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Role of de novo biosynthesis in ecosystem scale monoterpene emissions from a boreal Scots pine forest

R. Taipale[1], M. K. Kajos[1], J. Patokoski[1], P. Rantala[1], T. M. Ruuskanen[1,2], and J. Rinne[1]

[1]University of Helsinki, Department of Physics, P.O. Box 64, 00014 University of Helsinki, Finland
[2]University of Innsbruck, Institute of Ion Physics and Applied Physics, Technikerstr. 25, 6020 Innsbruck, Austria

Correspondence to: R. Taipale (risto.taipale@helsinki.fi)

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Abstract

Monoterpene emissions from Scots pine have traditionally been assumed to originate as evaporation from specialized storage pools. More recently, the significance of de novo emissions, originating directly from monoterpene biosynthesis, has been rec-
ognized. To study the role of biosynthesis in the ecosystem scale, we measured monoterpene emissions from a Scots pine dominated forest in southern Finland using the disjunct eddy covariance method combined with proton transfer reaction mass spectrometry. The interpretation of the measurements was based on a hybrid emission algorithm describing both de novo and pool emissions. During the measurement pe-
riod May–August 2007, the monthly medians of daytime emissions were 170, 280, 180, and 180 μg m^{-2} h^{-1}. The emission potential for both de novo and pool emissions exhibited a decreasing summertime trend. The ratio of the de novo emission potential to the total emission potential varied between 30% and 46%. Although the monthly changes were not significant, the ratio always differed statistically from zero, i.e., the role of de
novo biosynthesis was evident. The hybrid approach showed promising potential for the improvement of the ecosystem scale emission modelling. Given this feature and the significant role of biosynthesis, we recommend incorporating both de novo and pool emissions into the monoterpene emission algorithms for Scots pine dominated forests.

1 Introduction

Monoterpenes are deemed major contributors to aerosol particle formation and growth (e.g. Tunved et al., 2006; Hallquist et al., 2009), often cited as the key uncertainty in the current climate change research. Over the years, numerous studies have focused on monoterpene emissions from the Eurasian boreal zone, nowadays recognized as an important but still partly uncharted source (for a review, see Rinne et al., 2009). Long-term ecosystem scale flux measurements are a welcome addition to these studies due

to their spatial representativeness and capability to reveal seasonal changes.

The disjunct eddy covariance method (DEC; Rinne et al., 2001; Karl et al., 2002) has been widely applied to volatile organic compound (VOC) flux measurements at the ecosystem scale. It has usually been combined with proton transfer reaction mass spectrometry (PTR-MS), which is an online technique for measuring VOC concentrations (Lindinger et al., 1998; de Gouw and Warneke, 2007; Blake et al., 2009). This combination has yielded fundamental information on VOC emissions from various ecosystems (e.g. Warneke et al., 2002; Spirig et al., 2005; Holzinger et al., 2006; Brunner et al., 2007; Rinne et al., 2007; Davison et al., 2009; Bamberger et al., 2010; Holst et al., 2010; Langford et al., 2010; Misztal et al., 2010).

Scots pine is one of the dominant evergreen tree species in Eurasian boreal forests. Its monoterpene emissions have traditionally been assumed to originate as evaporation from large storage pools and thus modelled with temperature dependent algorithms (e.g. Tingey et al., 1980; Guenther et al., 1991, 1993). However, there is evidence that a substantial part of these emissions stems directly from de novo biosynthesis in a light and temperature dependent manner (Steinbrecher et al., 1999; Shao et al., 2001; Ghirardo et al., 2010). Process-based algorithms have been developed to take account of different physiological, phenological, and biochemical details of monoterpene biosynthesis (e.g. Niinemets et al., 2002; Bäck et al., 2005; Grote et al., 2006). The two origins of monoterpene emissions have been combined in hybrid algorithms which describe both pool and de novo emissions (e.g. Shao et al., 2001; Schurgers et al., 2009; Ghirardo et al., 2010).

