al.* 2000) and by contributing to secondary aerosol formation (Hoffmann *et al.* 1997, Andreae and Crutzen 1997, Bonn and Moortgat 2003, Bonn *et al.* 2004, 2009, Kulmala *et al.* 2004, Hallquist *et al.* 2009). In addition to terpenoids, plant emissions also include a cocktail of alkanes, alkenes, carbonyls, alcohols and acids (Kesselmeier and Staudt 1999). Short-chained oxygenated VOCs (oxVOC) such as formaldehyde, acetaldehyde, methanol, ethanol and acetone are characterized by longer atmospheric lifetimes and they affect the tropospheric chemistry for long, i.e. in the region of emission as well as in geographical areas far from their place of origin (Seco *et al.* 2007). However, their emission pathways and biological benefits are complex and still under discussion (Steiner and Goldstein 2007). In addition, stress responses of different plant species and resulting emissions differ. Hence, more emission measurements from different ecosystems are required in order to better understand their role in biosphere–atmosphere interactions and this study aims to focus on that.

Biogenic VOC emissions are controlled by both biotic and abiotic factors, such as the circadian clock, temperature, global radiation, atmospheric CO_2 concentrations, drought, air pollution (O_3) and mechanical injuries (Loreto and Schnitzler 2010). Nevertheless, the emissions are usually modeled using temperature only or temperature- and light-dependent algorithms (e.g. Guenther *et al.* 1995) despite the obvious need to include more biological realism in emission models (Niinemets *et al.* 2010). The established algorithms that have been applied in numerous emission studies are usually consistent with the measured emissions, providing the possibility

for comparisons between different ecosystems and tree species.

In this context, the hemiboreal zone ecosystems — characterized by mixed stands with both coniferous and deciduous trees, adapted to more moderate conditions than present in boreal environments — are of special interest as they are located in the transition zone between boreal and temperate forests. In the initial stages of succession, deciduous trees are dominating but in later stages they are gradually replaced by conifers (Noe *et al.* 2011). According to the ORCHIDEE model (Lathiere *et al.* 2005), future biogenic emissions from European areas would increase due to the expansion of temperate and boreal forests into new areas.

This study is the first attempt to quantify biogenic VOC emissions from a Norway spruce in a hemiboreal forest in Estonia by using on-line proton-transfer-reaction mass spectroscopy (PTR-MS; Lindinger *et al.* 1998), gas-chromatography mass spectrometry (GC-MS) and dynamic branch-enclosure (Bourtsoukidis *et al.* 2012) techniques. It uses the approach of Bourtsoukidis *et al.* (2012) with heated sampling lines made of glass in order to minimize adsorption and chemical reactions. This setup enabled us to quantify emission rates of 12 atmospherically relevant VOCs, among which are sesquiterpenes, extremely reactive compounds that have very short atmospheric lifetimes and are very difficult to detect (Duhl *et al.* 2008). Overall, we contribute to the global emission dataset by estimating average emission rates, emission potentials and temperature dependencies for several VOCs and by presenting atmospheric composition of critical gases in the atmosphere under autumn conditions.

Material and methods

Site description

The measurements were conducted at the SMEAR-Estonia experimental forest station, located in Järvelja in southeastern Estonia ($58^{\circ}16'N$, $27^{\circ}16'E$). The surrounding mixed forest belongs to the hemiboreal zone with moderately cool and moist climate and can be char-

acterised as remote and rural with low anthropogenic disturbances (Noe *et al.* 2011). While Norway spruce (*Picea abies*) is the dominant tree species, the stand structure is fairly complex. Co-dominant species such as silver birch (*Betula pendula*) and black alder (*Alnus glutinosa*) are responsible for the upper canopy layer emissions (16–20 m), while the presence of the suppressed tree layer receiving a smaller quantity of sunlight at the lower canopy (6–7 m) affects turbulent flows and fluxes within the forest (Noe *et al.* 2012).

Basic measurements

During an intensive three-week measurement campaign (26 September to 17 October 2012), environmental and meteorological parameters were continuously monitored at the Järvselja mixed forest station. Carbon dioxide (CO₂), methane (CH₄), water vapour (H₂O) and carbon monoxide (CO) were measured using a cavity ringdown spectroscopy analyser (Picarro G2301, Picarro Inc., Santa Clara, CA, USA) at 20 m representing the canopy-top conditions. Ambient air was sampled by two separate lines, one (made of Teflon®) for the standard gases (i.e. CO₂, CH₄, CO, H₂O) less affected by adsorption, and one (made of glass) for organics and ozone. For the standard gases, ambient air was drawn from a 35-meter Teflon® tube at 20 l min⁻¹. The sample flow through the PTR-MS and O₃ analyzers was diverted from the glass line and maintained at 0.4 l min⁻¹. The ozone trace gas analyser (Model 49i, Thermo Scientific, Franklin, MA, USA) used air from the glass line sampled at 1.5 l min⁻¹ applying a UV photometric method.

Solar radiation was measured using a pyranometer (SPLite, Kipp & Zonen, Delft, Netherlands) and a photosynthetic active radiation (PAR) sensor (LI190, LiCor Biosciences, Lincoln, NE, USA). Atmospheric pressure was measured by a digital barometer (Vaisala PTB330, Vaisala Oy, Helsinki, Finland). Wind speed was measured at 21-m height using a 3D sonic anemometer (CSAT3, Campbell Scientific, Logan, UT, USA). Precipitation was measured using a tipping bucket rain gauge (TR-4, Texas Electronics, Dallas, TX, USA).

Dynamic enclosure

In order to obtain VOC emission rates, a dynamic gas exchange enclosure (Bourtsoukidis *et al.* 2012) was installed on a healthy Norway spruce branch 16 m above ground. Prior to the measurement period, a new inlet line consisting of 19.4 m of heated ($T = 70\text{ }^{\circ}\text{C}$) and isolated glass tube (3 mm inner diameter) was constructed. Temperature (T) and relative humidity (RH) were continuously monitored inside the enclosure with a temperature-humidity sensor (Hobo U23-002 Pro v2, Onset data loggers, Germany), while ozone (O₃) mixing ratios were monitored using a dual-cell, UV photometric gas analyzer (model 49i, Thermo scientific, Franklin, MA, USA) and used for chemical loss corrections.

