BOREAL ENVIRONMENT RESEARCH 6: 237–249 ISSN 1239-6095
Helsinki 27 September 2001

Variation of the VOC emission rates of birch species during the growing season

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Hakola, H., Laurila, T., Lindfors, V., Hellén, H., Gaman, A. & Rinne, J. 2001. Variation of the VOC emission rates of birch species during the growing season. *Boreal Env. Res.* 6: 237–249. ISSN 1239-6095

The VOC emission rates of 16 *Betula pubescens* and 15 *Betula pendula* trees were measured during the 1997 growing season in southern Finland. Since the monoterpene emission rates of *Betula pubescens* showed large variations between the tree specimen, these measurements were continued in 2000 with two different clones. Both *Betula pubescens* and *Betula pendula* had low monoterpene emission rates early summer, but after the leaves were fully grown, darker and harder, *Betula pendula* initiated high monoterpene emission rates, whereas *Betula pubescens* showed large tree-to-tree variations. One of the studied clones initiated higher emission rates after the leaves had matured, whereas the emission rates of the other clone decreased a little. *Betula pubescens* also emitted linalool and sesquiterpenes. Linalool was the dominant emitted compound in June but later in summer the linalool emissions declined. Also the monoterpene emission pattern changed in the course of the growing season; at the time of leaf expansion the emission was composed of different monoterpenes, but later sabinene and *trans*-ocimene dominated. The seasonal changes in the emission rates were analysed using the Effective Temperature Sum (ETS, accumulated temperature above 5 °C). Monoterpene emissions, as well as those of linalool and sesquiterpenes, were dependent on temperature. When light was prevented from reaching the cuvette, the monoterpene emissions decreased, but sesquiterpene emissions did not. Physical disturbance of the leaves increased the emission rates of *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, 2-hexenal and 1-hexanol considerably.

Introduction

Boreal forests cover approximately 16 million square kilometers of the earth's surface (Archibold 1995). They are characterized by large volatile organic compound (VOC) emissions

with strong annual variations (Guenther *et al.* 1995). The emission characteristics of the European boreal ecosystem have been intensively studied during the last decade (Janson 1993, Janson *et al.* 1998, 1999, Hauff *et al.* 1999, Laurila and Lindfors 1999, Wilske and Kesselmeier 1999, Hakola *et al.* 2000), and the first emission inventories for North European forests have been published (Lindfors and Laurila 2000, Lindfors *et al.* 2000). Coniferous trees have been found to dominate the annual biogenic VOC emissions, but in the summer months the deciduous contribution to both monoterpene and isoprene emissions is considerable.

Temperature and the photosynthetically active radiation are the best-known environmental variables affecting the VOC emission rates in the short term. The emission rates of isoprene and monoterpenes are dependent on temperature, as shown in a number of studies (Lamb *et al.* 1985, Guenther *et al.* 1991, 1993), and isoprene emission rates are also dependent on light intensity. All the monoterpene emission rates were first considered to be independent of light, but recently studies have been published in which the short-term monoterpene emission rates of several plants have been shown to also depend on the photosynthetically active radiation (Bertin *et al.* 1997, Ciccioli *et al.* 1997, Schuh *et al.* 1997, Steinbrecher *et al.* 1997, Staudt *et al.* 2000).

Most of the published emission rate data feature only short-term variations, but there is also evidence that the plant developmental stages affect the emission rates. Schnizler *et al.* (1997) demonstrated how adding a correction term for the seasonality of isoprene synthase activity to the isoprene emission model improved the model results. Staudt *et al.* (2000) revealed large seasonal changes in both the quantity and quality of the monoterpene emissions of *Pinus pinea* L. and significant monoterpene emissions have been reported from *Salix phylicifolia* L. and *Populus tremula* L. soon after bud-break and prior to the beginning of the isoprene emissions (Hakola *et al.* 1998). Flowering also affects the VOC emissions; e.g., Arey *et al.* (1991a) measured significant linalool emissions from orange blossoms. According to Guenther (1997) the development of seasonally-dependent biogenic emission algorithms is far more uncertain than the parameterisation of the temperature and light dependencies of the emissions or the foliar density estimates.

Besides species-specific genetic coding, the phenological changes in plants are dependent on environmental factors such as temperature and the length of the day. The Effective Temperature Sum (ETS) [calculated as the accumulated daily average temperature sum above a threshold temperature, usually 0 or 5 °C ETS, and expressed in degree days (d.d.)] has been widely used for example, to estimate the time of onset of leafing and flowering of plants (Hari and Häkkinen 1991, Lappalainen 1993). Monson *et al.* (1994) applied ETS to predict the springtime induction of isoprene emission from aspen in different environments, and Hakola *et al.* (1998) used ETS to estimate the maturing of willow and aspen to the stage of isoprene emission.