A recent study demonstrated, using $^{13}CO_2$ labelling and PTR-MS analysis, that the ratio of de novo emissions to total emissions can be over 50% for Scots pine saplings (Ghirardo et al., 2010). It also indicated that a hybrid algorithm can track ecosystem scale measurements better than a conventional pool algorithm. Inspired by these findings, we propose a phenomenological approach to interpreting ecosystem scale monoterpene emissions. We first present a brief description of our continuous, round-the-clock DEC measurements during the summer 2007 and then utilize a simple hybrid

algorithm (Ghirardo et al., 2010) to examine seasonal changes in the proportion of de novo emissions and in the normalized emission, i.e., the emission potential. The ultimate goal is to determine whether the contribution of de novo biosynthesis to the total ecosystem scale emissions is observable and significant. This information could be useful when improving biological realism and ecosystem scale parameterizations in regional and global monoterpene emission inventories (Arneth et al., 2008; Niinemets et al., 2010a,b).

2 Methods

2.1 Flux measurements

The SMEAR II (Station for Measuring Ecosystem–Atmosphere Relations II) station of the University of Helsinki served as the measurement site (for a review, see Hari and Kulmala, 2005). It was situated at a rather homogeneous 45-year-old Scots pine (*Pinus sylvestris*) dominated forest in southern Finland (61° 51′ N, 24° 17′ E, 180 m a.s.l.). The forest had a relatively open canopy with a dry needle biomass density of 540 g m^{-2} (in 2005; Rinne et al., 2007) and an average tree height of 16 m. The stand also contained some Norway spruce (*Picea abies*), silver and downy birch (*Betula pendula* and *pubescens*), common aspen (*Populus tremula*), and grey alder (*Alnus incana*). The undergrowth consisted mainly of cowberry (*Vaccinium vitis-idaea*), bilberry (*Vaccinium myrtillus*), and mosses (*Pleurozium schreberi*, *Dicranum polysetum*).

The monoterpene flux measurements were conducted about 6 m above the forest canopy using the DEC method (Rinne et al., 2001; Karl et al., 2002). The measurement setup consisted of a sonic anemometer (Gill Instruments Ltd., Solent HS1199) and a PTR-MS instrument (Ionicon Analytik GmbH; Hansel et al., 1995; Lindinger et al., 1998). The heated sampling line was 30 m long, 8 mm in inner diameter, holding a continuous flow of 17.5 l min^{-1}, and made of Teflon (PTFE). A side flow of about 90 ml min^{-1} was taken into the PTR-MS through a PTFE tube, which was 1.3 m in length and

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1.6 mm in inner diameter. The total monoterpene concentration was derived from the molecular ion signal detected at 137 amu using an integration (dwell) time of 0.5 s. The flux averaging time was 45 min. Our DEC methods have been described in detail by Rinne et al. (2007) and Taipale et al. (2010). The PTR-MS measurement, calibration,
5 and concentration calculation methods have been presented by Taipale et al. (2008).

The measurement period was May–August 2007. The longest breaks were 26–27 June, 22–27 August, and 29–30 August. Only every third hour was allocated for the flux measurements since the PTR-MS was utilized also in concentration profile and shoot scale emission measurements. All flux measurements indicating emission were
10 included in the later analysis without applying any quality criterion, i.e., only negative values were filtered out. These negative fluxes made up 20% of the whole data and 80% of them were observed at night (20:00–08:00 LT). The final data included 151 observations from May, 159 from June, 176 from July, and 117 from August. The dismissal of the flux quality control was deemed justified as filtering based on the atmospheric
15 stability, the friction velocity, or the monoterpene flux uncertainty (Taipale et al., 2010) distorted the flux distribution by eliminating many near-zero observations.

2.2 Hybrid emission algorithm

The main objective of this study was to broaden the view on ecosystem scale monoterpene emissions by utilizing a simple hybrid emission algorithm to interpret the flux
20 measurements. The applied hybrid algorithm was the one formulated by Ghirardo et al. (2010) starting from the algorithms developed by Guenther et al. (1991, 1993). This choice was based on two reasons. First, the hybrid algorithm describes both pool and de novo emissions which seems necessary when modelling monoterpene emissions from coniferous forests (Steinbrecher et al., 1999; Shao et al., 2001; Ghirardo
25 et al., 2010). Second, its simple formulation with essentially only two free parameters is extremely suitable for the present purpose.

