JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. D13, 4161, 10.1029/2001JD000691, 2002

Monoterpene emissions from Scots pine (*Pinus sylvestris*): Field studies of emission rate variabilities

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Received 28 March 2001; revised 5 November 2001; accepted 16 November 2001; published 2 July 2002.

[1] Monoterpene emission rates from young and adult Scots pines (*Pinus sylvestris*), a typical central European conifer, were measured under ambient conditions using a dynamic enclosure chamber. We investigated diurnal and seasonal cycles of monoterpene emissions and branch-to-branch and plant-to-plant variabilities of emission rates. The four most abundant monoterpenes usually emitted from *Pinus sylvestris* were α-pinene, 3-carene, camphene, and β-pinene. Emissions of individual monoterpenes were highly correlated to each other and increased exponentially with temperature. We obtained β coefficients for the temperature dependence of different monoterpenes between 0.08 and 0.13 K^{-1}. The β coefficients varied with season by a factor of 2; the standard emission rates varied by more than 1 order of magnitude. Highest standard emission rates were found in April; lowest standard emission rates were found in July and October. In July and October the standard emission rates from two different branches of the same tree showed no significant differences; in September they differed by a factor of 2. Seasonal variations of a single branch and branch-to-branch variations in the spectrum of emitted monoterpenes were small. On the other hand, different individual Scots pines emitted a completely different spectrum of monoterpenes, indicating that the monoterpene emission spectrum is only typical for an individual plant but not for the whole plant species. The temperature normalized standard emission rates were found to be highly variable. Values for the sum of monoterpenes ranged between 0.06 and 3.7 μg g(dry weight)$^{-1}$ h^{-1} (micrograms monoterpenes per gram dry weight (dw) of needles and hour). Temperature-normalized monoterpene emission rates and temperature dependencies of the emissions were used to calculate monthly flux estimates of monoterpenes for the Hartheimer Wald. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* plant emissions, emission rates, monoterpenes, enclosure measurements

1. Introduction

[2] Volatile organic compounds (VOCs) are emitted in large quantities from the vegetation into the atmosphere. Biogenic VOCs influence the tropospheric concentration of the hydroxyl radical and thus have an impact on the oxidation capacity of the atmosphere [e.g., *Chameides et al.*, 1988]. In combination with sufficient levels of nitrogen oxides they lead to the production of ozone [e.g., *Trainer et al.*, 1987; *Fehsenfeld et al.*, 1992].

[3] Estimations of biogenic VOC emissions of single plants are based on algorithms using normalized, plant-specific emission rates and on the functional dependencies of those emissions on ambient parameters such as temperature and photosynthetic active radiation (PAR). In combination with ecosystem biomass and distribution data (leaf area indices, forest coverage, etc.), regional and global emission fluxes are calculated [e.g., *Lindfors et al.*, 2000]. *Guenther et al.* [1995] estimated the global biogenic VOC emissions to be 1150 Tg C yr^{-1}. The hydrocarbon with the largest contribution is isoprene with an annual flux of 503 Tg C yr^{-1}, whereas the estimated flux of all monoterpenes is 127 Tg C yr^{-1}.

[4] While isoprene emissions are coupled to the rate of biosynthesis and are therefore both temperature- and PAR-dependent [*Guenther et al.*, 1993], monoterpene emissions from coniferous plants are mainly reported to be only temperature-dependent [e.g., *Tingey et al.*, 1980; *Lamb et al.*, 1985; *Juuti et al.*, 1990]. Monoterpenes are stored in resin ducts of needles, and their emission is regarded as a result of evaporation out of these storage pools [e.g., *Dement et al.*, 1975; *Tingey et al.*, 1980, 1991]. The rate of monoterpene emissions was found to increase exponentially with temperature. A generally accepted algorithm to describe monoterpene emissions from plants was established by *Tingey et al.* [1991], in which the monoterpene emission rate is expressed as a product of a temperature-

0148-0227/02/2001JD000691

dependent term and a temperature-normalized standard emission rate. However, this standard emission rate is not a constant but varies because of unknown dependencies of the emissions.

[5] Only a little is known about a seasonal variability of standard emission rates of monoterpenes. *Janson* [1993] reported a seasonal variation of the standard emission rate of monoterpenes from *Pinus sylvestris* of a factor of 6 between May and August, measured at four sites in Sweden. In October he found standard emission rates a factor of 20 higher than the lowest value obtained at the end of May; he did not find an explanation for this. *Staudt et al.* [2000] investigated the seasonal variation in amount and composition of monoterpenes emitted by young *Pinus pinea* trees and reported a pronounced seasonal change in monoterpene emissions. They found lowest standard emission rates (normalized to both temperature and light intensity) during the winter months (December to February) and highest rates in summer (June to August) with an amplitude of a factor of ~45. In a recent paper, *Kim* [2001] reported results of studies with slash pine and loblolly pine saplings. He found higher monoterpene emission rates in spring than during the summer months and gave bud elongation during springtime and terpene pool variations as possible explanations for these findings.

[6] Also, for the branch-to-branch variability of standard emission rates, only limited data are available. Results reported in the literature contradict each other. *Street et al.* [1997] found no statistically significant differences in the isoprene emissions from two branches of a *Eucalyptus globulus* tree. On the other hand, *Guenther et al.* [1991] reported leaf-to-leaf variations in the emission rates from the same plant species (*Eucalyptus globulus*) of 62% for isoprene emissions and of nearly 80% for monoterpene emissions. The effect of stress was given as a possible explanation for these variations. *Bertin et al.* [1997] investigated monoterpene emissions from *Quercus ilex* (L.). They reported relatively low branch-to-branch and tree-to-tree variabilities in monoterpene emissions (4.4–19%) for measurements at branches at the top of the canopy but significantly higher variations when comparing Sun-exposed branches to shade-adapted branches. Here standard emission rates were different by 1 order of magnitude (21.4 μg g(dry weight)$^{-1}$ h^{-1} (micrograms monoterpenes per gram dry weight (dw) per hour) for Sun-exposed branches and 2.3 μg g(dw)$^{-1}$ h^{-1} for shade-adapted branches).

[7] Here we describe measurements of monoterpene emissions from Scots pine (*Pinus sylvestris*), a typical central European conifer. Measurements were conducted under ambient conditions at young pines and at branches of an adult pine in the Hartheimer Wald (southern Germany) using the branch enclosure technique described by *Komenda et al.* [2001]. We investigated the diurnal variation and temperature dependence of emissions from both the young and the mature pine. From measurements conducted on two branches on the same mature tree at different times of year, we derived seasonal and branch-to-branch variabilities of the standard emission rates. From measurements conducted on eight different specimens of young Scots pines, we derived the plant-to-plant variability of monoterpene emissions within that plant species. The data provide information on the natural variability of monoterpene emission rates from Scots pine and on the uncertainty of calculations of emission fluxes. Monoterpene emission rates from the two branches of the mature tree were used to calculate monthly flux estimates of monoterpenes for the Hartheimer Wald.

2. Experimental Methods

2.1. Sampling Site

[8] Measurements from the adult pine were conducted in a 40 year old pine plantation in the Hartheimer Wald (near Freiburg, southern Germany, 47°56′N, 7°37′E). On a total area of 10 × 1.5 km^2 the forest included Scots pine (*Pinus sylvestris*) and black pine (*Pinus nigra*). No other vegetation was present in significant amounts at this location. Long-term data for solar radiation, air temperature, precipitation, soil moisture, and other pertinent parameters (e.g., evapotranspiration and latent heat flux) were available for this field site. A detailed description is given by *Jaeger* [1997]. In 1998 the average height of the trees was 15 m. A 20 m high tower gave access to the forest canopy. We conducted four field campaigns at this site between April and October 1998. Between 40 and 57 samples were collected to quantify VOC emission rates during each campaign. Monoterpene emissions were measured from two branches of a Scots pine at canopy height using an enclosure technique. The first branch (A) was sunlit, positioned at the top of the canopy, with new needles contributing 63% of the dry weight. Some cones were present. The second branch (B) was shaded, located ~1.5 m below branch A in the same tree. The dry weight of its needles was 1.8 times larger than that of branch A with the new needles contributing ~48% to total needle dry weight. Between April and July the calculated dry weight of needles of branch A more than doubled. From July to September some needles on both branches became yellow, and both branches lost ~10% of their older needles. From September to October the branches again lost some old needles (~10%).

