

Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots pine (*Pinus sylvestris* L.)

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Abstract

Recent research pointed out the question of missing OH reactivity in a forest system and the question for unknown highly reactive biogenic emissions. In this study we show that coniferous forests are an important source of highly reactive hydrocarbons, the sesquiterpenes. We investigated the seasonality of terpene emissions from Scots pine to work out influences on atmospheric chemistry in different seasons for both mono- and sesquiterpenes. Especially sesquiterpenes (C₁₅) change dramatically in their contribution to the terpene emissions of Scots pine. Fourteen sesquiterpenes and oxygenated compounds were found in the emissions. In spring, the pattern was most complex with all 14 compounds being emitted, whereas in summer and fall it was reduced to 1,8-cineol and camphor. The emission pattern of the monoterpenes varied only slightly. The main compounds emitted were α -pinene, β -pinene, and 3-carene representing up to 90% of the total terpene emission. The total monoterpene emission rates varied from below detection limit to 460 pmol m⁻² s⁻¹ with highest emission rates found in June. Standard emission rates of the main compounds calculated from the monthly measured diurnal emission courses varied considerably over the year. Highest values were found in spring and early summer with up to 700 pmol m⁻² s⁻¹.

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1. Introduction

Plants emit a variety of trace gases, namely volatile organic compounds (VOCs). These emissions cover a large assortment of different hydrocarbons (Fehsenfeld et al., 1992). The Earth's northern hemisphere is covered with extensive

forests especially of coniferous character which represent a large source of biogenic emissions. It is known that conifers in the boreal region emit significant amounts of monoterpenes (Lerdau et al., 1997; Hakola et al., 2000, 2003; Tarvainen et al., 2005). Less is known about sesquiterpene emissions of conifers. Monoterpenes are emitted persistently from storage organelles (resin ducts) mainly as a function of the leaf temperature. However, there is also evidence that other parameters (light, draught, herbivore attack) affect the emissions

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(e.g. Steinbrecher et al., 1993; Litvak and Monson, 1998; Prieme et al., 2000; Shao et al., 2001).

The emitted compounds react with OH radicals and thus affect its tropospheric concentration (Thompson, 1992; Aschmann et al., 2002; Atkinson and Arey, 2003). Therefore, these VOCs may influence the oxidation capacity of the troposphere at least on a regional scale. Moreover, the degradation of VOCs in the presence of high NO_x concentrations leads to a net production of ozone and other photooxidants (Paulson and Seinfeld, 1992; Fehsenfeld et al., 1992). Beside their influence on the gas phase chemistry of the atmosphere, VOC's oxidation products can lead to the formation of secondary organic aerosols (Hoffmann et al., 1997; Vesala et al., 1998) and thus affect the net radiation of the troposphere at least on a regional scale (Brasseur et al., 1999).

The processing of VOCs with ozone results in OH production. It can be expected that a large amount of biogenic VOC (e.g. the highly reactive sesquiterpenes and oxygenated compounds) are processed within the canopy by this reaction. Indeed, recent observations show a missing OH reactivity especially in forest canopies, since the measured concentration of OH radicals is higher than that predicted by model calculations; mainly in the case of elevated temperatures where increased terpene emissions can be expected (Di Carlo et al., 2004; Holzinger et al., 2004). A reason for that may be the reaction of unknown, highly reactive VOCs with ozone to form these high OH concentrations. However, due to the lack of emission data this can only be speculated.

Here we report on emission studies carried out in 1998 and 1999 with Scots pine (*Pinus sylvestris* L.). The aim of the work was to shed light on the emission behaviour of this species in relation to the meteorological parameters air temperature and light intensity, and to investigate the influence of seasonal changes on the emissions as well. In order to evaluate the influence of air temperature and light on the emission, standard emission rates were calculated using algorithms presented by Guenther et al. (1993).

2. Materials and methods

2.1. The measurement site

Biogenic emissions were investigated in a stand of 40 years old Scots pines (*Pinus sylvestris* L.). The

stand has a total area of $10 \times 1.5 \text{ km}^2$ and is part of the "Hartheimer Wald" (Hartheim forest) near Freiburg, Southern Germany ($47^\circ 56' \text{N}$, $7^\circ 37' \text{E}$, 201 m a.s.l.). The climatic conditions in and above the stand are well documented by continuous measurements of the Meteorological Institute of the University of Freiburg (Jaeger and Kessler, 1996; Kessler and Jaeger, 2003). A detailed description of the site can be found in Jaeger et al. (1986). The mean canopy height of the investigated trees was about 15 m. The branches in the canopies were accessible from an 18 m-high tower.

