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ORIGINAL ARTICLE

Terpene emissions from European beech (*Fagus sylvatica L.*): Pattern and emission behaviour over two vegetation periods

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Abstract The source strength of volatile organic compounds (VOCs) emitted by vegetation is of great interest for the understanding of processes in atmospheric chemistry and climate change. In this study terpene emissions from branches of European beech (*Fagus sylvatica* L.) were studied in a deciduous forest. Using the branch enclosure technique changes in the emission pattern and the variation of emission rates over the year were investigated over two consecutive vegetation periods. More than 10 monoterpene compounds were found in the emissions, among which sabinene dominates. For most compounds the emission pattern changed only slightly over the year. Interestingly, two compounds tentatively identified as para-cymene and cis-ocimene showed differences in the emission behaviour in late summer compared to the other terpenes. In contrast to previous studies our investigation characterise European beech as a strong emitter. For the main compounds the emission rates changed up to two orders of magnitude as a function of temperature and light over the day. In general, highest emission rates were observed in summer and lowest in fall. A seasonality was characterized by a temperature independent decline of emissions in late summer, resulting in changes of the standard emission rate on the order of one magnitude. A standard emission factor of up to 3.5 nmol m^{-2} s^{-1} for the sum of measured terpenes was calculated. No emissions were found in early spring even though leaves were fully developed and temperature and light conditions were moderate. The results underline the importance of characterising the annual variation of the emission behaviour. Especially for the up-scaling to global VOC emissions, seasonal influences have to be considered to achieve realistic emission inventories.

Keywords Algorithm · ECHO · Long-term variation · Monoterpenes · Seasonality · VOCs

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1. Introduction

Volatile organic compounds (VOCs) have a decisive impact on atmospheric chemistry. Emission sources for these compounds are both anthropogenic and biogenic. Estimates of anthropogenic VOC emissions range between 56 Tg C yr^{-1} (Ehhalt *et al.*, 1986) and 98 Tg C yr^{-1} (Müller, 1992). In comparison, the emission rate from biogenic sources is estimated as 1150 Tg C yr^{-1} (Guenther *et al.*, 1995). Terpenes (isoprene, mono- and sesquiterpenes), especially, have a significant impact on atmospheric chemistry due to their high reactivity; they react rapidly with OH radicals thus affecting the tropospheric concentration of OH (Thompson, 1992; Aschmann *et al.*, 2002; Atkinson and Arey, 2003). Therefore, these VOCs may influence the oxidation capacity of the troposphere. 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). These reactions occur mainly in the boundary layer at the plant/atmosphere interface and in the canopy layer as the main region of biogenic VOC emissions (Ciccioli *et al.*, 1999; Makar *et al.*, 1999). Since ozone can damage plant tissues, these atmospheric processes can have a direct effect on the health of plants and thus have a feedback on the condition of an ecosystem. This is also connected to economical considerations since these effects can lead to significant losses in agricultural and forest productivity (Heck *et al.*, 1984).

Recent studies have indicated that, besides ozone, the photolysis of HONO plays an important role in OH radical formation (Kleffmann *et al.*, 2005). It was shown that photolysis of HONO is responsible for about half of the OH radical concentration observed in the canopy of a forest stand. Thus, it can be expected that a large amount of biogenic VOCs is photochemically processed within the canopy. Recent observations show a missing OH reactivity especially within forest canopies, since the measured concentration of OH radicals is lower than that predicted by model calculations (Di Carlo *et al.*, 2004; Holzinger *et al.*, 2004).

Monoterpenes are also known to be an important factor in particle formation as the oxidation products of these terpenes can lead to the formation of secondary organic aerosols (Hoffmann *et al.*, 1997; Vesala *et al.*, 1998). This was also shown for isoprene (Claeys *et al.*, 2004). Secondary organic aerosols can affect the radiation balance of the troposphere at least on a regional scale (Brasseur *et al.*, 1999) and can play a role in cloud formation (Lohmann and Feichter, 2004). The estimated emission rates of terpenes from vegetation on a global scale ranges from 250 to 450 Tg C yr^{-1} for isoprene and from 128 to 450 Tg C yr^{-1} for monoterpenes (Fall *et al.*, 1999). The range of these estimates is a result of the large uncertainties concerning both the character of biogenic VOC sources and their emission behaviour. In recent years it has been observed that plants emit very specific terpene compositions and show specialised emission behaviour (König *et al.*, 1995; Kesselmeier and Staudt, 1999; Owen *et al.*, 2001; Lerdau and Gray, 2003). While some of these compounds have clearly identified functions within plants (e.g. pollinator attraction, herbivore and pathogen defence, allelopathic functions, etc.), others are produced for reasons that are not yet fully understood.

In the past, *Fagus sylvatica* L. was characterised as a low monoterpene emitter in some studies (Hewitt and Street, 1992; König *et al.*, 1995; Simpson *et al.*, 1999), with normalised emission rates (emissions at 30°C and 1000 μmol m^{-2} s^{-1}) of only some μg g^{-1} leaf dry weight (LDW) h^{-1} (corresponding to some 100 μmol m^{-2} leaf area h^{-1}). In contrast, we observed significant emissions of monoterpenes at different times of the year released by beech. The amounts are comparable to emissions of other deciduous trees such as birch (*Betula pendula* Roth.), tea-leafed willow (*Salix phylicifolia*), aspen (*Populus tremula* L.),

or oak (*Quercus spec.*) as reported by other groups (Hakola *et al.*, 1998; König *et al.*, 1995; Sabillon and Cremades, 2001).

In recent studies on broad leaf trees it was observed that terpene emissions are highly dependent on ambient temperature and light intensity (e.g. Schuh *et al.*, 1997; Dindorf *et al.*, 2005). Furthermore, it is likely that terpene emissions change over the year due to the dependence of, for example, ontogenetic parameters and the developmental state of the plants. If so, this can lead to different standardised emission rates for an individual plant. In the last decade, a number of studies was carried out concerning different aspects of the seasonality of plant emissions (Harley *et al.*, 1994; Kempf *et al.*, 1996; Geron *et al.*, 2000; Petron *et al.*, 2001; Rapparini *et al.*, 2001; Hakola *et al.*, 2003; Kuhn *et al.*, 2004). Nevertheless, our knowledge about the seasonal influences on the emission behaviour is still quite limited. The present study investigates the seasonal changes in monoterpene emissions from branches of the wide spread European species *Fagus sylvatica* L. and year-to-year variations of emissions related to temperature and light intensity.

2. Materials and methods

2.1. The field site

Biogenic emissions were investigated at trees in a mixed deciduous forest located in the area of the Research Centre Jülich. Measurements were carried out in 2002 and 2003 during the European project "*E*mission and *CH*emical transformation of biogenic volatile *O*rganic compounds" – ECHO. The site has an area of about 350 ha and is located between the cities of Aachen and Cologne in a typical patched German landscape with a mean elevation of 90 m above sea level with an almost plain relief. The climatic conditions in the stand are well characterised by continuous measurements of parameters such as solar radiation, air temperature, precipitation and soil moisture (Bergs *et al.*, 1986; Polster *et al.*, 1986). Mean annual precipitation is about 685 mm and the average annual temperature is 9.7°C. Minimum and maximum temperatures for the years 2002 and 2003 are shown in Figure 1(a, b).