In this study, we present quantitative and qualitative seasonal changes in the VOC emission rates of the boreal deciduous trees *Betula pendula* Roth (silver birch) and *Betula pubescens* Ehrh. (downy birch) in 1997 and 2000. The seasonal variations of the emission rates are discussed in terms of the effective temperature sum. Compared with calendar dates, the use of ETS reduces variability between different years and geographical regions. According to the statistics of the Finnish Forest Research Institute, the leaves of *B. pubescens* at Ruotsinkylä research station emerged during the period 20 May–1 June in 1997 (corresponding to ETS 75–126 d.d.) and 7 May–10 May in 2000 (ETS 99–125 d.d.). The onset of leafing took place between 1 June–11 June in 1997 (ETS 126–239 d.d.) and 10 May–29 May in 2000 (ETS 125–250 d.d.). Although in 1997 the leaves were fully grown almost two weeks earlier than in 2000, the effective temperature sums are quite similar.

The results are compared to those of Hakola *et al.* (1998), who found that the emission rates of *B. pendula* were low in June and high in August. In addition to the environmental parameters, we studied the effect of physical disturbance on the VOC spectrum emitted by *B. pendula*, since e.g., König *et al.* (1995) have reported that *cis*-3-hexen-1-ol is among the three major VOCs emitted from *B. pendula*, and that

these emissions are at least partly caused by rough handling of the plants.

Also the monoterpene emission rates of Monterey pine have been found to increase due to the effects of rough handling (Juuti *et al.* 1990).

Experiments

The emission measurements were conducted at the Ruotsinkylä research station of the Finnish Forest Research Institute, 20 km north of Helsinki, Finland (60.4°N, 25.0°E). A branch of a tree was enclosed in a teflon bag with a teflon disc in front, in which the inlet and outlet ports were situated. Ambient air was pumped through the chamber at a rate of 8–20 l min^{-1}. The volume of the cuvette was about 20 liters and residence time of air in the cuvette was about 1–2 min. An ozone scrubber, consisting of a set of MnO_2-coated copper nets, was placed in the inlet tubing. Samples were collected from the inlet and outlet lines on adsorbents and in canisters. The emission rate (E) is determined as the mass of emitted compound per gram of dry leaf mass in unit time according to

$$E = (C_2 - C_1) F m_{dw}^{-1} \quad (1)$$

Here C_2 is the concentration of the emitted compound in the outgoing air, C_1 is the concentration in the incoming air, F is the flow rate into the cuvette, and m_{dw} is the dry leaf weight. The dry weight of the leaf biomass was determined by drying the leaves at 75 °C until weight consistency was reached.

In 1997, we measured the emissions of 16 *B. pubescens* and 15 *B. pendula* trees. The trees were young, with an average height of about 1–1.5 m. The measurements were carried out at irregular intervals throughout the growing season, with more intense sampling in spring in order to capture the onset of the monoterpene emissions. On each measurement day a different tree was sampled 2–4 times.

In 2000, two mature *B. pubescens* clones were studied. One was of Finnish origin (Finnish Forest Research Institute number E567, stem diameter 24 cm at a height of 1.5 m) and the other of German origin (Finnish Forest Research Institute number D2472, stem diameter 22 cm at a height of 1.5 m). In the following, the clones are referred to by their numbers E567 and D2472. The VOC emission rates of the mature clones were followed throughout the growing season by taking 2–8 samples once or twice a week. During the period of extensive leaf growth, a different branch was used for sampling on each measurement day, but after the leaves had reached their full size the same branch was sampled on two or three days. The tree was allowed to adapt to the cuvette conditions for one to two hours before the samples were taken at a flow rate of 100 ml min^{-1} for 10–20 min. First, a larger sample volume was collected on adsorbent for mass spectrometric analysis in order to confirm the identity of the compounds. After that, two to four samples were usually taken for quantification in selected ion mode (SIM). The samples did not show any clear trend during a day suggesting the adaption time was adequate. The adsorbent used in the measurements was 250 mg of Tenax-TA in 1997, and 100 mg of Tenax-TA/100 mg of Carbopack-B in 2000. Tenax-TA and Carbopack-B were chosen because they are hydrophobic, thus eliminating the need for sample drying. While Tenax-TA is a good adsorbent for monoterpenes and sesquiterpenes, it is not adequate for isoprene (Cao and Hewitt 1999). Thus, in 1997 isoprene was analyzed from canister samples. Carbopack-B is also a sufficiently good adsorbent for isoprene, and in 2000 no separate canister samples were needed for isoprene.

The adsorbent tubes were analyzed using a Perkin-Elmer ATD-400 thermodesorption unit, an HP 5890 gas chromatograph with an HP-1 column (60 m, i.d. 0.25 mm) and an HP-5972 mass selective detector. Calibration was performed using liquid standards in methanol solutions. The available standards were α-pinene, β-pinene, Δ^3-carene, limonene, camphene, an isomeric mixture of ocimenes, terpinolene, sabinene, *trans*-caryophyllene, linalool, 3-hexen-1-ol, 2-hexenal, 1-hexanol, and 3-hexenylacetate. Since no pure ocimene standard was available, ocimenes were quantified by assuming their response to be the same as that of α-pinene. α-Farnesene and *cis*-caryophyllene standards were not available either, and these compounds were quantified as *trans*-caryophyllene.