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The hybrid algorithm assumes that the monoterpene emission, E, has two independent origins, de novo biosynthesis and evaporation from specialized storage pools:

$$E = E_{\text{synth}} + E_{\text{pool}} = E_{0,\text{synth}} C_{\text{T}} C_{\text{L}} + E_{0,\text{pool}} \gamma. \tag{1}$$

Here $E_{0,\text{synth}}$ and $E_{0,\text{pool}}$ are the emission potentials for de novo and pool emissions. The synthesis activity factors for temperature and light, C_{T} and C_{L}, are the same as in the traditional synthesis algorithm (Guenther et al., 1991, 1993). They describe the dependence of enzyme activity on temperature and the dependence of electron transport rate on light. The temperature activity factor, γ, has the same form as in the traditional pool algorithm (Guenther et al., 1991, 1993). It describes the dependence of monoterpene saturation vapour pressure on temperature.

Equation (1) can be converted into the final hybrid formulation of Ghirardo et al. (2010):

$$E = E_0 \left[f_{\text{synth}} C_{\text{T}} C_{\text{L}} + (1 - f_{\text{synth}}) \gamma \right]. \tag{2}$$

Here $E_0 = E_{0,\text{synth}} + E_{0,\text{pool}}$ is the total emission potential and $f_{\text{synth}} = E_{0,\text{synth}} / E_0$ is the ratio of the de novo emission potential to the total emission potential.

In addition to Eq. (2), the conventional pool algorithm, $E_{\text{pool}} = E_{0,\text{pool}} \gamma$, was fitted to the measured emissions to have a point of comparison. It has been the established choice for Scots pine, especially when interpreting measurements (e.g. Janson, 1993; Rinne et al., 2000, 2007; Ruuskanen et al., 2005; Tarvainen et al., 2005; Hakola et al., 2006; Räisänen et al., 2009). The hybrid algorithm is a more recent rival, introducing de novo biosynthesis and thereby light dependence into the traditional monoterpene algorithm. Over the years, various hybrid formulations have been used, and not solely for Scots pine and monoterpenes (e.g. Schuh et al., 1997; Shao et al., 2001; Spanke et al., 2001; Haapanala et al., 2009; Schurgers et al., 2009).

To reveal seasonal changes in the monoterpene emissions, E_0, f_{synth}, and $E_{0,\text{pool}}$ were determined for May, June, July, and August using non-linear regression in the least squares sense (e.g. Seber and Wild, 1989). The 95% confidence interval was

calculated for each parameter to estimate whether the changes were statistically significant. The values of the other algorithm parameters, including the standard temperature and light (30 °C and 1000 µmol m^{-2} s^{-1}) and the temperature dependence coefficient in γ (0.09 °C^{-1}), were taken from Guenther (1997). Half-hour averages of air temperature (at 8.4 m) and photosynthetically active radiation (PAR, at 74 m) were used as the explanatory variables in the algorithms. They were acquired from a set of SMEAR II routine measurements (Junninen et al., 2009). Canopy shadowing effects were not considered when fitting the algorithms.

3 Results and discussion

3.1 Emissions, temperature, and PAR

Figure 1 shows the monoterpene emissions, air temperature, and PAR during the summer 2007. The monthly average temperatures from May to August were 9.2, 14.5, 15.4, and 15.5 °C. The corresponding averages at the Hyytiälä weather station, located about 500 m from the flux measurement site, for the reference period 1971–2000 were 8.8, 13.7, 15.5, and 13.4 °C (Fig. 1b; Drebs et al., 2002). Thus the summer 2007 was warmer than the average, especially in June and August.

