

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

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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 recognized. To study the role of biosynthesis at 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 correlation analysis and a hybrid emission algorithm describing both de novo and pool emissions. During the measurement period May–August 2007, the monthly medians of daytime emissions were 200, 290, 180, and 200 $\mu\text{g m}^{-2} \text{h}^{-1}$. The emissions were partly light dependent, probably due to de novo biosynthesis. 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, suggesting that the role of de novo biosynthesis was observable. Given the uncertainties in this study, we conclude that more accurate estimates of the contribution of de novo emissions are required for improving monoterpene emission algorithms for Scots pine dominated forests.

uncertainty in 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 poorly characterized 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 on-line 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 specialized storage pools and thus modelled with temperature dependent algorithms (e.g. Tingey et al., 1980; Guenther et al., 1991, 1993). However, there is increasing evidence that a substantial part of these emissions stems directly from monoterpene biosynthesis in a light and temperature dependent manner, without intermediate storage in specialized storage pools (Steinbrecher et al., 1999; Shao et al., 2001; Ghirardo et al., 2010). These de novo emissions have been described using both the traditional synthesis algorithm of Guenther et al. (1991, 1993) and more process-based algorithms including different physiological, phenological, and biochemical details of monoterpene biosynthesis (e.g. Ninemets et al., 2002; Bäck et al., 2005; Grote et al., 2006).

1 Introduction

Monoterpenes are estimated to be major contributors to aerosol particle formation and growth (e.g. Tunved et al., 2006; Hallquist et al., 2009), often cited as the key



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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 $^{13}\text{CO}_2$ 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 traditional pool algorithm. This paper attempts to estimate the contribution of de novo biosynthesis directly from DEC measurements during the summer 2007. We first analyse whether the measured emissions had a light dependent component 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. 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, operating at 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 PTFE tubing, which was 1.3 m in length and 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, 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 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). 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 stability, the friction velocity, or the monoterpene flux uncertainty (Taipale et al., 2010) would have distorted the flux distribution by eliminating many near-zero observations. In total, these quality criteria would have eliminated 23–42 % of the data, which also would have decreased the statistical significance of the analysis (see Sect. 3.2).

2.2 Hybrid emission algorithm

To estimate the contribution of de novo biosynthesis to the total ecosystem scale emissions, a simple hybrid emission algorithm was fitted to the flux measurements. The applied hybrid algorithm was the one formulated by Ghirardo et al. (2010) starting from the pool and synthesis algorithms developed by Guenther et al. (1991, 1993). A formulation with only two free parameters, both related to emission potentials, was chosen to achieve statistically significant results. The original constant values (Guenther, 1997) were used for the parameters related to the emission activity factors.

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

$$E = E_{\text{synth}} + E_{\text{pool}} = E_{0,\text{synth}} C_T C_L + E_{0,\text{pool}} \gamma. \quad (1)$$

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):

$$E = E_0 [f_{\text{synth}} C_T C_L + (1 - f_{\text{synth}}) \gamma]. \quad (2)$$

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 traditional 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 option, 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. The 95 % confidence interval was calculated for each parameter to estimate whether the changes were statistically significant. The regression analysis was based on the Levenberg–Marquardt method (e.g. Seber and Wild, 1989). The initial value was 10 % for f_{synth} and $100 \mu\text{g m}^{-2} \text{h}^{-1}$ for E_0 and $E_{0,\text{pool}}$. No predetermined upper or lower limits were used for these parameters. The regression and confidence interval calculations were conducted using the MATLAB functions "nlinfit" and "nlparci".

The values of the other algorithm parameters, including the standard temperature and light (30°C and $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) 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 input variables in the algorithms. They were acquired from a set of SMEAR II routine measurements (Junninen et al., 2009). Differences in PAR within the canopy were not considered when fitting the algorithms and bark biomass was not used as a proxy for storage pools.

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 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.

The range of the emissions was roughly $50\text{--}600 \mu\text{g m}^{-2} \text{h}^{-1}$ 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 (540g m^{-2}), the daytime emissions from Scots pine branches reported by Hakola et al. (2006) were typically $100\text{--}750 \mu\text{g m}^{-2} \text{h}^{-1}$ in May–August. On the other hand, the monoterpene emissions from the forest floor measured by Hellén et al. (2006) were clearly below $50 \mu\text{g m}^{-2} \text{h}^{-1}$ in summer. Thus we may suggest, consistently with Rinne et al. (2007), that the ecosystem scale emissions originated mainly from the aboveground biomass, i.e. from Scots pine needles and bark.

