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Terpenoid emissions from fully grown east Siberian *Larix cajanderi* trees

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Abstract. While emissions of many biogenic volatile organic compounds (BVOCs), such as terpenoids, have been studied quite intensively in North American and Scandinavian boreal forests, the vast Siberian boreal forests have remained largely unexplored by experimental emission studies. In this study the shoot-scale terpenoid emission rates from two mature *Larix cajanderi* trees growing in their natural habitat in eastern Siberia were measured at the Spasskaya Pad flux measurement site (62°15′18.4″ N, 129°37′07.9″ E) located on the western bank of the Lena river. The measurements were conducted during three campaigns: 3–24 June, 8–26 July, and 14–30 August, in the summer of 2009. A dynamic flow-through enclosure technique was applied for adsorbent sampling, and the samples were analysed offline with a gas chromatograph. Between 29 and 45 samples were taken from each shoot during all three campaigns. Seven different monoterpenes, six different sesquiterpenes, linalool isoprene, and 2-methyl-3-buten-2-ol (MBO) were identified. The monthly median value of the total terpenoid emissions varied between 0.006 and 10.6 μg g$_{dw}^{-1}$ h^{-1}. The emissions were dominated by monoterpenes, which constituted between 61 and 92 % of the total emissions. About half of the monoterpene emissions were comprised of Δ^3-carene; α- and β-pinene had significant emissions as well. Linalool emissions were also substantial, comprising 3–37 % of the total emissions, especially in June. Sesquiterpenes accounted for less than 3 % and isoprene less than 1 % of the total emissions. Based on the measured emission rates, the relative atmospheric concentration of each compound was estimated. Monoterpenes were the species with the highest relative concentration, while linalool and sesquiterpenes had a notably smaller contribution to the estimated atmospheric concentration than to the emission rates. A temperature-dependent pool algorithm with a constant β (0.09 °C^{-1} for monoterpenes and 0.143 °C^{-1} for sesquiterpenes) was used to normalize the measured emission data. For monoterpenes the emission potential varied between 0.5 and 18.5 μg g$_{dw}^{-1}$ h^{-1} and for sesquiterpenes between 0.02 and 0.4 μg g$_{dw}^{-1}$ h^{-1}.

1 Introduction

The boreal vegetation zone is the largest forested region on Earth (Bonan, 2008) and a major source of volatile organic compounds (VOCs) to the atmosphere (Guenther et al., 1995). Many dominant tree species in the Eurasian boreal region emit isoprene, mono- and sesquiterpenes (Rinne et al., 2009). These compounds have been shown to contribute to the regional formation and growth of secondary organic aerosol (SOA; e.g. Bonn and Moortgat, 2003;

Tunved et al., 2006), growing the initially formed nanoparticles to climatically relevant particle sizes (Kulmala et al., 2007, 2013). These are the particles that can act as cloud condensation nuclei (CCN) and scatter sunlight (Kerminen et al., 2005, 2012; Sihto et al., 2011; Paasonen et al., 2013). Paasonen et al. (2013) observed a direct connection between ambient monoterpene concentrations and CCN-sized particle concentrations. The VOCs also have an effect on the local air quality and participate in lower tropospheric ozone production (Seinfeld and Pandis, 1998).

A major part of the boreal forests lies in Eurasia, east of the Ural mountain range, i.e. in Siberia. The total forested area of Siberia is 6 million km^2, of which almost half is dominated by larch (*Larix* sp.) forests, corresponding to an area equal to one-third of the Eurasian boreal forest or taiga (Shepashenko et al., 1998). Larch species are characterized by soft deciduous needles that are shed every autumn. Three species, as well as several hybrids of these, are distinguished in Siberia: *Larix cajanderi*, *Larix gmelinii* and *Larix sibirica*, growing in the eastern, middle and western part of Siberia, respectively. The majority of Western scientific literature concentrates on *L. gmelinii* and *L. sibirica*, with *L. cajanderi* often being considered as a subspecies of *L. gmelinii*. However, in Russian literature all these three are recognized as separate species, and therefore the most detailed and complete information on the larch species in Russian forests has been available only in Russian (see Abaimov, 2010, and references therein).

Larch has been reported to emit significant amounts of mono- and sesquiterpenes (Isebrands et al., 1999; Ruuskanen et al., 2007; Ghirardo et al., 2010). Based on the measurements by Ruuskanen et al. (2007) and Ghirardo et al. (2010), terpenoid emissions from larch are higher than from other common boreal trees such as Norway spruce and Scots pine. However, these measurements were conducted with young seedlings either in the field or in laboratory, and have been restricted to measurements of European larch (*L. decidua*) and *L. sibirica*. Despite the vast area covered by *Larix* in the Eurasian boreal zone, to our knowledge no prior research has been conducted on the VOC emissions from these species in vivo. Also on a general scale the biogenic VOC (BVOC) source distributions across the Eurasian boreal zone and over the course of a growing season are poorly quantified and limited to a small number of mostly short-term studies in northern Europe and North America, with particularly few studies having been conducted in the Siberian forests (Rinne et al., 2009; Kulmala et al., 2011).

The aim of this study was to quantify and characterize the VOC emissions from fully grown mature larch trees in Siberia. The shoot-scale emissions from mature *L. cajanderi* trees growing in their natural environment were measured during one growing season. Thus, this study provides a unique data set for the emission potential for one of the major tree species of Siberian taiga that can be used in the upscaling of the VOC emissions of the Siberian Larch forests.

Additionally, based on the measured VOC emission by *L. cajanderi*, estimates for the fractional distribution of the air concentrations of the emitted compounds are given.

2 Methods

2.1 Measurement site

The shoot-scale BVOC emissions rates of *Larix cajanderi* were measured at the Spasskaya Pad flux measurement site (62°15′18.4″ N, 129°37′07.9″ E, 220 m a.s.l., Fig. 1), located on the western bank of the Lena river ca. 30 km to the northwest of the city of Yakutsk. The site is an experimental forest research station of the Russian Academy of Science, Institute for Biological Problems in Cryolithozone. The measurements were conducted during three campaigns in the summer of 2009: 3–24 June, 8–26 July, and 14–30 August.

Around the measurement site, the *L. cajanderi* forest extends over several kilometres in all directions except for small groves of birch and pine about 500 m south from the site. The canopy of the forest consists of *L. cajanderi* with a stand density of 840 trees ha^{-1}, leaf area index (LAI) of 1.56 and a mean tree height of approximately 18 m. The undergrowth consists mostly of cowberries (*Vaccinium vitis idaea*) (Ohta et al., 2008; Iida et al., 2009). The climate at the measurement site is classified as "Continental Subarctic climate with extremely severe winters (Dfd)" in the Köppen climate classification (Kottek et al., 2006), and the forest is underlaid by permafrost. The annual mean air temperature at the site is $-10.4\,°C$, with mean temperature of the coldest month, January, being $-39.5\,°C$ and that of the warmest month, July, $18.6\,°C$ (Dolman et al., 2004). During the three campaigns the mean daytime temperature on the measurement days was $26.8\,°C$ for the first, $26.0\,°C$ for the second and $19.0\,°C$ for the third campaign. The annual mean precipitation for the period from 1998 to 2006 was 259 mm (Ohta et al., 2008).