The automated cylindrical glass enclosure (15 l) remained open for most of the time to establish accurate ambient conditions for the branch enclosed and a minimum of artificial stress. The closing/opening times were 6/24 minutes, resulting in two emission rate measurements per hour and 48 per day. During one closure, 2.6 l min⁻¹ of air was transported down to the instruments. It was replaced by ambient air drawn from a leak at the branch passage into the enclosure in order to avoid under-pressure (Ruuskanen *et al.* 2005).

Temperature, relative humidity, ozone and volatile organic compound (e.g. monoterpenes) mixing ratios were continuously monitored inside the enclosure (*see* Fig. 1). During the closing period, the temperature rose on average by $1.6 \pm 0.8\text{ }^{\circ}\text{C}$ (mean \pm SD) and RH decreased by $1.5\% \pm 1.4\%$. O₃ mixing ratios decreased by $2.5 \pm 1.5\text{ ppb}_v$, due to reactions with the emitted VOCs and uptake by the needles. After opening the enclosure, the VOC and O₃ mixing ratios instantaneously reached the normal values, while temperature and RH needed at least 8 min to return to normal.

On 15 October, we chose to reverse the closing/opening times (24 min closed/6 min open) in order to find out if it affects the measurements. During this reverse operation period, the temperature inside the enclosure increased by $3.3 \pm 0.6\text{ }^{\circ}\text{C}$ compared with the ambient. Nevertheless, the measured emissions were similar to the ones measured earlier in the same temperature

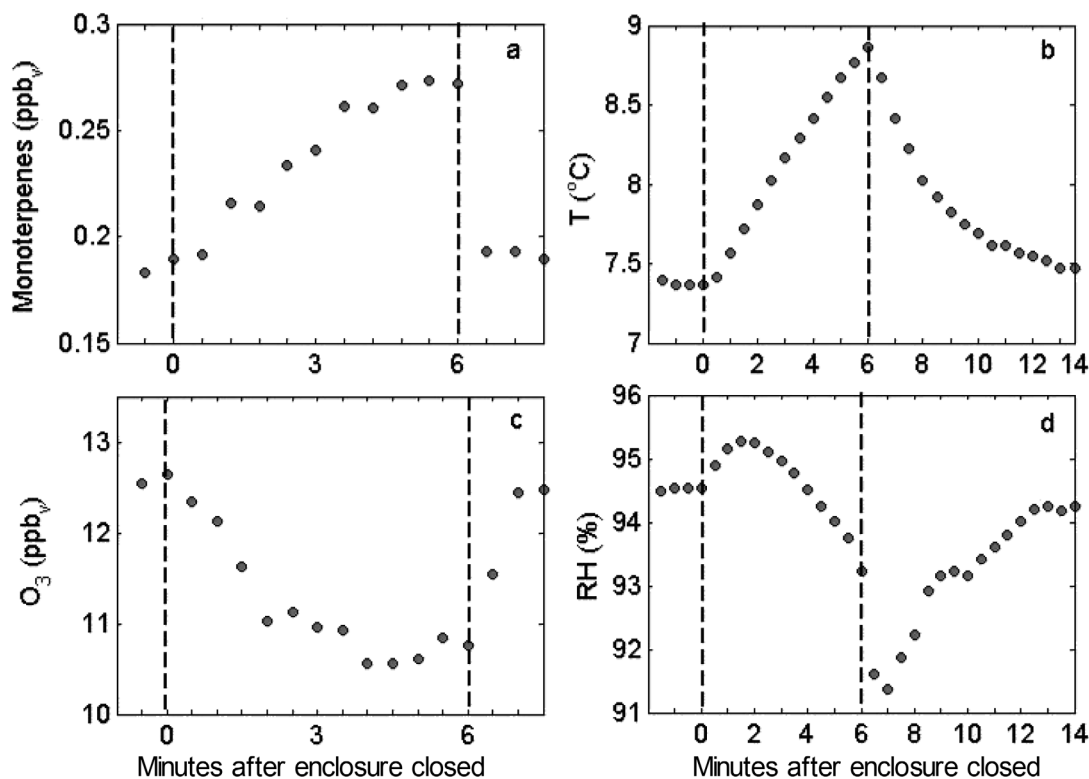


Fig. 1. Parameters measured inside the dynamic branch-enclosure and their behavior during a single closing cycle. Monoterpene mixing ratios (a) were raising until a steady-state was achieved. Temperature (b) was increasing, while ozone mixing ratios (c) were reduced due to reactions and uptake by the plant. Relative humidity (d) initially rose due to evaporation but later decreased due to temperature differences with the ambient environment.

range, hence prolonged closing time did not affect the results.

PTR-MS and GC-MS measurements

On-line VOC measurements were conducted using a commercial high sensitivity PTR-MS (Ionicon GmbH, Austria). Detailed description of the technique can be found in Lindinger *et al.* (1998), Blake *et al.* (2009) and references therein.

PTR-MS was operated under standard conditions with the drift-tube voltage and pressure adjusted to 600 V and 2.3 mbar, respectively. Optimization of the instrument resulted in a high and sustained primary ion signal ($[H_3O^+] = (4 \text{ to } 8) \times 10^7 \text{ cps}$), which enhanced the sensitivity of the measurements. The compounds that were continuously monitored during a PTR-MS

cycle of 36 s (and their protonated masses) were: formaldehyde ($m/z = 31$), methanol ($m/z = 33$), acetaldehyde ($m/z = 45$), ethanol and formic acid ($m/z = 47$), acetone ($m/z = 59$), isoprene ($m/z = 69$), methyl ethyl ketone (MEK, $m/z = 73$), main MT fragment ($m/z = 81$), total MT ($m/z = 137$), main SQT fragment ($m/z = 149$), methyl-salicylate (MeSA, $m/z = 153$), linalool ($m/z = 155$), pinonaldehyde ($m/z = 169$) and total SQT ($m/z = 205$). We considered mass 69 to correspond only to isoprene. However, other aldehydes and ketones that are detected at the same mass (Fall *et al.* 2001, Waneke *et al.* 2003) add some uncertainty to the monitored mixing ratios. Calibrations of the PTR-MS instrument were performed prior to the measuring period with a gas standard containing formaldehyde, methanol, acetaldehyde, ethanol, acetone, isoprene and α -pinene (L4763, Ionimed analytic GmbH, Austria), while SQTs were calibrated using a permeation oven tech-