The area has been a deciduous forest for more than 300 years and is surrounded by cultivated land. Analysis of the soil material (classified as a Stagno Luvic Pseudogleysol) showed characteristic features, which indicate optimal site qualities for the growth of deciduous trees. Main tree species in this forest are beech (*Fagus sylvatica* L.), birch (*Betula pendula* Roth) and oak (*Quercus spec.*).

2.2. Branch enclosure system and analytical techniques

The two investigated beech trees were about 160 years old. The canopy height was 28 m. The sunlit branches in the canopy were accessed from a tower of 24 m in height. Emission data were obtained from branch enclosure measurements on single branches located in the top of the canopy. Within the scope of two intensive ECHO field campaigns, two different enclosure systems on different branches in the canopy of the same tree were operated. For that time sample analysis were conducted with gas chromatography/mass spectrometry (GC-MS) of two different systems including GC with a single flame ionisation detector (GC-FID) and GC-FID with additional mass spectrometry (GC-FID-MS). For all other measurements over the vegetation periods of 2002 and 2003, the measurement system of the Research Centre Jülich was used (GC-FID-MS). Details of both measurement systems are given in Table 1 and in Sections 2.2.1 and 2.2.2.

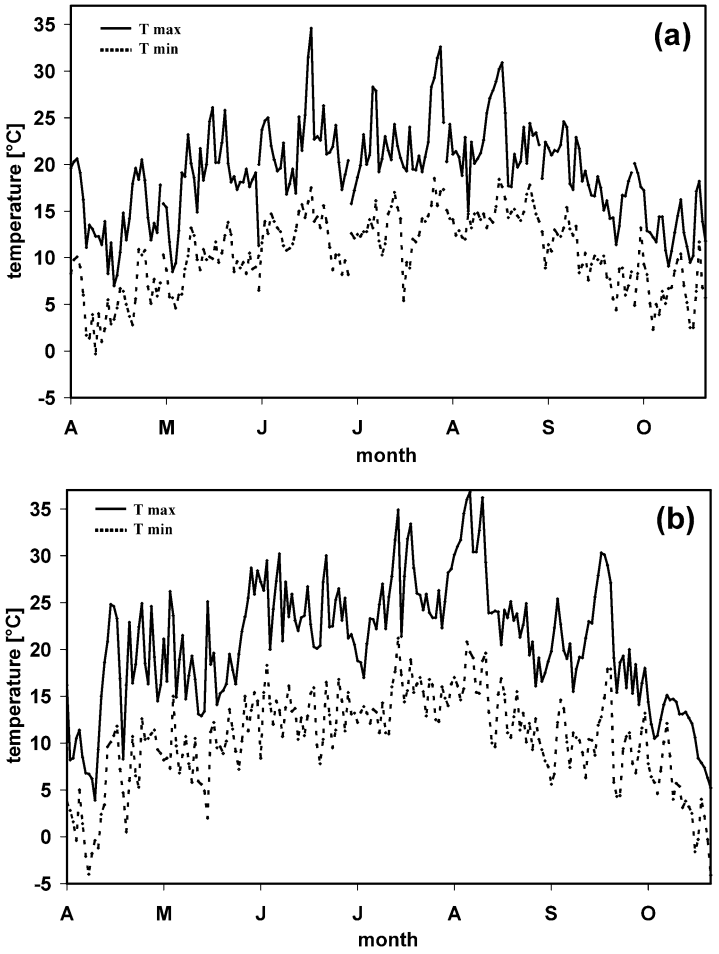

Fig. 1 Minimum and maximum temperatures measured from April to August at the field site for 2002 (a) and 2003 (b). The respective letter at x-axis is set at the 1st day of the corresponding month

2.2.1. Branch enclosure and analytical system of the Research Centre Jülich

Single branches in the canopy of two beech trees were enclosed in a 90 l Teflon-foil enclosure chamber and flushed with VOC-free air with a flow rate of 15–25 l min^{-1}. The enclosure volume was continuously mixed with a fan. Carbon dioxide concentration, temperature, photosynthetic active radiation (PAR) and relative humidity were measured continuously inside the branch enclosure systems. The dynamic branch enclosure system used by the Research Centre Jülich is described and characterised in detail by Komenda (2001) and Parusel (1996). After conditioning overnight, thus insuring that irritation induced emissions were settled, air from the enclosure chamber was sampled during the daytime on adsorption tubes (for specifications, see Table 1). Samples were taken for 30 min at a flow rate of 100 ml min^{-1} (normally about 20 samples between 4:00 am – 9:00 pm, at least from sun rise to sun set). Night-time measurements were omitted from the study because emission rates were

Table 1 Used branch enclosure- and measurement systems

Research Centre Jülich	
Enclosure system	
Type:	Dynamic FEP-foil chamber flushed with VOC- and ozone-free ambient air, the enclosure volume was continuously mixed with a fan.
Enclosure volume [l]:	90
Flow rate [l min^{-1}]:	15–25
Sampling/analytics	
Sampling and separation:	Sampling on adsorption tubes (Tenax TA / Carbotrap) Analysis : *Tekmar* AeroTrap thermal Desorber and *Tekmar* 6000 coupled with *Fisons* GC8060, column: DB5-MS, 30 m, 0.25 mm ID
Detection:	*Fisons* FID 80 and *Fisons* MD 800 (MS), EI mode
Max Planck Institute Mainz	
Enclosure system	
Type:	Two dynamic FEP-foil chambers comprising a branch enclosure and an empty reference chamber that were run simultaneously, both enclosures were flushed with ozone-free ambient air, the enclosure volume was continuously mixed with a fan.
Enclosure volume [l]:	75 branch chamber + 75 empty reference chamber
Flow rate [l min^{-1}]:	35 per chamber
Sampling/analytics	
Sampling and separation:	Sampling on adsorption tubes (Carbograph 1 / Carbograph 5), Analytics: thermal Desorber: *Perkin Elmer* ATD 400, Oven: *AutoSystems* XL, column: HP-1, 100 m length, 0.25 mm ID
Detection:	*Perkin Elmer* FID

below or at the detection limit. Enclosures were always removed from the branches between the different measurement campaigns (normally one 2–3-days-campaign per month).

Identification and quantification of the samples were performed in the laboratory of the Research Centre Juelich using thermodesorption coupled with GC-FID-MS. The GC temperature programme was run with an initial temperature of 70°C ramping with 5°C min^{-1} to 245°C. The MS was run in EI mode with a scan range of 45 to 240 m/z. The detection limit was about 50 ppt(v/v). 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 leaf surface area of the investigated branch.

