

## **A Revised Parameterisation for Emission Modelling of Isoprenoids for Boreal Plants**

R. Steinbrecher<sup>1</sup>, K. Hauff<sup>1</sup>, H. Hakola<sup>2</sup>, and J. Rössler<sup>1</sup>

(1) *Fraunhofer-Institut für Atmosphärische Umweltforschung (IFU),*

*Kreuzeckbahnstrasse 19*

*D-82467 Garmisch-Partenkirchen, Germany.*

(2) *Finnish Meteorological Institute, Air Quality Research Division (FMI)*

*Sahaajankatu 20 E*

*FIN-00810 Helsinki, Finland.*

### **Summary**

Boreal forests contribute a major fraction of the total amount of volatile organic compounds emitted in the Northern Hemisphere through their extended coverage and usually high temperatures in the summer. However, our understanding of the speciation and the source strength of VOC emissions from plants (BVOC) from the boreal region is limited due to the lack of studies. Emission rates normalised to a leaf temperature of 30°C and 1000 µE PAR for the sum of isoprenoids emitted from typical plant species in Finland's boreal region recorded during July/August decrease in the following order: *Salix caprea* (L.) > *Juniperus communis* (L.) > *Pinus sylvestris* (L.) > *Picea abies* ssp. *obovata* ([Ledeb.] Hult.) > *Ledum pallustre* (L.) >> *Betula pubescens* (Ehrh.). A revised parameterisation of monoterpene emission considers emission from reservoirs in the plants and emission from obviously *de novo* synthesised compounds. It is demonstrated that this new approach significantly improves the prediction of monoterpene emission from *P. sylvestris* and *P. abies* ssp. *obovata*.

### **Introduction**

Biogenic volatile organic compounds (BVOC) are emitted by many plant species [1]. Due to their high reactivity with OH-radicals, ozone and NO<sub>3</sub>-radicals, VOC significantly influence tropospheric air chemistry in southern latitudes [2] and also in the boreal regions as shown in this volume. Boreal vegetation is characterised as a major source of BVOC [1; 3]. Simpson et al. [3] pointed out that present BVOC emission inventories are quite uncertain and some of the tabulated emission rates may differ from actual rates by a factor of 10. One reason for this high uncertainty is the lack of emission data for key species in ecosystems covering large

areas. For Europe, Boreal BVOC emission estimates are based mainly on data by Janson [4] and Steinbrecher et al. [5] of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* [L.] Karst.) [1; 3]. Recent findings on the mechanisms involved in controlling monoterpene emission from Norway spruce (*Picea abies* [L.] Karst.), beech (*Fagus sylvatica* L.) and sunflower (*Helianthus annuus* L.) indicate that current parameterisations of monoterpene emission from plants need to be revised [6; 7]. Therefore, the goal of this study was to identify major BVOC emitted from typical Boreal plant species, to analyse the controlling factors of emission and to derive appropriate emission algorithms and emission factors for predicting realistic isoprenoid emission from Boreal vegetation.

## **Experimental**

### Location and plant material

The experiments were performed in 1996 and 1997 in July and August in Finland at two forest research sites: (1) in 1996 in the Pallas Ounastunturi National Park (68 °N, 25 °E) and (2) in 1997 in the Mekrijärvi area (63 °N, 31 °E). The following Boreal plant species were investigated: Siberian spruce (*Picea abies* ssp. *obovata* [Ledeb.] Hult.), Scots pine (*Pinus sylvestris* L.), Goat willow (*Salix caprea* L.), Downy birch (*Betula pubescens* Ehrh.), Common juniper (*Juniperus communis* L.) and Marsh tea (*Ledum pallustre* L.).

### Cuvette-measurements

Two flow-through enclosures were used for recording simultaneously two diurnal cycles of isoprenoid emission and CO<sub>2</sub>/H<sub>2</sub>O gas exchange from two twigs of each plant. Enclosures, called cuvettes in the following, were built mostly of Teflon (transparent foil; thickness: 50 µm; NOWOFOL, Siegsdorf, Germany). A fan was installed in each cuvette for mixing the air volume. Preconditioned air was used to flush the cuvettes continuously (MKS Instruments, München, Germany). The residence time of air in the cuvette was about 2 min. Ambient air humidity was adjusted to 5000 ± 500 ppmV by a cold trap. The concentration of water vapour in the cuvette inlet air was determined by dew point measurements (Walz, Effeltrich, Germany). The CO<sub>2</sub> concentrations were ambient. The absolute CO<sub>2</sub> mixing ratio in the cuvette inlet air and the differences in CO<sub>2</sub>- and water vapour concentration between cuvette inlet and outlet air were measured by an infrared absorption technique (BINOS, Rosemount, Hanau, Germany). Four NiCr-Ni-thermocouples in each cuvette were used for recording the leaf surface temperature. Sensors for recording the photosynthetic active radiation (PAR; LICOR LI 190SA; Walz, Effeltrich, Germany) were mounted on the cuvettes. The PAR