nique and a β -caryophyllene standard (W225207, Sigma-Aldrich, Inc.). Analytical fragmentation pattern were either derived experimentally or calculated according to the literature (Dhooghe *et al.* 2008, Kim *et al.* 2009, Demarcke *et al.* 2009). Additionally, tubing losses were quantified prior to the field campaign in laboratory tests and were extrapolated to the used length. Further information about the calibrations, the fragmentation pattern and the tubing losses can be found in Bourtsoukidis *et al.* (2012).

Supplementary gas-chromatography mass spectrometry (GC-MS) samples were collected from closed enclosure and from ambient air at the same height of 16 m with the aim to quantify individual and relative MT contributions. To adsorb the monoterpenes, multibed stainless steel cartridges (10.5 cm length, 3 cm inner diameter, Supelco, Bellefonte, USA) were used. These were filled with Carbotrap C 20/40 mesh (0.2 g), Carbopack C 40/60 mesh (0.1 g) and Carbotrap X 20/40 mesh (0.1 g) adsorbents (Supelco, Bellefonte, USA). The sampling took 30 min with a flow of 200 ml min⁻¹ yielding 6 l of air passing the adsorbent mesh. Subsequent GC-MS analysis was conducted using an automated cartridge desorber system (Shimadzu TD20) connected to the GC-MS system (Shimadzu 2010 Plus, Shimadzu Corporation, Kyoto, Japan) (for details see Copolovici *et al.* 2009, Toome *et al.* 2010).

Emission rate calculations

In general, a compound is assumed to be emitted if its mixing ratio increases when the enclosure is closed. This system may include chemical production of oxygenated species (oxVOC) and therefore emission needs to be treated as a sum of two processes, i.e. release and chemical gas-phase production. On the other hand, when the mixing ratio of the respective compound decreases when the enclosure is closed, we may attribute this behavior to deposition, plant uptake or chemical destruction. Here, we considered the emissions (i.e. the positive values) only when the difference between maximum and minimum values was higher than the standard deviation of the scattering signal when measuring stable

known concentrations in the laboratory.

Emission rate calculations were performed as described in Bourtsoukidis *et al.* (2012). In summary, the data measured during a closing period were corrected for ozone reactions, dilution with ambient air mixing ratios and deposition to enclosure's walls. The reaction rate constants were obtained from the literature (Atkinson and Arey 2003, Bouvier-Brown *et al.* 2009a) or, in case of MT, calculated from the individual composition derived from GC-MS measurements ($k_{\text{MT}+\text{O}_3} = 6.1 \times 10^{-17} \pm 1.5 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹). For SQT and since the quantification of the individual contributions could not be obtained from the GC-MS samples taken, we used the average ecosystem SQT reaction rate constant ($k_{\text{SQT}+\text{O}_3} = 3.3 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹; Bouvier-Brown *et al.* 2009b), whose uncertainty may be notable (close to 100%). However during the measurements, the O₃ values were quite small and the total uncertainty was found to be smaller than that for e.g. central Europe (Bourtsoukidis *et al.* 2012).

With respect to the corrections applied, dilution ($k_{\text{dil}} = 2.9 \times 10^{-3} \pm 0.2 \times 10^{-3}$ s⁻¹) was the dominant correction factor for the majority of the compounds measured, with a minor impact of dry deposition ($k_{\text{dep}} = 2.6 \times 10^{-5} \pm 0.2 \times 10^{-5}$ s⁻¹) on the monitored mixing ratios. In the case of SQT however, due to its highly reactive nature, the reactions with ambient O₃ were the main loss factor which should always be considered when measuring SQT in enclosure systems.

To calculate emissions rates, we applied the aforementioned corrections to the mass balance equation:

$$E = \frac{F}{B} \left[C_2 \exp \left(k_{\text{dil}} + k_{\text{VOC}} [\text{O}_3] + k_{\text{dep}} \right) \times t - C_1 \right] \quad (1)$$

where F is the total flow rate through the chamber, C_1 is the concentration at the last measurement interval before the enclosure closes, and C_2 is the last measurement conducted when the enclosure is closed. The outcome is corrected for dilution (k_{dil}), ozone reaction losses ($k_{\text{VOC}} \times [\text{O}_3]$) and dry deposition on the enclosure walls (k_{dep}). The time t is the closing period, while B is the total dry needle biomass of the enclosed branch ($B = 6.5 \pm 0.2$ g) which was determined by cutting the branch after the measurements and

drying the needles for a week at 70 °C in a temperature-controlled oven, until constant weight was achieved. All the emission data during the first diurnal cycle were excluded in order to avoid excess emissions due to mechanical stress that was applied when mounting the enclosure to the selected branch. We should note that the stepwise approach used in Bourtsoukidis *et al.* (2012) might overestimate the calculated emission rates for less reactive conditions and compounds. Therefore, Eq. 1 is an improved and updated version that should be used in emission rate calculations, since it reduces the uncertainty range and produces less scattering in the lowest values.

Results

Atmospheric conditions

During the entire measurement period, the ambient temperature (mean \pm SD) at the measuring height (T_{16m}) was 10.1 ± 4.1 °C (range = 0.5–19.5 °C). Detailed temperature data for the site can be found in Noe *et al.* (2012). The relative humidity ($89.5\% \pm 6.8\%$) ranged from 66.7% to 100%. The wind speed was 1.1 ± 0.7 m s⁻¹. Westerly winds dominated during the first week of the experiment, then the wind direction changed to southerly. During the last four days of the experiment, northern winds prevailed. The precipitation at the site was 0.13 ± 0.08 mm, and the atmospheric pressure 1002.4 ± 6.9 hPa. It was a period with rather constant but weak rainfalls. During the experiment, the radiation was already low (75 ± 45 W m⁻²), and PAR equalled 142 ± 85 μ mol m⁻² s⁻¹, with the daytime maximum around 440 μ mol m⁻² s⁻¹. Cloudy weather prevailed during most of the days.