2.2 Emission rate measurements

The measurements were done at the upper canopy of the *L. cajanderi* forest from two trees that could be easily accessed from a 15 m-high scaffolding tower. During each campaign, two fully sunlit shoots of these trees, labelled "A" and "B", were measured using a dynamic flow-through enclosure technique. For a more detailed description of the technique see Hakola et al. (2006). The measured shoots were enclosed in cylindrical Teflon chambers of 15 l volume. During the measurements, the chambers were flushed with a constant flow ($5\,L\,min^{-1}$) of VOC-free air, which was generated either by charcoal filter or catalytic zero air generator (Parker Balston, model 75-83-220, USA). When the BVOCs were not measured, the chambers were open to the ambient air from the other end of the cylinder. In order to minimize stress-induced emissions from the shoots, the chambers were put in place at least one day before the measurements started.
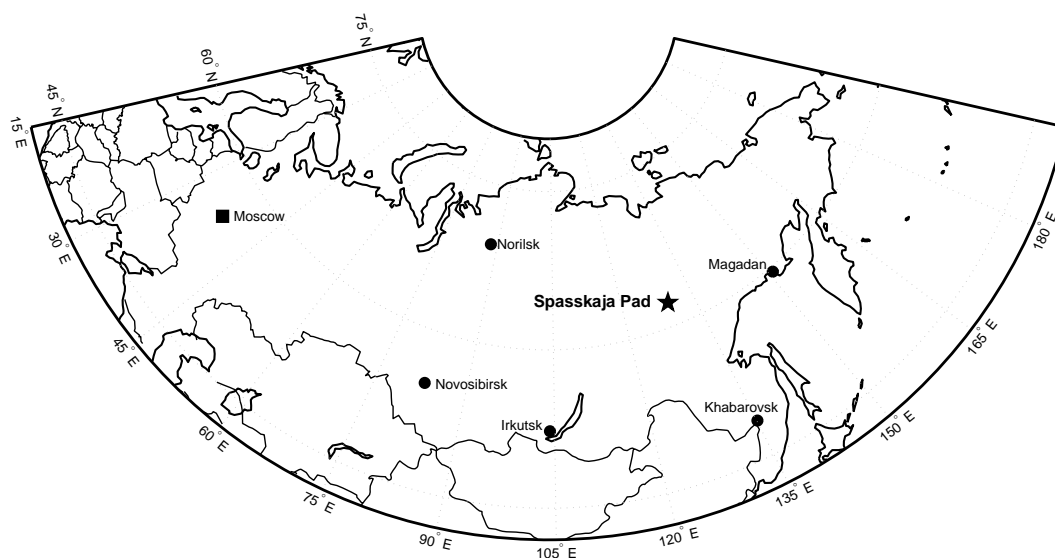
Fig. 1. Map showing the location of the Spasskaya Pad measurement site.

The two branches, the shoots of which were measured, were also attached to the scaffolding tower with ropes to prevent wind from moving the shoots and causing mechanical stress. Ozone was removed from the inlet air using MnO_2-coated copper nets to prevent oxidation of VOCs before sampling. Due to practical reasons, the measurements were conducted during daylight time between 8:00 and 20:00 local time.

The shoot-scale VOC emission rate (E, $\mu g\,g_{dw}^{-1}\,h^{-1}$) can be determined according to the equation

$$E = [(C_{out} - C_{in})F]/g_{dw}, \tag{1}$$

where g_{dw} (g) is the dry mass of the needles, C_{in} (μg) and C_{out} (μg) are the concentrations in the incoming and outgoing air, respectively, and F ($L\,min^{-1}$) is the flow rate of incoming air (e.g. Hakola et al., 2006).

For offline analysis, the VOCs were collected onto stainless steel adsorbent tubes (Perkin-Elmer, USA) filled with Tenax-TA and Carbopack-B for one hour at a flow rate of $220\,mL\,min^{-1}$. A total of 73 samples on 7 days, 62 samples on 6 days and 84 samples on 7 days were collected during the first, second and third campaign, respectively. Samples were taken from the early morning to late evening, covering a wide range of photosynthetically active radiation (PAR) and temperature values. In order to determine the background concentration of the VOC-free air, one to three adsorbent samples were taken from the zero air on each measurement day. The PAR was measured with a Li190 quantum sensor (Li-Cor Inc., USA), which was placed two metres away outside of the chamber. The radiation blocked by the Teflon film is assumed to be small enough not to have to be taken into account. Pape et al. (2009) reported that the transmissivity of a Teflon FEP film is above 90 % for the PAR radiation. The temperature inside the chamber was recorded using Tinytag (Gemini data loggers, UK) thermistor temperature sensors. After each of the measurement campaigns, the measured shoots were cut and their dry needle mass was determined.

The sample cartridges were sealed with brass (Swagelok, USA) caps and stored in a refrigerator before they were shipped to Finland. The cartridges were analysed within a month after sampling in the laboratory of the Finnish Meteorological Institute. The same laboratory has determined that when this type of sample cartridges, sealed with the same kind of caps, are stored properly, the samples remain stable for at least a month. VOC analysis was performed using a thermal desorption instrument (Perkin-Elmer Turbo-Matrix 650, Waltham, USA) attached to a gas chromatograph (Perkin-Elmer Clarus 600, Waltham, USA) with DB-5MS (60m, 0.25 mm, 1 μm) column and a mass selective detector (Perkin-Elmer Clarus 600T, Waltham, USA). The sample tubes were desorbed at 300 °C for 5 min and cryofocused in a Tenax cold trap (-30 °C) prior to injecting the sample into the column by rapidly heating the cold trap (40 °C min^{-1}) to 300 °C. Five-point calibration was utilized using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes and flushed in a nitrogen flow ($100\,mL\,min^{-1}$) for five minutes in order to remove methanol.

2.3 Emission potential calculations

In order to compare the measured emission rates to other emission studies, the emission rates need to be standardized so that the effects of environmental parameters such as changing temperature and light conditions are removed. A simple and commonly used method to standardize and model mono- and sesquiterpene emissions has been the use of temperature-dependent as well as temperature-

and light-dependent emission algorithms by Guenther et al. (1993, 1995, 1997). These algorithms have been widely used for different coniferous tree species growing in different environments from temperate to boreal regions (for review see Rinne et al., 2009). The traditional monoterpene emission algorithm (pool algorithm, Guenther et al., 1993), in which the emission is exponentially dependent on temperature, is implicitly based on evaporation of monoterpenes from storage pools:

$$E = E_{\text{pool}} \exp[\beta (T - T_{\text{S}})], \tag{2}$$

where E ($\mu g\,g_{\text{dw}}^{-1}\,h^{-1}$) is the measured emission, E_{pool} ($\mu g\,g_{\text{dw}}^{-1}\,{}^{-1}$) is the emission in standardized temperature T_{S} (30 °C), β (°C^{-1}) is a temperature dependence coefficient, which describes the strength of the temperature dependence, and T is the temperature inside the chamber. In some BVOC emission studies done in the northern regions, emissions have been standardized to 20 °C (e.g. Ekberg et al., 2009 and Haapanala et al., 2009). However, as the mean daytime temperature (from 08:00 to 20:00 local time) during the measurement days was 26.8 °C for the first, 26.0 °C for the second and 19.0 °C for the third campaign, the use of a standard temperature of 30 °C is more appropriate. This also makes the results easier to compare to most of the other emission studies.