An important message from Fig. 1 is that our flux measurement setup was sensitive enough to capture the daily and episodic changes in the emissions, which strengthens our earlier observations on the sensitivity (Rinne et al., 2007). Another salient point is the apparent correlation between the emissions, temperature, and PAR. The emissions were highest during the sunny and warm periods when the maximum temperatures were around 25 °C. At the onsets and ends of these periods, the changes in all three variables were distinct and rather coincident. However, the steep rise in the temperature in early May was not reflected on the emissions. Also the effects of the cloudy periods, indicated by the lower daytime PAR values, are hard to discern from the figure.

With regard to the range of the emissions, now roughly 50–600 μg m^{-2} h^{-1} in the daytime, previous shoot and ecosystem scale measurements at the site have yielded quite similar results (e.g. Rinne et al., 2000, 2007; Spanke et al., 2001; Ruuskanen et al., 2005; Tarvainen et al., 2005; Hakola et al., 2006). For instance, when multiplied by the needle biomass density (540 gm^{-2}), the daytime emissions from Scots pine branches reported by Hakola et al. (2006) were typically 100–750 μg m^{-2} h^{-1} in May–August. On the other hand, the monoterpene emissions from the forest floor measured by Hellén et al. (2006) were clearly below 50 μg m^{-2} h^{-1} in summer. Thus we may suggest, consistently with Rinne et al. (2007), that the ecosystem scale emissions originated mainly from the canopy, i.e., from Scots pine needles and bark.

To offer a more statistical view of the emissions, temperature, and PAR during the summer 2007, Fig. 2 illustrates the monthly variations by means of a box plot (e.g. McGill et al., 1978). The left and right boxes give the statistics of the daytime (08:00–20:00 LT) and night-time (20:00–08:00 LT) measurements, respectively. The numbers stand for the corresponding medians. The number of measurements included in each box varies between 52 and 96.

The monthly medians of the daytime emissions for May–August were 170, 280, 180, and 180 μg m^{-2} h^{-1}. As indicated by the confidence intervals around the medians, the daytime median for June was significantly higher than the other daytime values, which did not differ statistically from each other at the 95% confidence level. Also all night-time medians were similar. When calculated from all measurements, the monthly medians were 140, 180, 150, and 140 μg m^{-2} h^{-1} (not shown). Their differences were not significant, except for the increase between May and June.

The daytime median was always significantly higher than the corresponding night-time median. Such daily variation in the emissions was naturally expected. However, these were the first ecosystem scale measurements at a Scots pine forest extending over a summer that actually substantiated the expectations. This demonstrates the importance of long-term, round-the-clock measurements for emission algorithm comparisons and validations (see Sect. 3.3).

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Previous long-term shoot scale measurements at the site have shown a fairly clear seasonal cycle with peak emissions between late June and early August (Tarvainen et al., 2005; Hakola et al., 2006). Now the emissions peaked already in June, otherwise their monthly medians remained essentially invariable over the summer. This slight discrepancy vanishes when the emission potentials are considered, which indicates that the results do not differ much after the normalization to the standard light and temperature conditions (see Sect. 3.2).

The monthly medians of temperature and PAR were calculated using only the observations concurrent with the measured emissions to illustrate the variation in the input variables of the emission algorithms. The median daytime temperatures for May–August were 12, 17, 17, and 21 °C (Fig. 2b). At the 95% confidence level, May was significantly the coolest and August the warmest month, as demonstrated by both daytime and night-time medians. Given the absence of such increase in the median emissions, these temperature changes suggest that the monoterpene emission potential decreased towards the late summer. Of course, this reasoning is based on the traditional pool algorithm which assumes that emissions originate solely as evaporation from specialized storage pools.

The monthly daytime medians of PAR were 500, 990, 500, and 590 $\mu mol\,m^{-2}\,s^{-1}$ (Fig. 2c). The median for June was significantly higher than the other values, which were alike at the 95% confidence level. A similar occurrence was observed in the monoterpene emissions. Surprisingly, the monthly trends in the emissions and PAR resembled each other rather closely while the temperature variations had a divergent pattern. This resemblance is a qualitative hint that the ecosystem scale emissions might have depended also on light.