extinction of the Teflon foil was considered in the calculations. A PC controlled the solenoid valves for zero adjustment of the BINOS every 2 hours. Valve switching and measured parameters were recorded after A/D conversion. All sensors and flow controllers were calibrated before the field campaigns.

All given parameters are normalised to total leaf area. Total leaf area was obtained by multiplying the projected area as measured by a leaf area meter (LI-COR LI 3000, Walz, Effeltrich, Germany) by a factor of 2 for broad leaf species, a factor of 2.74 for Norway spruce [8] and a factor of 2.5 for Scots pine [9]. To calculate the total leaf area of Common juniper, a factor of 2.5 was used because the shape of juniper leaves is similar to that of Scots pine. Dry weight was determined after drying the collected leaves at 105°C for 48 hours. Gas exchange parameters, net CO<sub>2</sub> assimilation (A), transpiration (E), leaf to air water vapour pressure deficit ( $\Delta W$ ), leaf conductance for water vapour ( $g_{H_2O}$ ), and CO<sub>2</sub> mixing ratio inside the leaf ( $c_i$ ) were calculated using the equations given by Ball [10]. These gas exchange parameters were used to characterise the primary metabolism of the leaves and to identify injuries of the twig that could result from the enclosure of the twig in the cuvettes, which could lead to artefact emission. Twigs investigated were south-east/south exposed. In Pallas, twigs were measured at a height of 4 m above ground and in Mekrijärvi, at 1.5 m. Emission rates of conifers were determined on the basis of enclosed current year and last year shoots.

### GC-Measurements

The BVOC-mixing ratios in the cuvette inlet and outlet air were analysed with an online GC-system (HC1010 BTX Monitor, Airmotec, Illnau, Schweiz) after concentration of the sample air for 58 min (flow rate: 120 ml min<sup>-1</sup>) on mixed bed tubes (Carbosieve S-III/ Carboxen 1003 and Carbotrap, Supelco, München, Germany). The measurement frequency was 1.5 h. The trapped compounds were thermodesorbed at 350°C and cryo-focused at -30°C on a 18 cm \* 0.53 mm id capillary pre-column filled with Carbopack B (Supelco, München, Germany). The injection of the compounds on the capillary column (DB 1701, 12 m \* 0.18 id, 0.4 µm df; J&W, Köln, Germany) was achieved by heating the pre-column to 350°C within 1 sec. A linear temperature program starting at 35°C and ending at 150°C (rate: 8°C min<sup>-1</sup>) guaranteed the separation of the non-methane hydrocarbon fraction of the trapped compounds. All compounds were detected by FID and verified by GC-MS-analysis by H. Hakola, Finnish Meteorological Institute, Helsinki. Compounds were quantified according Steinbrecher *et al.*

[11] after checking periodically the GC performance in the field by a gaseous isoprene standard [12].

### Statistics

For investigating the influence of the various environmental and plant physiological parameters on the isoprenoid emission rate of oak species, the statistical software package of SPSS for Windows Ver. 6.1.2 (1995) was used. The relevant statistical procedures are given below.

### Revised parameterisation for monoterpene emission

In order to describe BVOC emission for terrestrial ecosystems, an extrapolation from measurements at the twig level has to be made. Guenther [13] described algorithms to predict BVOC emission from vegetation with leaf temperature and light intensity as the main controlling parameters. Up to now the isoprenoids, isoprene and monoterpenes, have been identified to be the dominate compounds in BVOC emission [14].