2.2. Branch enclosure system and analytics

Emission data were obtained using the branch enclosure technique. Enclosure measurements over a complete vegetation period raise the question of how to handle the plant material. Conducting the measurements over the year with different plant material can lead to additional problems in the interpretation of the results. It is known that pine trees show distinct differences in emissions pattern and emission strength (Janson, 1993; Komenda and Koppmann, 2002). Investigating always the same branches within an enduring vegetation period we could exclude these uncertainties arising from intra-specific variations in composition and amount of emissions. In this study emission rates are based on the total needle surface of the investigated branches. Long-term investigations have to account for the changes in total needle surface of a branch arising from the development of the needles over the year. The aim of the study was to analyse the emission behaviour at two individual branches over two vegetation periods. Therefore, the determination of the needle surface had to be done in a non-invasive way. The branches were photographed on a normalized reference paper board at the end of each measurement episode. From the monitoring of the development of single needles the changes of emitting surface were calculated (Table 1). Also the dropping of senescent needles was accounted for in this way. Both investigated branches looked healthy and showed no effects from aphids or other herbivores.

The two enclosure systems (based on the system described in detail by Holzke (2001) and Parusel (1996)) were made of Teflon foil bags (volume: 50 L each) flushed with VOC- and ozone free air (cleaned by a 1 L-charcoal filter) at a flow rate of $8\text{--}10 \text{ L min}^{-1}$. Carbon dioxide concentration, air

Table 1
Total needle surface

Date	Total needle surface (m ²)	
	Tree 1	Tree 2
<i>1998</i>		
3/31	0.049 ± 0.003	0.066 ± 0.003
4/28	0.056 ± 0.002	0.075 ± 0.003
6/04	0.087 ± 0.005	0.116 ± 0.004
7/06	0.112 ± 0.006	0.149 ± 0.007
8/26	0.131 ± 0.002	0.174 ± 0.003
9/16	0.125 ± 0.003	0.166 ± 0.005
10/21	0.125 ± 0.003	0.166 ± 0.005
<i>1999</i>		
5/06	0.092 ± 0.005	0.144 ± 0.004
7/21	0.185 ± 0.008	0.289 ± 0.009
10/13	NC	0.321 ± 0.008

Derived from the reference paper board based analysis of branch pictures. Pictures were taken with in every measurement campaign. The development of single needles were analysed to appreciate the changes of total emitting needle surface ± SD.

NC, not calculated.

temperature, photosynthetic active radiation (PAR) and relative humidity were measured continuously inside the enclosures which reached branches in 14 m height. After an overnight conditioning time, to make sure that irritation-induced emissions were settled, air from the enclosure chambers was sampled during daytime (normally 5:00 am–9:00 pm, at least from sun rise to sun set) every 2 h for a period of 30 min (night-time measurements were omitted from the study because emission rates ranged at the detection limit; blanks were taken two times the day). Samples were taken simultaneously at two branches of different trees with maximum delay time of half an hour for some measurements. The VOCs were trapped on adsorption tubes filled with Carbotrap and Tenax TA. Identification and quantification of the hydrocarbons were carried out in the laboratory applying thermodesorption coupled with GC/MS (Dani 6500 GC/Finnigan-MAT ITD 700; GC temperature programme: 37 °C for 2 min, first ramp: 8 °C min⁻¹ to 200 °C, second ramp: 10 °C min⁻¹ to 220 °C. Holding time 18 min; MS: EI mode, scan range 45–240 m/z). Detection limit: about 5 ppt(v/v). Analysis were carried out not later than 4 weeks after sampling. Meanwhile samples were stored at 8 °C in the dark. Most of the monoterpenes were identified by using reference compounds in a diffusion source. A detailed description is given in

Holzke (2001). Most of the sesquiterpenes and the oxygenated compounds were identified by comparison of library data for mass spectra and retention times (NIST, Gaithersburg, USA; Publisher Wiley-VCH, Weinheim; Kovats, 1958; Davies, 1990). Emission rates were calculated by multiplying the VOC concentration in the sample air with the air flow rate through the chamber divided by the total needle surface area of the investigated branch. To convert the numbers given here in units of pmol m⁻² s⁻¹ to emission rates in units of µg g(dw)⁻¹ h⁻¹, the factor $1.4 \times 10^{-5} \times Mw$ can be used where Mw is the molar weight of the respective compound (Heiden et al., 2003).

2.3. Modelling of the terpene emissions

We used the algorithms of Guenther et al., 1993, in the way of modelling the emissions out of pools and emissions deriving from de novo synthesis in combination. Standard emission rates E were calculated in the following way:

$$E = E_{\text{pool}} + E_{\text{synth}}, \quad (1)$$

with

$$E_{\text{pool}} = E_{\text{stand}}^p \left(\frac{\exp\left[\frac{C_{T_1}}{R} \left(\frac{T-T_s}{TT_s}\right)\right]}{C_{T_3} + \exp\left[\frac{C_{T_2}}{R} \left(\frac{T-T_M}{TT_s}\right)\right]} \right) \quad (2)$$

and

$$E_{\text{synth}} = E_{\text{stand}}^s C_L \left(\frac{\alpha L}{\sqrt{1 + \alpha^2 L^2}} \right) \times \left(\frac{\exp\left[\frac{C_{T_1}}{R} \left(\frac{T-T_s}{TT_s}\right)\right]}{C_{T_3} + \exp\left[\frac{C_{T_2}}{R} \left(\frac{T-T_M}{TT_s}\right)\right]} \right). \quad (3)$$