Carbon dioxide (CO₂), methane (CH₄), water vapor (H₂O) and carbon monoxide (CO) mixing ratios were continuously monitored at the top of the canopy (20 m; Fig. 2). The following ambient mixing ratios (mean \pm SD) were recorded: CO₂ 404 ± 13.6 ppm_v (range = 382.2–473.6 ppm_v), CH₄ 1.92 ± 0.03 ppm_v (range = 1.88–2.03 ppm_v), CO 0.13 ± 0.02 ppm_v (range = 0.11–0.18 ppm_v), and H₂O $0.99\% \pm 0.16\%$ (range = 0.59%–1.36%). Mixing ratios of these compounds

showed a distinct diurnal patterns (Fig. 3). Mixing ratios of CO₂ and CH₄ peaked during the night and decreased during the morning hours (~09:00). This decrease can be attributed to the biological activity of the forest (uptake by vegetation), and to the enhanced boundary layer vertical mixing during the daytime. The mixing ratio of CO was also reduced during the daytime but this reduction occurred around noon. Since CO is not used by vegetation but depends on atmospheric oxidation processes, we can conclude that this reduction was only due to atmospheric mixing and chemistry, i.e. its production was great during the morning hours while OH production and subsequent chemical loss of CO dominated around noon and later during the day. The only compound that was clearly increasing during the day was water vapour. This can be explained by plant transpiration, which is known to be elevated at higher daytime temperatures (Jasechko *et al.* 2013).

Emission of VOC

Emission rates of 12 atmospherically relevant BVOC were measured during the experiment (Table 1). In the reactive isoprenoid class, monoterpenes were the most emitted compounds, followed by sesquiterpenes and isoprene. Monoterpene emissions were almost eight times higher than those of sesquiterpenes and more than fourteen times higher than those of isoprene. Emissions of the lowest oxygenated compounds (oxVOC) were also quantified: higher values were recorded for acetone and lower for pinonaldehyde/limonaldehyde/phellandronaldehyde/caronaldehyde ($m/z = 169$) formed from the oxidation of endocyclic monoterpenes α -pinene, limonene, β -phellandrene and Δ^3 -carene.

Clear diurnal patterns were found for monoterpenes, sesquiterpenes, isoprene, ethanol + formic acid, acetaldehyde and acetone. Monoterpene emission rates peaked during the afternoon hours (13:00–15:00) and started to decrease thereafter, while sesquiterpenes rose earlier and developed a plateau until the late evening (Fig. 4). Ambient conditions during the entire measurement period varied (Fig. 5). While the first days were warm ($T > 10$ °C) with small

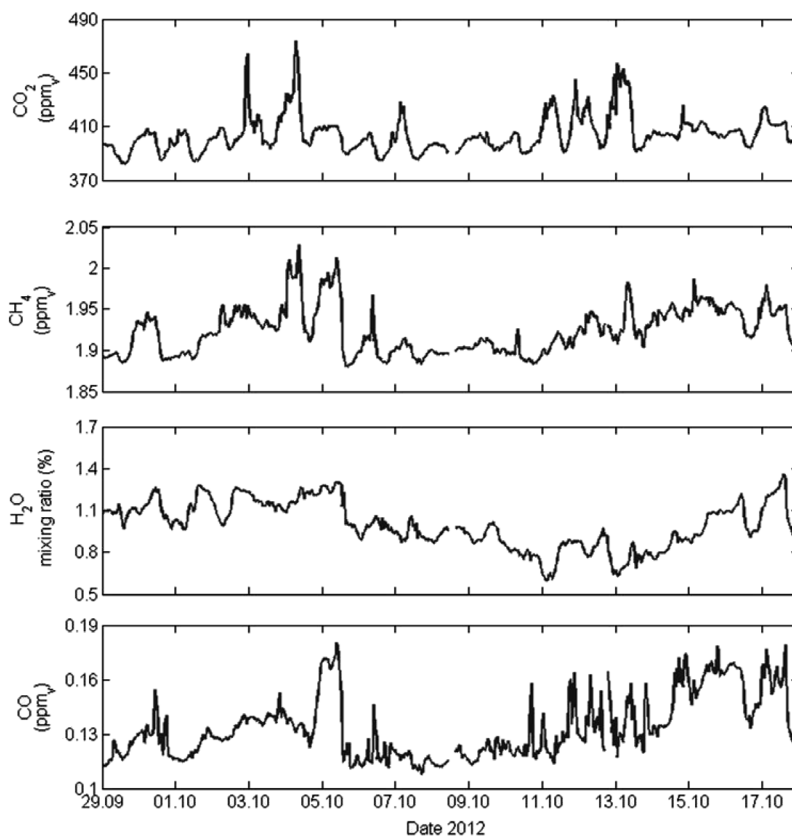


Fig. 2. Carbon dioxide (CO_2), methane (CH_4), water vapor (H_2O) and carbon monoxide (CO) mixing ratios during the campaign period. The measurements were conducted at the top of the canopy at 20 m.

ozone mixing ratios and highest VOC exchange rates, low temperatures even close to frost conditions at night were common after 10 October. This evidently affected the biogenic activity, i.e. the exchange rates such as the emission of monoterpenes.

Acetone and acetaldehyde showed a similar pattern to monoterpenes, however, a more steep decrease after the sunset especially in the case of acetaldehyde was found. This can be explained by atmospheric oxidation of terpenes as precursors for acetone and acetaldehyde. An emission burst during the first daytime hours was measured for the sum of ethanol and formic acid. During the first days of the campaign, the high ambient temperature differences between day and night resulted in a more distinct diurnal pattern.