The Isoprene emission rate,  $E_{iso}$ , may be calculated by using an emission factor,  $EF_{iso}$  (i. e. isoprene emission at a standard temperature,  $T_s$ , of 303 K) and a standard PAR of 1000  $\mu E$ , and adjusting this rate by temperature and light correction functions [13]:

$$E_{iso} = EF_{iso} \cdot C_{Liso} \cdot C_{Tiso} \quad (1)$$

where  $C_{Liso}$  is the correction term for light and  $C_{Tiso}$  that for leaf temperature  $T$  relative to standard conditions. Guenther [13] formulate these terms as:

$$C_{Liso} = \frac{\alpha \cdot c_{L1} \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \quad (2)$$

where  $\alpha = 0.0027$  and  $c_{L1} = 1.066$  are empirical constants, and  $L$  is the PAR ( $\mu E$ ). Temperature dependence  $C_{Tiso}$  is described by:

$$C_{Tiso} = \frac{\exp\left(\frac{c_{T1}(T - T_S)}{R \cdot T_S \cdot T}\right)}{0.96 + \exp\left(\frac{c_{T2}(T - T_M)}{R \cdot T_S \cdot T}\right)} \quad (3)$$

where  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $c_{T1}$  ( $95000 \text{ J mol}^{-1}$ ),  $c_{T2}$  ( $230000 \text{ J mol}^{-1}$ ), and  $T_M$  ( $314 \text{ K}$ ) are empirical coefficients. These parameters and algorithms were used to calculate emission factors by normalising measured emission rates to a leaf temperature of  $30^\circ\text{C}$  and  $1000 \mu\text{E PAR}$ .

Monoterpene emission from plants is often parameterised using the following equation [13]:

$$E_{mono} = EF_{mt} \cdot \exp(\beta(T - T_S)) \quad (4)$$

with  $EF_{MT}$  is the emission factor of monoterpenes at a leaf temperature  $T$  of  $30^\circ\text{C}$ ,  $\beta = 0.09^\circ\text{C}^{-1}$ ,  $T_S = 30^\circ\text{C}$  and  $T = T_{leaf} [^\circ\text{C}]$ .

This parameterisation for monoterpene emission from plants has been shown to be very crude [6; 7]. A theoretical reflection about the mechanisms involved in isoprenoid emission from plants with resin reservoirs leads to the conclusion that monoterpene emission from conifers is a result of emission from stored monoterpenes in resin vessels and emission from *de novo* synthesised compounds in the photosynthetic tissue of the needles. Therefore, total twig emission from conifers may be better parameterised by an algorithm taking into account the emission from pools and the emission related to actual synthesis. Equation (5) can be formulated as:

$$E_{term}(T, PAR) = E_{pool}(T) + E_{synthesis}(T, PAR) \quad (5)$$

Emission from pools in the plants is assumed to be only dependent on the vapour pressure of the compound of interest and the transport resistances in the leaves. Both parameters are temperature dependent and leaf temperature is taken as the main driving variable in describing pool emission from plants according to equation 4. Isoprenoid emission linked to *de novo* synthesis, possibly exclusively located in the photosynthetic tissue of the plant, is assumed to

**Table 1.** Specific leaf dry weight (SLW) for boreal plant species in Finland.

Plant species	SLW g dw m <sup>-2</sup> total leaf area	sd	number of twigs	number of plants
<b>Pallas 1996</b>				
<i>Betula pubescens</i>	36	-	1	1
<i>Picea abies</i> ssp. <i>obovata</i>	168	-	3	2
<i>Pinus sylvestris</i>	146	-	2	1
<b>Mekrijärvi 1997</b>				
<i>Betula pubescens</i>	47	-	1	1
<i>Ledum pallustre</i>	205	-	1	1
<i>Juniperus communis</i>	192	60	4	2
<i>Salix caprea</i>	50	-	2	1
<i>Pinus sylvestris</i>	159	38	6	3

sd = standard deviation

be dependent only on the rate of synthesis in the plant. This rate of synthesis is an enzymatic process, which is driven by the availability of substrate, energy and reduction equivalents. In plants the formation of these compounds is temperature and light dependent therefore leaf temperature and PAR are used for parameterisation isoprenoid emission rates according equations (1) to (3).

Equation (5) is a synthesis of equations (1) to (4) and in the following called the Pool/Synthesis -model, is tested against the classic procedure of emission rate parameterisation considering only pool emission (P-Model) (Figure 2) and than used to derive emission factors for key species in the Boreal region of Europe (Table 3).