2.2.2. Branch enclosure and analytical system of the Max Planck Institute for Chemistry

While accomplishing intensive measurement campaigns of the ECHO project during the summers of 2002 and 2003, enclosure measurements were carried out with a second enclosure system at the same tree specimen. In addition to physical parameters (PAR, ambient temperature, leaf temperature, and relative humidity), CO_2- and H_2O exchange was recorded by the use of an infrared gas analyser (model LI-7000, LI-COR Biosciences, USA). VOC

samples were collected for 60 min on solid adsorption tubes at flow rates of 150 ml min^{-1}. Analysis was performed at the Max Planck Institute for Chemistry, Mainz, Germany by GC-FID. Trace gas exchange rates were calculated according to Kuhn *et al.* (2002a) and Kuhn *et al.* (2002b) on a leaf area basis. Stomatal conductance was calculated according to Pearcy *et al.* (1989). The system applied by the Max Planck Institute is described in detail by Kesselmeier *et al.* (1996), Kuhn *et al.* (2002a) and Kuhn *et al.* (2002b).

2.3. Modelling of terpene emission

Monoterpene emission from European beech was calculated by a light and temperature dependent algorithms. This algorithm (in the following referred to as G97) was basically developed for isoprene emission by Guenther *et al.* (1993, 1995, 1997) but has also been used for the modelling of monoterpene emissions in the past (e.g. Schuh *et al.*, 1997; Hakola *et al.*, 1998; Owen *et al.*, 2001; Sabillon and Cremades, 2001; Kuhn *et al.*, 2002b; Staudt *et al.*, 2003; Dindorf *et al*, 2005). The G97 algorithm assumes a hyperbolic increase of VOC emission with light intensity leading to saturation. Concerning temperature the algorithm assumes a correlation of the leaf temperature to enzymatic processes leading to a temperature optimum of VOC emission at about 39°C. The light dependent term of the G97 function (in the following referred to as C_L) is specified by Equation 1. The temperature dependent term (in the following referred to as C_T) is specified by Equation 2. To calculate the actual VOC emission, both factors (C_L and C_T) are linked by multiplication with a standard emission factor (in the following referred to as SEF) that describes the basal VOC emission at standard light and temperature conditions (1000 μmol m^{-2} s^{-1}, 30°C, see Equation 3). We determined the standard emission factors (SEF) by a least squares fit of the measured and modelled emission rates.

$$C_L = \frac{\alpha \cdot C_{L1} \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \tag{1}$$

$$C_T = \frac{\exp\left(\frac{C_{T1} \cdot (T - T_S)}{R \cdot T_S \cdot T}\right)}{C_{T3} + \exp\left(\frac{C_{T2} \cdot (T - T_M)}{R \cdot T_S \cdot T}\right)} \tag{2}$$

$$\text{emission rate} = \text{SEF} \cdot C_L \cdot C_T \tag{3}$$

with: $\alpha = 0.0027$, $C_{L1} = 1.066$, C_L = light dependent term of the G97 function, C_T = temperature dependent term of the G97 function, $C_{T1} = 95000$ J mol^{-1}, $C_{T2} = 230000$ J mol^{-1}, $C_{T3} = 0.961$, L = actual light intensity [μmol m^{-2} s^{-1}], R = universal gas constant (8.314 J K^{-1} mol^{-1}), SEF = standard emission factor, T = leaf temperature [°K], $T_M = 314$ [°K], $T_S = 303$ [°K].

The branch enclosure and the PAR sensor were sometimes partly shaded by the measurement tower (normally between 12:00 am and 3:00 pm). Therefore, emission rates for these times were excluded from use in emission modelling.

2.4. The plant material

In this study emission rates are based on the total leaf surface area of the investigated branches. In its annual development, the leaf area changes from bud break until leaf maturity and senescence. Long-term investigations have to take into account these changes

in total leaf surface area. The aim of this study was to analyse the emission behaviour of individual branches over two vegetation periods. Thus, the surface determination had to be arranged in a non-invasive manner. Branches were photographed against a scale paper board with a defined grid surface without harvesting any leaf material. The total leaf area was determined by digital analysis of the photographs with the use of a reference area.

3. Results

3.1. The emission pattern

The main emissions were characterised by a mix of 10 terpenoids (Table 2 a and b). The dominant compound was the monoterpene sabinene. It contributed up to 60% to the total terpene emission. Besides sabinene, we also observed tricyclene, α-pinene, myrcene, β-pinene, limonene. In addition, para-cymene, β-phellandrene, cis-ocimene, α-terpinene and γ-terpinene were identified tentatively in the emission pattern. In general, the pattern of released monoterpenes remained unchanged throughout a vegetation period. However, in 2002, two terpenes showed an emission behaviour different to the other compounds. These were the tentatively identified compounds para-cymene and cis-ocimene. At the beginning of August no para-cymene emissions were detected while all other terpenes could be measured in the samples. In samples from August 15, 2002 para-cymene emissions were found again and emissions increased slowly until the final measurements conducted on September 13, 2002. Cis-ocimene emissions decreased strongly in samples collected on August 15, 2002 but increased again in the measurements of September.

In 2002, we investigated the emission pattern of two different branches of a single beech tree (cf. Table 2 a, tree I , branches a and b). These branches showed a similar emission pattern characterised by sabinene, tricyclene, α-terpinene and γ-terpinene as being the dominant compounds emitted. This was also found in 2003 (Table 2 b) where measurements were conducted at one branch in April/May and at another branch from July to October. In addition, the emissions of a branch with shaded leaves were investigated for five days at the end of July and the beginning of August 2003 (Table 2 b, tree I , branch e). This branch was growing about 3 meters below the main investigated branch from tree I. The leaves of branches at this height showed the typical anatomy of shaded leaves. However, the emission pattern was the same compared to the sunlit leaf branches previously mentioned.

The tree-to-tree variability in the emission pattern of two investigated trees was not pronounced since a branch of a second beech tree, investigated in July 2002, showed an emission pattern similar to the branch of the other investigated beech tree (Table 2 a, tree I, tree II).

However, from 2002 to 2003, a significant interannual variation in the contribution of individual terpenes to the total emission was observed for a single tree. Interestingly, the emission pattern of the investigated tree I in 2003 showed a much higher contribution of β-pinene to the total emission (up to 46.6%) throughout the year compared to 2002 (up to 3.2%). In correlation to this, the sabinene fraction in 2003 was half the fraction of the sabinene observed in 2002. For other compounds, little to no change in the contribution to the total terpene emission was observed (cf. Table 2 a and b). Similar results were obtained for all investigated branches.

Table 2 Contribution of individual monoterpenes to the total monoterpene emission 2002 and 2003 (in %).