The monthly medians of the daytime emissions for May–August were 198, 292, 182, and $204 \mu\text{g m}^{-2} \text{h}^{-1}$ (Table 1). As indicated by the 95 % confidence intervals, the daytime median for June was significantly higher than the values for May and July. Otherwise the daytime medians did not differ statistically from each other at the 95 % confidence level. The daytime values were significantly higher than the night-time values, which illustrates the diurnal variation in the emissions. The differences between the medians calculated from all measurements were not significant, except for the increase between May and June.

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 (Table 1) were calculated using the observations concurrent with the measured emissions. The median daytime temperatures for May–August were 12.3, 17.8, 17.6, and 20.9°C . This increasing trend was significant at the 95 % confidence level. The monthly daytime medians of PAR were 767, 1192, 706, and $762 \mu\text{mol m}^{-2} \text{s}^{-1}$. The median for June was statistically higher than the other values, which were alike at the 95 % confidence level. A similar seasonal pattern was observed in the monoterpene emissions.

Table 1 also shows the correlation coefficients between the emissions, temperature, and PAR for each month. Based on the confidence intervals, the correlations were significant but did not have clear diurnal or seasonal variations. The range was 0.43–0.66 for the emission–temperature correlation, 0.35–0.51 for the emission–PAR correlation, and 0.24–0.68 for the temperature–PAR correlation. The emission–temperature correlation for the daytime measurements in May and the night-time measurements in June and July as well as the daytime temperature–PAR correlation for May were not significant. Also the differences between the emission–temperature, emission–PAR, and temperature–PAR correlations were insignificant. This indicates a large

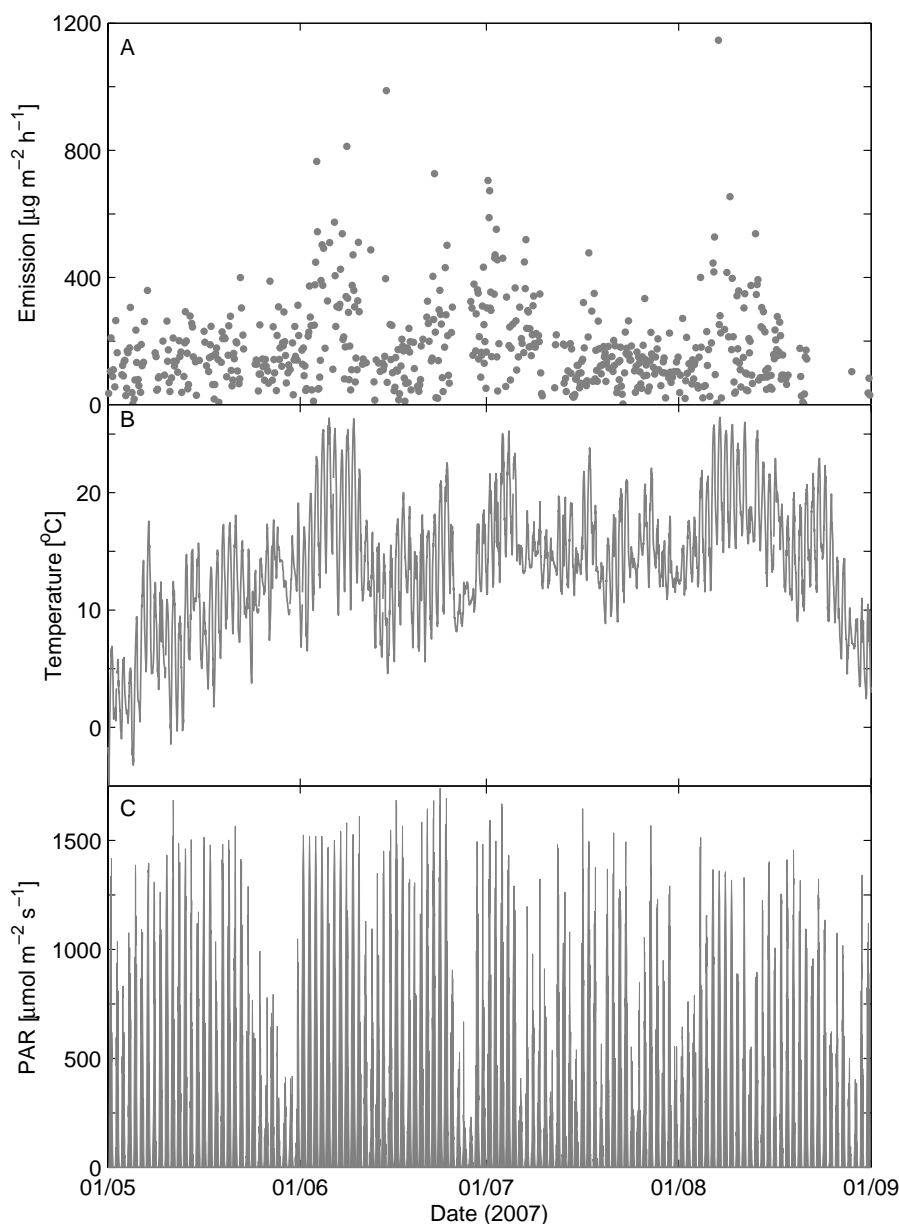


Fig. 1. Monoterpene emissions, air temperature, and photosynthetically active radiation (PAR) during the summer 2007.