## Results and discussion

### Isoprenoid emission of Boreal plant species

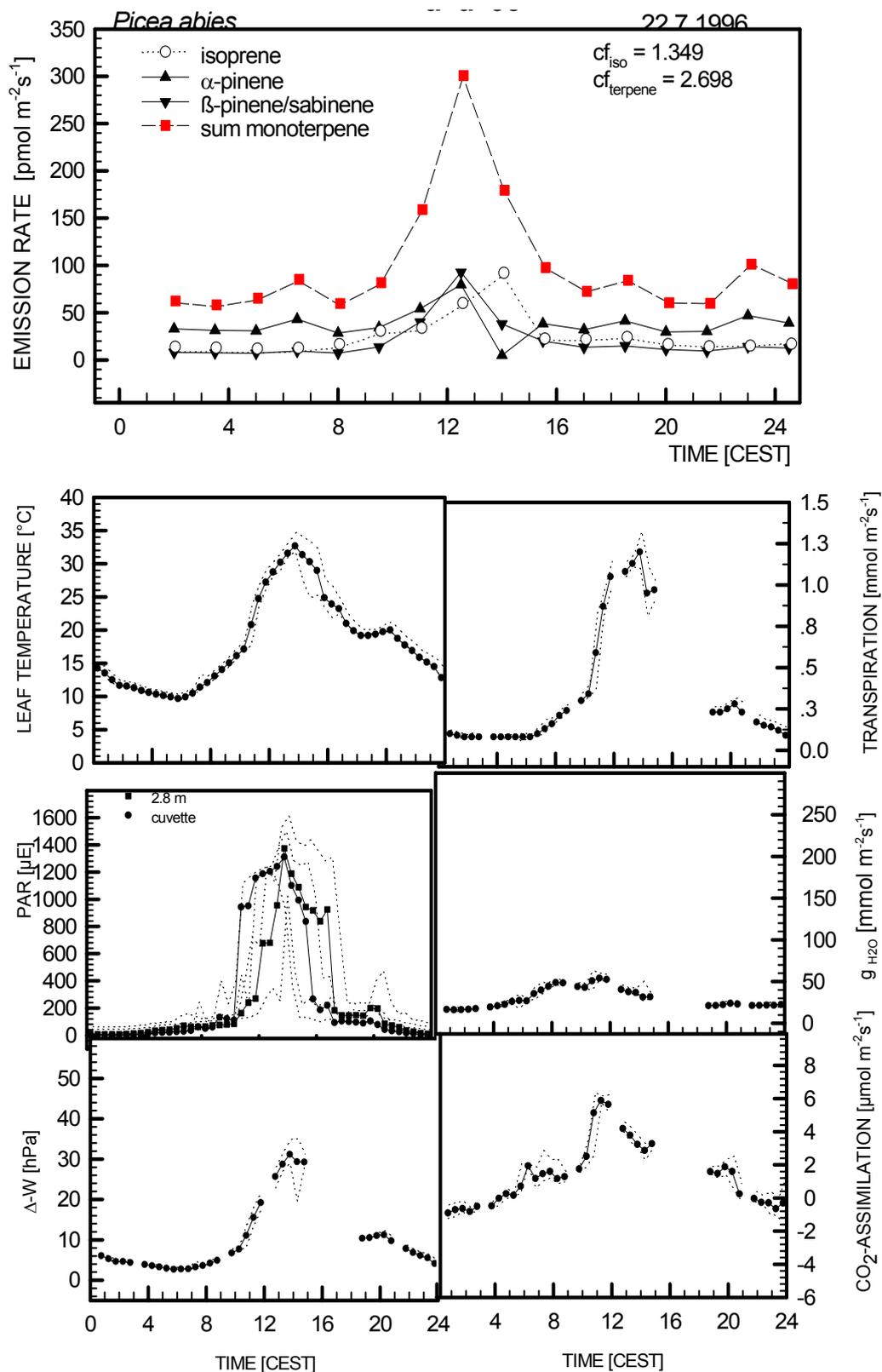
For calculating gas exchange from leaves, either leaf area (total or projected leaf area) or the dry weight can be used. In this paper, gas exchange rates are related to total leaf area. For converting leaf area based exchange rates to mass based rates, the specific leaf weight (SLW) is used. In Table 1 the SLW values (g dw m<sup>-2</sup> total leaf area) for the plants investigated are listed. The measured SLW for conifer species ranged between 146 g dw m<sup>-2</sup> for *P. sylvestris* and 168 g dw m<sup>-2</sup> for *P. abies* ssp. *obovata* and this range is comparable to literature values

[9]. The SLW for the other plant species ranged from 36 g dw m<sup>-2</sup> for *B. pubescens* in Pallas to 205 g dw m<sup>-2</sup> for *L. pallustre* in Mekrijärvi.