[9] The measurements with the young pines were conducted at the Forschungszentrum Jülich (western Germany). From 1996 to 1998, different 3–4 year old Pine seedlings were taken from the Hartheimer Wald. The young pines were dug out with the soil surrounding the roots and placed in pots. After being placed in pots, the young plants were acclimatized in pots in ambient conditions for 3 months. Before and between the individual experiments the plants were stored outside in Jülich under ambient conditions. Table 1 summarizes the age of investigated plants, date of emission rate measurements, temperature range inside the enclosure, dry weight of needles, and number of VOC samples.

2.2. Sampling Method

[10] The enclosure chamber and sampling system have been described in detail previously [*Komenda et al.*, 2001]. Briefly, the branches/plants were enclosed in chambers consisting of fluorinated ethylene propylene (FEP) copolymer foil (50 μm thickness) mounted in cylindrical frames. Both the pine and the frame of the enclosure were fixed in

Table 1. Summary of the Experiments: Age of Investigated Plants, Date of Emission Rate Measurements, Temperature Range Inside the Enclosure, Dry Weight of Needles, and Number of Volatile Organic Compound (VOC) Samples

Plant	Date	Temperature Range, deg°C	Dry Weight of Needles, g	Number of VOC Samples
Adult pine, branch A	April 1998	0–30	21	40
Young pine 1	June 1998	10–45	31	48
Young pine 2	June 1998	11–39	39	35
Adult pine, branch A	July 1998	5–35	44	57
Adult pine, branch B	July 1998	4–37	77	56
Young pine 3	August 1998	10–40	37	38
Young pine 4	August 1998	8–29	37	28
Adult pine, branch A	September 1998	1–30	38	52
Adult pine, branch B	September 1998	0–31	70	53
Adult pine, branch A	October 1998	0–29	37	48
Adult pine, branch B	October 1998	0–23	63	45
Young pine 5	May 1999	8–33	61	70
Young pine 5	July 1999	13–39	61	27
Young pine 6	June 1999	10–43	63	58
Young pine 7	June 1999	9–36	70	49
Young pine 8	May 1999	6–40	48	68
Young pine 8	July 1999	12–38	48	27
Young pine 8	August 1999	14–40	46	27

their position to reduce movement at higher wind speeds. The enclosure chambers, 30 L and 150 L in volume, were continuously flushed with hydrocarbon free air at flow rates of 6 L min^{-1} and 15 L min^{-1}, respectively. The air was provided by air supply systems that purified and dried ambient air, removing hydrocarbons and ozone from the inlet air. A Teflon-coated fan ensured a fast air mixing inside the chamber. CO_2 concentrations of the inlet air stream and inside the chamber were measured using an environmental gas monitor (EGM-2, PP systems). CO_2 was added from a cylinder to maintain ambient concentrations inside the chambers during photosynthetic activity. Air temperature, relative humidity, and PAR were measured inside the enclosures (HTR-1, PP systems) at an interval of 5 min. VOC inside the enclosure chamber were sampled by pumping air at a constant flow rate of 100 mL min^{-1} for 60 min through glass tubes (6 mm outer diameter and 180 mm length) packed with 100 mg of Tenax TA (60/80 mesh, Macheray and Nagel) and 50 mg of Carbotrap (20/40 mesh, Supelco). After sampling, the adsorption tubes were closed with Swagelok fittings and stored at room temperature in darkness. An automated sampling system allowed a continuous sampling with a time resolution of 1 hour. To reduce stress effects, the branches were placed inside the enclosures at least 12 hours prior to sampling. Samples were then collected for 3 consecutive days. Analysis of the tubes was performed within 4 weeks after sampling. Total needle surface and dry weight of the needles were determined after the last campaign and calculated for the previous experiments. Details of this procedure are given by *Komenda et al.* [2001].

2.3. Analytical Method

[11] Samples were analyzed using a gas chromatograph (GC 8000, Fisons Instruments) with a quadrupole mass spectrometer (MD 800, Fisons Instruments) and a flame ionization detector (FID) (FID 80, Fisons Instruments) in parallel. The VOCs were thermally desorbed (Aerotrap 6016, Tekmar) and separated on a DB-5MS column (30 m length and 0.25 mm ID, J&W). At the end of the chromatographic column the flow was split, introducing half of the flow into the quadrupole MS and half into the FID. Identification of the emitted species was achieved by comparison of the obtained spectra with library mass spectra (National Institute of Standards and Technology library) and comparison of the retention times with standard mixtures. Quantitative data are based on the FID signal only. A diffusion system was used for the preparation of standard mixtures to calibrate the system. Detailed descriptions of the analytical system and calibration technique are given by *Wedel et al.* [1998] and *Komenda et al.* [2001].

3. Results

3.1. Identified Compounds

[12] The following monoterpenes were identified as emission products from *Pinus sylvestris* and quantified during all field campaigns: α-pinene, camphene, sabinene, β-pinene, β-myrcene, 3-carene, limonene, β-phellandrene, and γ-terpinene. Also, p-cymene and 1,8-cineol were observed as emission products during all measurements. Other VOCs such as tricyclene, 2-carene, α-terpinene, and terpinolene were observed in very small amounts in a few samples only, and therefore no data are shown here.

[13] It should be noted that sabinene, p-cymene, and γ-terpinene could not be measured with the same high accuracy as the other monoterpenes. Tests revealed unspecified losses for sabinene and showed that γ-terpinene is converted into p-cymene in our analytical system. Therefore it could not be excluded that all p-cymene observed in our samples was due to this conversion and that there was no direct emission of p-cymene at all. Thus the emission rates of sabinene and γ-terpinene presented here are only lower limits, and those of p-cymene are upper limits.

3.2. Diurnal Variation of Emission Rates

[14] Figure 1 shows the diurnal variation of α-pinene emission rates over a time period of 3 days measured in September at a branch of an adult pine. Diurnal cycles like the ones shown here were observed during each field campaign and are therefore not shown in detail here. Obviously, the emission rates showed a significant diurnal

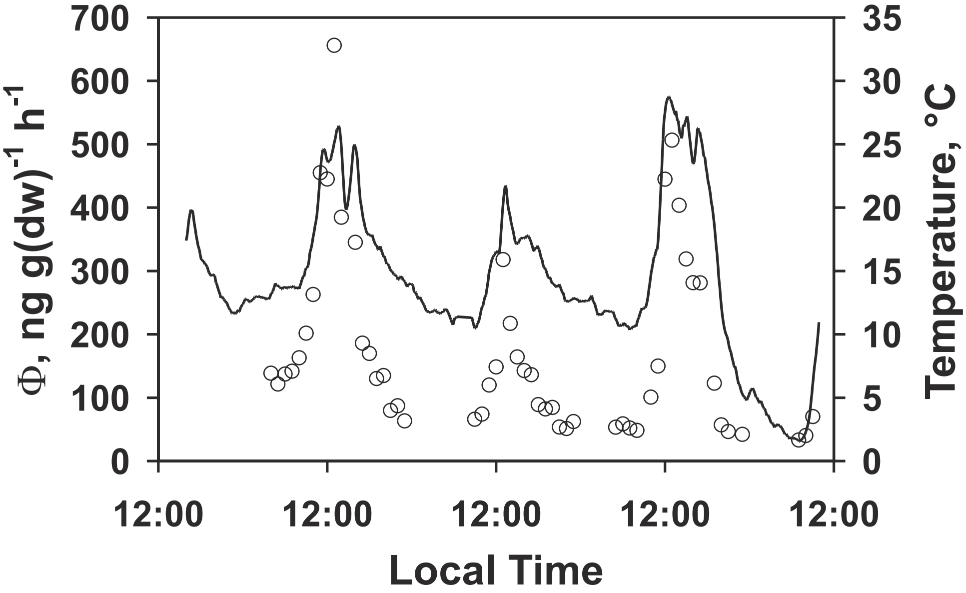

Figure 1. Diurnal variation of α-pinene emission rates (circles, see left axis) and temperature (solid line, see right axis) measured at branch A (16–19 September).