uncertainty in the estimates of the contribution of de novo emissions determined with the non-linear regression analysis (see Sect. 3.2). Further measurements are needed to reveal reasons for the insignificant night-time emission–temperature correlations.

Figure 2 illustrates the emission–PAR correlation in three narrow temperature ranges. A similar analysis was performed for six other ranges between 8 and 26 °C. All PAR observations above $10 \mu\text{mol m}^{-2} \text{s}^{-1}$ were included in the analysis. In addition to the three examples in Fig. 2, the emission–PAR correlation was significant in the ranges 10–12 and 16–18 °C. The correlation coefficients were 0.38 (0.08–0.61) and 0.25 (0.03–0.45), respectively.

The emission–temperature and temperature–PAR correlations were insignificant in all nine temperature ranges, indicating that the temperature dependence did not interfere with this analysis. Similarly, the emission–PAR and temperature–PAR correlations were insignificant in the PAR ranges 200–400, 600–800, and $1000\text{--}1200 \mu\text{mol m}^{-2} \text{s}^{-1}$. The emission–temperature correlations in these ranges were 0.38 (0.17–0.55), 0.45 (0.13–0.68), and 0.41 (0.10–0.65).

The medians in Fig. 2 indicate that the emissions at high PAR were statistically higher than the emissions at low PAR. A similar increase was present also in the ranges 10–12 and 16–18 °C. Based on the correlations and medians in the different temperature ranges, it seems that the ecosystem scale

Table 1. Monthly medians and correlations of the monoterpene emissions, air temperature, and photosynthetically active radiation (PAR) during the summer 2007. The values represent all, daytime (12:00–16:00), and night-time (00:00–04:00) measurements. The 95 % confidence intervals are in parentheses. Only statistically significant ($p < 0.05$) correlation coefficients (r) are shown.

	May	June	July	August
Median emission ($\mu\text{g m}^{-2} \text{h}^{-1}$)				
all	140 (126–154)	182 (157–207)	150 (137–164)	138 (116–160)
day	198 (172–224)	292 (243–340)	182 (146–218)	204 (149–258)
night	86 (63–109)	70 (44–100)	113 (83–144)	54 (37–71)
Median temperature ($^{\circ}\text{C}$)				
all	10.4 (9.4–11.4)	15.2 (14.4–16.0)	15.3 (14.8–15.8)	17.7 (16.8–18.5)
day	12.3 (11.1–13.6)	17.8 (16.7–18.9)	17.6 (16.6–18.5)	20.9 (19.2–22.7)
night	7.9 (5.4–10.4)	11.6 (10.2–13.0)	13.4 (13.0–13.8)	14.6 (13.3–15.9)
Median PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$)				
all	212 (140–284)	511 (373–650)	239 (174–303)	279 (178–380)
day	767 (599–935)	1192 (1068–1295)	706 (588–823)	762 (636–888)
Emission–temperature correlation				
all	0.45 (0.31–0.57)	0.54 (0.42–0.64)	0.43 (0.30–0.54)	0.56 (0.42–0.67)
day	–	0.57 (0.34–0.74)	0.48 (0.23–0.67)	0.66 (0.42–0.82)
night	0.45 (0.09–0.71)	–	–	0.55 (0.19–0.78)
Emission–PAR correlation				
all	0.50 (0.37–0.61)	0.49 (0.36–0.60)	0.42 (0.29–0.53)	0.50 (0.35–0.62)
day	0.44 (0.15–0.66)	0.35 (0.06–0.58)	0.38 (0.10–0.60)	0.51 (0.21–0.72)
Temperature–PAR correlation				
all	0.24 (0.08–0.38)	0.55 (0.43–0.65)	0.63 (0.53–0.71)	0.58 (0.45–0.69)
day	–	0.56 (0.32–0.73)	0.55 (0.31–0.72)	0.68 (0.45–0.83)
Number of measurements				
all	151	159	176	117
day	40	45	48	35
night	28	27	40	24

monoterpene emissions were partly light dependent. This result suggests that the role of *de novo* biosynthesis was observable. However, it can also be an indication of the correlation between PAR and the needle temperature. Then both storage pools and biosynthesis could have contributed to the light dependent increase in the emissions.