The light- and temperature-dependent algorithm, originally developed for isoprene emission, assumes that the emission originates directly from synthesis (de novo emission), and the functional form depends on light and temperature dependence of the synthesis (see also Grote and Niinemets, 2008). The synthesis algorithm is determined by

$$E = E_{\text{synthesis}} C_{\text{T}} C_{\text{L}}, \tag{3}$$

where E ($\mu g\,g_{\text{dw}}^{-1}\,h^{-1}$) is the measured emission, $E_{\text{synthesis}}$ ($\mu g\,g_{\text{dw}}^{-1}\,h^{-1}$) is the emission in normalized temperature (30 °C) and light (1000 μmol photons m^{-2} s^{-1}) conditions, and C_{T} and C_{L} are semi-empirical temperature- and light-dependent functions, respectively (see Guenther, 1997). As the early stages of monoterpene synthesis are similar to those of isoprene synthesis, the light- and temperature-dependent de novo emission algorithm has also been successfully applied to monoterpene emissions from certain tree species and ecosystems (Staudt and Seufert, 1995; Kuhn et al., 2002; Rinne et al., 2002), especially for species that do not store monoterpenes in specialized leaf structures.

2.4 Implications for the boundary layer VOC concentrations

The turbulent mixing in the atmosphere treats all trace gases in a similar way; thus their relative abundances in the boundary layer depend on relative emission and oxidation rates. When VOCs are emitted into the atmosphere, they are oxidized in reactions with hydroxyl radicals (OH), ozone (O$_3$)

and nitrate radicals (NO$_3$), leading to numerous oxidation products (Seinfeld and Pandis, 1998). If the oxidation products remain volatile, they undergo further oxidation until eventually CO$_2$ and H$_2$O are formed. Atmospheric oxidation can also lead to formation of less volatile VOCs, which contribute to formation and growth of SOA (Kroll and Seinfeld, 2008; Carslaw et. al., 2010).

When assuming a well-mixed boundary layer, the time derivative of the concentration of a certain VOC is

$$\frac{\partial [X]}{\partial t} = \frac{E_{\text{C}}}{h} - S, \tag{4}$$

where $[X]$ is the mean concentration of a certain VOC in the boundary layer, E_{C} is the canopy-scale emission to the boundary layer, S is the oxidation rate in the boundary layer, and h is the boundary layer height (see e.g. Seinfeld and Pandis, 1998). In Eq. (4) all other loss processes are neglected. Using the biomass density "bmd", the measured shoot-scale emission rates can be converted to canopy-scale emission as follows:

$$E_{\text{C}} = E \cdot \text{bmd}. \tag{5}$$

The oxidation rate can be written as

$$S = k_{\text{OH},X} [\text{OH}][X] + k_{\text{O}_3,X} [\text{O}_3][X] + k_{\text{NO}_3,X} [\text{NO}_3][X], \tag{6}$$

where $k_{\text{OH},X}$, $k_{\text{O}_3,X}$ and $k_{\text{O}_3,X}$ are the reaction rate constants of the oxidation reaction between hydroxyl radical, ozone and nitrate radical and compound X, respectively, and [OH], [O$_3$], [NO$_3$] and [X] are the concentrations of hydroxyl radical, ozone, nitrate radical and compound X, respectively. Oxidation due to ozone is important both during the day and at nighttime. OH and nitrate radical concentrations vary during the day; OH radicals are important in the daytime, when UV-radiation is available (Petäjä et al., 2009); and nitrate radical oxidation is only important at night (e.g. Williams et al., 2011; Rinne et al., 2012). Hence, the nitrate radical term can be neglected for daytime oxidation rates. Thus, by combining and reorganizing Eqs. (4), (5) and (6), the steady-state concentration of X is

$$[X] = \frac{E \cdot \text{bmd}}{h \left(k_{\text{OH},X} [\text{OH}] + k_{\text{O}_3,X} [\text{O}_3] + k_{\text{NO}_3,X} [\text{NO}_3] \right)}. \tag{7}$$

In Eq. (7) the boundary layer height and the biomass density is assumed to be similar for all VOCs, so the relative contribution of the emission of each VOC to the above-canopy atmospheric concentration can be written in a simplified form as

$$[X_{\text{rel}}] = \frac{E}{k_{\text{OH},X} [\text{OH}] + k_{\text{O}_3,X} [O_3]}. \tag{8}$$

Hydroxyl radical and ozone concentrations were not measured at the site; therefore typical daytime concentrations in boreal forest environment need to be used for estimating the

Table 1. Reaction rate constants (molecules $cm^{-3} s^{-1}$) of the oxidation reactions of the measured VOCs due to hydroxyl radicals and ozone.

		$k_{OH} \times 10^{12}$ [molecules $cm^{-3} s^{-1}$]	$k_{O_3} \times 10^{18}$ [molecules $cm^{-3} s^{-1}$]
	isoprene	101[a]	12.8[a]
	MBO	88.3	74
monoterpenes	α−pinene	53.7[a]	86.6[a]
	camphene	53[a]	0.9[a]
	β−pinene	78.9[a]	15[a]
	Δ^3−carene	88[a]	37[a]
	p-cymene	8.5	–
	limonene	171[a]	200[a]
	terpinolene	225[a]	1380[a]
sesquiterpenes	longicyclene	9.40[b]	44[b]
	iso-longifolene	96.2[b]	11[b]
	β−caryophyllene	145.9[a]	442[a]
	aromadendrene	62.5[b]	12[b]
	α−humulene	235.2[b]	870[b]
	alloaromadendrene	–	–
	farnesene	319.6[b]	10.4[b]
	linalool	119.6[b]	432[b]

[a] Atkinson (1994)
[b] Chemspider: http://www.chemspider.com/ (cited 25 January 2013). Predicted data are generated using the US Environmental Protection Agency's EPI Suite.

patterns of above-canopy concentrations of VOCs. The reaction rate constants due to hydroxyl radical and ozone for each considered VOC compound are listed in Table 1. Equation (8) does not give actual concentrations and the unit is arbitrary, but it can be used for calculating the fractional contribution of individual VOCs based on the measured emission rates. The reactive compounds, meaning those compounds whose fraction of the calculated air concentrations decreases significantly compared to the fraction of the emission rates, produce more first- or higher-generation oxidation products and are thus more likely to participate in SOA formation than less reactive compounds. This approach does not take into account any emissions from other tree species or the undergrowth.

3 Results and discussion

3.1 The VOC emission spectra

The first measurement day was 13 June 2009, and by then the *L. cajanderi* trees, from which the VOC emissions were measured, already had needles. The emission rates determined from the data are thus representative for *L. cajanderi* trees during the growing season, excluding the potentially important and different VOC emission spectra and rates during the burst of the needles or the initial growth of the needles. Hakola et al. (1998) found substantial monoterpene emissions from the *Populus tremula*, *Salix phylicifolia* and *Betula*

pendula species at the time when leaves were still young and emerging. The current measurements did not cover this season.

The speciation of the emissions from both of the trees during the three separate periods is depicted in Fig. 2. Throughout the summer, the total mass-based VOC emission spectra of both measured *L. cajanderi* trees were dominated by monoterpenes. Other emitted compounds were typically linalool, cineol, sesquiterpenes and very small contributions by isoprene and 2-methyl-3-buten-2-ol (MBO). The two trees were rather similar in terms of their emission spectra. The contribution of monoterpene emissions to the total emission from tree B (79–92 %) was higher than from tree A (61–92 %), especially in June. Linalool was another important contributor to the emission spectra of both trees – varying between 7 and 37 % for tree A and 3 and 19 % for tree B. The highest linalool emissions were measured in June, and they decreased during the summer and were lowest in August. For most of the time other measured VOCs, i.e. sesquiterpenes, isoprene, cineol and MBO, each constituted 1–3 % or less of the emissions of both trees.