variation, with maximum emission rates at daytime and lowest emission rates during the night. The emission rates of all other monoterpenes were highly correlated to those of α-pinene and generally followed the same diurnal cycle (Table 2). With only a few exceptions the correlation coefficients of the emission rates of an individual monoterpene versus those of α-pinene, R^2, were higher than 0.5. Therefore α-pinene is taken as an example for the dependencies of monoterpene emissions (e.g., from temperature), and the emissions of α-pinene are described in more detail in section 3.3.

3.3. Temperature Dependence of Monoterpene Emissions

[15] The diurnal cycle of monoterpene emission rates was a result of the diurnal cycle of temperature. Monoterpene emissions from coniferous plants are known to increase exponentially with temperature [e.g., *Tingey et al.*, 1980; *Lamb et al.*, 1985; *Juuti et al.*, 1990]. *Tingey et al.* [1991] explained the emissions of monoterpenes as a result of the diffusion out of storage pools in conifer needles. Increasing needle temperatures result in increasing vapor pressures and thus lead to higher emissions. On the basis of this model, *Schuh et al.* [1997] derived an algorithm to describe the temperature dependence of monoterpene emissions from pools:

$$\Phi_{\mathrm{voc}} = \Phi^{S}_{\mathrm{voc}} \exp\left[\frac{c_{TP}}{R}\left(\frac{T - T_S}{TT_S}\right)\right], \qquad (1)$$

where Φ_{VOC} is VOC emission rate, Φ^{S}_{VOC} is VOC emission rate under standard conditions, R is gas constant, T is temperature, T_S is standard temperature (25°C), and c_{TP} is an empirical parameter describing the temperature dependence of emissions.

[16] The algorithm most frequently used to describe the temperature dependence of monoterpene emissions is the approximation given by *Guenther et al.* [1993]:

$$\Phi_{\mathrm{voc}} = \Phi^{S}_{\mathrm{voc}} \exp[\beta(T - T_S)], \qquad (2)$$

where Φ_{VOC} is VOC emission rate, Φ^{S}_{VOC} is VOC emission rate under standard conditions; T is temperature; T_S is

Table 2. Calculated Correlation Coefficients (R^2) Determined for the Emission Rates of Individual Monoterpenes Versus the Emission Rate of α-Pinene

	28–30 April	7–11 July	16–19 September	20–23 October
3-carene	0.98	0.92	0.99	0.98
α-pinene	0.99	0.86	0.99	0.96
Camphene	0.92	0.91	0.97	0.94
β-myrcene	0.74	0.41	0.43	0.73
Sabinene	0.91	0.69	0.76	0.58
Limonene	0.80	0.11	0.95	0.87
β-phellandrene	0.94	0.55	0.97	0.89
γ-terpinene	0.92	0.36	0.85	0.73
p-cymene	0.86	0.04	0.93	0.85
1,8-cineole	0.90	0.60	0.83	0.83

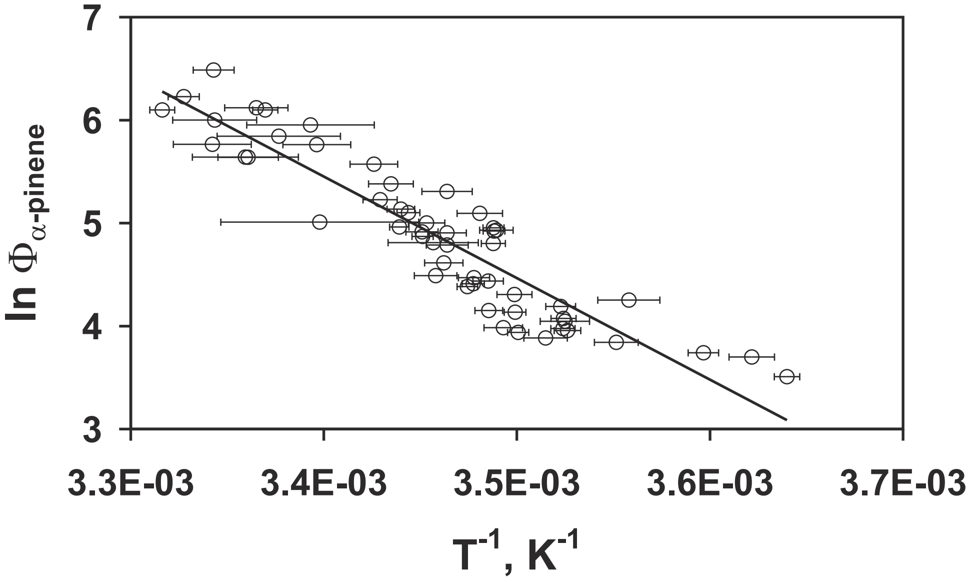

Figure 2. Plot of ln $\Phi_{\alpha\text{-pinene}}$ versus inverse temperature measured at branch A (16–19 September). Error bars indicate 1σ variance of temperature during sampling period. Line indicates regression line after least squares fit.

standard temperature (25°C or 30°C), and β is an empirical coefficient.

[17] This simpler algorithm makes the assumption that c_{TP}, which to a first approximation is the enthalpy of vaporization for the considered monoterpene, is not dependent on temperature within the range of physiological relevant temperatures. In the following we used equation (1) to describe our results. To make our data comparable to most results found in the literature which make use of equation (2), we also converted the obtained values for $c_{TP}R^{-1}$ to β by division by (298 K)^2.

[18] Figure 2 shows the natural logarithm of the emission rate of α-pinene versus the inverse temperature measured in September 1998 (same data set as in Figure 1). The error bars given in Figure 2 show the 1σ variance of the temperature during the 1 hour sampling period. We observed a significant linear relationship between ln$\Phi_{\alpha\text{-pinene}}$ and T^{-1} (n = 53 and R^2 = 0.85). This is in agreement with the algorithm given in equation (1).

[19] The parameter describing the temperature dependence of VOC emissions $c_{TP}R^{-1}$ can be derived from the slope of the fit; the standard emission rate Φ^S_{VOC} is calculated from the slope and the intercept. Table 3 summarizes the results for $c_{TP}R^{-1}$ and Φ^S_{VOC} for the investigated monoterpenes. The errors for $c_{TP}R^{-1}$ and Φ^S_{VOC} are 1σ variances and were derived from the fit to the data. For all monoterpenes a significant linear correlation between the logarithmic emission rate and the inverse temperature was found with correlation coefficients R^2 between 0.58 and 0.86. Values for $c_{TP}R^{-1}$ were of the order of 10^4 K and vary only slightly for the investigated monoterpenes between 8.9 × 10^3 K (camphene) and 11.6 × 10^3 K (3-carene). For T = 298 K, values of β between 0.10 and 0.13 K^{-1} were calculated. The emissions of 1,8-cineol showed a significantly higher temperature dependence ($c_{TP}R^{-1}$ = 19 × 10^3 K, β = 0.21 K^{-1}). The standard emission rates Φ^S_{VOC} of monoterpenes varied by 2 orders of magnitude between 5 ng g(dw)$^{-1}$ h^{-1} for γ-terpinene and 412 ng g(dw)$^{-1}$ h^{-1}