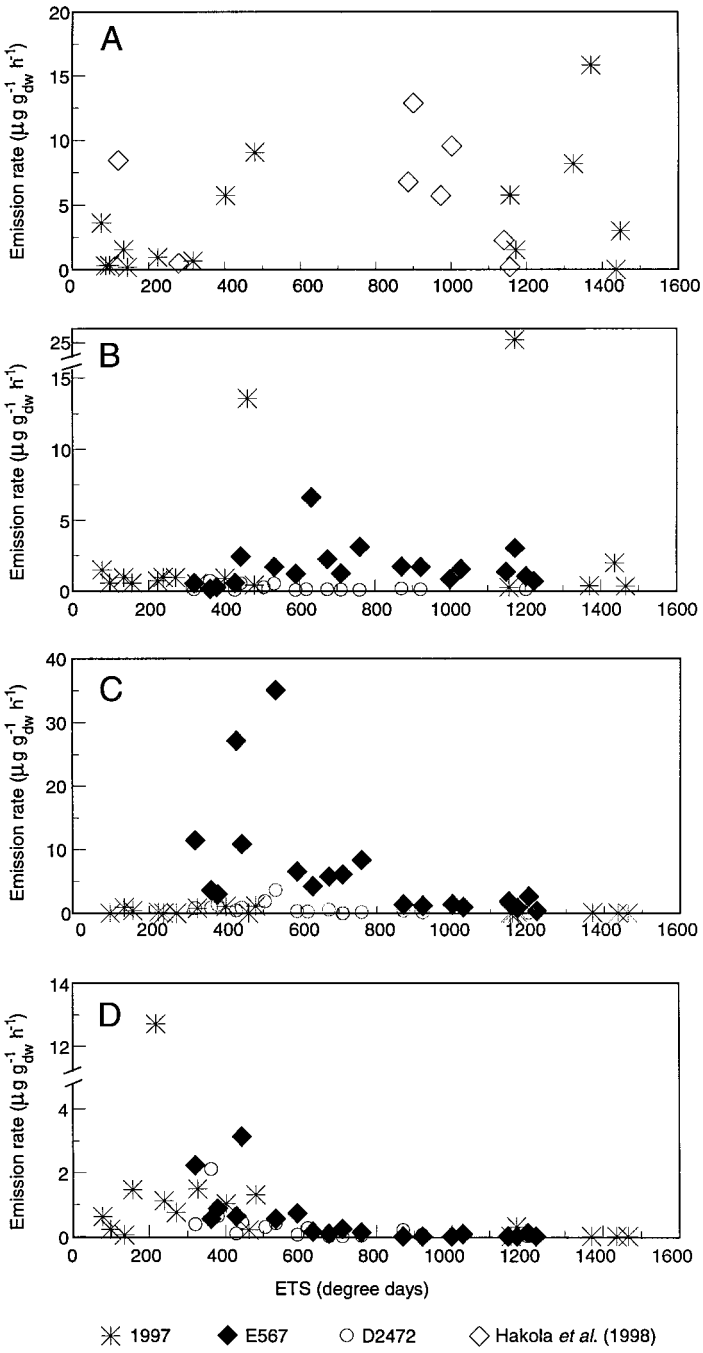

Fig. 1. Terpenoid emission potentials of *Betula pendula* and *Betula pubescens* as a function of the effective temperature sum (standardized to 30 °C in accordance with Guenther *et al.* (1991), linalool and sesquiterpenes are standardized to 30 °C using β coefficients from the present study). The *Betula pendula* monoterpene emission rate data from Hakola *et al.* (1998) is also shown. — **A**: monoterpene emission potentials of *Betula pendula*; — **B**: monoterpene emission potentials of *Betula pubescens*; — **C**: sesquiterpene emission potentials of *Betula pubescens*; — **D**: linalool emission potentials of *Betula pubescens*.

Light hydrocarbons were analyzed from canister samples. The 0.85-l stainless steel canisters were flushed several times prior to pressurizing them to ~200 kPa. The canister samples were analyzed using an HP-5890 gas chromatograph equipped with a flame ionization detector and an Al_2O_3/KCl PLOT column (50 m, i.d. 0.32). The sample volume was about 0.5 l (the exact sample volume was determined by measuring the pressure in the canister prior to and after the analysis) and the samples were preconcentrated in two liquid nitrogen traps, in a stainless steel loop (125 cm, 1/8´´) with glass beads and in a capillary trap. The sample was dried by passing it through a 10 cm long stainless steel tube filled with K_2CO_3 and NaOH. Calibration was performed with a UK National Physical Laboratory gaseous standard which contained isoprene and 26 other hydrocarbons, analyzed among the regular samples.

During sampling, temperature and relative humidity were measured inside and outside the enclosure using Vaisala temperature and humidity sensors (HMP35D). The photosynthetic photon flux density (PPFD) was measured by a quantum sensor (Li-Cor LI-190SZ). Hourly temperature data from the Helsinki-Vantaa airport, located about 7 km to the south from the measuring site, was used for the effective temperature sum (ETS) calculations. ETS was calculated in degree days (d.d.) as the accumulated daily average temperature above +5 °C.