Ruuskanen et al. (2007) reported *L. sibirica* to be a substantial sesquiterpene emitter, with 10 % of the emissions being sesquiterpenes. The tree measured by Ruuskanen et al. (2007) was a young, 5 yr-old *L. sibirica*, which was growing on a field in southern Finland where it had been planted three years earlier. The young age of the measured *L. sibirica* might have influenced the emission spectra. Of the emissions
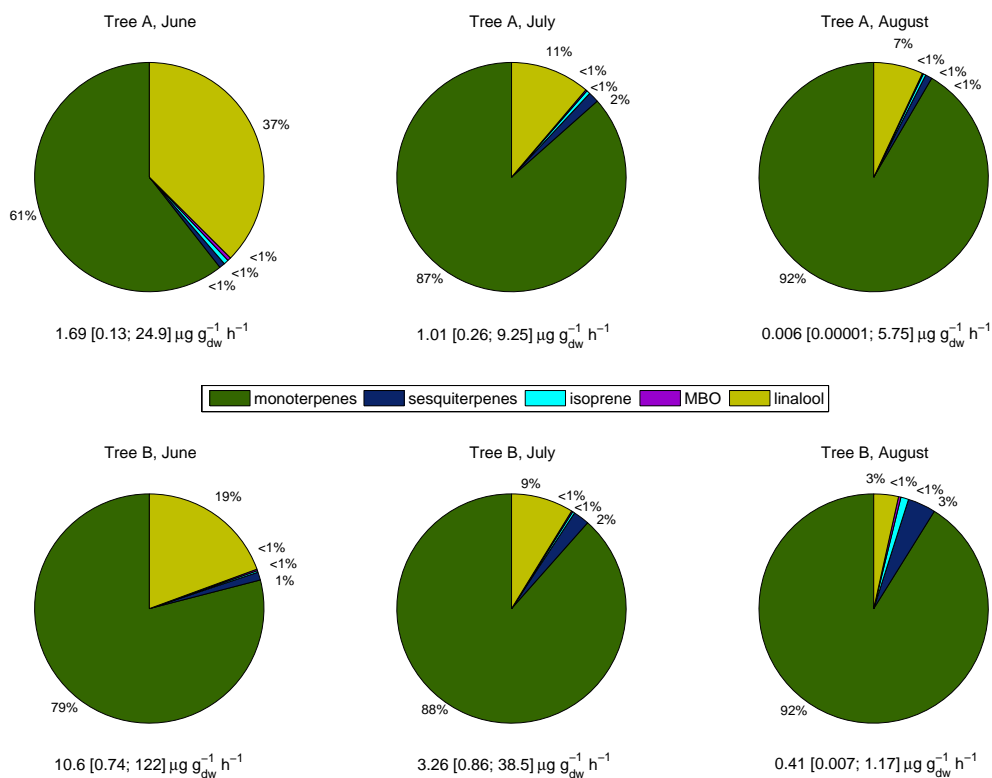
Fig. 2. Measured emission spectra of VOCs from the two *Larix cajanderi* trees during the measurement campaigns. Given below each pie chart are the monthly median and 5th and 95th percentile values of the total terpenoid emission rates.

of *L. cajanderi*, sesquiterpenes accounted for 1–2 % of the tree A and 1–3 % of the tree B emissions. In general, the fraction of sesquiterpene emission have been reported to be about 5–15 % of the total VOC emissions for boreal trees, such as pine and spruce (Rinne et al., 2009). The relative fraction of sesquiterpenes was rather constant throughout the summer, although the fraction increased from 1 to 3 % towards the end of the summer for tree B.

The monoterpene emission spectra were similar for both measured trees A and B, although the total emission rate of the monoterpenes was notably higher for tree B (Fig. 2.). The spectra of both trees remained also fairly constant throughout the growing season (Fig. 3). About half of the monoterpene emissions were comprised of Δ^3-carene. Other major compounds were α- and β-pinene, which accounted for 20–30 % and 10–15 % of the total, respectively. Also camphene, limonene, terpinolene and p-cymene were detected. Of interest, Ruuskanen et al. (2007) reported the emission spectrum of a young *L. sibirica* to be dominated by sabinene, a compound that was not detected for *L. cajanderi*. However, the same study showed Δ^3-carene and α- and β-pinene to also be important monoterpenes emitted by *L. sibirica*.

Whereas the sesquiterpene emission spectra for both measured trees were fairly similar, the spectra of the emissions from both trees changed from June and July to August (Fig. 4). In June and July sesquiterpene spectra were dominated by farnesene/alloaromadrendrene (these compounds coeluted so they cannot be separated from each other), which accounted for more than half of the sesquiterpene emissions. β-caryophyllene made up 17–29 % of the total sesquiterpene emissions. Other detected sesquiterpenes were α-humulene, aromadendrene, longicyclene and iso-longifolene. A few other sesquiterpenes were also detected, but due to the lack of suitable laboratory standards these could not be identified; besides, their contribution was negligible. The notable change in the spectra in August is most likely due to low overall emissions of sesquiterpenes in August, when the emissions were close to or below the detection limit and none of the measured sesquiterpenes were clearly dominating the spectra. The sesquiterpene emission spectrum of *L. cajanderi* was similar to the sesquiterpene emission spectra of *L. sibirica* as measured by Ruuskanen et al. (2007). Generally speaking, β-caryophyllene is usually reported as the most abundant sesquiterpene in sesquiterpene emission spectra of trees in the boreal zone. Also α- and β-farnesene and α-humulene are important sesquiterpenes from many tree species (Duhl et al., 2008).