E_{pool} = temperature dependent terpene emission from pools, E_{synth} = temperature and light dependent terpene emission from de novo synthesis, E_{stand}^p = standard emission factor, E_{stand}^s = standard emission factor, T = temperature (K), T_s = standard temperature (303 K), T_M = critical temperature of enzyme denaturising (314 K), C_{T_1} , C_{T_2} , C_{T_3} , α , C_L = empirical parameters, L = light intensity [$\mu\text{mol m}^{-2} \text{s}^{-1}$], R = gas constant R ($= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The algorithm was fitted by least-square fits of the standard emission factors. By that, the algorithm was used to simulate the measured emissions and to calculate standard emission rates normalized with air temperature and light intensity.

3. Results and discussion

3.1. The emission pattern

Scots pine is well known as a monoterpene emitter releasing α -pinene and 3-carene as main compounds (Simpson et al., 1999; Hauff et al., 1999; Komenda and Koppmann, 2002). However, the total terpene emission was found to be a mix of about 30 isoprenoids (mono-/sesquiterpenes and oxygenated compounds). Besides α -pinene and 3-carene we also observed β -pinene and camphene as main compounds in the emissions (see Table 2). These four compounds represented about 60–90% of the total terpene emission based on a molar carbon amount. This observation is in agreement with the two other studies carried out in 1998

(Komenda and Koppmann, 2002) and 1999 (Komenda et al., 2003) at the same site. For pine tree 1 an emission of these compounds was observed during the entire period of measurements. Interestingly, in the emission pattern of pine tree 2 almost no 3-carene was observed but pronounced higher rates of β -pinene (up to 40% higher than tree 1 at the 21st of October 1998; 15% on average for both years) occurred. No obvious differences in growth conditions and health were found for these two trees, which were growing at a distance of less than 10 m, growing on the same soil and controlled by the same ambient conditions. The observation of an individual emission pattern for Scots pine with no or low contributions of 3-carene to the emission was also reported by other groups (Hiltunen et al., 1975; Komenda and Koppmann, 2002; Tarvainen et al.,

Table 2
Percentages of the main compounds of the total terpene emission, tree 1 and 2

Date	Rate carbon (mol-%)				Rate of all main compounds of total terpene emission*
	α -pinene	β -pinene	3-carene	Camphene	
<i>Branch tree 1</i>					
1998					
3/31	28.5±4.7	1.9±2.9	51.6±7.8	9.0±4.2	91.0±3.6
4/28	25.9±5.8	4.1±5.3	48.4±15.2	5.9±1.6	84.3±4.8
6/04	12.1±4.1	3.6±2.0	67.7±9.9	2.9±1.0	86.3±3.9
7/06	31.0±7.0	4.8±3.7	39.9±11.7	4.6±1.2	80.4±11.3
8/26	15.7±7.9	25.6±9.2	30.7±10.6	2.4±1.2	74.4±8.1
9/16	32.3±4.9	4.2±1.1	47.8±4.5	5.1±0.9	89.4±3.7
10/21	29.5±4.4	2.8±1.4	56.2±7.9	2.3±1.0	90.7±2.7
1999					
5/06	16.9±6.1	3.1±2.5	50.7±20.1	3.0±1.4	73.7±13.1
7/21	20.7±3.1	0.9±1.1	68.9±4.1	1.5±1.6	92.0±3.1
10/13	NM	NM	NM	NM	NM
<i>Branch tree 2</i>					
1998					
3/31	39.1±5.6	20.0±3.7	0.4±1.2	10.2±1.8	69.7±7.8
4/28	40.3±5.2	22.6±5.7	0.7±13.1	9.1±1.7	72.7±5.3
6/04	36.6±6.6	15.6±2.1	0.3±0.3	12.1±1.57	64.7±7.3
7/06	39.5±11.1	16.3±5.5	0.3±1.6	9.0±3.4	65.1±8.7
8/26	47.2±6.3	22.3±5.9	0.8±3.9	7.0±1.8	77.3±5.5
9/16	56.5±2.3	13.2±1.0	4.6±4.8	10.9±2.5	85.2±2.3
10/21	29.8±3.6	43.2±4.4	0.6±2.1	1.4±1.1	75.0±4.5
1999					
5/06	28.8±9.8	20.7±6.3	0.2±0.3	12.4±2.5	62.0±8.6
7/21	54.0±4.2	12.4±2.3	0.7±2.5	16.8±4.2	84.0±5.0
10/13	54.9±6.2	15.2±6.3	5.8±7.0	11.3±6.8	87.2±7.1

Values are daily averages.

NM not measured.

*mono- and sesquiterpenes + ox. compounds.