When quantifying monoterpene emissions, it is important to know their individual composition, since different monoterpenes behave in a different manner with respect to atmospheric oxidation loss inside the enclosure when

it is closed. However, one should be aware of the chemodiversity of a forest as found by Bäck *et al.* (2012) for a Scots pine stand in Finland. In

Table 1. Mean emission rates (E_{mean} , $\text{ng g}_{\text{dw, needles}}^{-1} \text{s}^{-1}$) of the 12 oxVOC compounds from a Norway spruce measured in the closed enclosure.

Compound	$m/z = M_w + 1$ (g mole^{-1})	E_{mean} ($\text{ng g}_{\text{dw, needles}}^{-1} \text{s}^{-1}$)
Formaldehyde	31	5.1 ± 4.7
Methanol	33	9.7 ± 8.9
Acetaldehyde	45	13.7 ± 11.5
Ethanol + formic acid	47	9.9 ± 8.6
Acetone	59	27.6 ± 22.2
Isoprene	69	6.5 ± 5.2
Methyl ethyl ketone	73	2.6 ± 2.2
Methyl salicylate	153	5.9 ± 5.6
Linalool	155	4.1 ± 3.6
Pinonaldehyde/ caronaldehyde	169	3.7 ± 3.1
Total MT	139	93.2 ± 51.6
Total SQT	205	11.8 ± 8.3

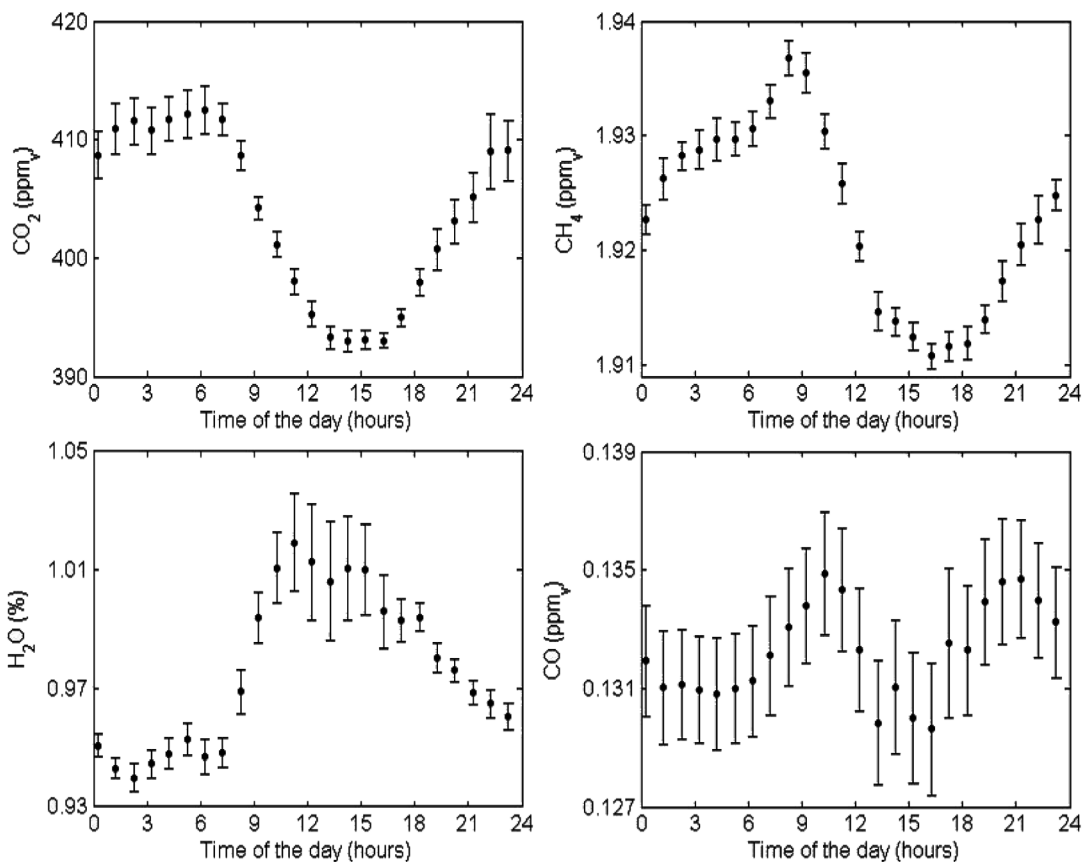


Fig. 3. Diurnal cycles of carbon dioxide (CO₂), methane (CH₄), water vapor (H₂O) and carbon monoxide (CO) during the campaign period.

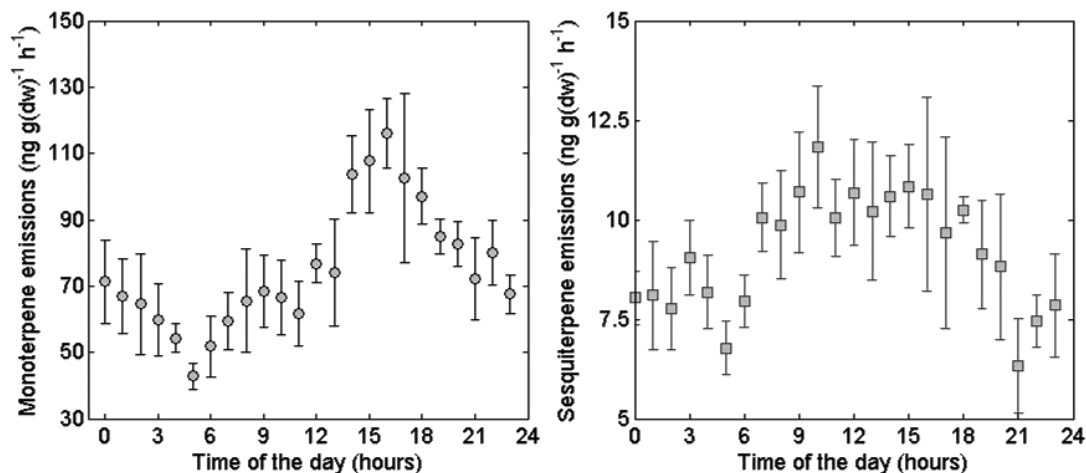


Fig. 4. Diurnal patterns of monoterpene (left) and sesquiterpene (right) emission rates during the campaign period.