Table 3. Temperature Dependence of VOC Emissions $c_{TP}R^{-1}$ and Standard Emission Rate Φ^S for Measurements at Branch A (16–19 September) Derived From the Linear Regression for the Plot of lnΦ Versus Inverse Temperature[a]

	N[b]	R^2	c_{TP} R^{-1}, 10^3 K	β, K^{-1}	Φ^S_{VOC}, ng g(dw)$^{-1}$ h^{-1}
3-carene	53	0.83	11.6 ± 0.7	0.13 ± 0.01	412 ± 34
α-pinene	53	0.85	9.9 ± 0.6	0.11 ± 0.01	361 ± 28
β-pinene	53	0.86	11.3 ± 0.6	0.13 ± 0.01	173 ± 13
Camphene	53	0.80	8.9 ± 0.6	0.10 ± 0.01	37 ± 3
β-myrcene	53	0.58	11.1 ± 1.3	0.12 ± 0.02	30 ± 5
Sabinene	37	0.77	10.1 ± 0.9	0.11 ± 0.01	19 ± 2
Limonene	51	0.77	9.9 ± 0.8	0.11 ± 0.01	13 ± 1
β-phellandrene	51	0.86	11.3 ± 0.7	0.13 ± 0.01	10 ± 1
γ-terpinene	37	0.77	10.7 ± 1.0	0.12 ± 0.02	5 ± 1
p-cymene	51	0.75	9.6 ± 0.8	0.11 ± 0.01	11 ± 1
1,8-cineole	39	0.81	18.7 ± 1.5	0.21 ± 0.02	27 ± 3

[a] The errors for $c_{TP}R^{-1}$ and Φ^S_{VOC} are 1σ variances and were derived from the fit to the data.

[b] Here n is the number of measurements.

Table 4. Temperature Dependence of VOC Emissions From a Branch of a Mature Scots Pine Measured at Different Times of Year[a]

	28–30 April	7–11 July	16–19 September	20–23 October	Mean Value
3-carene	13.6 ± 0.5 (36)	9.1 ± 1.4 (54)	11.6 ± 0.7 (53)	12.1 ± 1.5 (53)	11.6 ± 1.9
α-pinene	11.1 ± 0.5 (36)	8.1 ± 0.9 (54)	9.9 ± 0.6 (53)	7.6 ± 0.8 (53)	9.2 ± 1.6
β-pinene	12.0 ± 0.7 (36)	8.3 ± 1.2 (52)	11.3 ± 0.6 (53)	7.9 ± 1.0 (53)	9.9 ± 2.1
Camphene	9.4 ± 0.5 (36)	6.1 ± 1.2 (52)	8.9 ± 0.6 (53)	5.5 ± 0.7 (53)	7.5 ± 2.0
β-myrcene	9.0 ± 0.9 (36)	8.7 ± 1.6 (52)	11.1 ± 1.3 (53)	7.8 ± 1.0 (53)	9.2 ± 1.4
Sabinene	8.0 ± 0.5 (34)	5.5 ± 1.1 (29)	10.1 ± 0.9 (37)	4.0 ± 1.1 (52)	6.9 ± 2.7
Limonene	5.8 ± 0.5 (36)	5.4 ± 1.4 (45)	9.9 ± 0.8 (51)	6.7 ± 1.0 (53)	7.0 ± 2.1
β-phellandrene	10.7 ± 0.6 (30)	4.5 ± 1.1 (16)	11.3 ± 0.7 (51)	9.4 ± 1.2 (53)	9.0 ± 3.1
γ-terpinene	7.7 ± 0.8 (27)	7.0 ± 2.3 (21)	10.7 ± 1.0 (37)	5.9 ± 0.7 (53)	7.8 ± 2.1
p-cymene	8.7 ± 0.7 (35)	6.0 ± 1.4 (43)	9.6 ± 0.8 (51)	6.3 ± 0.8 (53)	7.6 ± 1.8
1,8-cineole	15.8 ± 0.6 (30)	14.3 ± 1.7 (40)	18.7 ± 1.5 (39)	8.5 ± 1.3 (53)	14.3 ± 4.3

[a] Data for $c_{TP}R^{-1}$ plus or minus standard deviation in 10^3 K obtained from linear regression of lnΦ versus inverse temperature. The number of samples is given in parentheses.

for 3-carene which was the most abundant monoterpene during that experiment.

3.4. Seasonal Variation of Emission Rates

[20] During four field campaigns between April and October 1998 the seasonal variability of monoterpene emissions from Scots pine was investigated. The growth of the branch during the course of the year was accounted for by measuring the length of the branch and calculating the total needle mass for each campaign individually. From the plots of lnΦ of each monoterpene versus T^{-1}, the parameter for the temperature dependence of VOC emissions $c_{TP}R^{-1}$ and the standard emission rates Φ^S were derived. Values for $c_{TP}R^{-1}$ and Φ^S are given in Tables 4 and 5, respectively.

[21] For individual monoterpenes the values for $c_{TP}R^{-1}$ showed a variation of about a factor of 2 with the time of year. The standard deviation of the mean value of all four campaigns for $c_{TP}R^{-1}$ was of the order of 15% (β-myrcene) to 40% (sabinene). Average values for $c_{TP}R^{-1}$ ranged between 6.9 × 10^3 K (sabinene) and 11.6 × 10^3 K (3-carene). From this values of β between 0.08 and 0.13 K^{-1} were calculated for $T = 298$ K.

[22] The standard emission rates Φ^S varied by up to a factor of 30 (β-pinene). For most of the investigated VOCs, highest standard emission rates were found in April, and lowest standard emission rates were found in July. For the sum of monoterpenes we found the highest standard emission rate in April, which then decreased by more than 1 order of magnitude to its lowest value in July and increased by a factor of 4 in September. Within the detection limit the standard emission rate observed in October was identical to the value observed in July. For α-pinene the standard emission rates varied by more than 1 order of magnitude between 75 and 917 ng $g(dw)^{-1}$ h^{-1}. The only compound showing a pronounced seasonal trend was 1,8-cineole. Emissions were highest in April (68 ng $g(dw)^{-1}$ h^{-1}) and declined continuously until October (2 ng $g(dw)^{-1}$ h^{-1}).

[23] Changes in the composition of monoterpene emissions from the same branch at different times of the year were small compared to the variations of the absolute amount of emissions. Table 6 summarizes the percent contributions of individual monoterpenes to the sum of emitted monoterpenes measured at branch A between April and October. Shown also is the mean value of the four field campaigns and the standard deviation. The monoterpene with the largest contribution to the sum of monoterpene emissions was always 3-carene, followed by α-pinene and β-pinene. On average, 42% of the emitted mass of monoterpenes were emitted as 3-carene, 30% were emitted as α-pinene, and 15% were emitted as β-pinene. The average contribution of all the other monoterpenes was smaller than 5% each.

3.5. Branch-to-Branch Variability

[24] To test the variability of VOC emissions from different branches of the same plant, a second branch (branch B)

Table 5. Standard VOC Emission Rates Φ^S in ng $g(dw)^{-1}$ h^{-1} From the Same Branch (Branch A) of a Mature Scots Pine Measured at Different Times of Year[a]

	28–30 April	7–11 July	16–19 September	20–23 October
3-carene	1725 ± 82	85 ± 17	412 ± 34	122 ± 20
α-pinene	917 ± 58	75 ± 12	361 ± 28	78 ± 11
β-pinene	832 ± 64	28 ± 6	173 ± 13	29 ± 5
Camphene	63 ± 4	10 ± 3	37 ± 3	10 ± 2
β-myrcene	64 ± 8	15 ± 4	30 ± 5	7 ± 1
Sabinene	41 ± 3	14 ± 4	19 ± 2	5 ± 2
Limonene	40 ± 5	5 ± 2	13 ± 1	4 ± 1
β-phellandrene	34 ± 3	3 ± 1	10 ± 1	3 ± 0.5
γ-terpinene	23 ± 3	4 ± 2	5 ± 1	2 ± 0.4
p-cymene	25 ± 3	5 ± 2	11 ± 1	4 ± 1
1,8-cineole	68 ± 4	48 ± 8	27 ± 3	2 ± 0.4
Sum of monoterpenes	3739 ± 120	240 ± 22	1061 ± 47	260 ± 24
Temperature range, deg °C	0–29.5	5.0–35.3	1.0–29.5	0–28.7

[a] Data are obtained from linear regression of lnΦ versus inverse temperature.