3.2 Emission potentials and the role of *de novo* emissions

Between May and August, the emission potential decreased from 1100 to 630 $\mu\text{g m}^{-2} \text{h}^{-1}$ in the hybrid algorithm and from 810 to 500 $\mu\text{g m}^{-2} \text{h}^{-1}$ in the pool algorithm (Fig. 3). 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 or in the monoterpene composition. 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

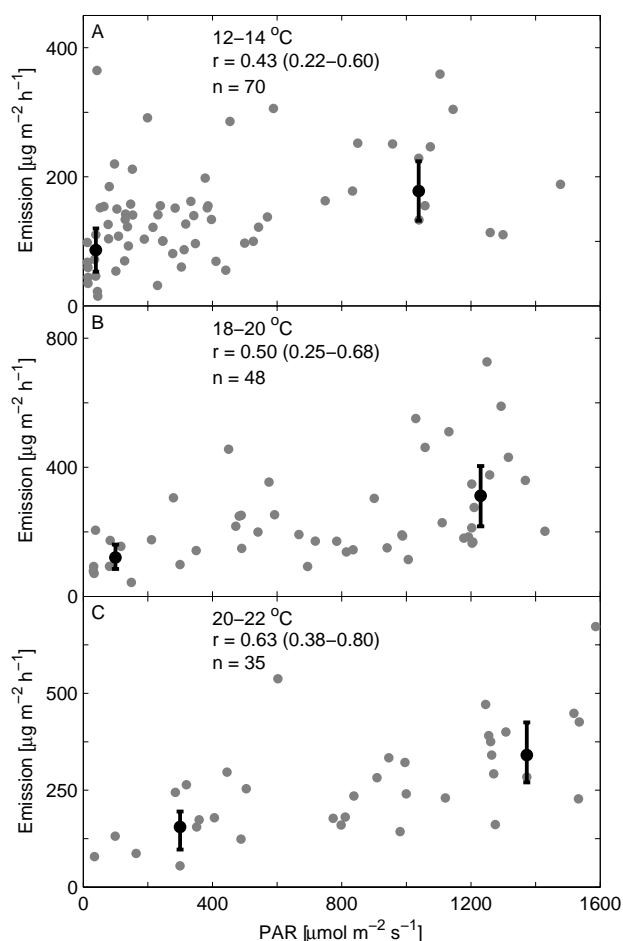


Fig. 2. Monoterpene emissions as a function of photosynthetically active radiation (PAR) in three temperature ranges. The grey dots show the individual measurements, r is the correlation coefficient, and n is the number of measurements. The black dots show the medians for the observations at low PAR (below the 25th percentile) and high PAR (above the 75th percentile). The numbers in parentheses and the error bars represent the 95 % confidence intervals. Only observations at PAR higher than $10 \mu\text{mol m}^{-2} \text{s}^{-1}$ were included in the analysis.

can also reflect seasonal variation in 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, not forgetting that emissions from the 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 approach to assessing the role of biosynthesis at the ecosystem scale. The ratio of the de novo emission potential to the total emission potential ranged between 30 % (7–52 %) and 46 % (22–69 %).

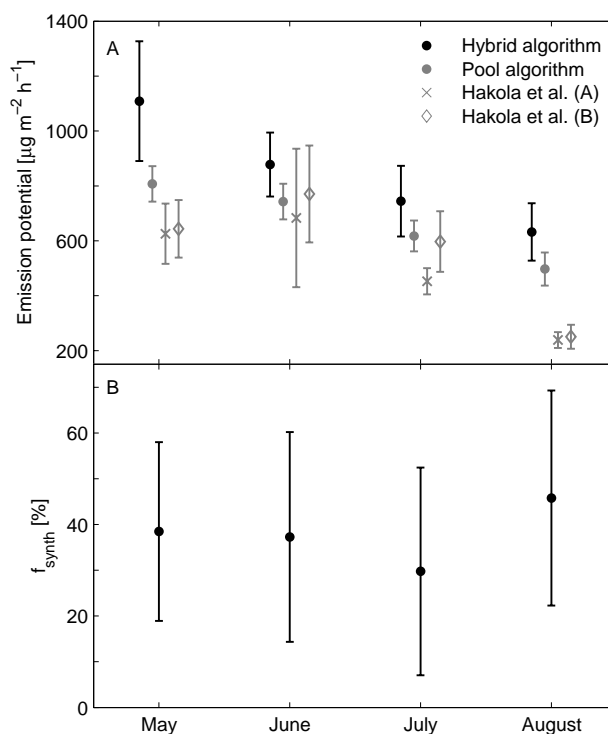


Fig. 3. (A) Monthly variation in the total emission potential and the pool emission potential during the summer 2007. The pool emission potentials based on measurements with two Scots pine branches were derived from the results of Hakola et al. (2006) using a needle biomass density of 540 g m^{-2} . (B) Ratio of the de novo emission potential to the total emission potential (f_{synth}). The error bars represent the 95 % confidence intervals.