	Tricyclene	α-pinene	Sabinene	Myrcene	β-pinene	3-carene	α-terpinene*	Para-cymene*	Limonene	β-phellandrene*	Cis-ocimene*	γ-terpinene*
							(**a**) 2002					
							Tree I (2002)					
Branch a (April-Oktober)												
Mean	11.1	1.4	61.2	1.2	1.8	1.4	7.9	1.6	1.5	2.5	0.4	7.7
Standard deviation	1.0	0.8	4.1	1.0	0.9	0.4	0.8	1.0	0.3	0.3	0.6	1.3
Branch b (June)												
Mean	10.9	2.0	59.6	1.4	3.2	1.2	7.5	1.6	1.6	2.5	1.2	7.3
Standard deviation	2.6	1.7	12.8	0.7	2.1	1.1	2.3	0.7	0.6	0.7	1.2	2.0
							Tree II (2002)					
Branch a (July)												
Mean	9.4	0.7	62.3	2.3	1.4	1.1	7.4	2.7	1.6	2.5	0.0	8.6
							(**b**) 2003					
							Tree I (2003)					
Branch c (May)												
Mean	3.3	3.9	24.0	2.4	46.6	0.7	6.1	2.0	0.9	1.2	0.7	3.2
Standard deviation	2.1	3.5	14.9	1.0	23.7	0.4	2.9	1.4	0.6	0.9	0.9	2.1
Branch d (July-September)												
Mean	4.5	1.3	37.8	3.5	33.8	1.1	7.3	2.1	1.1	1.7	0.4	5.4
Standard deviation	0.7	0.5	2.7	2.5	4.2	0.7	0.9	1.8	0.5	0.6	1.0	1.0
Branch e (July-August, shade leaves)												
Mean	4.7	1.8	34.7	3.9	34.6	1.1	7.3	3.3	1.4	1.9	0.4	5.0
Standard deviation	0.7	1.2	3.8	1.2	1.2	0.8	1.3	1.2	3.8	1.2	1.2	0.8

*Compound identification uncertain

3.2. Diurnal variation of the emissions

In general, the emission rates of monoterpenes showed a pronounced diurnal cycle. Highest emission rates were found for conditions with highest temperatures and photosynthetic active radiation (PAR). This diurnal emission behaviour was found for measurements conducted over several days (Figure 2). For example, the diurnal course of the emission rates per leaf area is shown for June 12, 2002 in Figure 3(a) as a function of time. The emission rates varied by one order of magnitude during the day depending on the prevailing temperature and light conditions. For this specific day, measurements were carried out in parallel for two branches of the same tree (Figure 3(a)) and were combined with measurements of the CO_2 assimilation rate and the stomatal conductance for one of these branches (Figure 3(c)). As shown by the graph, the observed net assimilation rates indicated a typical diurnal periodicity that followed light intensity and temperature. In general, all investigated parameters showed pronounced diurnal cycles. The temperature- and light conditions for this day are given in Figure 3(b).

Since ambient temperature and light intensity are often highly correlated a light dependence of emissions could be hardly recognised under field conditions. In a first approach the influence of light was characterised at some very hot days with night time temperatures above 20°C that occurred in June 2002. Figure 4 shows emission rates for the main compound sabinene and temperature / light intensity measured in the morning hours of June 18, 2002. It is clear that almost no emissions appeared in the absence of light even though temperature conditions were moderate at 20 to 30°C. After sunrise, emissions began to increase. In the ensuing course of the day emissions appeared to be mainly temperature dependent and less light dependent when light saturation is reached. The light saturation of monoterpene emissions of beech is discussed in more detail by Dindorf *et al.* (2005).

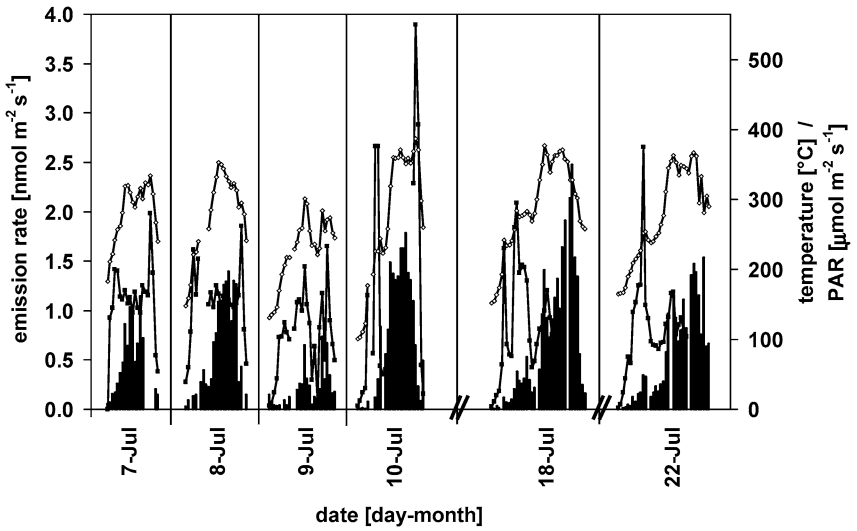

Fig. 2 Diurnal course of terpene emission in July 2003. Black bars: Emission rate of the sum of terpenes. Open diamonds, black line: Temperature inside the enclosure (multiplied by a factor of 10). Filled squares, grey line: PAR inside the enclosure. All data are mean values taken over 30 min