3.2 Emission potentials and the role of de novo emissions

Figure 3 reveals the main results of this study. First, the monoterpene emission potential had a decreasing summertime trend in both the hybrid and pool algorithm. Second, the contribution of de novo biosynthesis to the ecosystem scale emissions differed from

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zero throughout the summer.

Between May and August, the emission potential decreased from 1100 to 630 μg m^{-2} h^{-1} in the hybrid algorithm and from 810 to 500 μg m^{-2} h^{-1} in the pool algorithm. The trend was statistically significant in both cases, indicating that the potential of the forest to emit monoterpenes diminished over the summer. A similar decline in the pool emission potential has been observed also in shoot scale measurements at the same site (Tarvainen et al., 2005; Hakola et al., 2006). For example, the results of Hakola et al. (2006) correspond fairly well with our ecosystem scale pool emission potential (Fig. 3a). Thus, concordant with the conjecture in the previous section, the monoterpene emissions seem to have originated mainly from the canopy also in view of the emission potentials. August was an exception with a higher ecosystem scale result, reflecting that other sources possibly had a more central role in late summer.

According to the pool algorithm, our results suggest that the monoterpene diffusion rate from the storage pools into the atmosphere decreased towards the late summer, probably due to changes in the diffusivity of this pathway. A substantial diminution of the pool size seems unlikely as the storage in needles typically exceeds the annual emission at least by five times (see e.g. Rinne et al., 2009). The trend in the total emission potential can also reflect seasonal variation in the monoterpene biosynthesis in Scots pine. Without further evidence, it is probably safest to assign the decrease in both emission potentials to changes in Scots pine needles and bark, not forgetting that emissions from undergrowth, litter, and soil can occasionally be substantial at the site (Hellén et al., 2006). Root-associated fungi occurring in boreal forest soils are an interesting and yet rather unexplored monoterpene source, even though their emissions appear to be dominated by oxygenated VOCs (Bäck et al., 2010).

Figure 3b shows the outcome of our phenomenological approach to assessing the role of biosynthesis in the ecosystem scale. The ratio of the de novo emission potential to the total emission potential ranged between 30% and 46%. The monthly changes were not significant at the 95% confidence level and hence the seasonal variation in biosynthesis (Fischbach, 2001) could not be determined from our results. However, the

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ratio always differed statistically from zero. Thus de novo biosynthesis had a significant role in the ecosystem scale monoterpene emissions.

The contribution of de novo emissions was lower, although not significantly, than in the shoot scale measurements of Ghirardo et al. (2010). Their result for Scots pine saplings was 58%, which does not differ from our results when the uncertainties in both studies are taken into account. The age and habitat of the trees, the season, and the measurement scale could probably explain even a more pronounced difference. In addition to the mature Scots pine trees, the ecosystem scale measurements included emissions from the undergrowth, litter, and soil. It is also possible that emissions from bark, presumably originating mainly from pools, had a stronger effect in the ecosystem scale than for the saplings.

This study probably gives the first direct suggestion of the significance of biosynthesis in ecosystem scale monoterpene emissions. The result may be considered more corroborating than surprising as laboratory experiments have clearly demonstrated the substantial contribution of both pool and de novo emissions (Shao et al., 2001; Ghirardo et al., 2010). Recently, there has been a debate on whether process-based or semi-empirical algorithms should be used when modelling monoterpene emissions at different scales (e.g. Grote and Niinemets, 2008; Niinemets et al., 2010a,b). Although inadequate for such speculation, our results offer one important guideline to follow in the context of Scots pine forests: the algorithm should describe emissions from both storage pools and biosynthesis.

3.3 Implication for emission modelling

Figure 4 illustrates one interesting consequence of the incorporation of biosynthesis into the monoterpene emission algorithm. It shows the median daily cycle for each month as given by the measurements and the two algorithms. The measurements confirmed earlier results (Rinne et al., 2000, 2007; Ruuskanen et al., 2005; Tarvainen et al., 2005; Hakola et al., 2006) without new major revelations about the daily patterns. Instead, the algorithm results offered more insight into the ecosystem scale modelling.