3.2 Measured emission rates

During all three campaigns the measured emission rates of *L. cajanderi* had a distinct daily pattern following both
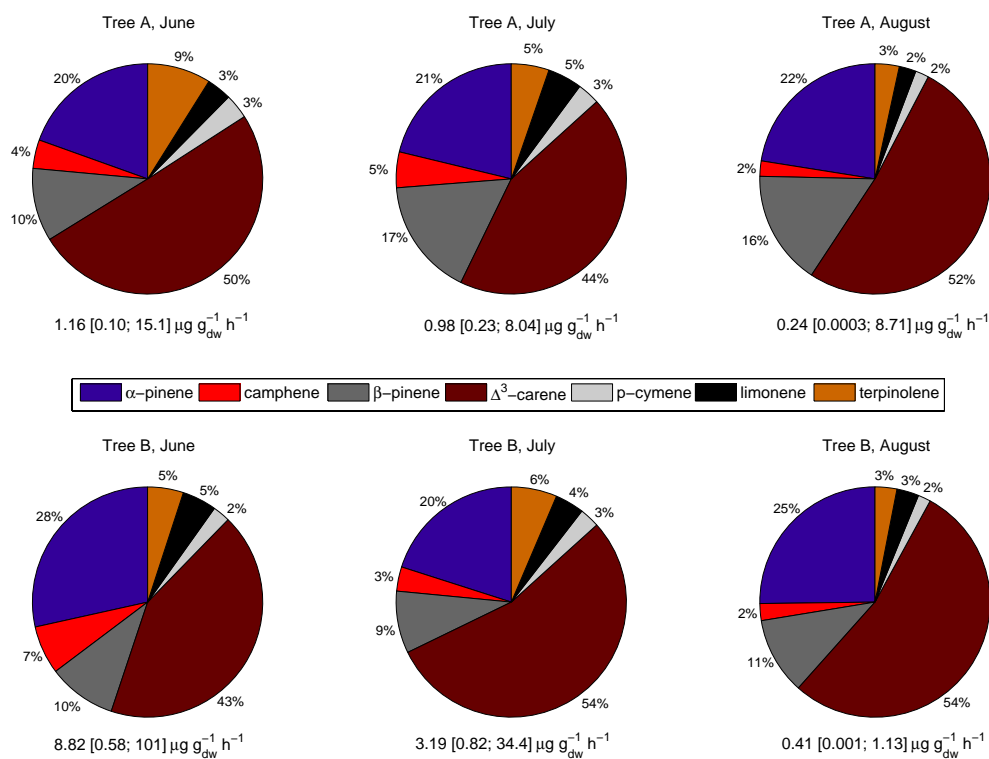
Fig. 3. Measured emission spectra of monoterpenes from the two *Larix cajanderi* trees during the measurement campaigns. Given below each pie chart are the monthly median and 5th and 95th percentile values of the total monoterpene emission rates.
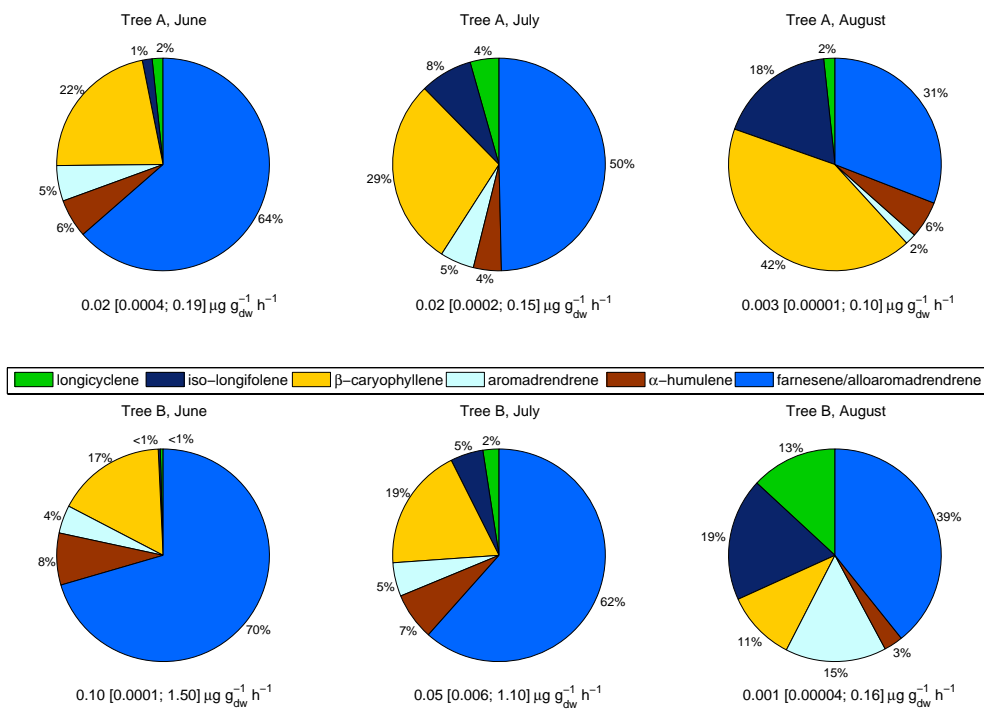
Fig. 4. Measured emission spectra of sesquiterpenes from the two *Larix cajanderi* trees during the measurement campaigns. Given below each pie chart are the monthly median and 5th and 95th percentile values of the total sesquiterpene emission rates.

Table 2. The calculated emission potentials E_{pool} and $E_{synthesis}$ ($\mu g\,g_{dw}^{-1}\,h^{-1}$) of mono- (MT) and sesquiterpenes (ST) at standard conditions (30 °C and 1000 μmol photons $m^{-2}\,s^{-1}$) using a temperature-dependent pool algorithm (Guenther et al., 1993) and a temperature- and light-dependent synthesis algorithm (Guenther, 1997). The pool emission potential was determined in two different ways: by keeping the β value constant (0.09 °C^{-1} for mono- and 0.143 °C^{-1} for sesquiterpenes) and by keeping β as a free parameter. The correlation coefficient is indicated by r, and the number in the brackets illustrates how many data points were used for calculating the emission potential.

		pool, constant β		pool, variable β			synthesis	
		E_{pool}	r	E_{pool}	β	r	$E_{synthesis}$	r
MT Tree A	June	2.20 ± 0.96	0.28 (34)	1.90 ± 2.00	0.13	0.28 (34)	2.40 ± 0.97	0.35 (33)
	July	1.50 ± 0.57	0.35 (32)	1.50 ± 0.79	0.10	0.35 (32)	2.30 ± 0.77	0.31 (17)
	August	1.80 ± 2.06	0.06 (45)	1.50 ± 2.30	0.03	0.08 (45)	5.00 ± 4.70[a]	0.80 (3)
	All	1.90 ± 0.54	0.32 (111)	1.70 ± 0.84	0.12	0.32 (111)	2.40 ± 0.61	0.32 (53)
MT Tree B	June	18.50 ± 6.80	0.70 (28)	10.10 ± 8.10	0.30	0.72 (28)	21.60 ± 6.80	0.66 (23)
	July	7.40 ± 2.50	0.81 (30)	2.10 ± 1.30	0.43	0.93 (30)	8.00 ± 2.60	0.66 (26)
	August	0.46 ± 0.14	0.31 (39)	0.42 ± 0.15	0.05	0.30 (39)	0.51 ± 0.20	0.56 (28)
	All	9.60 ± 2.60	0.57 (97)	3.80 ± 2.30	0.40	0.66 (97)	11.50 ± 2.80	0.54 (77)
ST Tree A	June	0.03 ± 0.01	0.31 (34)	0.03 ± 0.03	0.13	0.31 (34)	0.04 ± 0.02	0.37 (32)
	July	0.02 ± 0.01	0.12 (32)	0.03 ± 0.02	0.05	0.17 (32)	0.05 ± 0.02	0.06 (17)
	August	0.03 ± 0.03	0.22 (45)	0.03 ± 0.03	0.06	0.25 (45)	0.09 ± 0.06[b]	0.74 (5)
	All	0.03 ± 0.01	0.32 (111)	0.03 ± 0.01	0.09	0.32 (111)	0.04 ± 0.01	0.31 (54)
ST Tree B	June	0.36 ± 0.18	0.69 (28)	0.17 ± 0.18	0.34	0.71 (28)	0.44 ± 0.14	0.68 (22)
	July	0.23 ± 0.09	0.75 (30)	0.05 ± 0.07	0.52	0.87 (30)	0.27 ± 0.11	0.64 (26)
	August	0.04 ± 0.02	0.43 (39)	0.001 ± 0.004	1.63	0.75 (39)	0.05 ± 0.03	0.69 (16)
	All	0.25 ± 0.06	0.67 (97)	0.08 ± 0.06	0.45	0.76 (97)	0.31 ± 0.08	0.62 (64)

[a] Only three data points.
[b] Only five data points.

temperature and light. Figure 5 shows the mono- and sesquiterpene emission rates, temperature and the PAR radiation during the second campaign in July. The highest emission rates were measured in June, when temperature and PAR were high and the needles were still growing.