The VOC emission of attached twigs from eight typical boreal plant species was investigated over 38 diurnal cycles. The dominant C<sub>5</sub> to C<sub>10</sub> VOCs emitted by the plants were the isoprenoids. The monoterpene  $\alpha$ -pinene dominates the emission pattern for *J. communis*.  $\beta$ -pinene and  $\Delta^3$ -carene are the main compounds for *P. sylvestris* and myrcene is characteristic for the emission of *L. pallustre*. Other monoterpenes such as camphene, sabinene, limonene and p-cymene/1,8-cineol were emitted in traces. *B. pubescens* is a very low emitter of isoprenoids with emission rates < 20 pmol m<sup>-2</sup> s<sup>-1</sup>. *S. caprea* is a strong isoprene emitter (see Table 3). In the following the diurnal behaviour of isoprenoid emission from *P. abies* ssp. *obovata* is described and discussed in more detail.

The diurnal behaviour of isoprenoid emission and gas exchange of Siberian spruce and its relation to PAR and leaf temperature values is shown in Figure 1 exemplified for July 22nd 1996. This day was a warm and sunny day with leaf temperatures of up to 35°C and PAR values of up to 1400  $\mu$ E around noon. During that time, the sum of monoterpenes emitted by a Siberian spruce twig amounted to 300 pmol m<sup>-2</sup> total leaf area s<sup>-1</sup>. Main isoprenoid compounds in the VOC emission pattern were  $\alpha$ -pinene,  $\beta$ -pinene/sabinene and isoprene. Maximum values of the single compounds reached ca. 100 pmol m<sup>-2</sup> s<sup>-1</sup>. Other monoterpenes such as myrcene,  $\Delta^3$ -carene, limonene,  $\beta$ -phellandrene and 1,8 cineol/p-cymene were emitted in significantly lower amounts by spruce twigs. Isoprene was emitted by Siberian spruce with values up to 90 pmol m<sup>-2</sup> s<sup>-1</sup>.

In general, the emission rates are correlated with temperature and light (Figure 1). A correlation with transpiration and net CO<sub>2</sub>-assimilation may be anticipated on the basis of the diurnal cycle. A Kendall correlation analysis of the complete data set for Siberian spruce revealed no significant correlation with net CO<sub>2</sub>-assimilation and the isoprenoid emission (P > 0,05). The correlation with transpiration is quite close with coefficients  $r_{\text{kendall}}$  ranging from 0.38 for  $\alpha$ -pinene to 0.45 for camphene. On the other hand no correlation between isoprene emission and leaf conductance for water vapour could be detected ruling out any significant influence of stomatal opening on isoprenoid emission of Siberian spruce.



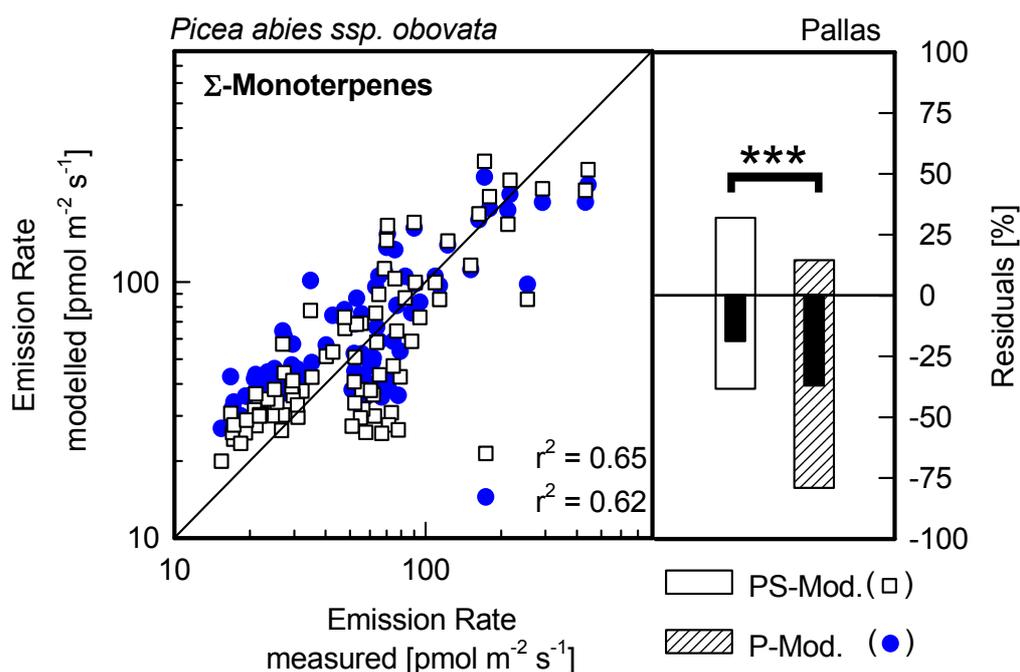
**Figure 1.** Isoprenoid emission rates and plant physiological parameters of a Norway spruce twig and environmental parameters in the Pallas area, Finland. The twig southerly exposed was growing at 1.5 m above ground. The dashed lines represent the min. and max. values of the shown parameters. For abbreviations see text.