Every month the hybrid algorithm reproduced the daily variation somewhat better than the pool algorithm, reducing especially the night-time overestimation. Such behaviour was noticed also by Ghirardo et al. (2010).

This observation can be considered a tentative indication. The algorithms should be contrasted with independent measurements to get more reliable estimates of their performance. However, the hybrid algorithm already has one clear advantage making it an advisable alternative to the pool algorithm. It is biologically more realistic (Ghirardo et al., 2010). This fundamental benefit seems to be accompanied by a practical one, the improvement of the ecosystem scale modelling of monoterpene emissions.

In recent emission inventories for Europe (Karl et al., 2009; Keenan et al., 2009), for instance, the contribution of freshly synthesized monoterpene emissions from Scots pine has already been taken into account by using hybrid algorithms. However, the partition between pool and de novo emissions is still poorly known. The work of Ghirardo et al. (2010) gave the first quantitative result, now complemented by our assessment at the ecosystem scale. Seasonal changes in the partition as well as the detailed structure of a sound and practical hybrid algorithm await to be determined.

4 Conclusions

Our analysis based on the micrometeorological flux measurements above a boreal Scots pine forest revealed four important features of the ecosystem scale monoterpene emissions. (1) The emissions peaked in June, otherwise their monthly medians remained essentially constant during the measurement period May–August 2007. The monthly medians of PAR showed similar behaviour while the monthly median temperatures had an increasing trend. (2) Both the hybrid and pool algorithm indicated that the monoterpene emission potential decreased over the summer. These ecosystem scale results were concordant with the trend in the pool emission potential derived from previous shoot scale measurements. (3) The ratio of the de novo emission potential to the total emission potential differed significantly from zero throughout the summer.

Since the monthly changes were masked by the large uncertainties, their determination should be the subject of further studies. (4) The hybrid approach appeared to be a promising enhancement to the ecosystem scale emission modelling as it tracked the daily cycles better than the conventional pool algorithm.

Although highly accurate estimates were not achieved, the main result of this study seems beyond dispute. The role of de novo biosynthesis in the ecosystem scale emissions was statistically significant. Thus we recommend incorporating biosynthesis into the algorithms for monoterpene emissions from Scots pine dominated forests.