VOC emission rates

Seasonal variation of the VOC emission rates

Both *Betula* species were found to be copious monoterpene/sesquiterpene emitters. The emission rates as well as the compound patterns changed in the course of the season.

B. pendula emitted only monoterpenes. High monoterpene emission rates were measured soon after bud burst when leaves were still growing. These first high emission rates may be residuals from monoterpene pool in buds. The buds of birches contain 4%–6% of volatile oils whereas their leaves contain only 0.05%–0.1% (Lievonen 1982), and the emission rates of stored monoterpenes are known to be dependent on their concentrations in the foliage (Lerdau *et al.* 1995). The emission rates declined for about a month. After the leaves had reached their full size and were darker and harder the emission rates increased. This change in emission rates took place after ETS exceeded 400 d.d. (Fig. 1A). The emission rates then remained substantial, but showed quite large variations until the leaves started to turn yellow and the measurements were brought to an end (Table 1).

A clear seasonal variation was also expected for the monoterpene emission rates of *B. pubescens*, but the measurements conducted in 1997

Table 1. The emission potentials of *B. pendula* and *B. pubescens* (average ± standard deviation, μg g_{dw}^{-1} h^{-1}) for different seasons. For *B. pubescens*, the data set from 1997 and the two clones measured in 2000 are shown separately due to large variations. The β-coefficients used in the standardization were 0.09 $°C^{-1}$, 0.18 $°C^{-1}$, and 0.19 $°C^{-1}$ for monoterpenes, linalool, and sesquiterpenes, respectively. Number of observations are given in parentheses.

	B. pendula, 1997	*B. pubescens*, 1997	*B. pubescens*, 2000, E567	*B. pubescens*, 2000, D2472
	Monoterpenes	Monoterpenes	Monoterpenes	Monoterpenes
ETS < 80	3.63 ± 0.38 (2)	1.47 ± 0.14 (2)	No data	No data
80 < ETS < 400	0.68 ± 0.57 (14)	0.72 ± 0.24 (18)	0.31 ± 0.21 (6)	0.31 ± 0.43 (6)
ETS > 400	7.71 ± 4.64 (12)	5.49 ± 9.22 (16)	1.71 ± 1.40 (46)	0.17 ± 0.18 (23)
	Linalool	Linalool	Linalool	Linalool
ETS < 600	–	1.79 ± 3.27 (26)	1.20 ± 0.99 (15)	0.67 ± 0.89 (15)
ETS > 600	–	0.06 ± 0.13 (10)	0.08 ± 0.17 (37)	0.07 ± 0.10 (14)
	Sesquiterpenes	Sesquiterpenes	Sesquiterpenes	Sesquiterpenes
	–	0.31 ± 0.53 (36)	6.94 ± 10.85 (52)	0.81 ± 0.95 (29)

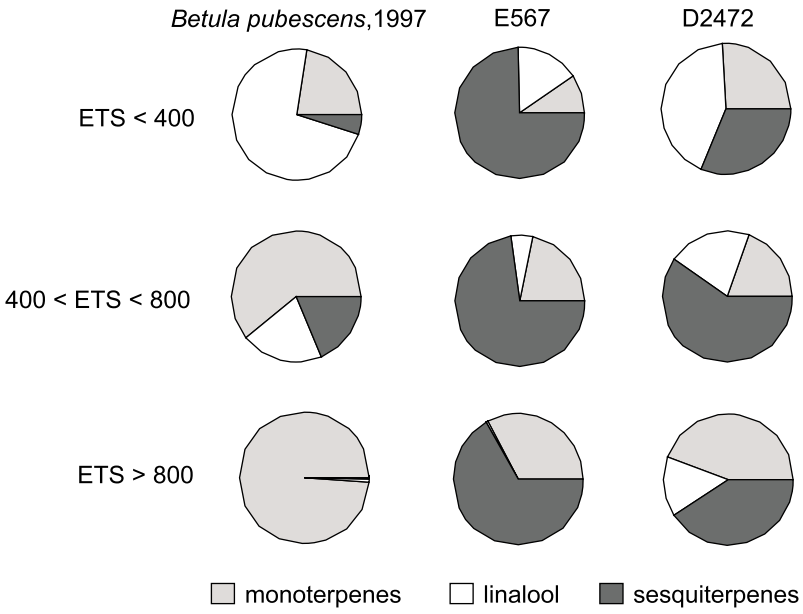

Fig. 2. Variation of the relative amounts of monoterpenes, linalool, and sesquiterpenes in the emissions of *Betula pubescens* during the growing season. The phases of the growing season are categorized by the ETS values (in degree days). In 1997, 400 and 800 d.d. were reached on 25 June and 24 July, and in 2000 on 18 June and on 21 July, respectively.

showed surprising variability. As with *B. pendula*, the emission rates of *B. pubescens* were low in June, but during the period when *B. pendula* had high monoterpene emissions, the emission rates of *B. pubescens* were much more variable. Of the four individual *B. pubescens* trees measured in July–August 1997, two emitted a high amount of monoterpenes (mean emission potential 20 μg g^{-1}_{dw} h^{-1}) while two emitted very little (mean emission potential 0.6 μg g^{-1}_{dw} h^{-1}). To test whether these differences were tree-to-tree or day-to-day variations, the measurements were repeated in summer 2000 with the two mature *B. pubescens* clones. Again, the emission rates of both clones were low in early summer, but after the ETS value of 400 d.d. was exceeded (19 June 2000), one of the clones (E567) initiated higher monoterpene emissions while the other (D2472) did not (Fig. 1B). The difference in emission rates between the *B. pubescens* specimen can be due to different genetic origin. *B. pubescens* has more genetic variation than *B. pendula* and biodiversity could be responsible for the emission variability found in 1997, when a different tree was used for sampling on each measurement day.