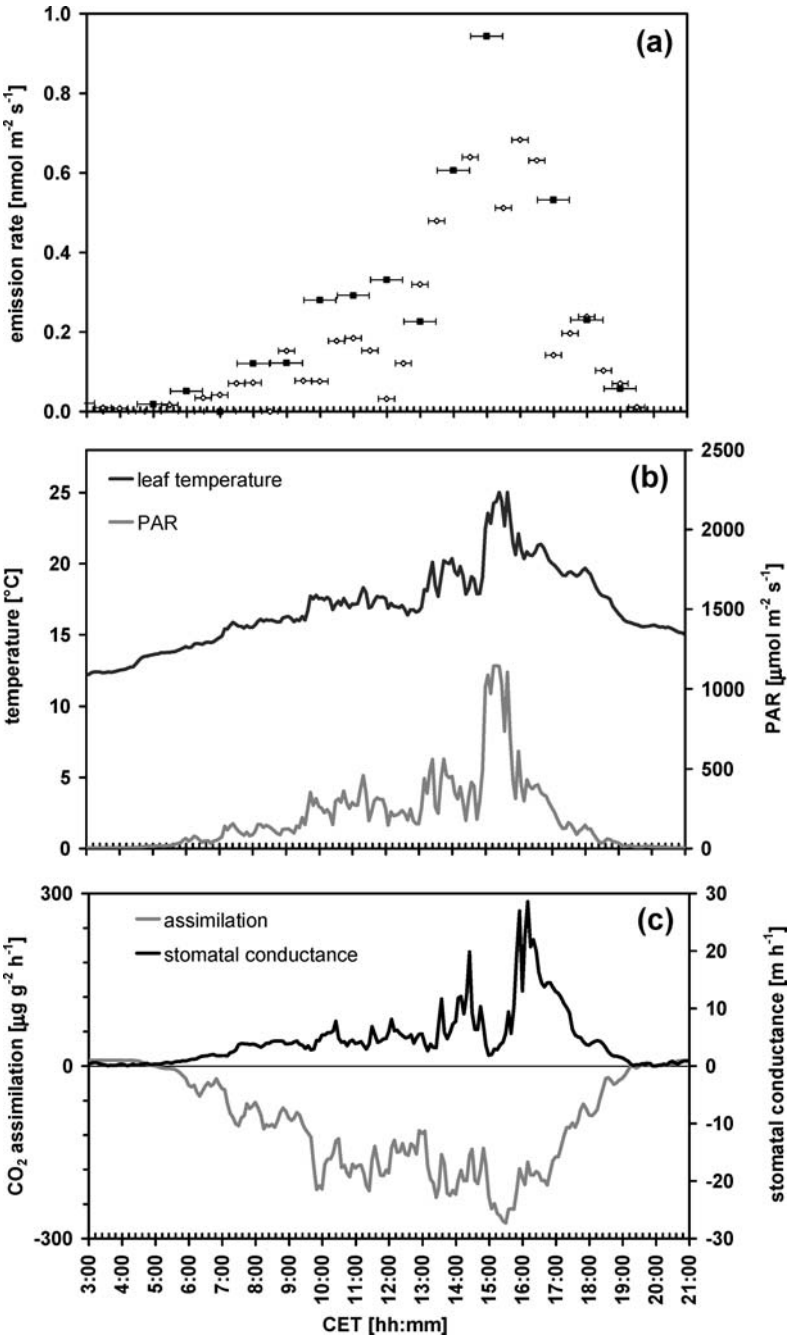

Fig. 3 Diurnal variation of emission and photosynthesis on June 12, 2002. Emission rate sum of terpenes (a): measurements performed by the Research Centre Jülich (open diamonds) and the Max Planck Institute (filled squares), horizontal bars give the duration of sampling; meteorological parameters (b): Leaf temperature (black line), photosynthetic active radiation PAR (grey line) and physiological parameters (c): stomatal conductance (black line), CO_2 assimilation rate (grey line)

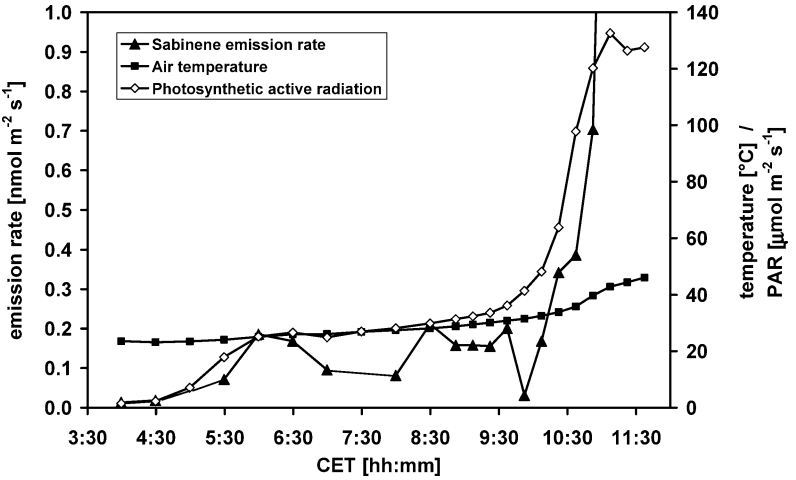

Fig. 4 Sabinene emission induction by light on a very hot day. Emission rates and prevailing temperature and light conditions, measured on June 18, 2002; Times are mean values of 30 min samples until 8:30 am followed by 15 min samples until noon

3.3. Seasonal variation of the emissions and year-to-year differences

In the past it was 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 beech was investigated over nearly two whole vegetation periods in several campaigns from April to October in 2002 and 2003. We found that the emission from beech shows a strong seasonal variation. In 2003, the measured emission rates of monoterpenes (the sum of all quantified compounds) increased in spring and reached a maximum in July (Figure 5 a,b) with average daytime emission rates (8:00 am to 4:00 pm) up to 1.4 nmol m^{-2} s^{-1}. At some days with significantly higher temperatures than average (35–40°C), emission rates were much higher with values of 6 nmol m^{-2} s^{-1} (data not shown). Emissions were found to be lowest in September where daytime average values of only 0.01 nmol m^{-2} s^{-1} and 0.03 nmol m^{-2} s^{-1} were measured in 2002 and 2003, respectively (cf. Table 3). Indeed, temperature and light intensity values were comparable to summertime measurements in these specific years. Emission rates measured at the beginning of May 2003 were comparably low. Investigating the branch in early spring (April 23 to 25) in the state of fully

Table 3 Mean daytime emission (8 am–3 pm) per leaf area in 2002/2003, in (nmol m^{-2} s^{-1})

Date	Temperature (°C)	Light (PAR) (μmol m^{-2} s^{-1})	Sabinene	α-pinene	Sum of terpenes
20/6/2002	24.2	152	0.243	0.019	0.397
18/7/2002	20.6	170	0.611	0.036	0.957
13/9/2002	25.5	90	0.015	bdl	0.007
14/5/2003	13.8	116	0.002	0.025	0.035
18/7/2003	31.1	132	0.148	0.125	0.362
16/9/2003	24.1	64	0.009	0.011	0.029

bdl = below detection limit

Table 4 Standard emission factors (SEF) for the sum of main monoterpene emission of European beech, calculations were done with the G97 for 30°C and 1000 μmol m^{-2} s^{-1}

		Sum of terpenes	
Date	Tree/branch	Standard emission factor (SEF) (nmol m^{-2} s^{-1})	Correlation of measured and modelled emissions r^2
		2002	
10/06		2.49	0.674
11/06		2.07	0.173
12/06	I/b	1.12	0.775
18/06		1.73	0.686
20/06		1.73	0.488
21/06		0.46	0.416
16/07		2.04	0.895
18/07	I/a	3.49	0.907
13/08		0.49	0.734
15/08		0.10	0.147
13/09		0.06	0.181
		2003	
07/05		0.20	0.591
12/05		0.14	0.322
13/05		0.23	0.433
14/05	I/c	0.24	<0.1
16/05		0.44	0.826
20/05		2.01	0.682
22/05		0.49	0.310
07/07		1.27	0.908
08/07		1.28	0.896
09/07		1.36	0.856
10/07		2.46	0.511
16/07	I/d	1.14	0.649
18/07		1.07	0.839
22/07		1.24	0.946
23/07		1.30	0.845
24/07		1.15	0.788
16/09		0.12	0.436

expanded leafs no emissions were found in both years, even though temperature and light intensity values were moderate and comparable to values at the end of June (measurements in 2002) and at the beginning of July (measurements in 2003) where significant emissions appeared.

Temperature- and light normalised emissions changed over the year. Table 4 gives the standard emission factors (SEF) calculated with the algorithm by Guenther (1997) by a least squares fit. In 2002 changes were in the range of 1–2 orders of magnitude. Highest SEFs were found on June 10 and 11 and with a particularly high value on July 18. On August 13 and 15 SEFs decreased significantly and reached a value of 0.06 nmol m^{-2} s^{-1} on September 13. In 2003, especially, SEFs showed a pronounced seasonal course. In May, values were comparably low (0.14 to 0.49 nmol m^{-2} s^{-1}) with one exception on May 20, 2003 (2.01 nmol