Table 6. Contribution of Individual Monoterpenes to the Sum of Monoterpenes in Percent and Mean Value Plus/Minus Standard Deviation for Measurements at Branch A at Different Times of Year

	28–30 April	7–11 July	16–19 September	20–23 October	Mean
3-carene	46	35	39	47	42 ± 5.6
α-pinene	25	31	34	30	30 ± 4.0
β-pinene	22	12	16	11	15 ± 5.1
camphene	1.7	4.2	3.4	3.7	3.3 ± 1.1
β-myrcene	1.7	6.4	2.8	2.8	3.4 ± 2.1
sabinene	1.1	5.9	1.8	1.9	2.7 ± 2.2
limonene	1.1	2.3	1.2	1.5	1.5 ± 0.5
β-phellandrene	0.9	1.4	0.9	1.0	1.1 ± 0.2
γ-terpinene	0.6	1.6	0.5	0.8	0.9 ± 0.5

was enclosed in a separate enclosure chamber during the last three campaigns. The second branch, which was located ~1.5 m below the first branch, was older, was 2 times larger, and had a smaller amount of new needles compared to the first branch. Figure 3 shows the percent contributions of individual monoterpenes to the sum of monoterpene emission rates, averaged over the course of the year. The composition of monoterpene emissions was found to be similar for the selected branches.

[25] The absolute values of the standard emission rates of monoterpenes Φ^S are summarized in Table 7. Generally, the standard emission rates measured in July and October were similar between the two branches. Taking the 1σ error of the calculated standard emission rates, only the emissions of 3-carene of branch B were significantly higher in July. In September the standard emission rates calculated for the measurements at branch B were approximately a factor 2 larger than measured in July. This increase in the emissions between July and September was also observed for branch A. Here the standard emission rate of the sum of monoterpenes increased by a factor of 4. Emissions from branch A were thus almost twice as high as from branch B in September.

3.6. Plant-to-Plant Variability

[26] In order to estimate plant-to-plant variability in emission rates of monoterpenes, experiments were conducted under similar conditions with eight specimens of 3–4 year old Scots pines. These plants were of the same origin and were treated equally during the measurements. Table 8 summarizes values for Φ^S for the most abundant monoterpenes from these studies.

[27] The sum of the standard emission rates of all monoterpenes varied by more than 1 order of magnitude between 58 and 644 ng $g(dw)^{-1}$ h^{-1} for measurements with different plants. The plant-to-plant variability of the emission rates of individual monoterpenes was even larger. The largest variation was observed for 3-carene, which was the most abundant monoterpene emitted from pine 8 with a standard emission rate of 313 ng $g(dw)^{-1}$ h^{-1}, but it was almost absent in the emissions from plant 5 with a standard emission rate <1 ng $g(dw)^{-1}$ h^{-1}. For measurements con-

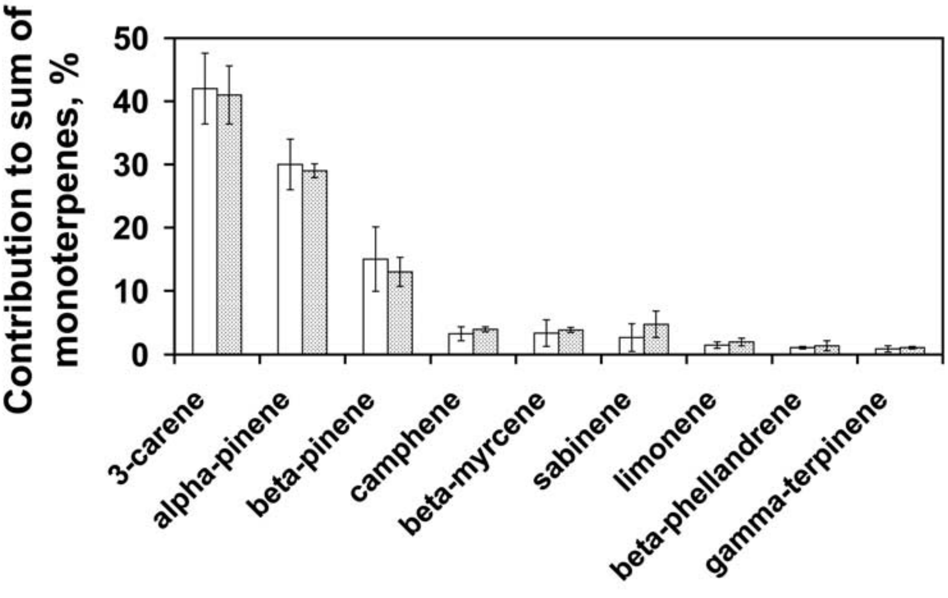

Figure 3. Percent contributions of individual monoterpenes to the sum of the monoterpene emission rates, averaged over the course of the year, for branch A (open bars) and branch B (shaded bars). The error bars give the 1σ variance of the contribution.

Table 7. Standard VOC Emission Rates Φ^S in ng g(dw)$^{-1}$ h^{-1} Measured at Two Different Branches of a Mature Scots Pine at Different Times of Year[a]

	7–11 July		16–19 September		20–23 October	
	Branch A	Branch B	Branch A	Branch B	Branch A	Branch B
3-carene	85 ± 17	124 ± 19	412 ± 35	223 ± 31	122 ± 20	119 ± 11
α-pinene	75 ± 12	85 ± 13	361 ± 28	190 ± 31	78 ± 11	77 ± 10
β-pinene	28 ± 6	36 ± 7	173 ± 13	97 ± 18	30 ± 5	31 ± 6
Camphene	10 ± 3	14 ± 2	37 ± 4	23 ± 6	10 ± 2	10 ± 3
β-myrcene	15 ± 4	13 ± 2	30 ± 5	24 ± 7	7 ± 1	9 ± 9
Sabinene	14 ± 4	14 ± 3	19 ± 3	43 ± 32	5 ± 2	7 ± 4
Limonene	6 ± 2	6 ± 1	13 ± 1	9 ± 4	4 ± 1	7 ± 1
β-phellandrene	3 ± 1	7 ± 3	10 ± 1	7 ± 2	3 ± 0.5	2 ± 1
γ-terpinene	4 ± 2	4 ± 1	5 ± 1	7 ± 5	2 ± 0.4	3 ± 2
p-cymene	5 ± 2	5 ± 1	11 ± 1	8 ± 3	4 ± 1	7 ± 2
1,8-cineole	48 ± 8	43 ± 6	27 ± 3	16 ± 2	2 ± 0.4	2 ± 1
Sum of monoterpenes	240 ± 22	302 ± 25	1061 ± 47	624 ± 59	260 ± 24	266 ± 19

[a] Data are obtained from linear regression of lnΦ versus inverse temperature.

ducted at the same plant at different times, variations of the sum of Φ^S were quite high. For plant 5 this variation was about a factor of 2 (218–457 ng g(dw)$^{-1}$ h^{-1}); for plant 8 variations of a factor of 4 (120–644 ng g(dw)$^{-1}$ h^{-1}) were found.