In addition to monoterpenes, *B. pubescens* also emitted sesquiterpenes (Fig. 1C) and linalool, an oxygenated monoterpene (Fig. 1D). *Cis*- and *trans*-caryophyllene were among the main compounds emitted by the mature *B. pubescens* clones. The young trees measured in 1997 also emitted another sesquiterpene, tentatively identified as α-farnesene. The caryophyllene emission rates of the mature clones reached high levels before those of monoterpenes and remained substantial until 800 d.d. was reached (Fig. 1C and Table 1). The linalool emission rates showed a clear seasonality: in 2000 they were already high when the measurements were started, declining after about 600 d.d. (26 June 2000) and becoming extremely low after 800 d.d. (22 July 2000) (Fig. 1D and Table 1). Linalool emissions from *B. pubescens* are not related to flowering as is the case with orange trees (Arey *et al.* 1991a), since the flowering of birches takes place already at about 50 d.d. (Lappalainen 1993). In 2000, 50 d.d. was achieved on 25 April. The seasonal variation of the relative abundances of the emitted compounds was quite different between the studied *B. pubescens* trees. Figure 2 shows the relative contributions of linalool, mono-, and sesquiterpenes to the emissions of *B. pubescens* before 400 d.d., be-

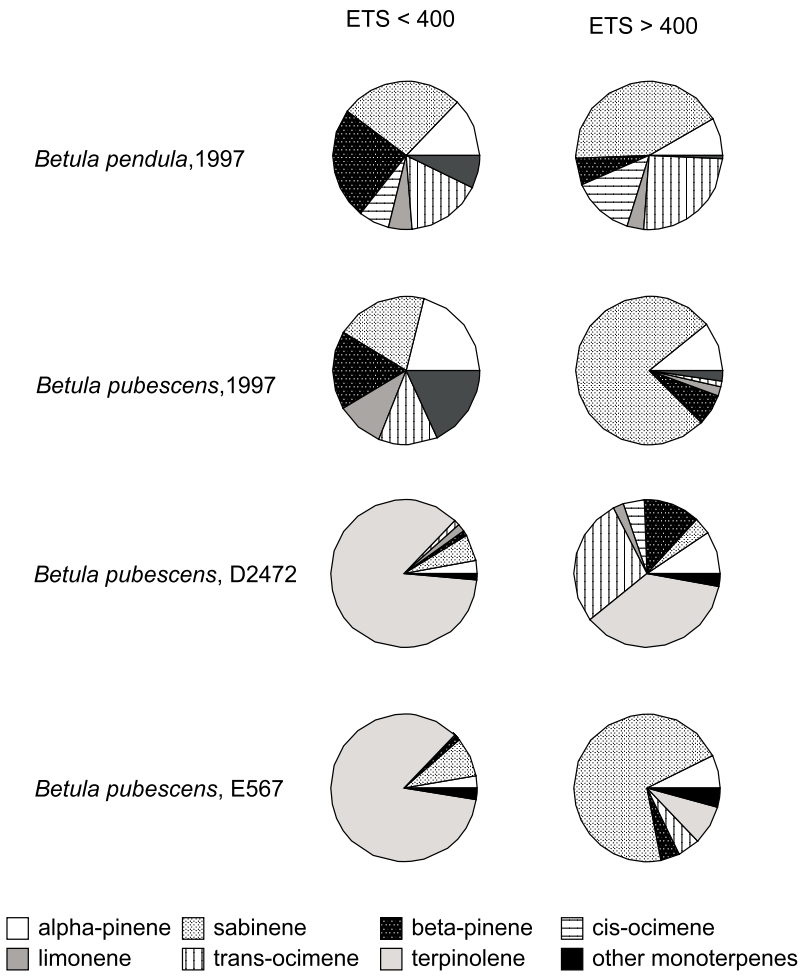

Fig. 3. Mean composition of emitted monoterpenes before and after 400 degree days. In 1997 and 2000, 400 d.d. were reached on 25 June and on 18 June, respectively.

tween 400 and 800 d.d. and after 800 d.d. These limits were chosen, because after 400 d.d. the monoterpene emissions generally increased, while after 800 d.d. the linalool emissions were almost absent. The linalool emissions dominate early in the growing season, but after 400 d.d. is exceeded, the role of monoterpenes becomes more important. Later in the summer the emissions of young *B. pubescens* trees mainly consist of monoterpenes (Fig. 2), whereas the relative contribution of sesquiterpene emissions is significant for the mature trees throughout the growing season. On the basis of our data, it remains unclear whether the sesquiterpene emissions become more important as the tree gets older, or whether this result is due to the large tree-to-tree variations observed in the *B. pubescens* emissions. About half of the measured *B. pubescens* trees initiated higher monoterpene emissions after 400 d.d. while the other half did not.

