History effect of light and temperature on monoterpenoid emissions from *Fagus sylvatica* L.

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Abstract

Monoterpenoid emissions from *Fagus sylvatica* L. trees have been measured at light- and temperature-controlled conditions in a growth chamber, using Proton Transfer Reaction Mass Spectrometry (PTR-MS) and the dynamic branch enclosure technique.

*De novo* synthesized monoterpenoid Standard Emission Factors, obtained by applying the G97 algorithm (Guenther, 1997), varied between 2 and 32 μg C m⁻² h⁻¹ and showed a strong decline in late August and September, probably due to senescence.

The response of monoterpenoid emissions to temperature variations at a constant daily light pattern could be well reproduced with a modified version of the MEGAN algorithm (Guenther et al., 2006), with a typical dependence on the average temperature over the past five days.

The diurnal emissions at constant temperature showed a typical hysteretic behaviour, which could also be adequately described with the modified MEGAN algorithm by taking into account a dependence on the average light levels experienced by the trees during the past 10–13 h.

The impact of the past light and temperature conditions on the monoterpenoid emissions from *F. sylvatica* L. was found to be much stronger than assumed in previous algorithms.

Since our experiments were conducted under low light intensity, future studies should aim at confirming and completing the proposed algorithm updates in sunny conditions and natural environments.

1. Introduction

Vegetation plays an important role in earth–atmosphere interactions due to its importance for the carbon cycle but also as a source of a variety of reactive volatile organic compounds. The global annual flux of non methane volatile organic compounds (NMVOC) emitted from vegetation is estimated to be 1150 Tg C y⁻¹ (Guenther et al., 1995). With respective estimates between 454 and 601 Tg C y⁻¹ and between 32 and 127 Tg C y⁻¹, isoprene and monoterpenes represent a large part of the NMVOC flux (Arnth et al., 2008). The large variability of these estimates, especially for monoterpenes, reflects a lack of observations for constraining the emission models. Whereas on a global scale monoterpenoid emission rates are only ~15% of isoprene emission rates, a recent NMVOC inventory predicts equal isoprene and monoterpane emission rates in Europe (Karl et al., 2009), showing the relative importance of the latter species in Europe.

Accurate estimates of these emissions are needed, because atmospheric oxidation of these compounds has an important impact on the budget of oxidants, in particular ozone (O₃) and the hydroxyl radical (OH) (Seinfeld and Pandis, 1998). Furthermore, isoprenoids represent a large source of Secondary Organic Aerosol (SOA) due to the gas-to-particle conversion of low-volatility oxidation products (Kulmala et al., 2004), and the large variability on global monoterpenoid emission rates results in very high uncertainties on bottom-up estimates of global biogenic SOA fluxes (Hallquist et al., 2009).

Many plant species (e.g. most conifers) store monoterpenes in special storage tissues or organs and the diffusion of monoterpenes out of these structures is driven by temperature (Kesselmeier and Staudt, 1999). However, several plant species, which lack these storage compartments, are known to emit *de novo* biosynthesized
monoterpenes. These emissions are driven by light and temperature in a similar way as for isoprene emissions (Staudt and Seufert, 1995). Moreover, they appear also to depend on light and temperature levels experienced by the plant in the previous hours, days or even weeks. The dependence on temperature during previous days or weeks has been observed in the case of isoprene (Monson et al., 1994; Sharkey et al., 1999; Pétron et al., 2001; Rapparini et al., 2004) and 2-methyl-3-buten-2-ol (MBP) (Gray et al., 2003, 2006). This dependence is apparently due to changes in the concentration of enzymes responsible for the production of these compounds (Schnitzler et al., 1997) and is consistent with their hypothesized role as thermal protectant (Sharkey et al., 2008). Since non-oxygenated monoterpenes might contribute to heat stress resistance (Copolović et al., 2005), temperature history effects as observed for isoprene can be expected for monoterpenes as well. Indeed, dependence on past temperature and light levels has been reported for (de novo synthesized) monoterpenic emissions from Quercus ilex L. (Staudt et al., 2003). The acclimatization time was observed to vary from a few days to several weeks, and down-regulation of the emission capacity was found to be slower than upregulation. In addition, monoterpenic emissions are expected to depend on past environmental conditions during the previous minutes or hours, due to the布尔ian transient storage pools, as suggested for instance by the observed temporal dynamics of 13C incorporation into newly synthesized monoterpenoid emissions (Noe et al., 2006, 2010). The time-lag between monoterpenic production and emission is compound-specific and depends on the Henry’s law constant and the octanol/water partitioning coefficient.