Emission of isoprenoids and transpiration from leaves is driven physically by leaf temperature through an increase of vapour pressure of the compounds and therefore the high  $r_{\text{kendall}}$  values between these parameters have been expected ( $r_{\text{kendall}}$  of 0.60 for the sum of monoterpenes;  $P < 0,001$ ). In general,  $r_{\text{kendall}}$  values for the pair transpiration/emission are somewhat lower with values ranging from 0,38 to 0.45 ( $P < 0,01$ ) compared to  $r_{\text{kendall}}$  values for the pair leaf temperature/emission with values ranging from 0.43 to 0.57 ( $P < 0,001$ ). On the basis of this analysis and to avoid cross-correlation between parameters, it was decided to use only leaf temperature in the parameterisation approach. PAR and leaf temperature also show a significant correlation ( $r_{\text{kendall}} = 0.43$ ). In order to separate the influence of light and temperature on the emission of isoprenoids from Siberian spruce a partial correlation analysis was performed excluding the influence of leaf temperature or light on the emission in different analysis steps. It became clear that a significant fraction of the observed variation, e.g. 46% of the variation of the  $\alpha$ -pinene emission, can be explained by the variation of PAR only. Therefore, PAR is considered as second parameter in modelling isoprenoid emission from Siberian spruce.

Similar diurnal cycles of isoprenoid emission, gas exchange and environmental parameters were recorded for other plant species and for these plants as well light and temperature are main factors in controlling isoprenoid emission and gas exchange.

### Emission modelling

The diurnal cycles of isoprenoid emission of the Boreal plant species and corresponding PAR and leaf temperature values were used in emission modelling according to the procedures described above. The new approach (Pool/Synthesis (PS)-model), and the classic monoterpene emission model (P-model) were used in predicting emission rates for the typical Boreal tree species Siberian spruce and Scots pine. Measured PAR and leaf temperature values were used in a non-linear regression analysis to derive emission factors for the different models, different emission processes, and different compounds. The emission factors,  $EF_{\text{pool}}$ , valid for pool emission in the PS model were calculated on the basis of night time values. For calculating the emission factors  $EF_{\text{synthesis}}$  in the PS model only day time values were considered ( $\text{PAR} > 10$ ). Emission factors  $EF_{\text{MT}}$  valid for the P-model were calculated by not splitting the data sets into daytime and night time values.



**Figure 2.** Isoprenoid emission modelling and model performance. Statistical significance is calculated by the Wilcoxon paired sampled test: \*\*\*  $P < 0.001$ ; open and dashed bars represent the 25 and 75 percentiles, respectively;  $r^2$  expresses the variability of the emission rates explained by the Pool/Synthesis (PS-Mod.) and Pool-Model (P-Mod.) approach.

### Siberian spruce

The performance of the PS-model and the P-model for predicting the emission rates of the sum of monoterpenes from Siberian spruce are compared in a scatter plot (Figure 2). It is demonstrated by the greater shared variance,  $r^2$ , and a residual analysis that the measured emission rates of Siberian spruce are significantly better parameterised by the PS-model with consideration of *de novo* synthesis of monoterpenes ( $r^2 = 0,65$ ) than by the P-model with consideration of emissions from pools only ( $r^2 = 0,62$ ). A further reduction of the remaining variability between measured and modelled emission rates by adjusting parameters  $\beta$ ,  $\alpha$ ,  $C_{LI}$ ,  $C_{Liso}$  and  $C_{Tiso}$  in the parameterisations could not be achieved.