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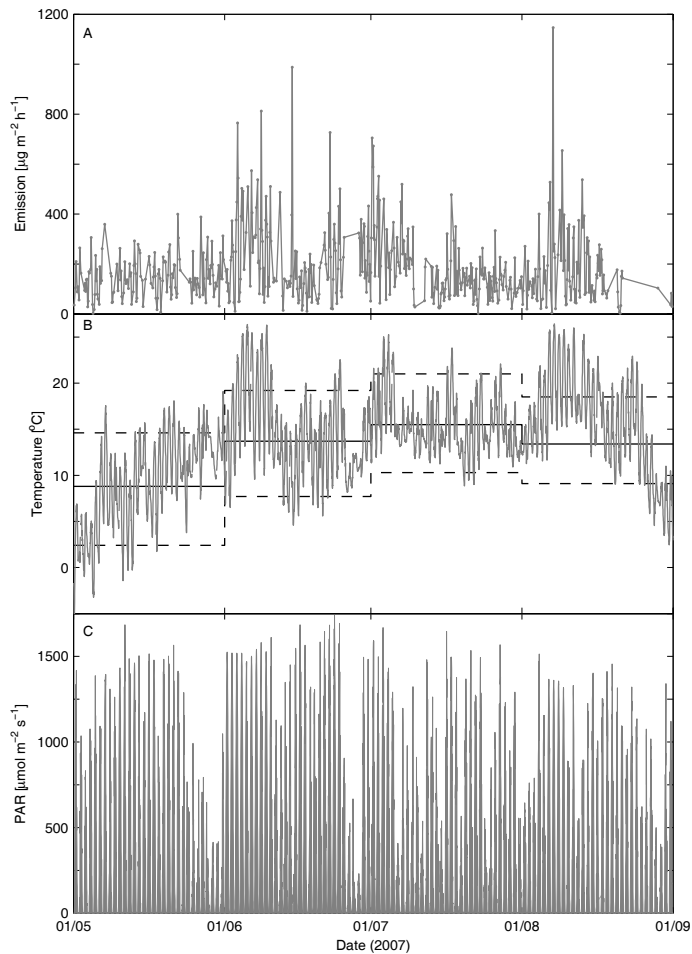
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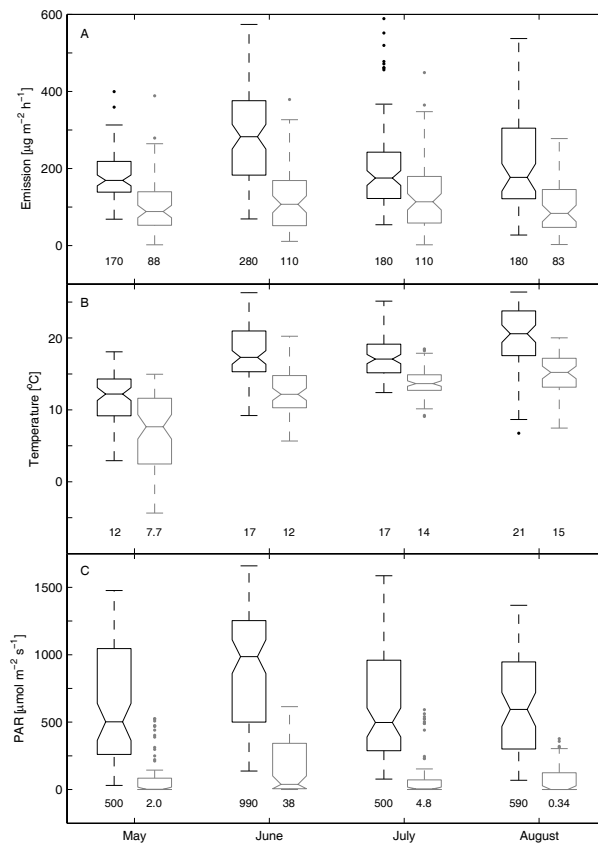
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Fig. 1. Monoterpene emissions, air temperature, and photosynthetically active radiation (PAR) during the summer 2007. The black lines in Panel (B) show the monthly average temperatures and the monthly averages of daily maxima and minima at the Hyytiälä weather station for the reference period 1971–2000 (Drebs et al., 2002).