Also the monoterpene emission pattern changed in the course of the growing season (Fig. 3). During the period of extensive leaf growth, the monoterpenes emitted by young *B. pendula* and *B. pubescens* trees were quite evenly distributed between the different compounds, whereas the mature clones mainly emitted terpinolene in early summer. After 400 d.d. all trees mainly emitted ocimenes and sabinene. The ocimene and sabinene emissions declined at the end of September, when the leaves began to turn yellow. According to the

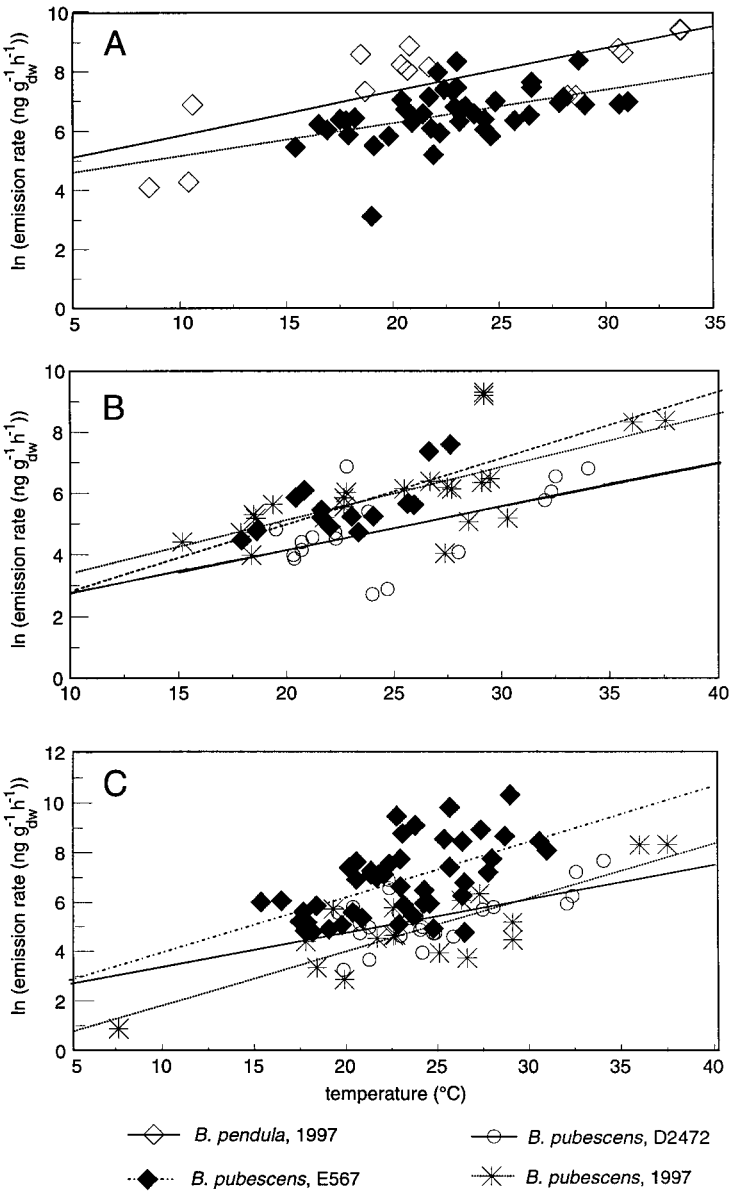

Fig. 4. Terpenoid emission rates as a function of temperature. Monoterpene emission rates of the two strong emitters, *Betula pendula* and *Betula pubescens* clone E567 after 400 degree days (**A**), linalool emission rates of *Betula pubescens* prior to 600 degree days (**B**) and all sesquiterpene emission rates of *Betula pubescens* (**C**) are plotted.

statistics of the Finnish Forest Research Institute the yellowing of the leaves of *B. pubescens* took place 4 October–21 October in 1997 (ETS 1476-1489) and 25 September–7 October in 2000 (ETS 1348-1422). Our measurements were finished already when the leaves started to turn yellow.

Small amounts of alkenes were found to be emitted by *B. pubescens* soon after bud burst. These emissions declined as the leaves matured, but for the period 80–130 d.d. the average emission rates of ethene, propene and 1-butene were 0.32 ± 0.41, 0.08 ± 0.08, and 0.07 ± 0.04 μg g_{dw}^{-1} h^{-1}, respectively.

The effect of temperature and light on the emission rates of *Betula pubescens*

The emission rates of monoterpenes are strongly dependent on temperature. The relationship of monoterpenes from pools is usually described by

$$E = E_s \exp[\beta(T - T_s)] \quad (2)$$

where β is an empirically determined coefficient, T is the leaf temperature, T_s is the standard temperature, and E_s is the emission rate at the standard temperature. On the basis of reported measurements, Guenther *et al.* (1993) suggested a best estimate of β = 0.09 for the temperature coefficient for all monoterpenes and plants.