The measured emission rates of tree B were substantially higher than those of tree A, up to 10 times higher in June and July. In August when the overall emission rates were low, the emissions from tree B were almost two orders of magnitude higher than from tree A. From the measured branches, one shoot from both trees was enclosed in the chamber for VOC sampling. The measured shoot of tree A remained in place, but the shoot of tree B was moving occasionally due to wind. Since mechanical stress is known to lead to high emissions of VOCs stored in the leaves, this movement could underlie the different emission rates (Niinemets et al., 2011). Another and possibly more important cause for difference in measured emission rates between the two trees could be that parts of the branches of tree B were probably affected by some herbivore. After the first campaign white "cotton like" spots were seen on several branches of tree B. These white spots could be caused by *Adelges geniculatus*, which is hosted by larch. The Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape (BFW) describes the symptoms of the *Adelges geniculatus* attack resulting in

bent needles with white waxy wool (http://bfw.ac.at/ws/sdis.schadenstyp_e?sdis_id_in=79, cited on 20 December 2012). This type of waxy wool, i.e. the white spots, was clearly seen in photographs taken of tree B. Sesquiterpene emissions especially can be related to herbivore attacks the tree may have experienced. Haapanala et al. (2009) found large α-farnesene emissions from mountain birches in northern Sweden two years after an outbreak of autumnal moth; when the measurements were repeated the following year, α-farnesene was no longer observed. However, in the case of mechanical or herbivore-attack-induced stress, one expects not only different rates of emissions but also different emission spectra, which were not observed in this study (Haapanala et al., 2009; Duhl et al., 2013). The similar emission spectra of trees A and B do not support the hypothesis that either of the trees would have been more stressed than the other. It should be noted that these results are based on measurements of two trees only; thus the cause of the difference in emission rates remains unsolved. It is possible that the difference in the observed emission rates reflects within-species variation of *L. cajanderi*. Monoterpene emission potential variation of more than one order of magnitude has been reported by, for example, Hakola et al. (2001) for *Betula pubescens* and Haapanala et al. (2009) for *Betula pubescens* spp. *czerepanovii*.
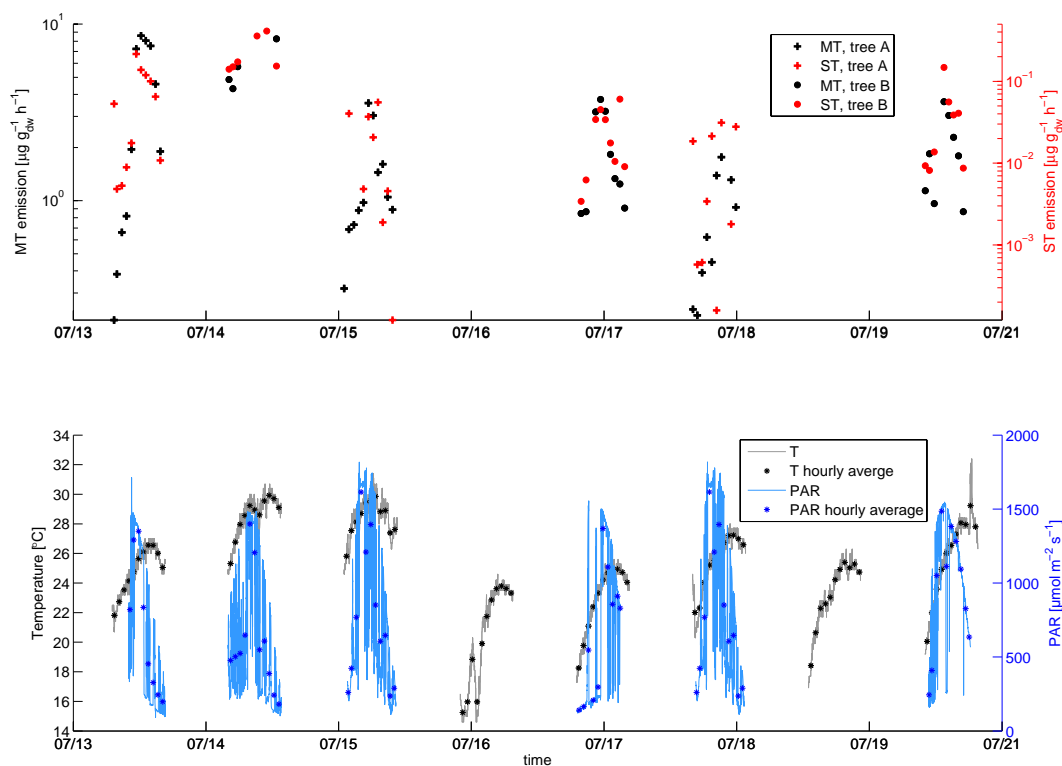
Fig. 5. An example of the measured mono- and sesquiterpene emission rates (top) and temperature and photosynthetically active radiation (PAR) (bottom) between 13 and 15 July 2009.

Also Bäck et al. (2012) have reported intra-species variation in the monoterpene emission profile from *Pinus sylvestris*.

3.3 Emission potentials

The emission potentials were determined using both pool and synthesis algorithms (Table 2). The calculations were done for standard conditions of 30 °C for temperature and 1000 µmol photons m^{-2} s^{-1} for the radiation. In the pool algorithm, a value of 0.09 °C^{-1} was chosen for parameter β °C^{-1}, which is commonly applied for monoterpenes (e.g. Guenther et al., 1993, 1995; Lindfors et al., 2000). There is no widely adopted value of β for sesquiterpenes; however, based on measurements in boreal forest, Tarvainen (2008) recommended a "generic" β value of 0.19 °C^{-1} for sesquiterpene emissions. In this study (i) a β value of 0.143 °C^{-1}, which was found from the nonlinear regression calculations for *L. sibirica* (Ruuskanen et al., 2007), was used, and (ii) β was kept as a free parameter when fitting the algorithm to the observations.

Recently it has become evident that monoterpene emissions from some coniferous trees can have two parallel sources: one directly from synthesis and the other one as evaporation from large storage pools (Shao et al., 2001; Ghirardo et al., 2009). Linear combination of de novo and evaporative algorithms has been used to describe the monoter-

pene emission via parallel sources from boreal coniferous trees and ecosystems (Steinbrecher et al., 1999; Shao et al., 2001; Ghirardo et al., 2009; Taipale et al., 2011). However, according to Ghirardo et al. (2009) only a small part of the emission from *L. decidua* originated directly from synthesis, and thus it is rather probable that the contribution of the de novo emission is small also for *L. cajanderi*. The applicability of the hybrid model was also tested, but due to a limited number of measurements the results were not reliable.

Measured mono- and sesquiterpene emissions rates of *L. cajanderi* seemed to follow both pool and synthesis algorithm equally well (Table 2). In general the emission rates of tree B follow both pool and synthesis algorithms better than those of tree A for both mono- and sesquiterpenes. In field conditions, especially in the boreal forest in the summertime, the temperature and radiation may be strongly coupled, which makes it difficult to distinguish whether enhanced emissions were caused by increases in the radiation, temperature or both. The emission potentials obtained with the synthesis algorithm were higher than those obtained with the pool algorithm, yet the difference was within the uncertainty range.