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Fig. 2. Monthly variation in the monoterpene emissions, air temperature, and photosynthetically active radiation (PAR) during the summer 2007. Eight values above $600\,\mu g\,m^{-2}\,h^{-1}$ are not shown in Panel (A). The left and right boxes represent the daytime (08:00–20:00 LT) and night-time (20:00–08:00 LT) measurements. The line in the middle of each box and the number below show the median. The lower and upper line are the 25th and 75th percentile, the distance between them is the interquartile range. The error bars extend from the top or bottom of the box to the furthest data value within 1.5 times the interquartile range. The values beyond the error bars are outliers. The notches show the 95% confidence interval for the median. If notches of two boxes do not overlap, the difference between medians is statistically significant.
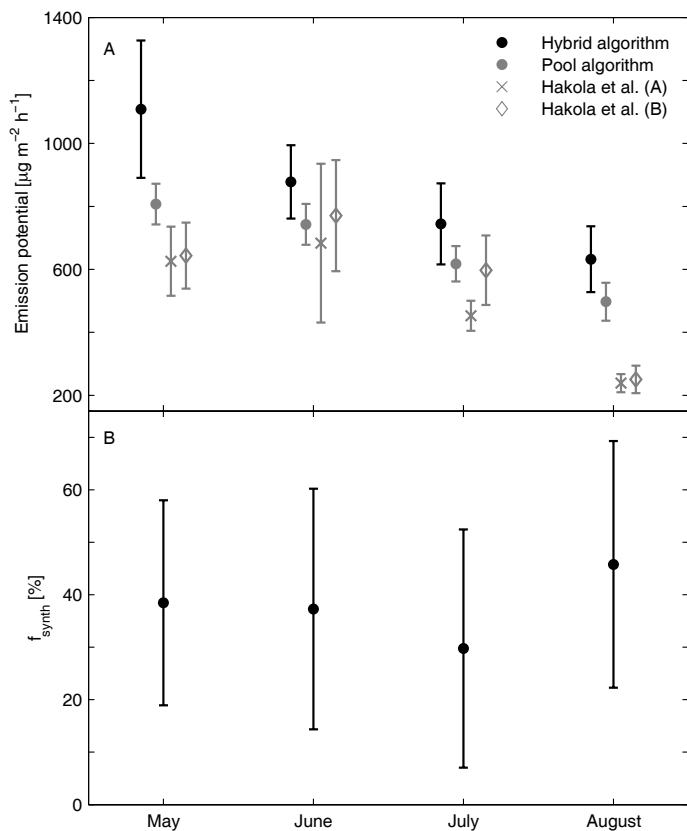
Fig. 3. (A) Monthly variation in the total emission potential and the pool emission potential during the summer 2007. The pool emission potentials based on measurements with two Scots pine branches were derived from the results of Hakola et al. (2006) using a needle biomass density of $540\,\mathrm{g\,m^{-2}}$. **(B)** Ratio of the de novo emission potential to the total emission potential (f_{synth}). The error bars represent the 95% confidence intervals.

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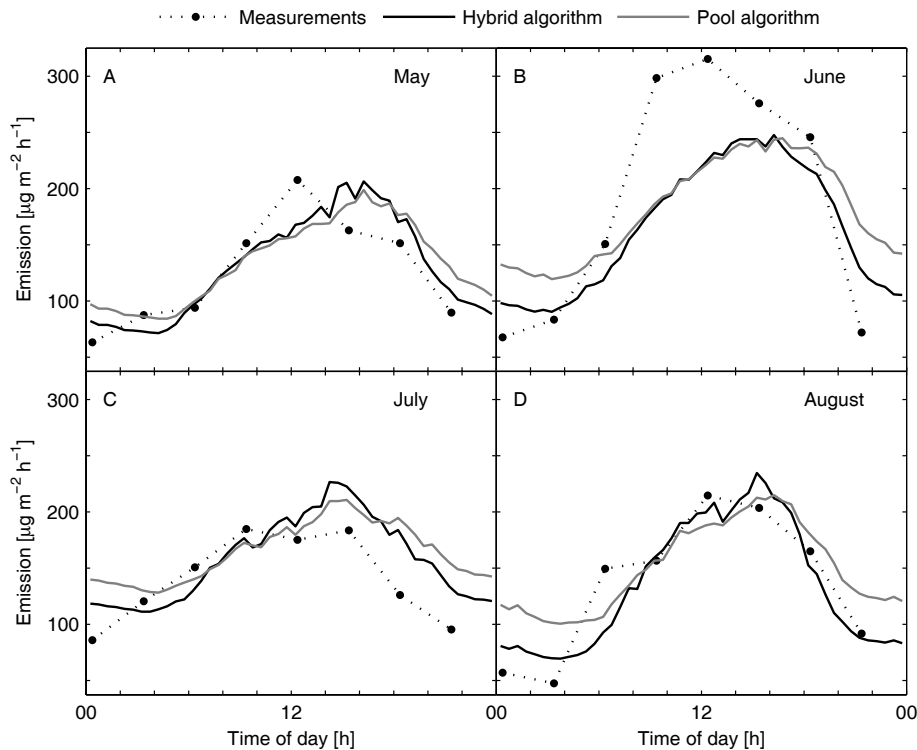
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Fig. 4. Median daily cycles of the monoterpene emissions during the summer 2007 as given by the measurements and the two algorithms.