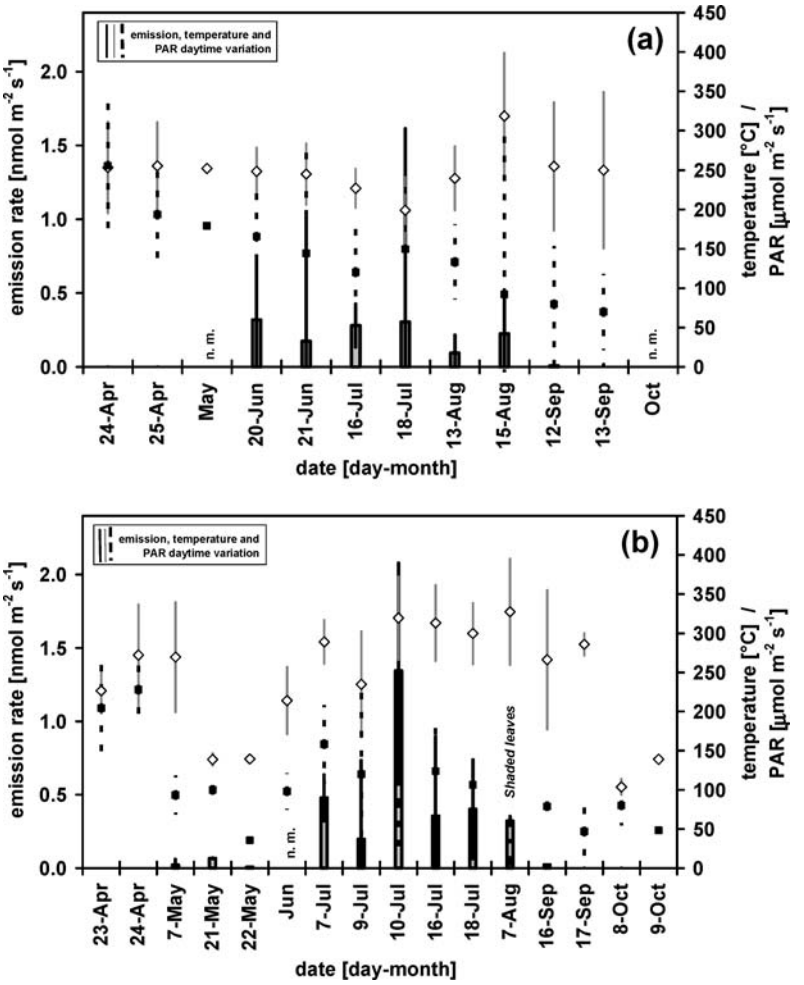

Fig. 5 Emission rate of the sum of monoterpenes at different times of the year for 2002 (a) and 2003 (b). Bars: Emission rate per leaf area and time. Open diamonds: Temperature inside the enclosure (multiplied by a factor of 10). Filled squares: PAR inside the enclosure. All data are median values obtained between 8:00 am and 4:00 pm CET. Small vertical bars give the daytime variation of emission rate, temperature and PAR; n.m. = not measured

m^{-2} s^{-1}). Also on September 16, 2003 only a small SEF was measured (0.12 nmol m^{-2} s^{-1}). In July the SEF appeared to be constant within the range of 1.07 to 1.36 nmol m^{-2} s^{-1} with an exception for measurements on July 10, 2003 (2.46 nmol m^{-2} s^{-1}).

Meteorological data show that in the year of 2003, from May to September, median temperatures were about 2°C higher compared to the same period in 2002 and longer warmer periods were found in 2003 (Figure 1a,b). Even though emission rates were expected to be higher in 2003, the observed emission rates in fact tended to be lower. Even the peak emission rates measured on July 18, 2003 (sum of terpenes) were at least a factor of 2–3 lower than the corresponding value for 2002 (Table 3). Emissions for the rest of the year 2003 appeared to be in the range of the emissions of the colder year 2002.

4. Discussion

Within the scope of the ECHO project, investigations on the long-term emission behaviour of the wide spread deciduous tree *Fagus sylvatica* were conducted in the field applying the branch enclosure technique. In the past, European beech was characterised as a low monoterpene emitter (Hewitt and Street, 1992; König *et al.*, 1995; Simpson *et al.*, 1999). However, we found this species to be an important biogenic source of monoterpene emissions.

4.1. The emission pattern

Fagus sylvatica can be characterized as a monoterpene emitter. The pattern of leaf volatiles reported here is similar to that found in other studies (König *et al.*, 1995; Tollsten and Müller, 1996; Schuh *et al.*, 1997; Kahl *et al.*, 1999), where sabinene and β-pinene were found to be the main constituents of *Fagus* leaf volatiles. These results differ from VOC flux measurements carried out above a beech stand in June 1996 (Gallagher *et al.*, 2000). The most abundant compounds found above the beech canopy were Δ3-carene followed by α-pinene and β-pinene. From the sixteen compounds detected, eight were consistently observed: α-pinene, β-pinene, sabinene, Δ3-carene, cymene, limonene, γ-terpinene and linalool. However, a comparison with our results is complicated because of the possibility of transport processes in and above the canopy while flux measurements.

A different emission behaviour for the emissions tentatively identified as para-cymene and cis-ocimene was observed. This may indicate a specific physiological role for these compounds. However, the variations measured in August and September ranged from very low emission values to near the lower limit of detection. Therefore, a quantitative treatment of the results is difficult and must be very cautiously addressed. The emission of volatile compounds from plant tissue has been recognised to be very important to the interaction between plants and insects, both in the attraction of pollinators and as a defence against herbivores (Harborne, 1988; Pichersky and Gershenzon, 2002). Defence mechanisms of plants against herbivore or pathogen can be an induced mechanism, in which the synthesis of defensive compounds is triggered in response to attack, or a constitutive one (for a review, see Gatehouse, 2002). In our investigation emission rates are mainly correlated with prevailing temperature and light intensity conditions. These emissions are a mixture of about 10 major compounds and some compounds with minor emission rates at the lower limit of detection. It is known that complex mixtures of compounds are more effective in herbivore defence compared to admitting the same compounds singly (Hummelbrunner and Isman, 2001). Because plants usually present defences as a suite of compounds, and not as individual ones, it is thought that the minor constituents found in low concentration may act as synergists, enhancing the effectiveness of the major constituents through a variety of mechanisms (Berenbaum, 1985). Complex mixtures are also likely to be more durable with respect to insects evolving resistance and developing behavioural desensitisation (Bomford and Isman, 1996).

In our investigation, we found only representatives of monoterpenes for beech emissions. However, Tollsten and Müller (1996) also found low emissions of sesquiterpenes, which are mainly assigned to be irritation induced. In contrast to Tollsten and Müller (1996) no sesquiterpene emissions were observed throughout the years 2002 and 2003.

4.2. Diurnal variation of the emissions

Although synthesis and emission of some of these isoprenoids are wounding or feeding induced (Bohlmann *et al.*, 1997; Steele *et al.*, 1998) an obvious temperature dependence of