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 ratio always differed statistically from zero, thus suggesting that 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 at the ecosystem scale than for the saplings.

This study probably presents the first direct attempt to estimate the importance of biosynthesis in ecosystem scale monoterpene emissions. The analysis revealed significant correlations between the emissions and PAR, but the

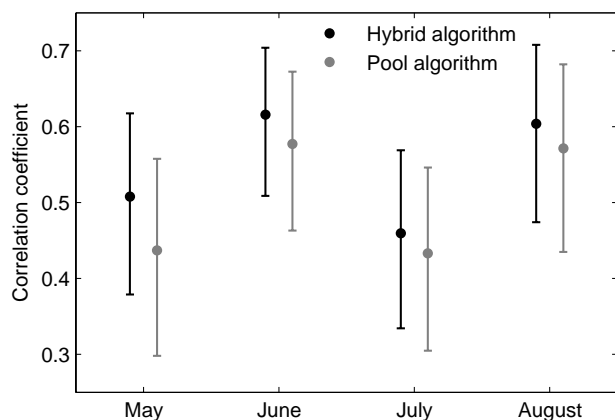


Fig. 4. Monthly correlations between the measured monoterpene emissions and the emissions given by the two algorithms during the summer 2007. The error bars show the 95 % confidence intervals.

estimates of the contribution of de novo emissions were sensitive to the amount of data and thus highly uncertain. For example, when the amount of data was reduced by applying flux quality criteria or using only daytime measurements, the hybrid algorithm produced results which did not demonstrate a significant contribution from biosynthesis at the 95 % confidence level. Despite this sensitivity to the amount of data, the results in Fig. 3 were reproducible in the sense that they were independent of the initial values in the non-linear regression analysis.

3.3 Implication for emission modelling

Figure 4 shows the correlations between the measured emissions and the emissions given by the two algorithms. The range of the correlation coefficient was 0.46–0.62 for the hybrid algorithm and 0.43–0.58 for the pool algorithm. The seasonal changes and the differences between the algorithms were not significant. In this sense, the algorithms performed equally well. However, they should be contrasted with independent measurements to get more reliable estimates of their performance and predictive power. By employing an independent value for the proportion of de novo emissions, Ghirardo et al. (2010) observed that the hybrid algorithm captured diurnal variation in ecosystem scale emissions somewhat better than the pool algorithm, reducing especially night-time overestimation.

Recently, there has been a debate on whether process-based or semi-empirical algorithms should be used when modelling monoterpene emissions at different scales (Grote and Niinemets, 2008; Niinemets et al., 2010a,b). Our results are inadequate for such speculation, but previous laboratory experiments have clearly demonstrated the substantial contribution of both pool and de novo emissions from Scots pine (Shao et al., 2001; Ghirardo et al., 2010). Thus hybrid algorithms seem biologically more realistic than pool algorithms.

In recent emission inventories for Europe (Karl et al., 2009; Keenan et al., 2009), for instance, the contribution of de novo 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 more qualitative assessment at the ecosystem scale. Seasonal changes in the partition as well as the detailed structure of a sound and practical hybrid algorithm remain as important research objectives.

4 Conclusions

Our analysis based on the DEC measurements above a boreal Scots pine dominated forest revealed five 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. The emissions were partly light dependent, which probably was an indication of the role of de novo biosynthesis.
3. Both the hybrid and pool algorithm demonstrated 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.
4. The ratio of the de novo emission potential to the total emission potential differed significantly from zero throughout the summer. However, more reliable estimates of the contribution of de novo emissions are needed for improving monoterpene emission algorithms.
5. In this study, the hybrid algorithm did not perform statistically better than the traditional pool algorithm.

Although highly accurate estimates were not achieved in this work, the results of ^{13}C labelling experiments (Shao et al., 2001; Ghirardo et al., 2010) have clearly shown the significance of de novo emissions. Given this strong biological support, we recommend comparing hybrid and pool algorithms when modelling monoterpene emissions from Scots pine dominated forests.

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