In Table 3 the emission factors for the PS-model of each isoprenoid emitted from Siberian spruce are shown. The emission of all monoterpenes exhibits a significant fraction due to actual synthesis of the compounds and for  $\alpha$ -pinene, the major compound emitted, the fraction of *de novo* synthesis could be estimated to be approximately 50% of the total amount released.

**Table 2.** Isoprenoid emission modelling for Scots pine.

<i>Pinus sylvestris</i>					Mekrijärvi	
Isoprenoid	PS-Model <sup>a</sup>		n	P-Model <sup>a</sup>	Model-Performance	
	Ef <sub>pool</sub>	Ef <sub>synthesis</sub>			Ef <sub>mt</sub>	r <sup>2</sup> <sup>c</sup>
α-pinene	77 (10)	39 (5)	55	109 (4)	0.88	***
camphene	19 (4)	14 (3)	56	30 (2)	0.51	***
β-pinene	12 (4)	13 (7)	55	24 (5)	0.08	***
sabinene	40 (3)	0	56	40 (3)	0.56	—
myrcene	14 (3)	25 (1)	54	33 (2)	0.91	***
Δ <sup>3</sup> -carene	72 (5)	0	56	72 (5)	0.43	—
limonene	21 (2)	0	54	21 (2)	0.28	—
p-cymene/ 1,8 cineol	7 (2)	40 (2)	54	40 (2)	0.91	***
Σ terpenes	245 (44)	144 (27)	56	367 (19)	0.72	***

<sup>a</sup> Emission factors Ef<sub>pool</sub>, Ef<sub>synthesis</sub> and Ef<sub>mti</sub> in pmol m<sup>-2</sup> total leaf area s<sup>-1</sup>,

() = asymptotic std. error

<sup>b</sup> Wilcoxon paired sample test: ns: P > 0.05; \*\*\*: P < 0.001

<sup>c</sup> low r<sup>2</sup>-values (PS model approach) are mainly due to intra-species variation (see text).

### *Scots pine*

A similar emission model comparison was performed for data from Scots pine. The results are presented in Table 2. For all monoterpenes showing a significant emission related to *de novo* synthesis in the needles, the PS-model improved the prediction of emission rates significantly. In contrast to Siberian spruce some monoterpenes emitted from Scots pine show no significant influence of actual synthesis on total isoprenoid emission and the release of the monoterpenes Δ<sup>3</sup>-carene, sabinene and limonene likely originates from the reservoirs only. This finding underlines the necessity of compound specific emission modelling.

Variability of emission rates from individual plants of the same species at comparable light and leaf temperature values increases the uncertainty of predicted emission rates. This variability may be called intra-specific and is due to the fact that plants of the same species are usually genetically different. As a result, it is likely that the same plant species have different abilities to adapt to environmental conditions such as light, temperature, soil

moisture, nutrients, etc. and as a consequence the emission rates under comparable environmental conditions may be variable. As shown in Table 2 this finding seems to be compound specific because some of the monoterpenes exhibit a distinct intra-specific variability indicated by low  $r^2$  values (e.g. 0.08 for  $\beta$ -pinene) but others like  $\alpha$ -pinene and myrcene show high  $r^2$  values (0.88 and 0.91, respectively) and emission rates are obviously not greatly affected by genetic predisposition. This low variability is associated with high emission factors due to the term describing emission resulting from *de novo* synthesised compounds in the leaves. The emission of these compounds is controlled by dynamic light and temperature dependent plant physiological processes, ruling out the genetic variation within one plant species. This genetic variability has been proven for the resin content of conifers and is used in chemotaxonomy of plants (e.g. [15]).