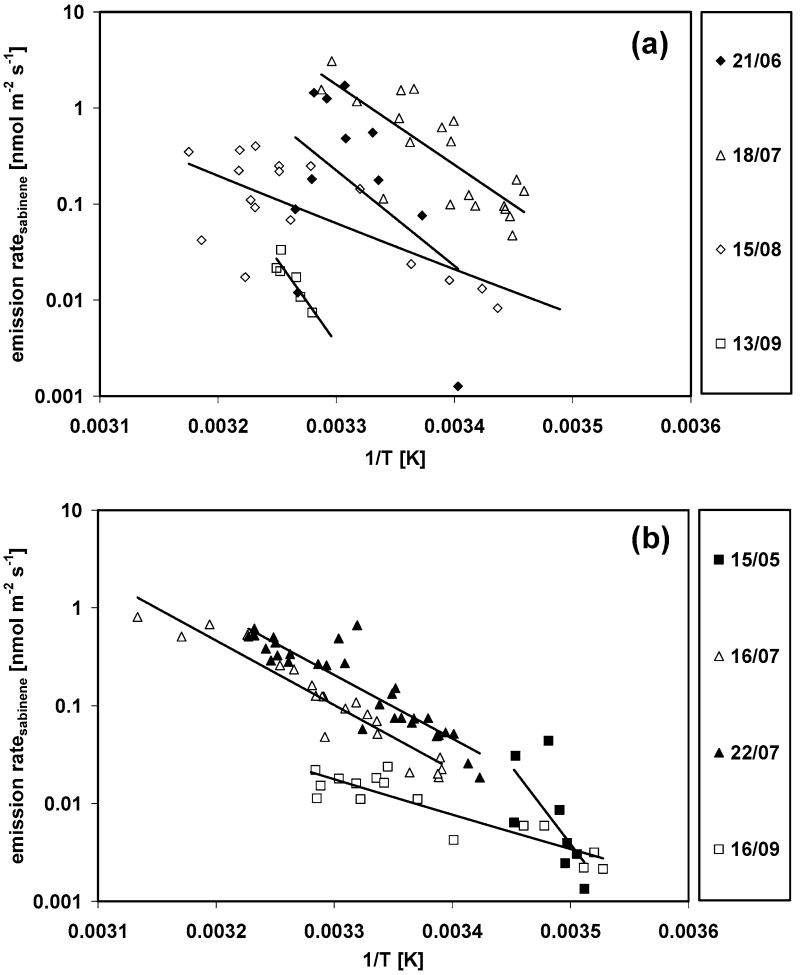

Fig. 6 Changes in the temperature dependence of sabinene emissions for different seasons for 2002 (a) and 2003 (b). Data points represent mean values of 30 min samples. Correlation coefficients (r^2) for 2002: 21/06: 0.209, 18/07: 0.632, 15/08: 0.487, 13/09: 0.795; for 2003: 15/05: 0.450, 16/07: 0.919, 22/07: 0.844, 16/09: 0.495.

the major emissions was observed. However, the measurements of very warm days in 2002, especially on the 18th of June show that there is an induction of the sabinene emission by light. Based on the fact that sabinene emissions from *Fagus* derive from *de novo* synthesis mainly (Kahl, 1997), it is suitable that emission activity needs light for activating terpene synthases and/or for the availability of terpene precursor molecules synthesised from photosynthetic fixed carbon. In some studies, light-induced monoterpene emissions were also found for other species emitting terpenes from *de novo* synthesis. In these studies, emissions appear to be mainly temperature dependent and less light dependent in the later course of the day when light saturation is approached (Loreto *et al.*, 1996; Schuh *et al.*, 1997; Staudt, 1997; Shao *et al.*, 2001; Dindorf *et al.*, 2005).

4.3. Seasonal and interannual variation of the emissions

By investigating a individual beech tree throughout two vegetation periods an insight into the variation of the source strength of biogenic emissions of a widespread European tree species was developed. Non-normalized emissions were highest in summer, in general, following the course of the ambient temperature in its diurnal variation. However, a more thorough analysis of the data reveals that other parameters beside temperature also influence emissions from beech. Plotting the emission rates as a function of the inverse ambient temperature (as an Arrhenius-type plot) shows that the functional dependence of the emissions from temperature (i.e. the emission potential) changed significantly with season. Figure 6(a) is a plot of the dominantly-emitted compound sabinene throughout 2002. In general, the temperature dependence of the emissions tended to decrease during August and September. In June and July, the terpene emission potential was much higher in comparison. At comparable temperature conditions, sabinene emissions were about one to two orders of magnitude lower in August and September than in June and July. However, the data scatter was pronounced during September measurements. The significance of the temperature dependence for the individual measurement periods is very different. Measurements at the same tree in 2003 showed better correlations for the temperature dependence of the sabinene emission (Figure 6(b)), especially in the July measurements. Similar to 2002, emission rates in 2003 tended to be lower in September than in July. Furthermore, emissions measured in spring (May 15, 2003) tended to be lower. Obviously, the temperature dependence of the sabinene emission rates had changed and the potential of emissions had shifted to higher values in summer.

In an earlier study such seasonal variations were also reported for Tea-leafed willow (*Salix phylicifolia*), Aspen (*Populus tremula*), and Silver birch (*Betula pendula*) by Hakola *et al.* (1998) for the boreal region. Emissions of Willow and Aspen showed highest values in May and they decreased until September. For Birch, emission rates were highest in August and lowest in June and September. Ambient air measurements above a boreal coniferous forest in Finland validate the observed seasonality of VOC emissions (Hakola *et al.*, 2003).

Zhang *et al.* (1999) found differences in the emission rates for Silver birch measured in the month of June and August with significantly lower levels of volatiles in August. These measurements were conducted at different branches as leaf area was determined directly after each sample. Sabinene and β-pinene (among several other compounds) were found in the June samples but not in the samples of August.

The seasonality of monoterpene emissions was also observed by Rapparini *et al.* (2001) for the deciduous trees Apple (*Malus domestica*) and Cherry (*Prunus avium*), attributing these emissions to ecological functions throughout plant development. At full bloom, the release of monoterpenes from apple flowers was 366 ng g^{-1} dry weight (DW) h^{-1}. The emission rate of cherry flowers was 1213 ng g^{-1} DW h^{-1}. Terpene emissions dramatically decreased at fruit-set and ripening stages for both species, reaching the lowest values at harvest time when leaves were fully mature (3–9 ng g^{-1} DW h^{-1}). For beech, an induction of terpene emissions while flowering in early spring was not observed within our measurements but monoterpene release started some weeks after full leaf expansion. This delay in the emissions in spring was also reported for isoprene emissions from aspen where emissions started 4 weeks after leaf emergence (Monson *et al.*, 1994). The delay occurred despite the presence of positive net photosynthesis rates. In another study that investigated velvet bean, it was found that the delay time between onset of positive net rates of photosynthesis and the induction of isoprene emissions is in the range of 3 to 4 days (Harley *et al.*, 1994). This indicates that there are other (physiological and/or ontogenetic) parameters that are responsible for the induction of the emissions. These parameters seem to be less dependent on direct meteorological factors,

since emission strength differed in both spring and fall, while the temperature (and light) conditions were almost identical.

As our plots (Figure 6 a,b) show, a different emission behaviour for different seasons is likely. For 2003, standard emission factors (SEFs) differ in the range of one order of magnitude over the year, with the highest value in July and lower values in May and September (Table 4). Measurements in 2002 showed much higher SEF values for June 10 and 11 compared to SEFs on June 12, 18, 20 and 21. Another high value was found for July 18. SEFs decreased in August and September, comparable to results in 2003. Schuh *et al.* (1997) obtained SEFs for beech from laboratory experiments as best fit values of 720 ± 70 pmol $m^{-2}s^{-1}$ in spring and 93 ± 6.8 pmol $m^{-2}s^{-1}$ in fall. Our results obtained in May and September field campaigns appear to be in the same range.