The temperature dependences of our measured emission rates are depicted in Fig. 4. The data was fitted to Eq. 2, and the β-coefficients together with the correlation coefficients are given in Table 2. Generally the correlation between the emission rates and temperature is rather poor, but for monoterpene emissions the β-coefficient is, however, close to the generally used 0.09 °C^{-1} (Table 2). In this analysis we only included the data obtained after 400 d.d. for the trees that initiated higher monoterpene emission rates at that time (all *B. pendula* data and *B. pubescens* clone E567 data). The poor correlation is likely due to light that also affects at least part of the emission. Recently studies have been published in which the short-term monoterpene emission rates have been shown to depend on the photosynthetic photon flux density (PPFD) for *Quercus ilex* L. (Bertin *et al.* 1997), sunflower and beech (Schuh *et al.* 1997), and *Pinus pinea* (Staudt *et al.* 2000). These conclusions were drawn using diurnal variations in the emissions, but there are also other studies where artificial darkening has been applied to confirm the PPFD dependence of at least some terpenoid compounds (Staudt *et al.* 1997). As our measurements were always carried out at approximately the same time of day, ± 2 hours around midday, we have no data corresponding to either dawn or sunset. Based on our regular samples, neither the sum of terpenes nor any individual terpenoid compound exhibited any clear dependence between the normalised emission rate and PPFD. This was the case for both *Betula* species in the 1997 measurements and for both *B. pubescens* clones in 2000.

However, during the 2000 measurements, an experiment was conducted, in which a branch of clone E567 was covered and samples were collected from the dark cuvette. Emissions of almost all monoterpenes decreased when the cuvette was darkened, whereas the sesquiterpene emission rates were not much affected (Table 3). Linalool emission rates also decreased but not as much as those of monoterpenes. After the cuvette was exposed to light again, the emission rates started to increase. The emissions did not decrease sharply with the sudden darkness, but declined gradually within an hour indicating that there is a time lag while the plant adapts the emission rate to the new light conditions. This time lag can cause the observed lack of correlation between the emission rates and light intensity for samples taken in the natural environment where the light conditions are constantly varying. The assessment of the temperature and light dependence of the terpenoid emission rates must therefore be based on laboratory experiments where plants can be studied in a controlled environment.

Table 2. β-coefficients according to Eq. 1 and the correlation coefficient R between the emission rate and temperature. The monoterpene data for ETS > 400 d.d. and linalool data for ETS < 600 d.d. are included in the analysis. Two and three asterisks indicate significance at the 1% and 0.1% risk levels, respectively. N is the number of measurements.

Terpenoids	β °C^{-1}	R	N
Monoterpenes			
B. pendula, data set from 1997	0.15	0.76***	15
B. pubescens, E567	0.11	0.47**	42
Sesquiterpenes			
B. pubescens, data set from 1997	0.22	0.83***	17
B. pubescens, D2472	0.14	0.56**	26
B. pubescens, E567	0.22	0.57***	47
Linalool			
B. pubescens, data set from 1997	0.17	0.68***	23
B. pubescens, D2472	0.14	0.57*	17
B. pubescens, E567	0.22	0.70**	14

In addition to monoterpenes, we applied the exponential relationship presented in Eq. 2 to analyse the temperature dependence of the linalool and sesquiterpene emission rates (Table 2). On the basis of our results, this relationship can be used as an approximation for the temperature dependence of these compounds. However, for linalool, only days before 600 d.d. were taken into account, since after that the linalool emissions declined for reasons other than temperature. The 1997 data set contained trees that did not emit sesquiterpenes at all, regardless of temperature; those trees were not included in this analysis. The averages of the experimental β-coefficients (0.18 $°C^{-1}$ and 0.19 $°C^{-1}$ for linalool and sesquiterpenes, respectively) were used to calculate the standard emission potentials for these compounds.

The effect of rough handling of the leaves on VOC emissions

In addition to the terpenoids, also other oxygen-

Table 3. The effect of light on the emission rates (ng g^{-1}_{dw} h^{-1}) of *B. pubescens* (clone E567). The branch was covered after the second sample was taken and remained in the dark while samples 3, 4 and 5 were collected. The samples were collected on 7 July 2000, and the sampling time was 15 min.

Sample number	1	2	3	4	5	6	7
Sampling start at	10:01	10:17	10:38	10:54	11:14	11:37	11:53
Temperature (°C)	23	22.1	22.1	22.3	21.7	22.2	21.7
PPFD	256	122	4	3	4	216	325
Relative humidity in the cuvette	76	78	83	80	81	79	80
Relative humidity outside	64	67	64	66	66	70	73
α-Pinene	307	181	41	0	0	138	99
Sabinene	3366	2318	562	116	50	1627	1061
β-Pinene	127	124	20	16	0	69	37
Δ^3-Carene	5	1	0	0	0	0	6
cis-β-Ocimene	36	16	12	0	6	14	9
Limonene	46	42	11	0	2	10	14
1,8-Cineol	4	7	0	1	2	8	1
trans-β-Ocimene	75	56	19	3	2	19	17
Linalool	47	35	26	14	10	24	20
Terpinolene	53	39	6	0	5	25	12
Caryophyllene	758	1248	816	883	619	1042	931

Table 4. The effect of pressing of the branch on the emission rates (ng g^{-1}_{dw} h^{-1}) of *B. pubescens*. On 18 June 1997, two 20 min samples were taken, after which the cuvette was opened and the branch was pressed between the hands. Two samples were taken after disturbing the branch.