2005). Considering that our investigated trees grew up under similar conditions we have no explanation for the observed differences in the emission pattern. Schnitzler et al. (2004) proposed a genetic background that leads to differences in the expression of terpene synthases for individual trees according to their parent genes. For our study this could only be speculated as we do not have data of terpene synthase activities for the trees of the “Hartheimer Wald”. Comparing the main compound α -pinene with 3-carene the present study shows a significantly different 3-carene-to- α -pinene ratio for June. It was higher by a factor of three compared to the rest of the year for this tree. It has been argued that 3-carene acts as a protective agent against feeding, mainly produced in young needles (Larsson and Tenow, 1980). This could explain the high emission rates measured on 4 June 1998 (Fig. 2) as the development of new needles occurred mainly in June. In fact temperature normalized emission rates of 3-carene found for tree 1 during this month were significantly higher compared to other months of the year (Table 4).

In addition to monoterpenes the investigated pines emitted a wide variety of sesquiterpenes and oxygenated hydrocarbons. In March/April we observed up to 14 different compounds (cf. Table 3). Highest emission rates were found for 1,8-cineole and camphor. In August, September and October 1998 the emission of sesquiterpenes and oxygenated hydrocarbons decreased considerably and was finally restricted to the compounds 1,8-cineole and camphor. The differences in the sesquiterpene emission pattern indicate a plant physiological role played by these compounds. It is known that they have an essential biological function as to be signal transmitting compounds in plant/plant (Kelsey and Locken, 1987) and plant/insect interaction (Threlfall and Whitehead, 1991; Steele et al., 1998). However, concerning the seasonal emission behaviour from vegetation under ambient conditions there is very little information in the literature on single components (Isidorov et al., 1985; Ciccioli et al., 1999; Hakola et al., 2003; Tarvainen et al., 2005). To our knowledge, the present study is the first in which a wide range of emissions of sesquiterpenes and oxygenated compounds was investigated systematically for nearly a whole vegetation period using the branch enclosure technique. For the vegetation in the USA it was reported that about 9% of the NMHCs emitted are sesquiterpenes (Helmig et al., 1994). Although the

emission rates of sesquiterpenes and oxygenated compounds were comparable small in our study (up to about 6% of the total terpene emission) they are still important as they influence tropospheric chemistry due to their extremely high reactivity (Shu and Atkinson, 1995). The degradation of sesquiterpenes yields reaction products both in gas and aerosol phases (Jaoui and Kamens, 2003). Our results are compatible with the possibility that especially in spring sesquiterpenes might influence extraordinarily the OH reactivity in a forest system. Calculating on a reacted mass basis, sesquiterpenes like β -caryophyllene and α -humulene also have much higher aerosol formation potentials than monoterpenes (Griffin et al., 1999). Their contribution to secondary aerosols is currently not clear, but may be significant depending on their actual emissions. In addition, their role in atmospheric processes remains uncertain due to the lack of the identification and quantification of reaction products from their atmospheric oxidation.

The observed seasonality of sesquiterpene emissions might lead to distinct chemical regimes at different times of the year. This seasonality in the sesquiterpene pattern was also observed in a study carried out in California's South Coast Air Basin for Black Sage (*Salvia mellifera*). Here the percentage of the sesquiterpenes of the total terpene emission was significantly higher in spring compared to the rest of the year (Arey et al., 1995). Sesquiterpenes contributed up to 70% to the total emissions in March but this value decreased down to 1–2% in August and September.

3.2. Variation of the emission rates

Concerning their emission behaviour monoterpenes, in general, showed a pronounced diurnal cycle. Highest emission rates were found for conditions with highest air temperatures and PAR. Fig. 1 shows the diurnal variation for one day in August with emission rates varying by a factor of 10. These variations were mainly correlated with air temperature, as these trees emit hydrocarbons from storage organelles. This observation is in agreement with the results of other groups achieved for the boreal region (e.g. Janson, 1993; Rinne et al., 2000). However, it was also reported that additional, especially ecophysiological parameters influence the emission behaviour of plants (Janson, 1993; Rapparini et al., 2001). Therefore, the variability of the emissions of Scots pine was investigated over

Table 3
Mean day time emission rates for sesquiterpenes and oxygenated compounds, tree 1 and 2