effect, contrary to the entire terpene emission, the terpene composition might change remarkably among trees. We used GC-MS in order to determine relative monoterpene contributions, in the

closed enclosure (Table 2). The compound that contributed the most to the monoterpene emissions by the Norway spruce branch was α -pinene followed by Δ^3 -carene. In order to distinguish

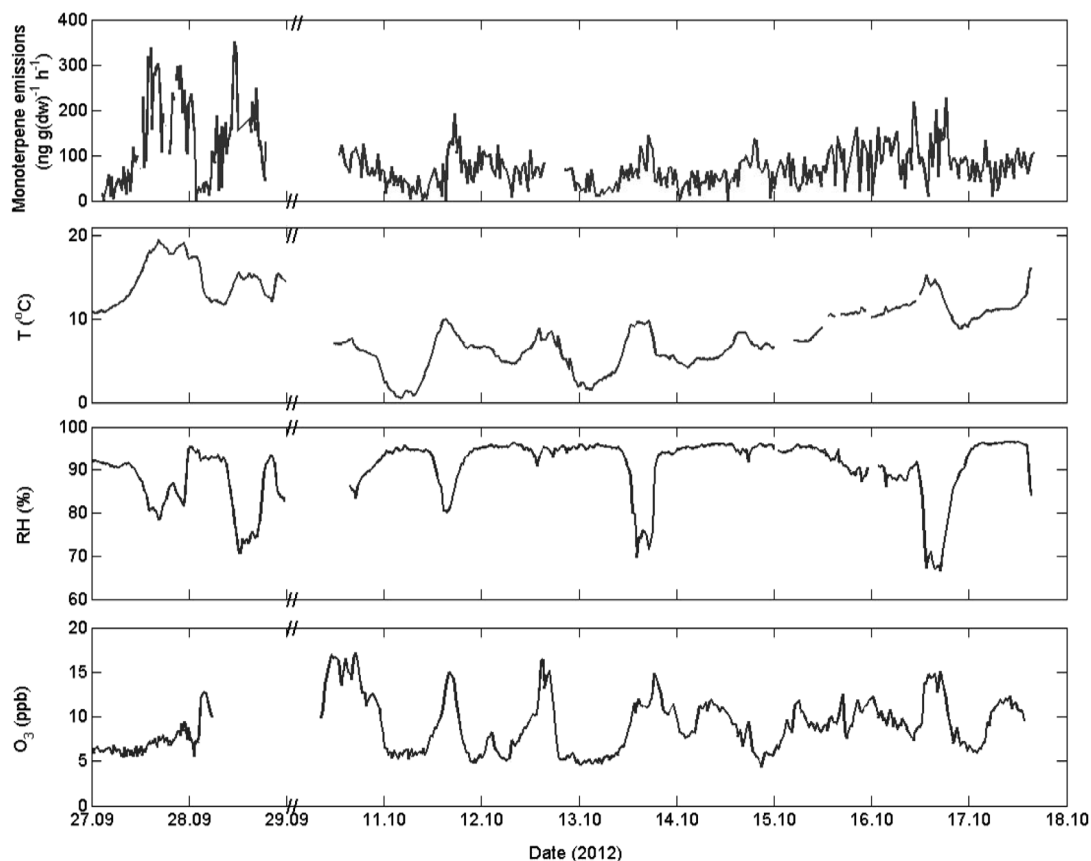


Fig. 5. Monoterpene emission rates along with temperature, relative humidity, and ozone concentrations measured when the branch enclosure was closed.

between the emissions from the branch and the ambient-air monoterpenes resulting from emissions and transport, GC-MS samples were also collected at the same height but outside the enclosure. The dominant monoterpene found in the ambient air was Δ^3 -carene followed by α -pinene. Other monoterpenes could not be identified in the ambient air because of their small amounts. Similarly, sesquiterpenes could not be identified in three samples analyzed. However, traces of longifolene were found in the samples taken from closed enclosure, probably due to its reduced reactivity with ozone.

Temperature effect

Almost all BVOC emission measured responded to the temperature changes (Fig. 6). To analyze

this dependence the following exponential function between temperature and emissions (Guenther *et al.* 1995) was used:

$$E = E_{30(T)} \times \exp[\beta \times (T - T_s)] \quad (2)$$

Here, E is the emission rate ($\text{ng g}_{\text{dw, needles}}^{-1} \text{h}^{-1}$) for the individual VOCs measured at temperature T

Table 2. Monoterpene composition in the closed enclosure determined by GC-MS.

Monoterpene	Relative contribution (%)
α -pinene	58.7 \pm 10.2
Δ^3 -carene	25.8 \pm 11.9
Camphene	6.8 \pm 2.4
Limonene	4.3 \pm 4.3
β -pinene	3.8 \pm 2.7
β -phellandrene	1.2 \pm 1.2

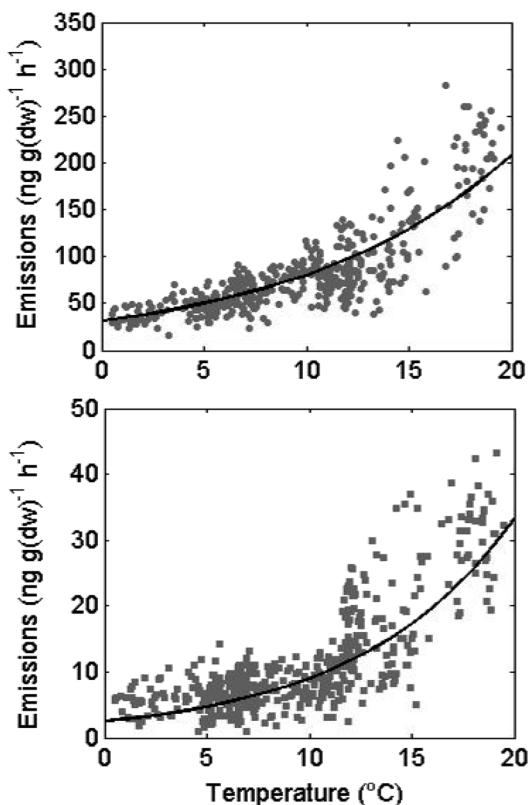


Fig. 6. Regressions of monoterpene (top) and sesquiterpene (bottom) emission rates on temperature. For r^2 values see Table 3.