For the first time, comprehensive information is given on isoprenoid compounds emitted from typical boreal plant species (Table 3). Emission factors including error estimates are listed for each plant species and each isoprenoid emitted. Significant sources for isoprene are Goat willow and Siberian spruce with emission factors of  $1783 \pm 98 \text{ pmol m}^{-2} \text{ s}^{-1}$  and  $53 \pm 4 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively. All other plant species investigated are significant monoterpene emitters with an emission factor range from  $136 \pm 19 \text{ pmol m}^{-2} \text{ s}^{-1}$  for Marsh tea to  $389 \pm 71 \text{ pmol m}^{-2} \text{ s}^{-1}$  for Scots pine in the Mekrijärvi area. The emission factors of Scot pine grown in the Pallas area were somewhat lower ( $248 \pm 137 \text{ pmol m}^{-2} \text{ s}^{-1}$  for the sum of monoterpenes) compared to those of Scots pine grown in the Mekrijärvi area ( $389 \text{ pmol m}^{-2} \text{ s}^{-1}$  for the sum of monoterpenes), possibly reflecting the effect of different climates during the growing season. In general, emission factors derived by non-linear regression using the PS-model show an asymptotic standard error on the order of 20 to 50%. This uncertainty is mainly due to intra-species variability discussed above, measurement errors of leaf temperature and PAR and the analysis of small data sets.

## Conclusions

This investigation of the BVOC emissions from important boreal plant species demonstrates the importance of the isoprenoids. It has been shown that this isoprenoid emission is parameterised better by an approach considering *de novo* synthesis of monoterpenes in the leaves in addition to emission from reservoirs. It has also been demonstrated for Scots pine that monoterpene emission due to *de novo* synthesis in the plants exhibits a significantly

**Table 3. Emission factors of investigated boreal plant species from Pallas area (1996) and Mekrijärvi area (1997)**

plant species:	$\alpha$ -pinene		Camphene		$\beta$ -pinene		sabinene		myrcene		$\Delta^3$ -carene		limonene		p-cymene/ 1,8-cineol		$\Sigma$ MT		isoprene E <sub>f<sub>s</sub></sub>		
	E <sub>f<sub>p</sub></sub>	E <sub>f<sub>s</sub></sub>																			
<b>Mekrijärvi</b>																					
<i>Pinus sylvestris</i> (n=56)	77 (10)	39 (5)	19 (4)	14 (3)	12 (4)	13 (7)	40 (3)	0 (3)	0 (3)	14 (3)	25 (1)	72 (5)	0 (2)	21 (2)	0 (2)	7 (2)	40 (2)	245 (44)	144 (27)	d	
<i>Juniperus communis</i> (n=32)	70 (24)	127 (39)	3 (1)	0 (1)	10 (2)	0 (2)	31 (2)	0 (2)	0 (2)	6 (2)	16 (3)	30 (11)	22 (7)	11 (3)	20 (6)	4 (1)	11 (2)	134 (26)	237 (54)	nd	
<i>Ledum pallustre</i> (n=22)	21 (2)	0 (2)	D	D	27 (2)	0 (2)	43 (9)	0 (9)	0 (9)	72 (11)	0 (11)	13 (1)	0 (1)	28 (6)	0 (6)	0 (1)	0 (1)	136 (19)	0 (19)	nd	
<i>Salix caprea</i> (n=8)	d		D	D	d	d	d	d	d	d	d	d	d	d	d	d	d	-	-	1783 (98)	
<b>Pallas</b>																					
<i>Pinus sylvestris</i> (n=94)	81 (16)	30 (28)	Nd	Nd	d	d	15 (7)	26 (13)	0 (7)	78 (22)	35 (38)	nd	nd	nd	nd	187 (50)	61 (87)	187 (50)	61 (87)	d	
<i>Picea abies ssp. obovata</i> (n=79)	47 (10)	45 (14)	10 (2)	3 (2)	11 (10)	62 (12)	3 (3)	11 (4)	0 (3)	10 (3)	9 (4)	9 (4)	21 (5)	23 (4)	16 (6)	154 (24)	87 (31)	154 (24)	87 (31)	53 (4)	

Emission factors E<sub>f<sub>pool</sub></sub> and E<sub>f<sub>synthesis</sub></sub> in pmol m<sup>-2</sup> total leaf area s<sup>-1</sup>  
 d: detected; nd : not detected; detection limit: 1 pmol m<sup>-2</sup> s<sup>-1</sup>  
 MT: Monoterpenes; (): asymptotic std. error  
 n: number of emission samples analysed

lower deviation from measured values compared to the monoterpenes likely emitted from resin pools only. Therefore, the environmental parameters leaf temperature and PAR seem to overrule a possible intra-specific variation of the plants, which is known for the monoterpene composition of the resins from conifers. The results of this investigation will improve BVOC emission modelling and in consequence photochemistry/transport models will provide realistic prognoses of photooxidant distributions in Northern Eurasia.

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