	Mean emission rate ($\text{pmol m}^{-2} \text{s}^{-1}$)									
	1998							1999		
	3/31	4/28	6/04	7/06	8/26	9/16	10/21	5/06	7/21	10/13
<i>Tree 1</i>										
γ -cadinene	0.02	0.13	0.21	0.03	bdl	bdl	bdl	2.65	0.65	NM
δ -cadinene	0.07	0.07	0.22	0.02	bdl	bdl	bdl	2.28	1.08	NM
α -muurolene	0.04	0.05	0.25	0.02	bdl	bdl	bdl	1.74	0.67	NM
Aromadendrene	bdl	0.03	0.16	bdl	bdl	bdl	bdl	bdl	bdl	
β -caryophyllene	bdl	0.34	0.92	0.03	bdl	bdl	bdl	16.38	1.48	NM
β -cedrene	0.02	0.08	2.41	0.12	bdl	bdl	bdl	11.15	3.55	NM
β -bourbonene	bdl	0.01	0.02	0.01	bdl	bdl	bdl	0.34	bdl	NM
α -ylangene	bdl	0.01	0.15	bdl	bdl	bdl	bdl	0.22	0.01	NM
Bornyl acetate	bdl	bdl	0.09	0.06	bdl	bdl	bdl	0.31	0.01	NM
Verbonene	0.13	0.05	0.12	0.18	0.01	0.01	bdl	3.91	4.23	NM
Methylsalicylate	bdl	bdl	0.04	0.15	bdl	bdl	bdl	0.32	0.13	NM
α -terpineol	bdl	0.02	0.91	0.09	0.01	bdl	bdl	4.47	0.57	NM
4-terpineol	0.08	0.01	0.24	0.16	0.01	bdl	bdl	3.32	1.51	NM
Camphor	0.52	1.10	0.44	5.02	0.22	0.09	0.06	4.06	1.34	NM
Nopinene	0.15	0.04	0.24	0.04	0.01	bdl	0.01	0.28	0.09	NM
1.8-cineole	0.76	2.34	14.09	5.45	2.54	0.14	0.12	8.73	29.49	NM
<i>Tree 2</i>										
γ -cadinene	0.53	0.21	0.63	0.07	0.04	bdl	bdl	1.51	0.37	0.01
δ -cadinene	0.12	0.17	0.56	0.05	0.02	bdl	bdl	1.40	0.67	0.01
α -muurolene	0.10	0.09	0.22	0.03	0.01	bdl	bdl	0.94	0.23	bdl
Aromadendrene	0.10	0.11	0.13	0.01	bdl	bdl	bdl	bdl	0.04	bdl
β -caryophyllene	0.36	0.22	0.98	0.07	0.04	bdl	bdl	1.97	bdl	bdl
β -cedrene	0.37	0.17	2.76	2.14	0.20	0.01	bdl	10.72	0.56	bdl
β -bourbonene	0.11	0.08	0.07	bdl	bdl	bdl	bdl	bdl	bdl	bdl
α -ylangene	0.14	0.07	0.12	0.01	bdl	bdl	bdl	bdl	bdl	bdl
Bornyl acetate	0.10	0.18	0.18	0.02	bdl	bdl	bdl	0.88	bdl	0.05
Verbonene	0.58	0.26	0.72	0.19	0.05	0.03	0.01	2.52	1.07	3.18
Methylsalicylate	0.04	0.07	0.10	0.09	0.01	bdl	bdl	0.12	0.15	bdl
α -terpineol	0.04	0.05	0.44	0.05	0.01	bdl	bdl	0.21	0.01	0.71
4-terpineol	0.01	0.01	0.42	0.05	bdl	bdl	bdl	bdl	bdl	0.39
Camphor	2.45	0.93	1.01	0.52	0.97	0.42	0.18	0.66	0.31	69.0*
Nopinene	0.07	0.05	0.11	0.03	0.03	0.01	0.01	0.48	0.12	10.4
1.8-cineole	2.39	3.95	12.82	14.93	1.34	0.10	0.12	12.25	8.12	2.23

Averages were taken from measurements between 8:30 a.m and 6:30 p.m.

NM, not measured; bdl, below detection limit.

*Value doubtful.

nearly a complete vegetation period from March to October in 1998 and partially in 1999.

During the course of the year we found that the emissions from Scots pine show a strong seasonal variation. The emission rates of terpenes (the total of all detected compounds) increased in spring and reached a maximum in June (Fig. 2(A)). In 1998 average daytime emission rates of the total of terpenes were up to $460 \text{ pmol m}^{-2} \text{ s}^{-1}$ for tree 1 (averages were taken from measurements between 8:30 am and 6:30 pm). Highest average emission rates of tree 2 were about $300 \text{ pmol m}^{-2} \text{ s}^{-1}$,

observed in June. Emissions were lowest in September when values of only about $20 \text{ pmol m}^{-2} \text{ s}^{-1}$ were measured. Emission rates in fall were about one order of magnitude lower than emissions in spring, even though the conditions of average light intensity and air temperature were similar for both seasons (cf. Figs. 2(B) and (C)). Similar observations were made in a pine stand in Sweden (Janson, 1993), where highest emissions were found in summer too (measured in June, July 1989/1990) with 3 to 4 times lower values in spring and in late summer (measured in May 1990, August 1989/1990 and October 1990).