($^{\circ}\text{C}$), $E_{30(\text{T})}$ is the emission potential (basal emission) at standardized temperature ($T_s = 30\text{ }^{\circ}\text{C}$), and β ($^{\circ}\text{C}^{-1}$) is an empirical coefficient (known as the β factor) that is based on the best fitting

Table 3. Results of nonlinear regression analysis between VOC emission rates and temperature. E_{30} is the emission potential ($\text{ng g}_{\text{dw_needles}}^{-1} \text{h}^{-1}$) at $30\text{ }^{\circ}\text{C}$, β ($^{\circ}\text{C}^{-1}$) is the coefficient describing the strength of the temperature dependence and r^2 describes the quality of exponential fitting between temperature and emission rates.

Compound	E_{30}	β	r^2
Formaldehyde	41.3 ± 28.6	0.12 ± 0.07	0.29
Methanol	68.5 ± 34.1	0.11 ± 0.05	0.54
Acetaldehyde	157.9 ± 64.8	0.12 ± 0.04	0.72
Ethanol	105.5 ± 35.3	0.13 ± 0.05	0.65
Acetone	289.9 ± 76.8	0.14 ± 0.04	0.68
Total MT	539.5 ± 63.3	0.10 ± 0.02	0.80
Total SQT	112.8 ± 19.3	0.13 ± 0.04	0.71

between temperature and emission rate.

Nonlinear regression analysis was performed for all the 12 compounds monitored (see Table 3). While the highest emission rates were usually measured under elevated temperatures, the exponential relationship described was not applicable to all of the compounds investigated. For MEK, MeSA, linalool and pinonaldehyde/caronaldehyde, the fitting between the aforementioned variables was very poor ($r^2 < 0.2$) and therefore these compounds were excluded from further analysis. The unclear temperature dependency is likely to be caused by two overlapping processes, i.e. emission of the precursor or compound and oxidation strength. The highest emission potential was calculated for monoterpenes and the lowest for formaldehyde. While the monoterpene emission potential was, similarly to the emission rates, higher than the one for sesquiterpenes, slightly stronger temperature dependencies were found for sesquiterpenes. However, the calculated β factor for sesquiterpenes was within the uncertainty values of the β factor for monoterpenes.

Mechanical stress

As noted above, the first day of the campaign was excluded from the analysis because of the mechanical stress applied to the branch during the installation process. This caused a substantial increase in emissions rates. During the first day, sesquiterpene emissions (mean \pm SD) were most affected and instantly induced, with the rates being almost three times higher ($42.6 \pm 9.1 \text{ ng g}_{\text{dw_needles}}^{-1} \text{h}^{-1}$) than the corresponding emission rates at similar temperatures ($15.7 \pm 5.8 \text{ ng g}_{\text{dw_needles}}^{-1} \text{h}^{-1}$; $11.7\text{ }^{\circ}\text{C} < T < 13.9\text{ }^{\circ}\text{C}$). Other sensitive compounds whose emissions increased during the installation process were methanol, acetaldehyde, ethanol and acetone, while only a moderate impact was detected for monoterpenes, isoprene, MEK and MeSA.

Higher emissions were also measured in windy conditions (wind speed $> 2 \text{ m s}^{-1}$). Sesquiterpenes were the most affected with their emission rates being almost double than the average ones ($E_{\text{SQT,wind}>2\text{m/s}} = 21.1 \pm 11.1 \text{ ng g}_{\text{dw_needles}}^{-1} \text{h}^{-1}$ compared with $11.8 \pm 8.3 \text{ ng g}_{\text{dw_needles}}^{-1} \text{h}^{-1}$; see

Table 1). Emission rates of methanol increased by almost 50%, while those of ethanol, acetaldehyde, monoterpenes and acetone only slightly.

Discussion

Branch enclosure techniques have been used for biogenic VOC emissions studies since the late 1920s (Isidorov 1990) with thousands of enclosed branches, leaves and plants (Guenther *et al.* 2006). Vegetation enclosures can be static or dynamic (Ortega and Helmig 2008, Ortega *et al.* 2008). In our study, we used a dynamic branch enclosure with automatic opening and closing. After testing VOC mixing ratios during one closure, we chose to keep the enclosure closed for six minutes in a half-hour cycle in order to assure steady-state of monitored mixing ratios. Ruuskanen *et al.* (2005) used a closing time of less than two minutes, assuming an underestimation of about 10% in the calculated emissions, due to a non-steady state. Our measurements indicate that for a 15-l enclosure, at least four-minute closing time is required in order to achieve a steady-state and minimize the uncertainty in emission calculations. Similarly, Kolari *et al.* (2012) suggested that the closing time should be at least three minutes as a compromise between maximum accuracy and minimum changes in the enclosure's environment. Additionally, the branch enclosure should not be leak-tight in order to prevent under-pressure caused by pumping the air out into the instruments (Ruuskanen *et al.* 2005). We prolonged the PTR-MS inlet with a 3-mm heated glass tube. Glass is well known to be chemically inert that reduces VOC sampling losses, and it has been found to be favourable for sesquiterpene measurements in earlier studies (Helmig *et al.* 2003). Isolating and heating up the lines in combination with large flows and short residence times results in minimized losses and highest measurement accuracy.

We measured emission rates of 12 VOCs, but clear diurnal patterns were found for only half of them. Cojocariu *et al.* (2004) found that acetone emissions from Norway spruce were higher during the afternoon and late evening and steeply declined after sunset. Same was found by Karl *et al.* (2004) in tropical rainforest. In our

experiment, acetone emissions were higher than those of acetaldehyde. Same was found by Grabmer *et al.* (2006), who investigated emissions from Norway spruce twigs during a summer campaign. We also found higher daytime emissions of acetaldehyde with a similar and even stronger decrease after sunset. Previous studies (Graus *et al.* 2004, Holzinger *et al.* 2000) also showed a difference in acetaldehyde emissions during light-dark transitions as a result of "pyruvate overflow mechanism" (Karl *et al.* 2002). Acetaldehyde is emitted from vegetation as a result of different processes including leakage from stomata during oxidation of ethanol (Kreuzwieser *et al.* 1999).