[28] As can already be assumed from Table 8, different specimens of young Scots pines emitted completely different spectra of monoterpenes. As an example for this large variability, Figure 4 shows the percent contributions of individual monoterpenes to the sum of monoterpene emission rates for pines 5 (open bars) and 8 (shaded bars), respectively. The spectrum of emitted monoterpenes from plant 5 was dominated by α-pinene with an average contribution of 72% to the sum of monoterpenes, whereas 3-carene contributed <1%. On the other hand, 3-carene was the most abundant monoterpene in the emissions from plant 8 (48% on average). Here the contribution of α-pinene was only of the order of 21%.

4. Discussion

4.1. Monoterpene Emission Pattern

[29] Generally, the composition of VOC emissions measured in this study is typical for Scots pine and is in agreement with results reported in the literature. The major emission products from *Pinus sylvestris* were usually α-pinene and 3-carene [*Isidorov et al.*, 1985; *Petersson*, 1988; *Janson*, 1992, 1993; *Rinne et al.*, 2000]. The observed contributions of β-pinene (up to 22%) and camphene (up to 18%) were higher than reported elsewhere. Our results showed that all other emitted monoterpenes contributed <10% to the sum of monoterpenes.

[30] Surprisingly, different individual Scots pines emitted a completely different spectrum of monoterpenes. A noteworthy point was the observation that one of the young plants (plant 5) did not emit 3-carene in significant amounts (<1 ng g(dw)$^{-1}$ h^{-1}, corresponding to 0.1% of the total sum of monoterpene emissions) but that this monoterpene was one of the major constituents in the emissions of the other plants. On the other hand, seasonal variations in the emission spectrum from the same plant were much smaller than the plant-to-plant variability. Also, the monoterpene emission spectra (averaged over the course of the year) from two branches of the same tree were identical.

[31] Differences in monoterpene emissions might be attributed to differences in enzyme activity or enzyme composition. Several monoterpenes are synthesized by specific enzymes [*Croteau*, 1987; *Gershenzon*, 1994; *Bohlmann et al.*, 1997]. If in one plant the 3-carene synthesizing enzyme was inactive or absent, this plant could not emit 3-carene. Since the presence of enzymes is genetically controlled, the difference in monoterpene composition could be the result of genetic differences. This is the first report of such large intraspecific variability in monoterpene composition of emissions from *Pinus sylvestris* growing at the same origin. *Nerg et al.* [1994] investigated the monoterpene concentrations in young seedlings of Scots pine from nine different seed origins growing in three locations of different latitudes in Finland and Estonia. They reported a geographical trend in the terpene composition in pine shoots, with highest proportional quantities of 3-carene in the most southern origins and lowest quantitites in the northern regions (~54% at 58°N and ~25% at 68°N). The contribution of α-pinene to the terpene composition showed an opposite trend (~25% at 58°N and ~50% at 68°N). In other studies each species of tree was reported to have its own distinctive leaf oil composition [e.g., *Schindler and Kotzias*, 1989; *Roussis et al.*, 1995].

[32] *von Rudloff and Lapp* [1992] investigated the needle oil terpene composition of Ponderosa pine (*Pinus ponderosa*) from various sites in the United States. They report that investigations of the leaf oil composition of three to five trees from the same location provided almost identical data, unfortunately without giving any numbers. Even for trees from different sites, they found only small variations.

[33] Our results of the gas-phase emissions of monoterpenes from Scots pine seem to contradict previous studies. Either the intraspecific variation of the monoterpene composition of the needle oil is significantly higher for Scots pine (*Pinus sylvestris*) than reported in the literature for other pine species, or the differences in the gas-phase emissions are induced by other, unknown factors. A latitudinal influence on terpene compositions, as proposed by *Nerg et al.* [1994], cannot explain the results observed in this study, since the investigated plants grew at the same location. We are aware of the fact that our database is small; nevertheless, our results seem to indicate that the composi-

tion of emitted monoterpenes could be regarded as a fingerprint for an individual *Pinus sylvestris* plant but not a general species specific fingerprint, as is often suggested in the literature for most monoterpene-emitting plant species.

4.2. Temperature Dependence of Monoterpene Emissions

[34] Our observation of monoterpene emission rates increasing exponentially with temperature confirmed the results reported in the literature [e.g., *Tingey et al.*, 1980; *Lamb et al.*, 1985; *Juuti et al.*, 1990]. For monoterpenes we observed values for $c_{TP}R^{-1}$ between 6.9 × 10^3 K and 11.6 × 10^3 K. For T = 298 K the derived value of β was between 0.08 and 0.13 K^{-1}. *Guenther et al.* [1993] suggested a value of 0.09 K^{-1} as best estimate for all monoterpenes and plants, which is within the range of our observations. In a more recent publication, *Rinne et al.* [2000] reported a value for β of 0.146 K^{-1} for the temperature dependence of monoterpene emissions from *Pinus sylvestris*, which is only slightly higher than the upper limit of our observations.

4.3. Standard Emission Rates of Monoterpenes

[35] The standard emission rates Φ^S measured at the branch of an adult pine (branch A) at different times of year showed larger variations than the parameter describing the temperature dependence $c_{TP}R^{-1}$. Values for Φ^S varied by more than 1 order of magnitude between April and October. Generally, highest standard emission rates were found in April. Standard emission rates of monoterpenes were ∼1 order of magnitude lower in July then increased in September by a factor of 4 and decreased in October to values comparable to those in July. The studies conducted at a second branch (branch B) of the same tree showed the same type of seasonal variation. In July and October the standard emission rates of monoterpenes from branch B were similar to those from branch A. The only exception was 3-carene which was emitted in larger amounts from branch B in July. From July to September, standard emission rates from branch B increased by a factor of 2. For branch A the emission rates increased by a factor of 4.

[36] Since the standard emission rates are already normalized to a specific temperature (in this case 25°C) and since the temperature range was very similar during all four campaigns, variations in the temperatures cannot explain the observed differences. Only little is known about the seasonal variation of the standard emission rate of monoterpenes. *Janson* [1993] measured monoterpene emissions from *Pinus sylvestris* at different times of year between May and October. He found high standard emission rates in early May which decreased to lowest values at the end of May. In June and July, standard emission rates were a factor of 3–4 higher than at the end of May and August. He concluded that emission rates of monoterpenes are enhanced during periods of active needle growth and monoterpene biosynthesis. Though we have no evidence to corroborate this hypothesis, it seems to be a plausible explanation. Nevertheless, this does not explain the increase in standard emission rates between July and September. The observation of two

Table 8. Standard VOC Emission Rates Φ^S in ng $g(dw)^{-1}$ h^{-1} From Enclosure Studies With Eight Different 3 to 4 Year Old Pine Seedlings and Plant-to-Plant Range of Emissions[a]