Dependence of emissions on past radiation levels is suggested from the observed hysteretic behaviour of monoterpenic emissions from Fagus sylvatica L. reported by Dindorf et al. (2005) in natural environmental conditions, with higher emissions in the afternoon than in the morning at constant light and temperature levels. Note that dependence on past radiation levels could be (at least partly) due to leaf heating (Gray et al., 2006).

The history effects observed for isoprene emissions have been parameterized in the algorithm of Guenther et al. (1999, 2006). However, the shape of the response curve to past weather conditions is highly uncertain, despite its demonstrated importance in the simulation of seasonal variations of isoprene emissions. Furthermore, its applicability to the emissions of other NMVOCs is questionable.

Due to the strong co-variation of temperature and light in natural conditions, it is often difficult to separate the effects of both parameters on BVOC emissions. Therefore the present study focuses on the light and temperature dependence of monoterpenic emissions by F. sylvatica L, a common European tree species, measured under controlled light and temperature conditions in a growth chamber.

2. Experimental set-up and methods

Experiments were carried out successively on two three-year old beech (F. sylvatica L.) trees. Both trees were grown in outdoor conditions and were allowed to acclimate to the growth chamber conditions for at least one month prior to the start of the measurements. VOC emissions were obtained by putting a single branch of each tree in a dynamic enclosure system and continuously monitoring the emitted species with a Proton Transfer Reaction Mass Spectrometer (PTR-MS). These continuous measurements were occasionally complemented by enclosure air sampling, followed by off-line analysis by Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GC-MS) for VOC speciation.

2.1. Controlled environment

In the growth chamber (2 × 1.5 × 2 m; height × width × length) the trees were subjected to a controlled light and temperature regime. The daily light pattern was simulated by varying the light intensity in eight steps by means of a set of 40 fluorescent lamps (type PHILIPS Master TL-D fluorescent lamps 36W/830 warm white, super 80). The maximum photosynthetic photon flux density (PPFD) that was obtained at branch level was 150 μmol m−2 s−1. The incident PPFD was monitored by a quantum sensor (LI-190SA, LI-COR, USA), positioned next to the branch enclosures at the same height of the leaves of the enclosed branch. The daily PPFD pattern imposed on the enclosed branch of the second tree is shown in the upper graph of Fig. 2 and is similar to the one imposed on the enclosed branch of the first tree.

For the second tree, a horizontal Teflonated grid was used to gently flatten the leaves and to avoid leaf overlap with the aim to ensure a homogeneous light distribution over the leaves enclosed. The total leaf area and total leaf dry weight were 0.181 m2 and 0.89 g for the enclosed branch of the first tree and 0.0120 m2 and 0.59 g for the enclosed branch of the second tree.

The temperature in the growth chamber was controlled by means of an air conditioning system. During the experiments with the first tree, daily averaged leaf temperatures of the enclosed branch were 21°C (13/16/07), 19.5°C (17/18/07) and 18°C (20/22/07). Measurements taken during temperature transition periods were excluded from the analysis. During the experiments with the second tree, the leaf temperature for the enclosed branch varied between 17 and 27°C, as shown in Fig. 3 (upper graph). The air temperature outside and inside the enclosures was monitored by thermosets (type 10k, NTC, Omega, NL). Leaf temperature was measured by an infrared thermocouple (type IR/c:1X, Exergen, MA, USA), mounted in a Teflon housing and installed in the cuvette about 5 mm under the surface of a single beech leaf. Relative humidity sensors were installed in the outlet line of each cuvette (type HH-3610, Honeywell, NJ, USA) and in the growth chamber itself (type RHa, Rotronic, CH).