Ethanol emissions were on average slightly lower than those of acetaldehyde but inside the uncertainty range. While ethanol emissions are often associated with anaerobic stress conditions such as flooding, drought or frost (Rottenberger *et al.* 2008, Bourtsoukidis *et al.* 2014), studies on coniferous trees (Schade and Goldstein 2001, Grabmer *et al.* 2006) revealed a similar diurnal pattern with a burst during morning and a peak around midday, addressing their connection with stomatal conductances. Relatively small emissions were also measured by us for methyl salicylate. Karl *et al.* (2008) reported significant ecosystem-scale emissions of MeSA, pointing out the role of this compound as a chemical warning signal that indicates ecosystem-scale stresses. They also measured strong emissions of MeSA when differences between night and day temperatures were large. Since we carried out our measurements in autumn, the small measured emission rates in combination with the absence of large temperature changes between night and day indicate that the selected tree did not experience considerable thermal stress.

Isoprene emissions remained low during our measuring period, especially during the second half. Norway spruce is considered to be a weak isoprene emitter (Kesselmeier and Staudt 1999, Grabmer *et al.* 2006, Filella *et al.* 2007) and the emissions are known to be driven by a combination of temperature and light conditions (Guenther *et al.* 1993, 1995). Both were moderate during our measurements.

Emissions of monoterpenes we measured were on average more than seven times higher

than those of sesquiterpenes (*see* Table 1). Tarvainen *et al.* (2005) reported sesquiterpene emission rates from pine trees to be 2%–5% of the total monoterpene emissions ($E_{MT}/E_{SQT} = 20\text{--}50$) in southern Finland and 40% ($E_{MT}/E_{SQT} = 2.5$) in northern Finland. It is worth mentioning is that their emission measurements were conducted on trees with different ages and heights. It is therefore difficult to define a specific ratio between monoterpenes and sesquiterpenes ingeneral without considering the tree species, leaf age, stand composition, adaptive mechanisms of the investigated trees, and environmental conditions, which depend on e.g. latitude and seasonality.

In this study, we calculated emission potentials and temperature dependencies according to the storage pool algorithm given by Eq. 1. The low ambient ozone concentrations found during the measuring period did not induce any ozone stress and therefore sesquiterpene emissions were considered to be only temperature-dependent (Bourtsoukidis *et al.* 2012). The temperature dependency of sesquiterpenes was found to be slightly higher than that of monoterpenes. This observation is in line with the previous studies carried out in the boreal environment but on pine trees (Tarvainen *et al.* 2005, Hakola *et al.* 2006). However, Helmig *et al.* (2007) reported a wide range of monoterpene and sesquiterpene temperature dependencies for pine trees (β factors: $0.07\text{--}0.28\text{ }^{\circ}\text{C}^{-1}$ and $0.05\text{--}0.29\text{ }^{\circ}\text{C}^{-1}$, respectively), and Bourtsoukidis *et al.* (2012) a wide variability of calculated daily sesquiterpene temperature dependencies along an eight-month period of observations for a spruce tree in central Europe (β factors: $0.02\text{--}0.27\text{ }^{\circ}\text{C}^{-1}$).

Disturbance such as mechanical stress resulting from installation and/or operation of the enclosure can induce emission responses from vegetation (Ortega and Helmig 2008). Guenther *et al.* (1994) pointed out that an error in monoterpene emissions can result from mechanical disturbances, which can enhance monoterpene emission rates up to 50 times (*see* Juuti *et al.* 1990) due to rough handling of the branches. Vercammen *et al.* (2001) found monoterpene and sesquiterpene emissions to be 2–3 orders of magnitude higher as a result of a disturbance. Our measurements showed enhanced emissions after the installation process with sesquiterpene

emissions to be the most affected, the increase being the same as presented by Vercammen *et al.* (2001). Apart from isoprenoids, we also found increased methanol emissions resulting from mechanical stress during the first measurement day. As it was pointed out by Loreto and Schnitzler (2010), methanol emissions can also be induced by mechanical wounding.

When measuring VOC emissions from living plants, it is always important to quantify the disturbance duration and exclude the data obtained from that period. Ortega *et al.* (2008) suggested waiting for a complete diurnal cycle before sampling in order to allow vegetation to adapt to new conditions. Since there is no *a priori* knowledge of the adaptive responses of a plant, and since each experimental technique involves handling of a living organism, the type and amount of VOCs emitted by a plant as a results of stress (Jansen *et al.* 2009) should be quantified before any analysis of emission measurements.

Conclusions

We quantified emission rates, emission potentials and temperature dependencies for 12 atmospherically relevant biogenic VOCs, for a spruce in a hemiboreal forest in autumn. By applying a dynamic branch enclosure and by using heated and isolated glass tubing for carrying the air down to the PTR-MS inlet, we were able to quantify sesquiterpene emission rates despite their seasonally low values and their high reactivity, which usually leads to short atmospheric lifetimes (*see e.g.* Duhl *et al.* 2008). We can conclude that for a 15-l enclosure, the closing time should be at least four minutes in order to achieve steady-state of the mixing ratios. Additionally, we found increased emissions rates after the installation process. Therefore, mechanically-induced emissions that result from a rough handling of the branch should always be considered and quantified before analyzing the data.

Emissions rates and emission potentials of monoterpenes were almost eight and five times higher, respectively, than those of sesquiterpenes but their temperature dependency was found to slightly smaller for monoterpenes. Additionally, we found small emission of oxygenated VOCs

of varying strength (acetone > acetaldehyde > ethanol + formic acid > methanol > formaldehyde). It is, therefore, important to focus also on such emissions apart from isoprenoids in order to quantify the entire non-methane-hydrocarbon exchange. Nevertheless, more data for longer periods are needed in order to quantify emissions and atmospheric mixing ratios in a conclusive manner.

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