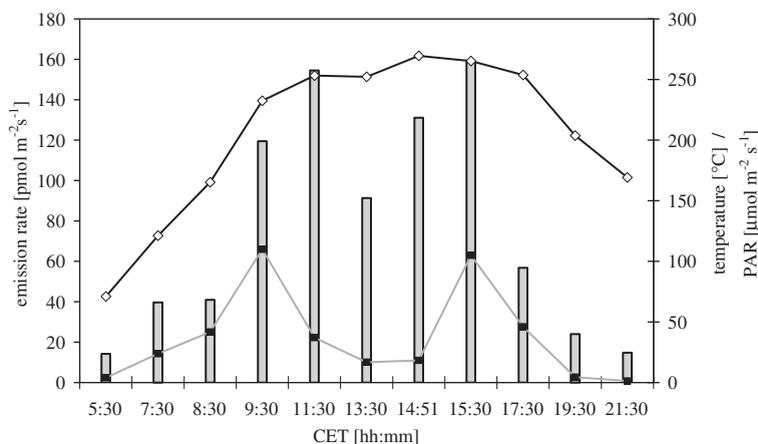


Fig. 1. Diurnal course of terpene emissions. Bars: emission rate (total of terpenes), open diamonds, black line: temperature (multiplied by 10) inside the enclosure system, filled squares, grey line: PAR inside the enclosure system, data show mean values of 30 min samples (time axis: starting time of samples) from tree 2 on 26 August 1998.

Seasonal variations for the boreal region were also reported for tea-leaved willow (*Salix phylicifolia*), aspen (*Populus tremula*), and silver birch (*Betula pendula*) by Hakola et al. (1998). Emissions of willow and aspen showed highest values in May decreasing until September. Birch emission rates were highest in August and lowest in June and September. Ambient air measurements above a boreal coniferous forest in Finland agree with this observation of a seasonality of VOC emissions (Hakola et al., 2003). The conformity of the findings in the boreal region and our results for emission measurements in southern Germany makes it reasonable that there is no obvious geographical influence on the emission behaviour at least concerning these two regions in northern and middle Europe.

3.3. Seasonal variation of the standard emission rates

The diurnal cycle indicated that emissions of terpenes are only dependent on the ambient temperature. However, we found that emission rates at comparable temperature ranges but in different seasons differed. Plotting the emission rates against the inverse ambient temperature (Arrhenius plot) shows that the emission potential (so the absolute emission rate at a given temperature) changes with the season. Fig. 3 shows that for α -pinene as an example. In spring (measurements in March and April) the terpene emission potential was much higher for the ambient temperature compared to the following seasons. In late summer (measurements in August, September, and October)

the potential decreased clearly. Within comparable temperature conditions α -pinene emissions were about one order of magnitude lower compared to spring emissions. However, the individual slopes of the temperature dependence for the different seasons did not change remarkably while the absolute terpene emission rates changed significantly. A reason for that decrease of the absolute terpene emission rates might be a depletion of plants terpene pools later in the year. However, it was reported that emission from de novo synthesis also occurs besides a pool emission for coniferous trees (Kahl, 1997; Staudt, 1997). Therefore emissions will not automatically cease at the end of the year when terpene pools might be depleted.

In the past it was found that reduced emissions reported in summer and fall are correlated with the activity of some terpene synthases (Lehning et al., 1999). Recently, a seasonality was reported for monoterpene synthases for *Quercus ilex* L. (Fischbach et al., 2002). This indicates that the emissions are not only dependent on exogenous but also on endogenous parameters such as the developmental state of the investigated branches. This may be an explanation for the results reported here about seasonal changes in terpene emission rates. However, this can only be confirmed by combining measurements of the emission behaviour and synthase activity in *Pinus sylvestris*.

3.4. Modelling of the terpene emissions

Applying the G93 as described before terpene emissions can be modelled, however, only for a