	Seedlings and Time of Measurement								Range
	1 June 1998	2 June 1998	3 August 1998	4 August 1998	5 May 1999	5 July 1999	6 June 1999	7 June 1999	8 May 1999	8 July 1999	8 August 1999	
α-pinene	35 ± 3.8	66 ± 14	283 ± 19	46 ± 5.1	330 ± 37	165 ± 41	23 ± 1.3	15 ± 1.7	134 ± 21	35 ± 2.7	46 ± 4.6	15–330
3-carene	58 ± 7.0	84 ± 18	50 ± 3.2	36 ± 3.9	0.6 ± 0.3	0.3 ± 2.3	22 ± 1.1	22 ± 1.7	313[b]	50 ± 3.2	54 ± 4.7	0.3–313
β-pinene	10 ± 1.3	27 ± 5.5	13 ± 1.9	5.0 ± 18	32 ± 3.4	8.6 ± 1.7	4.5 ± 0.3	6.4 ± 1.1	104 ± 17	18 ± 1.2	23 ± 2.3	5–104
Camphene	19 ± 2.0	12 ± 2.3	22 ± 2.0	8.3 ± 4.2	13 ± 1.3	18 ± 3.3	13 ± 0.9	8.4 ± 1.0	13.4 ± 1.4	6.5 ± 1.0	10 ± 1.4	7–22
Sabinene	11 ± 1.7	12 ± 7.2	7.2 ± 2.1	5.1 ± 192	2.7 ± 0.7	1.4 ± 0.4	2.8 ± 0.2	2.5 ± 0.3	31 ± 4.3	4.7 ± 0.8	5.1 ± 1.2	1–31
β-myrcene	8.1 ± 0.9	9.2 ± 3.1	20 ± 1.5	7.1 ± 3.7	9.5 ± 1.5	5.2 ± 1.5	2.5 ± 0.2	1.9 ± 0.4	23 ± 4.3	3.2 ± 0.7	5.6 ± 0.9	2–23
Limonene	4.4 ± 0.7	4.6 ± 1.5	12 ± 0.7	4.0 ± 12	54 ± 4.7	17 ± 5.6	1.0 ± 0.07	1.2 ± 0.3	12 ± 1.6	1.7 ± 0.2	1.7 ± 0.4	1–17
β-phellandrene	5.7 ± 1.5	3.3 ± 5.2	3.8 ± 0.7	2.9 ± 10	15 ± 1.5	2.4 ± 0.5	0.7 ± 0.04	0.5 ± 0.07	14 ± 2.2	1.0 ± 0.1	1.4 ± 0.3	1–15
1,8-cineol	9.1 ± 0.9	10 ± 2.3	2.7 ± 0.4	ND	2.7 ± 0.4	1.5 ± 0.2	2.5 ± 0.2	1.6 ± 0.1	4.5 ± 0.2	1.9 ± 0.3	3.3 ± 0.4	2–10
Sum	151	218	411	117	457	218	70	58	644[b]	120	147	58–644

[a] Errors are 1σ errors from fits to the data; ND means not detected.

[b] Only lower limit, because the peak of 3-carene, was often out of the linear range.

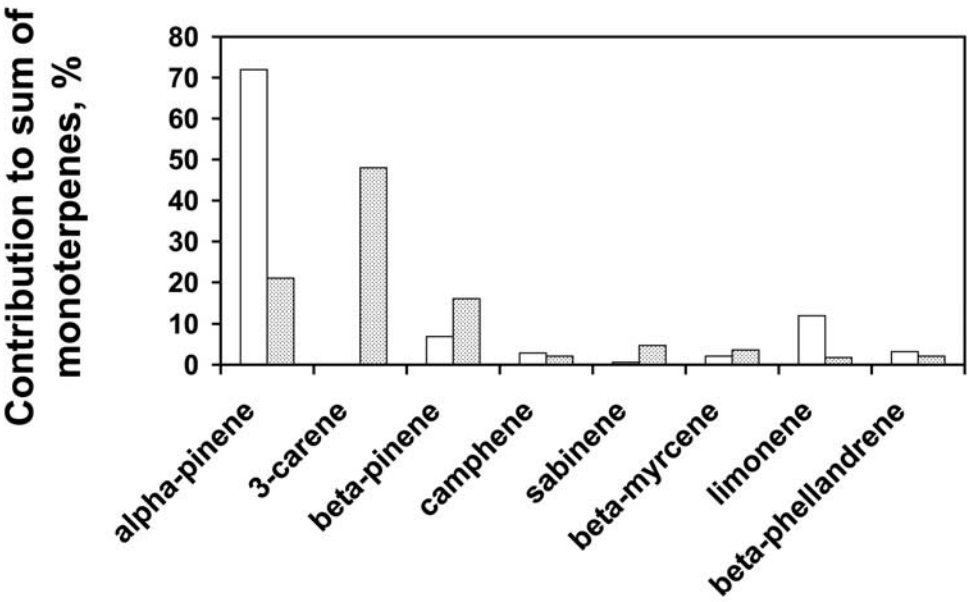

Figure 4. Percent contributions of individual monoterpenes to the sum of the monoterpene emission rates from two different individual young Scots pines. Open bars indicate plant 5; shaded bars indicate plant 8.

separate branches of the same plant showing this increase indicates a systemic response of the plant to an unknown parameter. Stress on the plant is a possible explanation for that observation. Many natural (e.g., heat, drought, and insects) and anthropogenic (e.g., ozone smog, acid rain, and oversupply of nitrogen) factors can serve as stress to plants. For a few of those stressors the impact on monoterpene emissions has been investigated in the past. Though there are too few data available to identify the specific stressor that probably led to the increase in the standard emission rates in September, we can exclude certain forms of stresses and speculate about those that are possible in the following.

[37] *Kainulainen et al.* [1998] and *Lindskog and Potter* [1995] investigated the influence of elevated ozone concentrations and found no significant increase in monoterpene emissions after ozone fumigation of Scots pine (*Pinus sylvestris*) and Norwegian spruce (*Picea abies*), respectively. Therefore high ozone concentrations can be ruled out as an explanation.

[38] *Bertin and Staudt* [1996] investigated water stress effects on monoterpene emissions from Holm oak (*Quercus ilex*) and reported a decrease in monoterpene emissions after a long period of drought. Although there was no rainfall during the campaigns themselves, there was sufficient rain 2 weeks prior to the experiments. Thus stress due to drought can be excluded as well.

[39] In laboratory studies with young Scots pine seedlings, elevated temperatures ($T > 30°C$) were observed as stress factors leading to an increase in monoterpene emissions (J. Wildt, unpublished data, 1998). The factor of increase observed in these studies was on the same order of magnitude as the increase in the standard emission rates between July and September. However, during the experiments in September, only temperatures below 30°C have been observed, and also in a 4 week period prior to the campaign, temperatures did not exceed this value. Therefore temperature stress is unlikely to explain the elevated standard emission rates in September.

[40] Under mechanical stress, plants have been observed to emit higher amounts of monoterpenes [e.g., *Juuti et al.*, 1990; *Yatagai et al.*, 1995]. *Juuti et al.* [1990] reported an increase in monoterpene emission rates by factors of 10–50 during rough handling of Monterey pine (*Pinus radiata*) in their enclosure system; 1–2 hours after the "contact stimulation" emission rates were again within the normal range. During our experiments the mounting procedure was similar during each campaign, and the branch was not treated differently in September. The sampling was started at least 12 hours after mounting the branch inside the enclosure. Therefore it can be assumed that the plant did not suffer from mechanical stress during the experiment.

[41] Under pathogen (J. Wildt, unpublished data, 1998) and herbivory attack [*Turlings and Tumlinson*, 1992; *Priemé et al.*, 2000] plants have been observed to emit higher amounts of monoterpenes. Although no pathogen or herbivory was observed on the investigated branches, it cannot be assumed that other parts of the tree were not affected. The plant-herbivory defense mechanism of release of monoterpenes has been observed to be systemic; that is, monoterpenes are released not only by the attacked part of the plant but by the whole organism [*Turlings and Tumlinson*, 1992; *Röse et al.*, 1996; *Paré and Tumlinson*, 1997a, 1997b, 1998]. Thus a pathogen or herbivory attack is one possible explanation for the increase in the emission rates.

[42] Table 9 compares the range of standard emission rates of monoterpenes observed within the scope of this study to results reported in the literature for Scots pine.

Table 9. Comparison of Monoterpene Emission Rates From *Pinus sylvestris*^{a}

Emission Rate, μg g(dw)$^{-1}$ h^{-1}	Reference
12.1^b (7.7)	*Isidorov et al.* [1985]
0.8^c (1.3)	*Janson* [1993]
6^b (3.8)	*Staudt* [1997]
0.06–0.64^d	this work, young pines
0.24–3.7^d	this work, mature pines

^{a}Numbers in parentheses were calculated for a temperature of 25°C.
^{b}Value is normalized to 30°C.
^{c}Value is normalized to 20°C.
^{d}Value is normalized to 25°C.