Similarly to the measured emission rates, the determined emission potentials were highest in June for both trees A and B, and they decreased towards August. Similar decreasing trends during growing season have been observed also for
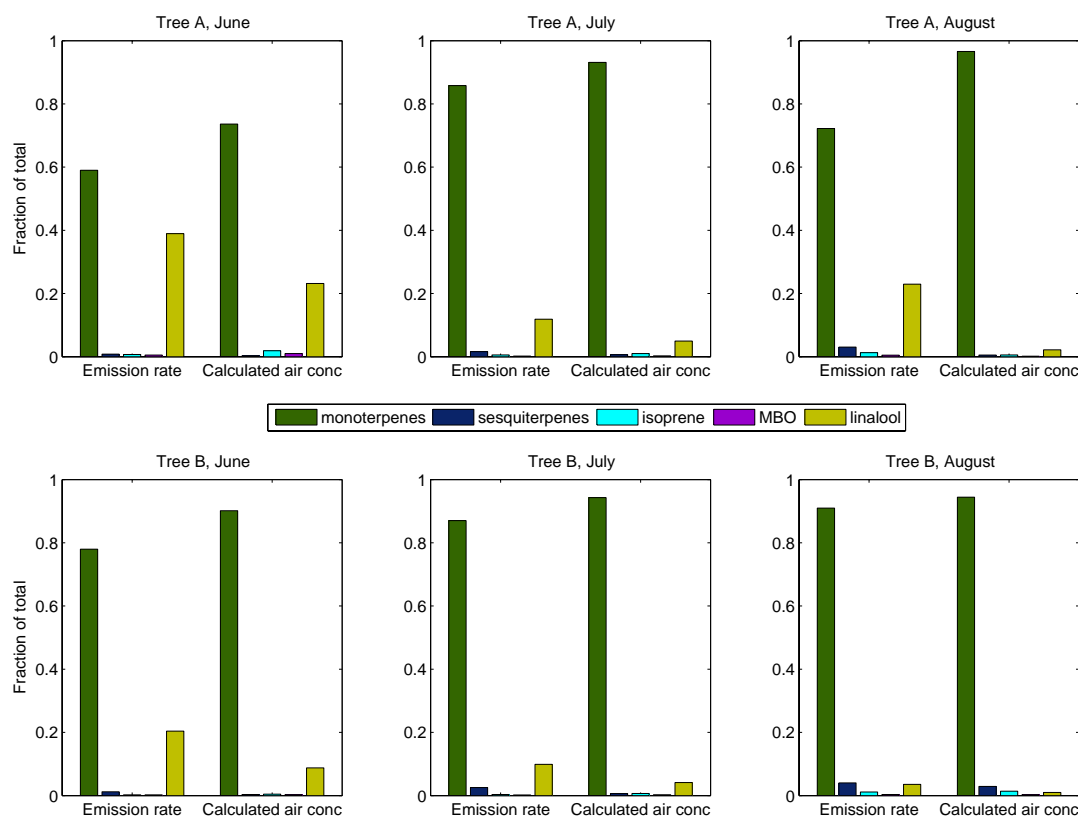
Fig. 6. Relative emission rates of the measured VOCs and their calculated air concentrations due to oxidation with OH and ozone.

other boreal tree species, e.g. *Pinus sylvestris* (Tarvainen et al., 2005; Hakola et al., 2006). Reflecting the high emission rates, the mono- and sesquiterpene emission potentials of tree B were high compared to tree A. The normalized monoterpene emission potential, using the temperature-dependent pool algorithm with constant β (Guenther et al., 1993), varied between 1.5 and 2.2 $\mu g\,g_{dw}^{-1}\,h^{-1}$ for tree A and 0.5 and 18.5 $\mu g\,g_{dw}^{-1}\,h^{-1}$ for tree B. In June and July the emission potential of tree B was almost an order of magnitude higher than that of tree A, whereas in August the monoterpene emission potential of tree A was more than four times higher than that of tree B. The monoterpene emission potentials of tree B are comparable to those of *L. sibirica*, which have been reported to be 5–21 $\mu g\,g_{dw}^{-1}\,h^{-1}$ by Ruuskanen et al. (2007).

Several studies have been done on the monoterpene emissions of other boreal tree species. Normalized pool emission potentials of 0.2–4.4 $\mu g\,g_{dw}^{-1}\,h^{-1}$, 0.2–8.3 $\mu g\,g_{dw}^{-1}\,h^{-1}$, 0.7–7.7 $\mu g\,g_{dw}^{-1}\,h^{-1}$ and 0.2–5.5 $\mu g\,g_{dw}^{-1}\,h^{-1}$ have been determined for *Pinus sylvestris*, *Picea abies*, *Betula pendula* and *Betula pubescens*, respectively (Janson et al., 1999; Hakola et. al., 2001, 2006; Ruuskanen et. al., 2005; for review see Rinne et al., 2009). The results of this study are in the same range as the previous measurements, indicating that monoterpene emissions of *L. cajanderi* are comparable to other boreal tree species. For sesquiterpenes less data are available in the published literature. The temperature-dependent pool emission potential algorithm yielded values of 0.02–0.03 $\mu g\,g_{dw}^{-1}\,h^{-1}$ for tree A and 0.04–0.4 $\mu g\,g_{dw}^{-1}\,h^{-1}$ for tree B, which were lower than emission potentials of *L. sibirica* (0.4–1.5 $\mu g\,g_{dw}^{-1}\,h^{-1}$; Ruuskanen et al., 2007).

The β values obtained from the pool algorithm, when varying β, for the monoterpene emissions of tree A are all somewhat close to the commonly used value 0.09 °C^{-1}. The mean of all the β values for tree A is 0.10 °C^{-1}. Yet, for tree B the mean β value is 0.30 °C^{-1}, which is clearly higher than 0.09 °C^{-1}. However, in August the β value for tree B is significantly lower than during the other months (0.05 °C^{-1}); furthermore, in August the β values of both trees are comparable with each other. In the case of sesquiterpenes the β values of tree A are clearly lower (mean β is 0.083 °C^{-1}) and β values of tree B substantially (mean 0.243 °C^{-1}) higher than the value 0.143 °C^{-1} that was used for constant β calculations.

3.4 Estimated relative air concentrations

In order to assess the role of VOC emissions in the atmospheric chemistry and SOA formation, relative above-canopy concentrations of monoterpenes, linalool, sesquiterpenes, isoprene and MBO were estimated for each of the three campaigns (Fig. 6). For the most reactive compounds,
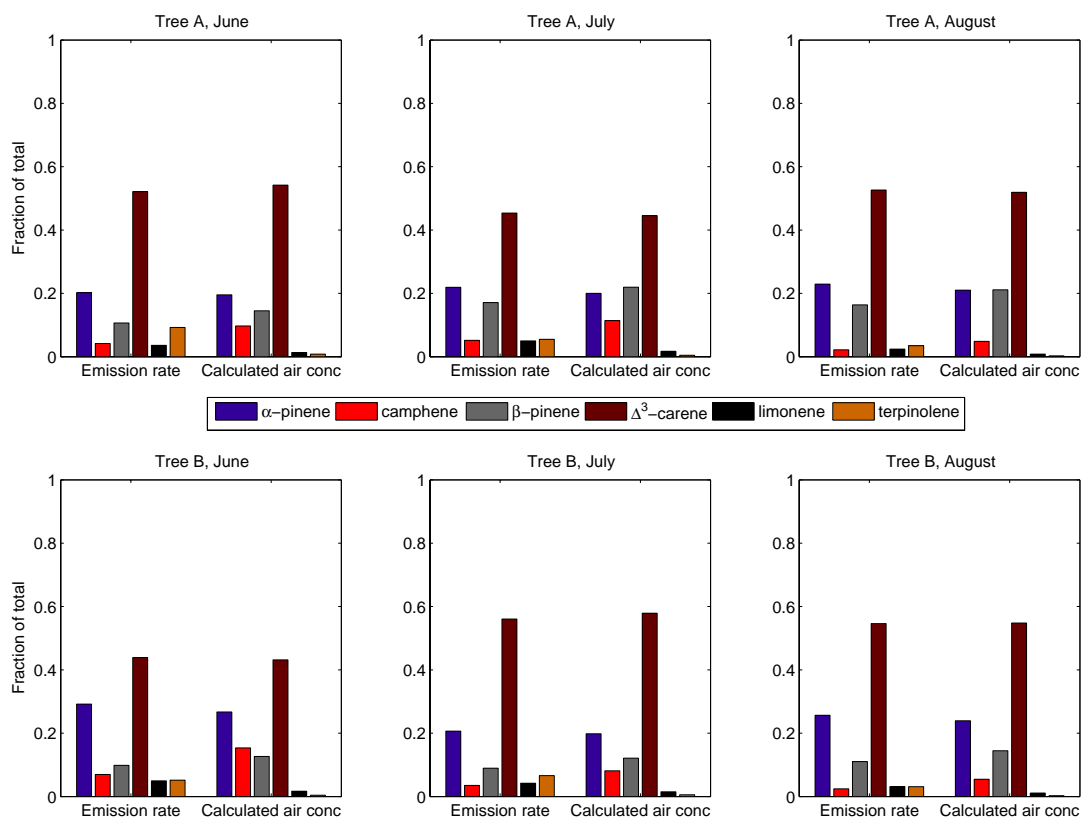
Fig. 7. Relative emission rates of monoterpenes: Δ^3-carene, α-pinene, β-pinene, terpinolene, camphene, limonene and p-cymene, and their calculated air concentrations due to oxidation with OH and ozone.