2.2. Branch enclosure system and incoming air supply system

The dynamic branch enclosure system consists of a transparent cylindrical box with a volume of 12.2 L and is shown in Fig. 1. Dynamic enclosure system containing a branch of a Fagus sylvatica L. tree (second tree).
Fig. 1. The external frame is made of a transparent polymethylmethacrylate (PMMA) base plate, three PMMA rings and three aluminum bars, which hold a cylindrical 50 μm thick perfluoroalkoxy Teflon (PFA) envelope (Norton, Saint-Gobain Performance Plastics, NJ, USA) with a solar transmission of 96%. The base plate contains two PFA gas feedthroughs (bulkheads) for incoming and exiting air, as well as a Teflon feedthrough for electrical connections inside the cuvette. The emitted biogenic volatile organic compounds (BVOCs) and the incoming air are efficiently homogenized by means of a Teflon ventilator, which is

Fig. 2. Hourly averaged PPFD values (upper graph) and monoterpenoid emission rates for the second tree (lower graph), with (circles) and without (diamonds) correction for nighttime emissions. The values represent averages over the entire experimental period.

Fig. 3. Temporal evolution of leaf temperature and monoterpenoid emission rates (μg m⁻² h⁻¹) for the enclosed branch of the second beech tree.
mounted on the base plate. The air exit opening of the cuvette is sufficiently large to avoid overpressure in the cuvette. While enclosing the branch in the cuvette, extreme care was taken not to bend the branch too much and not to injure any leaves, in order to avoid unwanted stress-induced BVOC emissions.

Ambient air from above the roof of the building was pumped by a diaphragm pump (MD4, Pfeiffer Vacuum, Germany) and purified by a dust filter (2 μm pore size Zefluor™ PTFE Membrane Filter, Pall, MI, USA) and an ozone filter, consisting of a set of 12 MnO2-coated copper nets (type ETO341FC004, Anyasco, Germany) housed in an aluminum filter holder. The air was subsequently sent through a set of two active coal filters (Airpel 10, Organosorb 10-CO, Desotec, Belgium), the combination of which resulted in an optimal pore size distribution for absorption of VOCs. To prevent carry-over of carbon powder a second dust filter was placed downstream the active coal filters. The purified air was then distributed to three flow meters (5860S (0–30 L min⁻¹), BROOKS Instrument, PA, USA), all followed by manual ball valves (type SS-43S4, Swagelok, OH, USA). By adjusting the valve settings, all cuvettes were provided with identical dust-, O3- and VOC-free air at 333 K (293 K). Ozone levels in the incoming air were regularly checked at the cuvette inlet with an ECC Ozonesonde (EN-SCI, Inc., Boulder, USA) and were found to be below 2 ppbv at all times.

The PTR-MS ion signal at /m/z 137 was used to monitor the sum of monoterpenes. Mono- terpene calibration was performed regularly by using a gravimetric growth chamber. Cuvette air samples were taken occasionally and analyzed off-line by TD-GC-MS (Jøø et al., 2010) to determine the monoterpenoid emission pattern. These analyses revealed the presence of linalool which also contributes to the ion signal at /m/z 137 and therefore interferes with monoterpene detection. Consequently, the BVOC emissions that were inferred from the PTR-MS ion signal at /m/z 137 included both monoterpenes and linalool and will be called monoterpenoid emissions hereafter. A fraction of the ion signal at /m/z 137 can also be due to the emission of α-farnesene, a sesquiterpene which was also observed by TD-GC-MS (Jøø et al., 2010). However, this fraction was estimated to be at most 3–5% and was therefore neglected in the further analysis.

The procedure to determine accurate monoterpenoid emission rates, taking into account the experimentally determined monoterpene calibration factor, the ratio of the detection sensitivity of monoterpenes (mainly sabinene) to the one of linalool at /m/z 137, as well as the fractional contribution of both species to the sum of monoterpenoids (as determined by TD-GC-MS), has been described in detail in by Jøø et al. (2010).

### 2.4. Emission algorithms

Monoterpene emissions by *F. sylvatica* L. are known to be temperature and light dependent. Since, however, small nighttime emissions have been observed, probably due to a temperature-dependent release from non-specific storage pools (Schuh et al., 1997), we write the emission (E in μg m⁻² h⁻¹) of monoterpenoids by *F. sylvatica* L. as

\[
E = E_{ns} + E_p
\]

where \(E_{ns}\) is the newly synthesized emission component and \(E_p\) represents the release from storage pools. The light and temperature-dependent part, \(E_{ns}\), has been often described by the emission algorithm of Guenther (1997) originally developed for isoprene:

\[
E_{ns,G97} = \gamma_{age} \cdot \gamma_T \cdot \gamma_p \cdot \gamma_S\]

where \(\gamma_{age}\) accounts for these variations due to phenology. Several choices are possible for the response functions \(\gamma_T\) and \(\gamma_P\): (1) Guenther (1997) (G97), (2) Schuh et al. (1997) (S97), (3) Guenther et al. (2006) (G06), (4) Gray et al. (2006) (Gray), and (5) a modified form of the G06 algorithm (G06a), with parameters fitted using the measurements presented in the next Section.