Literature for this specific pine species is scarce, and therefore only a small amount of data is available. It has to be noted that standard emission rates from *Isidorov et al.* [1985] and *Staudt* [1997] were normalized to 30°C; those given by *Janson* [1993] were normalized to 20°C. Since a 5 K difference in temperature has a substantial influence on the standard emission rate, the values given in the literature were converted into emission rates normalized to 25°C. Equation (2) and a value of $\beta = 0.09$ K^{-1} were used for that conversion. The corresponding emission rates are given in parentheses. The comparison of standard emission rates shows that for the young pines the observed range of emission rates was lower than the values reported in the literature. Only the standard emission rate of *Janson* [1993] was close to the upper limit of the observed range. Owing to the much higher emission rates in April from branch A of the adult pine the range of standard emission rates was closer to the values observed in other studies. Nevertheless, emission rates reported by *Staudt* [1997] and especially by *Isidorov et al.* [1985] were higher than the range of standard emission rates observed within this study. It cannot be excluded that stress to the plant or systematical differences in the normalization to needle weight were responsible for that difference.

4.4. Calculated Canopy Fluxes for the Hartheimer Wald

[43] The observed seasonal and plant-to-plant variations in the standard emission rates of monoterpenes are of prime importance with regard to calculation of fluxes of these compounds into the atmosphere. Usually, plant species-specific standard emission rates are taken from the literature, and emission algorithms such as the one presented by *Guenther et al.* [1993] (see equation (2)) are taken to calculate emission rates of biogenic VOCs from different plant species on regional and global scales.

[44] To show the effect of the observed variations on such extrapolations, we calculated total monoterpene fluxes for the Hartheimer Wald based on the results of the outdoor enclosure measurements with the adult pine. Neither a seasonal cycle in the standard emission rates or stress effects are included in any existing model describing VOC emissions from plants. Lacking such a model, we used equation (2) to simulate emission fluxes from the Hartheimer Wald for different times of year. Monoterpene fluxes from the Hartheimer Wald were calculated using values for the standard emission rate Φ^S and the parameter describing the temperature dependence $c_{TP}R^{-1}$ obtained from the measurements at branch A at different times of the year. Since the values for $c_{TP}R^{-1}$ only showed minor variations with season, we took the mean value of $c_{TP}R^{-1}$ for each compound. As standard emission rates, which showed seasonal variations of >1 order of magnitude but no clear trend, we took the lowest and highest value to give a range of monoterpene fluxes. These were calculated for the monthly mean temperatures measured in the Hartheimer Wald (H. Mayer, unpublished data, 1999). Emission rates normalized to dry weight of the needles were first converted into emission rates per projected needle surface and then converted into emission rates per land area using a leaf area index of 2.07 for the Hartheimer Wald (H. Mayer, unpublished data, 1999).

[45] Figure 5 shows the simulated flux of the sum of monoterpenes and the monthly mean temperatures. The simulated seasonal cycle follows the cycle of temperature, and highest monoterpene fluxes are expected for July, which is the month with the highest average temperature (19°C). For July the range of the calculated monoterpene flux is between 16 and 260 ng m^{-2} s^{-1}. This large range is a result of the high variation of the standard emission rate observed during our measurements. *Rinne et al.* [2000] measured monoterpene emissions from a *Pinus sylvestris* forest in Finland using a micrometeorological gradient method. Within a temperature range of 5°C–25°C they reported monoterpene fluxes between a few ng m^{-2} s^{-1} and >100 ng m^{-2} s^{-1}. From their observations they calculated an emission flux potential for T = 30°C of 268 ng m^{-2} s^{-1}. The range of our calculated flux potential at T = 30°C is 54–941 ng m^{-2} s^{-1}. Despite the large variation and uncertainties our estimated fluxes are thus of the same order of magnitude as those given by *Rinne et al.* [2000], and they may be typical for midlatitude pine forests.

5. Summary

[46] In this study, monoterpene emissions from Scots pine (*Pinus sylvestris*) have been measured using a dynamic branch enclosure technique. From the diurnal cycle we were able to derive a temperature dependence that is in agreement with results reported in the literature. We conducted measurements at the same branch between April and October and derived a seasonal variability of emissions. The temperature dependence of emissions showed only small variations with season. Of major importance were the obtained results for the standard emission rates, which are often used for extrapolations of emission rates to regional and global scales. These standard emission rates showed variations of >1 order of magnitude but no clear seasonal trend. Measurements conducted at two different branches of the same tree allowed us to derive a branch-to-branch variability of emissions. The emission spectrum of monoterpenes from these two branches was similar. In July and October also, the absolute emission rates were similar. In September both branches emitted higher amounts of monoterpenes than during the other campaigns, but the increase in the emission rates was different by a factor of 2 between the branches. From studies with eight different individual young pines a plant-to-plant variability in monoterpene emissions was derived. Surprisingly, different individual plants showed completely different compositions of monoterpene emis-

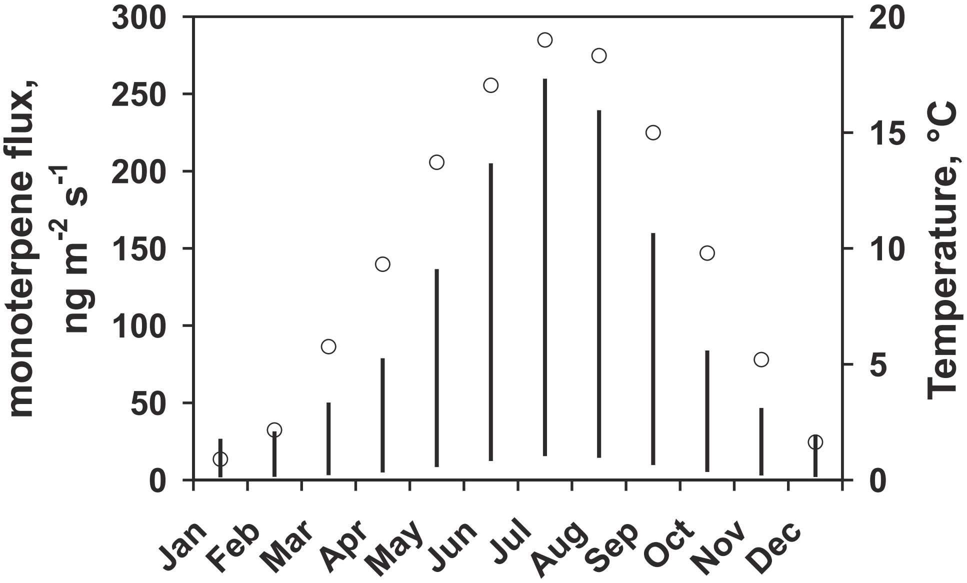

Figure 5. Calculated flux of monoterpenes for the Hartheimer Wald. The bars represent the range between lowest and highest emission rates based on the observed range of standard emission rates measured at branch A at different times of year (left axis). Circles show the monthly mean temperatures (right axis).

sions, indicating that there is no typical fingerprint for the monoterpene emissions of that plant species.

[47] Our results indicate that the current models describing monoterpene emissions from Scots pine are insufficient. Only the temperature dependence of monoterpene emission seems to be described adequately. The large variability in the standard emission rates, however, is a strong indication that other parameters, neglected by the algorithms, also influence the amount of emissions. For example, a seasonal cycle of the standard emission rate and the influence of stress are not taken into account. Without a better understanding of the processes leading to the emissions of monoterpenes, estimations of emissions rates remain uncertain.

[48] **Acknowledgments.** This work was supported financially by the German Ministry for Education, Science, Research and Technology under grant 07TFS24. The authors thank H. Mayer (Meteorologisches Institut der Universität Freiburg) and J. Wildt (Institut für Chemie der Belasteten Atmosphäre, Forschungszentrum Jülich) for making available unpublished data.

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