the fraction of the relative ambient concentration is smaller than their fraction from the measured emissions. These compounds are oxidized faster by OH and O_3 and their SOA formation potential is higher than for less reactive compounds. This approach assumes that the atmospheric concentrations were only due to the emissions from *L. cajanderi*, so the possible contribution from the undergrowth and the small amount of other tree species is neglected. The calculation was done separately for the emission rates obtained from the measurements for trees A and B because of the large difference in the absolute emission rate values of the two trees. For mono- and sesquiterpenes weighted mean reaction rate constants, which take into account the emission spectra, were used (Table 1). Because no ozone oxidation reaction rate constant for p-cymene exists in the literature, p-cymene was omitted from the calculations. The calculations were done using a typical summer daytime maximum value of 10^6 molecules cm^{-3} for hydroxyl radical (Petäjä et al., 2009) and 35 ppb for ozone (Luybovtseva et al., 2005), based on measurements in Hyytiälä, Finland.

Figure 6 shows that, similarly to the measured emission rates, monoterpenes formed the main fraction of the total calculated air concentrations for both trees A and B, in the case of tree A especially so towards the end of the summer. As linalool and most of the observed sesquiterpenes are very re-

active, their contributions to the calculated air concentrations were notably smaller than their contribution to the emission rates. For linalool, due to high emissions in June and a decreasing emission trend during the summer, the calculated air concentration was high in June and negligible in August. Even though the sesquiterpene emission rates remained rather constant as the summer progressed, their contribution to the calculated air concentrations increased, especially in the case of tree B. For isoprene both the emission rates and the calculated atmospheric concentrations were negligible for both trees A and B.

The relative air concentrations for individual monoterpene species, as well as the emission rates, are shown in Fig. 7. Δ^3-carene, which has the highest emission rate, also dominates the calculated monoterpene air concentrations. For α-pinene the fraction in air concentrations is slightly smaller compared to emission rates, whereas for β-pinene and camphene the situation is opposite. The most reactive of the observed monoterpenes, limonene and terpinolene have the largest decrease when comparing the fraction in measured emission rates to the calculated air concentrations. As a comparison, in Scots pine (*Pinus sylvestris*)-dominated boreal forest the measured main monoterpene species in the summertime is α-pinene, which corresponds to about half of the monoterpene concentration (Hakola et al., 2012). The

same study showed that Δ^3-carene, β-pinene, limonene and camphene are the other important contributors to the total monoterpene emission, and that the rest of the detected monoterpenes are less significant.

4 Conclusions

The shoot-scale emission rates of VOCs from *Larix cajanderi* were dominated by monoterpenes, between 61 and 92 % of the total emission. Also linalool emissions were substantial (3–37 % of the total), especially in June. Sesquiterpenes accounted for less than 3 % of the total emission. Isoprene, cineol and MBO were also detected, but their shared percentage was about 2 % of the total. The emission spectra of monoterpenes remained somewhat constant throughout the summer. Δ^3-carene constituted about half of the monoterpene spectra. Other significant compounds were α- and β-pinene. In June and July more than half of the sesquiterpene spectra consisted of farnesene/alloaromadrendrene. In August the sesquiterpene emissions were close to detection limits and none of the compounds were dominating the spectra.

In June, when the linalool emission rate was highest, its impact on air chemistry and SOA formation was also the greatest. Nevertheless, due to their high emission rates monoterpenes contribute most to the air chemistry during the whole summer. As the atmospheric oxidation reaction rates of the main monoterpenes emitted by *L. cajanderi* are all in the same range, the calculated relative air concentrations of monoterpenes closely reflect their relative emission rates. The calculated relative abundance of sesquiterpenes is even smaller than their relative emission rates due to their high reactivity.

Large differences were observed in the emission rates of the two trees. Possibly, the measured shoots of tree B were exposed to mechanical stress; additionally, other parts of tree B may have been influenced by a herbivore attack. However, based on measurements of only two trees, it cannot be concluded whether these stress factors explain the different emission rates or if it is caused by tree-to-tree variation.

The normalized emission potentials of both mono- and sesquiterpenes were highest in the early summer and decreased towards the end of the summer. For the two measured trees A and B, the monoterpene emission potential using the temperature-dependent pool algorithm with constant β were 1.5–2.2 $\mu g\,g_{dw}^{-1}\,h^{-1}$ and 0.5–18.5 $\mu g\,g_{dw}^{-1}\,h^{-1}$, respectively. These results are consistent with previous measurements done for other boreal tree species, except for the highest emission potential values of tree B. The emission potentials of tree B were higher than those observed for other boreal tree species with the exception of *L. sibirica*. The normalized sesquiterpene emission potentials were between 2 and 3 % of those of monoterpenes, 0.02–0.03 $\mu g\,g_{dw}^{-1}\,h^{-1}$ for tree A and 0.04–0.4 $\mu g\,g_{dw}^{-1}\,h^{-1}$ for tree B.

The structure of today's global BVOC emission models, which linearly upscale the leaf emission potentials, requires robust information on this variable for the vegetation functional unit of the models (Arneth et al., 2008; Niinemets et al., 2010a, b). Naik et al. (2004) and Schurgers et al. (2009) adopted a value of 2.4 $\mu g\,g_{dw}^{-1}\,h^{-1}$ as leaf emission potential for the boreal needle-leaf summer green plant functional type. This value is comparable to the measurements of tree A. However, if values of tree B were to be adopted, or some average of the two, modelled monoterpene emissions over a large part of the boreal forest would increase substantially (Arneth et al., unpublished data). As a result, this would increase the derived SOA and regional radiative forcing due to SOA (Makkonen et al., 2012). Based on these measurements, robust advice on the emission potential to be used for boreal larch in global models cannot be provided. Thus more emission measurements need to be done on several individual *L. cajanderi* trees and also on different larch species. However, the data provide evidence that previous modelling studies have underestimated the emission factors, and that estimates of monoterpene emissions across Siberia have to be revised.

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