Day	18 June	18 June	18 June	18 June
Time	11:55	12:20	12:50	14:05
Temperature (°C)	18	18	19	22
		Pressing		
2-Hexenal	9	10	36565	138
3-Hexen-1-ol	61	42	90065	742
1-Hexanol	9	19	3369	87
3-Hexenylacetate	67	32	11170	212
Monoterpenes	304	134	99	74
trans-Caryophyllene	0	27	296	88
Linalool	178	201	278	182

ated compounds than linalool have been detected in plant emissions. Arey *et al.* (1991b) found *cis*-3-hexenylacetate and *cis*-3-hexen-1-ol in the emissions of agricultural plant species, while König *et al.* (1995) found *cis*-3-hexenylacetate, *cis*-3-hexen-1-ol and hexanal in the emissions of various agricultural plant species and trees. König *et al.* (1995) determined *cis*-3-hexen-1-ol to be among the three major VOCs emitted by birches; they also concluded that these emissions were at least partly caused by rough handling of the plants. This was also very clearly found in the present study.

To test the effect of rough handling on the emissions, an experiment was carried out during the 1997 measurements in which the cuvette was opened and the *B. pubescens* branch was pressed between the hands a couple of times, without causing permanent damage to the leaves. Two samples were taken from the cuvette before and two after this treatment. The emission rates obtained in this experiment are presented in Table 4. After disturbing the plant, large increases in *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, 2-hexenal and 1-hexanol emission rates were detected. Subsequently, the emission rates decreased again and the sample taken one hour later was already close to the normal value. The handling did not have much effect on the monoterpene emissions, but it did cause some *trans*-caryophyllene emission.

Summary and conclusions

The emissions of *B. pendula* consisted only of monoterpenes and demonstrated clear seasonal variation. The high emission rates measured soon after bud break are likely to be residuals from the buds. The emissions declined for about a month, to increase again after the ETS value of 400 d.d. was exceeded. The standard emission potentials of *B. pendula* are presented in Table 1.

Sixteen young *B. pubescens* trees were measured during the growing season of 1997 and the emission rates of two mature *B. pubescens* clones were followed throughout the growing season of 2000. The standard emission potentials are presented in Table 1 separately for the young trees and the mature clones. All trees measured before ETS had reached 400 d.d. demonstrated low monoterpene emission rates, with the exception of the first measurement, which was carried out soon after bud break. After 400 d.d. pronounced tree-to-tree variations were observed. One of the clones emitted monoterpenes with high rates and continued to do so until the end of the growing season, whereas the emissions of the other clone stayed at a low level. Clear tree-to-tree variations explain the deviations observed in the 1997 measurements and they are likely to be due to different genetic origins.

Even though the 1997 data set included some low-emitting specimen, the average monoterpene emission rate of young *B. pubescens* trees was clearly higher than the average of the mature clone with higher monoterpene emissions (Table 1). On the other hand, the sesquiterpene emission rates of younger trees were much lower than those of the clones. It is possible that the observed differences are not only tree-dependent, but also related to the age of the trees.

Linalool emission rates were highest early in the growing season and declined after midsummer. At the time of high emission rates, the contribution of linalool to the total VOC emission of the trees was considerable.

The monoterpene emission pattern changed during the growing season; terpinolene was the main monoterpene emitted by the mature *B. pubescens* trees, whereas the young *B. pubescens* and *B. pendula* had a more evenly distributed monoterpene pattern. After 400 d.d. sabinene and the ocimenes were clearly dominant.

Monoterpene emission rates are dependent on light intensity and temperature. The sesquiterpene and linalool emission rates also depend on temperature, but their light dependence is less obvious. Controlled laboratory experiments are needed to quantify the temperature and light dependencies of the terpenoid emissions.

Physical disturbance of the plants caused very high emission rates of *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, 2-hexenal and 1-hexanol. Emission algorithms should also be formulated for these and other compounds, whose emissions are presently poorly understood.

Acknowledgments. We wish to thank Prof. Kubin, Mr. Poikolainen, Mr. Kananen and Mr. Lehtonen at the Finnish Forest Research Institute for co-operation, Mika Aurela for programming the data acquisition system and Jaakko Vesterinen for technical assistance. This work was funded by the Academy of Finland and the European Commission DG XII (contract number ENV4-CT95-0022). Janne Rinne gratefully acknowledges the Maj and Tor Nessling's Foundation for financial support.

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Received 6 April 2001, accepted 31 May 2001