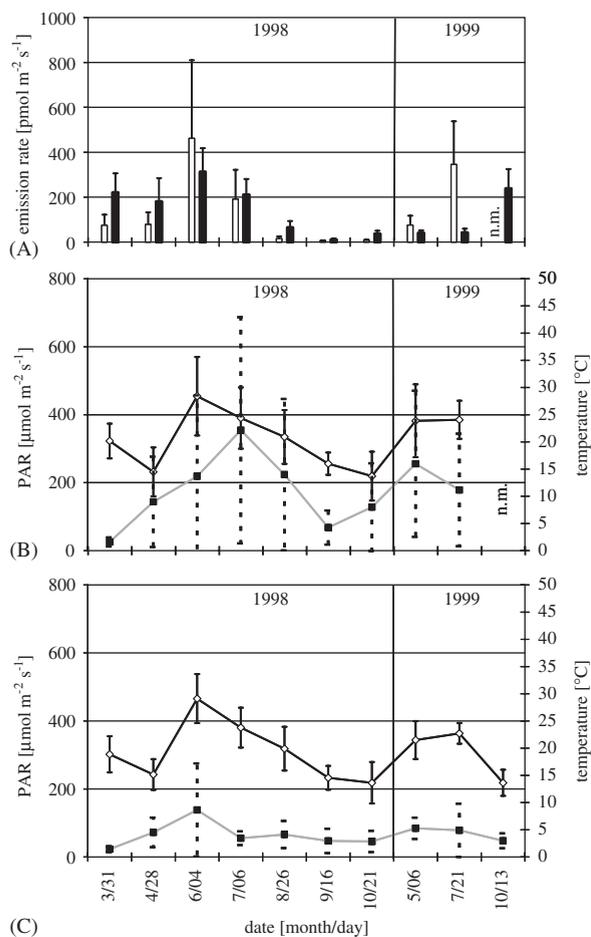


Fig. 2. Seasonal variation in daytime emission, air temperature and light intensity for the years 1998 and 1999. (A) average of the total terpene emission of *Pinus sylvestris*, open bars: branch of tree 1; filled bars: branch of tree 2. (B) average temperature and light intensity inside the enclosure system of tree 1; open diamonds, black line: temperature; filled squares, grey line: PAR. (C) average temperature and light intensity inside the enclosure system of tree 2; open diamonds, black line: temperature; filled squares, grey line: PAR. Averages were taken from measurements between 8:30 am and 6:30 pm. Error bars represent the SD of the average daytime value, n.m. = not measured.

short period of time, typically some days. In order to match the long-term measurements, the algorithm had to be adapted by varying the emission factors (see Eqs. (2) and (3) in Section 2) individually for every month (cf. Fig. 4). Therefore, standard emission rates calculated from the adjusted algorithm varied up to two orders of magnitude for the year 1998 and up to one order of magnitude for the year 1999 (Table 4). In general, standard emission rates for the main emitted compounds were highest in spring and early summer and decreased consider-

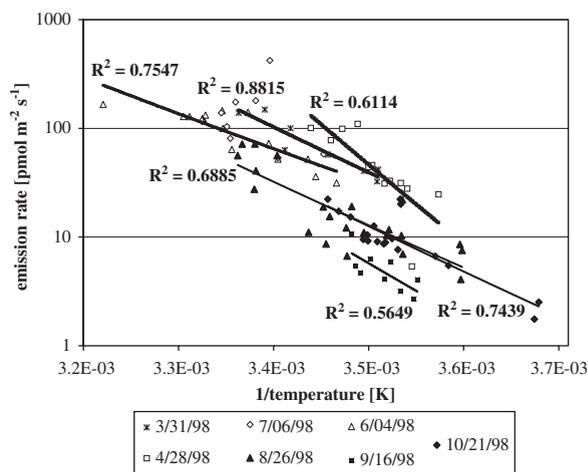


Fig. 3. Changes of the temperature dependence of the α -pinene emission for different seasons measured at a branch of tree 2, emission rates are given on logarithmic scale.

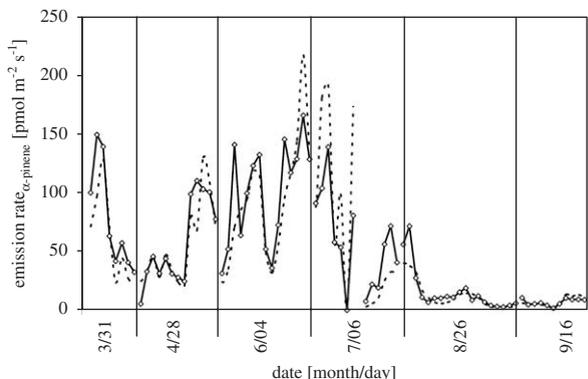


Fig. 4. Simulation of the daytime variation of α -pinene emission 1998 at tree 2 using the Guenther et al. (1993) algorithm G93. Open diamonds with solid line: measured daytime emission rates (one data point correspond to a 30 min sample), dashed line: simulated emission rates using the G93, for details see text.

ably in August, September and October. The deduced variation of standard emission rates is comparable to a recent study for *Pinus sylvestris* where seasonal variations in the standard emission rates of monoterpenes of about a factor of 6 were observed (Komenda et al., 2003). Our results for *Pinus* are also in agreement with observations by Staudt et al. (2002), which were carried out with *Quercus ilex* L. in field and laboratory studies. Here the monoterpene emission behaviour of this species was investigated under different growth conditions related to light intensity and temperature. Under field conditions Staudt et al. (2002) estimated that the standard emission rate of sun-adapted current-year leaves decreases from approximately

Table 4
Calculated standard emission rates for main monoterpenes emitted by Scots pine

Date	Standard emission rate ($\text{pmol m}^{-2} \text{s}^{-1}$)					
	α -pinene		β -pinene		3-carene	
	Tree 1	Tree 2	Tree 1	Tree 2	Tree 1	Tree 2
<i>1998</i>						
3/31	97.8	350.7	3.06	450.6	220.2	NC
4/28	106.0	375.2	16.3	309.9	278.3	NC
6/04	154.9	114.2	32.6	59.1	415.9	NC
7/06	93.8	709.5	14.2	562.7	80.5	NC
8/26	5.1	164.1	14.2	76.4	10.2	NC
9/16	10.2	109.0	2.04	31.6	15.3	NC
10/21	14.2	89.7	1.02	130.5	43.8	NC
<i>1999</i>						
5/06	15.3	33.6	5.1	22.4	35.6	NC
7/21	122.3	82.5	6.1	22.4	424.1	NC
10/13	NC	1288.7	NC	399.7	NC	NC

Calculations were done with the G93 for 30°C and $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$.
NC, not calculated.