The G97 and G06 models were originally developed for isoprene emissions using experimental emission rate data from several tree species; the S97 algorithm was developed using sunflower as a model plant and beech to confirm its applicability for other plant species; the Gray algorithm was developed to parameterize the impact of both instantaneous and past temperatures for methylbutenol (MBO) emissions from needles of ponderosa pine trees.

The response function \(\gamma_T\) in the G97 algorithm (Guenther, 1997) is given by:

\[
\gamma_T,G97 = \frac{\exp\left(\frac{C_{T1} (T-T_0)}{R + C_{T1}}\right)}{C_{T3} + \exp\left(\frac{C_{T2} (T-T_0)}{R + C_{T2}}\right)}
\]

\[
C_{T1} = 95 \text{ 000 J mol}^{-1}, \quad C_{T2} = 230 \text{ 000 J mol}^{-1}, \quad C_{T3} = 0.961 \text{ are empirical coefficients}, \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ is the universal gas constant}, \quad T \text{ is leaf temperature [K],} \quad T_0 = 314 \text{ K}, \quad T_3 = 303 \text{ K.} \quad \text{The corresponding light response function is given by:}
\]

\[
\gamma_P,G97 = C_{L,G97} \cdot \frac{a_{G97} \cdot L}{\sqrt{1 + a_{G97}^2 \cdot L^2}}
\]

where \(L\) is the photosynthetic photon flux density (PPFD) in μmol m⁻² s⁻¹, whereas \(a_{G97} = 0.0027\) and \(C_{L,G97} = 1.066\) are empirical coefficients.
Whereas the temperature dependence of the emissions according to Schuh et al. (1997) is very similar to the response function of G06, the light dependence of the S97 algorithm is a sigmoidal curve expressed as:

\[
\gamma_{P,S97} = C_{L,S97} \cdot \left( \frac{a_{S97} \cdot L}{1 + a_{S97} \cdot L^2} \right)^2
\]

where \(a_{S97}\) and \(C_{L,S97}\) are equal to \(a_{G97}\) and \(C_{L,G97}\), respectively.

The temperature response function in Gray et al. (2006) which achieves the best agreement with their MBO flux measurements involves a correction factor to the G97 algorithm:

\[
\gamma_{T,Gray} = \gamma_{T,G97} \cdot \left( 0.822 \cdot \frac{T - T_0}{30} + 0.805 \cdot \frac{T_{24d} - T_0}{30} - 0.601 \right)
\]

where \(T_0 = 273 K\) and \(T_{24d}\) is the average daily maximum temperature for the previous 7 days.

The isoprene emission algorithm in MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006) incorporates a dependence of the emissions on leaf age and soil moisture, as well as updated temperature and light response functions accounting for the observed role of past meteorological conditions. Both MEGAN (G06) and a generalized form of the MEGAN algorithm (G06a) will be tested against our measurements. The temperature response function of G06 is:

\[
\gamma_{T,G06} = E_{opt,G06} \left( \frac{C_{T2} \cdot \exp(C_{T1} \cdot x)}{C_{T2} - C_{T1} \cdot (1 - \exp(C_{T2} \cdot x))} \right)
\]

with

\[
x = \frac{\left( T_{opt,G06}^{-1} - T^{-1} \right)}{R}
\]

where \(R, C_{T1}\) and \(C_{T2}\) are as in Eq. (4); \(E_{opt,G06a}\) is the maximum normalized emission capacity, and \(T_{opt,G06a}\) is the temperature at which \(E_{opt,G06a}\) occurs. These quantities depend on the average leaf temperature over the past 24 h \((T_{24d})\) and the past \(m\) days \((T_{md})\) and are given by:

\[
T_{opt,G06a} = 313 + 0.6 \cdot (T_{md} - 297)
\]

\[
E_{opt,G06a} = 2.038 \cdot \exp(\alpha_1 \cdot (T_{24d} - 297) + \alpha_2 \cdot (T_{md} - 297))
\]

where \(m, \alpha_1\) and \(\alpha_2\) are adjustable parameters (note that \(m = 10, \alpha_1 = 0.05\) in MEGAN).