The temperature and light conditions that a leaf has been exposed to during the previous hours to days appear to significantly influence emissions, but this has not been well characterized so far (Harley *et al.*, 1997; Sharkey *et al.*, 1999). For moss (*Sphagnum spec.*) and also for oak (*Quercus spec.*) it was observed that preceding temperature and, to a lesser degree light conditions, affect normalised emission rates (Hanson and Sharkey, 2001). By changing the plant's growth conditions, changes in emission rates occurred within several hours to some days. These results are similar to those of field studies which showed that the meteorological conditions from the previous 6 h to 2 d are highly correlated with emission potential (Sharkey *et al.*, 1999; Geron *et al.*, 2000). These results were confirmed by Staudt *et al.* (2002), who investigated the emission behaviour of Holly Oak (*Quercus ilex* L.) in field and laboratory studies under different growth conditions by varying light intensity and temperature. Under field conditions they estimated that the standard emission rate of sun-adapted current-year leaves decreases from approximately 8 nmol m^{-2} s^{-1} in summer to 0.8 nmol m^{-2} s^{-1} in winter. This was accompanied by a decrease of the daily average temperature from 23°C to 7°C and a decrease of the daily accumulated global radiation from 22 to 6 MJ m^{-2} d^{-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 a period of 8 months (Staudt *et al.*, 2003). This indicates that the 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).

In regard to the emission potential, we observed considerable differences between 2002 and 2003. In general, standard emission rates tended to be lower in 2003, even though the mean temperature was higher compared to 2002 and longer warm periods occurred. In particular, in July most of the SEFs appeared to be lower than expected after taking the previous measurements of 2002 into account. An explanation may be found in the preceding meteorological situation at the measuring site, concerning precipitation and the subsequent induction of drought stress. Figure 7 shows the annual course of precipitation and the SEFs calculated for 2002 and 2003. It is seen that 2003 was a much drier year (compared to 2002) with some long periods completely lacking in rainfall. As most of the SEF values in July 2003 were comparably low, drought may be (aside from light intensity and temperature conditions) another environmental factor influencing the emission behaviour of the investigated tree. Evidence for such an influence on the emission behaviour was obtained from isoprene emissions of red oak (*Quercus rubra*) in a recent study (Funk *et al.*, 2005). It was observed that drought periods of 20 days depressed standard emission rates by a factor of 4. However, emission rates increased again when wet periods followed. In contrast, short time variations of precipitation (day to day) sometimes influenced the emissions and sometimes did not show any effect.

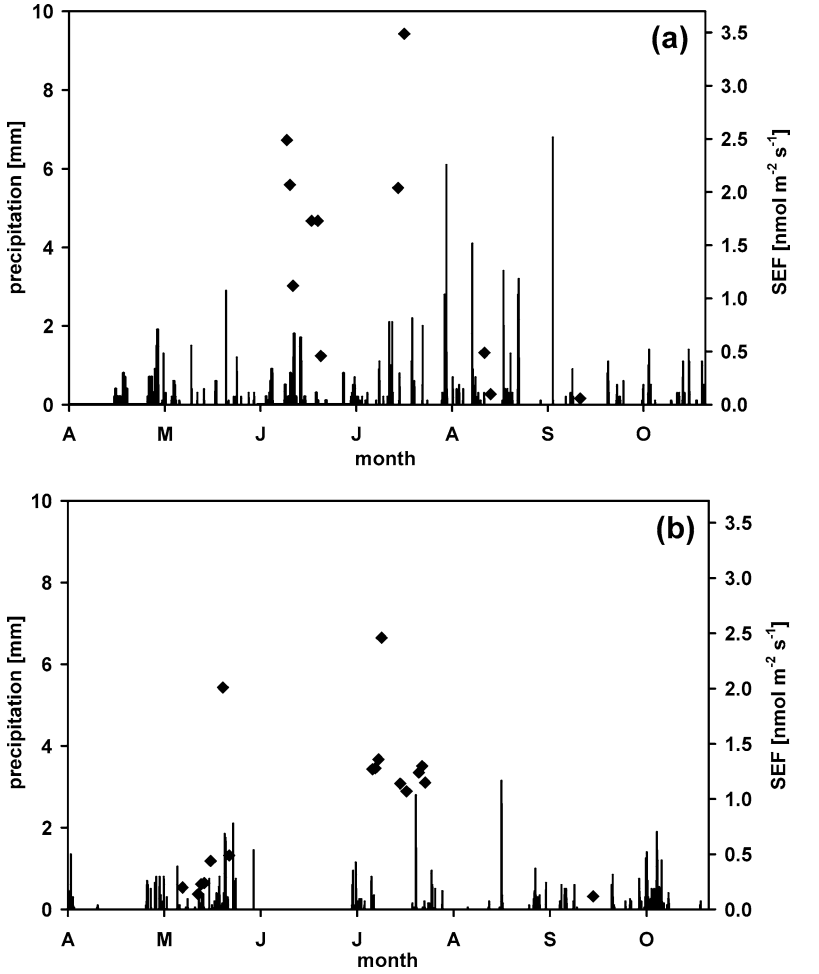

Fig. 7 Precipitation at the measurement site (bars) and SEFs calculated from branch enclosure measurements (grey diamonds) for 2002 (a) and 2003 (b). The respective letter at x-axis is set at the 1st day of the corresponding month.

Moreover, previous studies observed reduced emissions in summer and fall to correlate with the activity of some terpene synthases (Lehning *et al.*, 1999). For isoprene, this was reported for velvet bean (Kuzma and Fall, 1993) and for the European oak *Quercus robur* L. (Schnitzler *et al.*, 1997). Recently, a seasonality concerning occurrence and activity was also reported for monoterpene synthases for *Quercus ilex* L. (Fischbach *et al.*, 2002). This indicates that the emissions are not only dependent of exogenous but also of endogenous parameters such as the developmental state of the investigated branches. This may explain the results reported here concerning seasonal changes in terpene emission rates. The results of the latter investigations underline the importance of conducting measurements at different times of the year during the vegetation period, in order to characterise biogenic emissions and to understand the emission behaviour of plants in general.

5. Conclusions

We reported emission studies for European beech carried out in the vegetation periods of 2002 and 2003 in a Forest near Jülich, Germany. The results of several field campaigns showed that beech is a reasonable monoterpene emitter, releasing mainly sabinene. The terpene emission rates varied with season with highest values in June and July. The results of our field studies showed that, as a first approximation, emission models like the G97 are useful tools to describe the emission behaviour as a function of temperature and light. However, the results also indicate the influence of other factors on the terpene emission, that can be seen in the variation of standard emission rates over the course of the year and, also, in year-to-year variations of the emissions. The seasonal variations indicate that the emission behaviour of terpenes is linked to synthase activity which is dependent on a plant's developmental state. Our results also underline that future algorithms for the prediction of the emission behaviour of terpenoids have to take into account physiological and ontogenetic parameters. This is also necessary for realistic estimates of the impact of biogenic emissions on local and regional tropospheric photochemistry and the necessary up scaling for investigating the impact on global climate. Although the dataset of our measurements is small, our findings may indicate that the widely used algorithms to model monoterpene emissions may not be applicable to predict the seasonal variation of monoterpene emissions from beech.

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