$8 \text{ nmol m}^{-2} \text{ s}^{-1}$ in summer to $0.8 \text{ nmol m}^{-2} \text{ s}^{-1}$ in winter, which was accompanied by a decrease of the daily average temperature from 23 to 7°C and a decrease of the daily sum of global radiation from 22 to $6 \text{ MJ m}^{-2} \text{ day}^{-1}$ (Staudt et al., 2002). In contrast, forcing constant growth conditions in the laboratory they found that standard emission rates of full-light-grown plants were almost stable over an 8-month period (Staudt et al., 2003). This indicates that terpene emissions of plants are also subject to the influence of growth conditions comparable to other physiological aspects of development e.g. bud break, leaf expansion and growth, or fruit ripening.

Applying the G93 with and without the light dependence term (Eq. (3) in Section 2) the influence of light on the emission behaviour was also investigated. Calculated standard emission rates showed no significant differences for all investigated seasons (Fig. 5). This is in contrast to other coniferous species like *Pinus pinea*, which also shows a significant light effect in its emissions (Staudt, 1997) or *Picea abies* which shows an influence of temperature and light intensity on the emission of monoterpenes (Steinbrecher et al., 1993). For *Pinus sylvestris* a small influence of light on the emission behaviour of monoterpenes was found in a laboratory study (Shao et al., 2001). A low PAR dependence was observed for the α -pinene

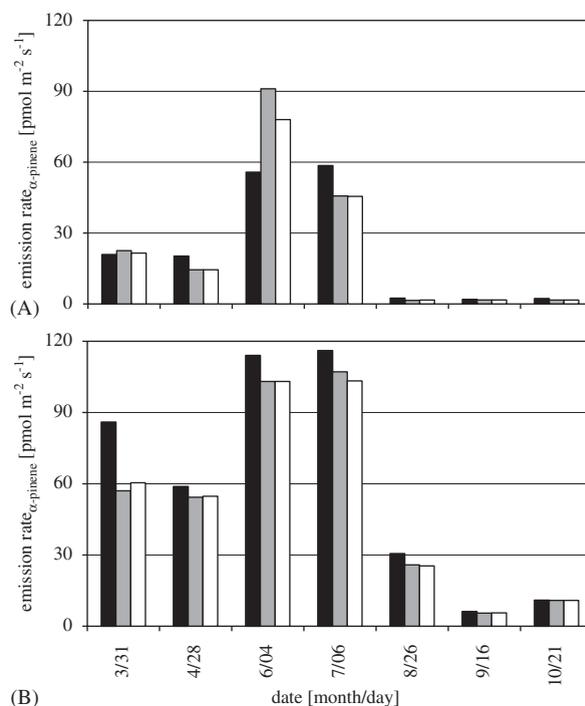


Fig. 5. Simulation of the α -pinene average day time emission 1998 applying different terms of the Guenther-algorithm G93. (A) branch of tree 1, (B) branch of tree 2, black bars: measured average daytime emission rate (averages were taken from measurements between 8:30 am and 6:30 pm), grey bars: simulated average daytime emission rate applying the temperature term combined with the light term, open bars: simulated average daytime emission rate applying only the temperature term.

and camphene release from the plant. Light intensities up to about $300 \mu\text{mol m}^{-2} \text{ s}^{-1}$ triggered the release of these terpenes. This shows that the PAR saturation of this monoterpene emission occurs already at levels of about 15% of full sunlight. Therefore, all measurements conducted above 15% of full sunlight intensity will show no PAR dependence. Moreover, as temperature dependence of the emission is much stronger (shown in this study) the low PAR dependence could not be detected under conditions in the field where temperature and irradiation are correlated. Even in the laboratory study by Shao et al. (2001) a PAR dependence of the emissions of β -pinene and 3-carene was not detectable within the error of measurements.

4. Conclusion

In this study, a significant seasonality of terpene emissions is shown which influences the chemistry of

the atmosphere in and above a coniferous forest stand. Especially, sesquiterpenes change dramatically in their contribution to the total terpene emissions of Scots pine. In spring the pattern was most complex with 14 compounds being emitted, whereas in summer and fall it was reduced to 1,8-cineol and camphor. Also the changes in the standard emission rates of the main emitted monoterpenes α -pinene, β -pinene, and 3-carene means a change of the VOC source strength and therefore the presence of reactive compounds for chemical processes in and above the stand. The study confirms that an emission algorithm such as the G93 is able to predict the average emissions adequately on a short-time scale but do not consider the ability of plants to adapt their terpene biosynthesis capacity dynamically over the year to changing environmental conditions. The seasonal variations indicate that the temperature dependence of the terpene emission from *Pinus sylvestris* is linked to the synthase activities governed by the plant's developing state. The results underline that future algorithms for the prediction of emissions of terpenoids have to take into account physiological and ontogenetic parameters. This is also indispensable for realistic estimates of the impact of biogenic emissions on local and regional tropospheric photochemistry and the up scaling to global climate scenarios.

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