The light response function in G06a is expressed as:

\[
\gamma_{P,G06a} = C_{L,G06a} \cdot \frac{a_{G06a} \cdot L}{1 + a_{G06a}^2 \cdot L^2}
\]

with

\[
a_{G06a} = a_3 \cdot (0.004 - 0.0005 \cdot \ln(P_{10d}))
\]

\[
C_{L,G06a} = 0.0468 \cdot \exp(\alpha_4 \cdot (P_{nh} - P_0)) \cdot P_{10d}^{0.6}
\]

where \(P_{nh}\) and \(P_{10d}\) [\(\mu mol\) m\(^{-2}\) s\(^{-1}\)] are the PPFD averages over the last \(n\) hours and 10 days, respectively. \(P_0\) is equal to 200 \(\mu mol\) m\(^{-2}\) s\(^{-1}\) for sunlit leaves and 50 \(\mu mol\) m\(^{-2}\) s\(^{-1}\) for shaded leaves, respectively. \(a_3\) and \(\alpha_4\) are adjustable parameters \((n = 24, a_3 = 1\) and \(\alpha_4 = 0.0005\) in MEGAN). Due to the constant diurnal PPFD pattern in our experiments, \(P_{10d}\) and \(P_{24d}\) are constant and both equal to 50 \(\mu mol\) m\(^{-2}\) h\(^{-1}\).

3. Results and discussion

The first part of this section deals with small nighttime ion signals that were observed at \(m/z\) 137, and how these were accounted for in the derivation of standard emission factors for the newly synthesized monoterpensoids. Subsequently, the performance of the different emission algorithms in describing the experimental results will be assessed and the effect of previous temperature and light conditions on the emissions will be quantified.

3.1. Nighttime emissions and standard emission factors

The temporal evolution of the monoterpene emission rate from a branch of the second \(F. sylvatica\) L. tree is shown in Fig. 3, along with the variation in leaf temperature, from August 24th until October 15th. Gaps in the data are mainly due to instrumental problems and power failures. Monoterpene emissions clearly followed the daily imposed PPFD profile (Fig. 2) and responded to a large extent to leaf temperature variations. However, in late September and early October this response was masked by a general decline of the emissions, which was observed over the entire period and which is discussed in more detail in Section 3.2.

This light and temperature dependence of monoterpene emissions by \(F. sylvatica\) L., with emissions close to zero at darkness, is in agreement with what has been reported previously by several authors (Schuh et al., 1997; Spirig et al., 2005; Holzke et al., 2006; Moukhtar et al., 2005; Dindorf et al., 2006). In the beginning and at the end of the experimental period the emission rate at zero PPFD was found to be negligible. Between August 28th and September 4th and between September 9th and September 18th, small PTR-MS ion signals at \(m/z\) 137 appeared in dark conditions, amounting to at most 12% of the maximum daytime emission rate, with the exception of one day at which a value of 20% was reached (September 2nd). Schuh et al. (1997) previously reported small emissions of \(\alpha\)-pinene at zero light flux in growth chamber experiments on \(F. sylvatica\) L., indicating the presence of non-specific storage pools. The monoterpene emission pattern in our experiments, however, contained no \(\alpha\)-pinene but was mainly composed of sabinen, linalool, ocimene and an unidentified monoterpene, as determined by GC–MS analysis of sampled air from the branch enclosure (Joó et al., 2010). Sabinen was the predominant \(C_{10}H_{16}\) compound and linalool was always present in non-negligible amounts.

Although the nighttime emission rates calculated from the PTR-MS ion signal at \(m/z\) 137 are considered to be monoterpene emission rates, it cannot be excluded that other BVOCs (e.g., sesquiterpenes for which temperature-dependent dark emissions can be expected) also contributed to this ion signal to some extent.

In order to separate this limited light independent contribution from the major light dependent contribution to the monoterpene emission rates, linearly interpolated dark emission rates were subtracted from the hourly averaged daytime emission rates. Emission rates obtained at 11 PM of the day of the measurement and 11 PM of the previous day were used for this interpolation. The influence of this correction on the hourly averaged emissions over the entire experimental period is shown in Fig. 2. In the following discussion, the corrected, daytime emission data are compared with literature data and tested against existing emission algorithms for newly synthesized monoterpensoids.
The values of the daily standard emission factors ($\varepsilon_{CGF}$, see Eq. (2)) inferred from the measured monoterpenoid emission rates of the second tree are found to vary between 100 and 1550 µg m$^{-2}$ h$^{-1}$ or 2 and 32 µg gDW h$^{-1}$, in good agreement with literature data reported for F. sylvatica L. in recent years (Schuh et al., 1997; Kahl et al., 1999; Spirig et al., 2005; Moukhtar et al., 2005; Dindorf et al., 2006), which have been recently compiled in Table 3 of Dindorf et al. (2006), and with the values adopted in the two most recent European plant-specific BVOC inventories, 22.1 µg gDW h$^{-1}$ (Karl et al., 2009) and 10.0 µg gDW h$^{-1}$ (Schurgers et al., 2009).

3.2. Response of monoterpenoid emissions to temperature variations at constant daily PPFD pattern

The temporal variation of the standard emission factors $\varepsilon_{CGF}$ for the second tree is shown in Fig. 4.

The SEFs are normalized by their value on August 24 (1020 µg m$^{-2}$ h$^{-1}$). Two features are prominent: a general decrease of the SEF during the course of the experimental period, very probably related to senescence, and a large peak around September 1st. The effect of senescence is crudely parameterized by an exponential decrease of the leaf age activity factor (Eq. (3)) with time:

$$\gamma_{\text{age}} = \exp\left[-\frac{(t - t_0)}{t_i}\right]$$

(15)

where $t_i$ (~18 days) is a characteristic time for the effect of senescence, fitted from the measurements, and $t_0$ is August 24th. As seen in Fig. 4, $\gamma_{\text{age}}$ decreased by almost an order of magnitude in less than 6 weeks. Although such a fast decline might be partly due to the unusual environment of the growth chamber, it is qualitatively consistent with the seasonal decline of the SEFs reported e.g. by Schuh et al. (1997).

The maximum SEF on September 1st (~50% above the initial SEF on August 24th) occurred at the end of a 5-day period with warmer temperatures (up to 26 °C, see Fig. 2). Taking the effect of senescence (i.e. $\gamma_{\text{age}}$) into account, the emission capacity approximately doubled in response to the 5 °C warming imposed on the tree in this period. In the following days, the decrease in temperature was immediately followed by an abrupt decrease in SEF amounting to a factor of 5 in only one week. The dependence of SEF on temperature history suggested by this pattern is much stronger than in existing emission algorithms accounting for temperature history effects, such as MEGAN and the algorithm developed by Gray et al. (2006) (green and yellow curves on Fig. 4). It is, however, similar in magnitude to the acclimation of isoprene emission capacity by Quercus macrocarpa to changes in growth temperature observed by Pétron et al. (2001): a 5 °C warming was found to double the emission capacity of Q. macrocarpa, while a subsequent cooling led to a strong reduction in SEF, by a factor up to 4 on a time scale of several days. The monoterpenoid emission capacity of Q. ilex has been observed by Staudt et al. (2003) to respond even more drastically to the temperature regime: in so-called shaded conditions (PPFD $\leq$ 300 µmol m$^{-2}$ s$^{-1}$), the emission capacity increased by almost an order of magnitude in less than one week when the growth temperature was increased by 10 °C.

The observed temporal evolution of the daily SEF values was used to constrain the temperature dependence of the algorithm G06a, by minimizing the root mean square deviation between modeled and observed daily SEFs. The best match was found when including a strong dependence on the average temperature over the last 5 days ($m = 5$), with $a_2 = 0.21$ in Eq. (11). Dependence on the average temperature over the last day was weak ($a_1 = 0.03$).

The temporal evolution of the SEF for the first tree (Fig. 5) provides some confirmation of the parameterized influence of past temperature on the emissions.

The reasons for the small increase during the first days (before 16/07) are unclear, since temperature remained constant during that period. Afterwards, the SEF steadily declined in response to a decrease in temperature, in agreement with the G06a algorithm constrained by data from the second tree, and in reasonable agreement with the algorithm of Gray et al. (2006). The effect of senescence was assumed to be unimportant during that period.

3.3. Response of monoterpenoid emissions to PPFD variations at fixed temperatures

Fig. 6 illustrates the response of monoterpenoid emissions to PPFD during selected days for the second tree. Temperature was constant during each series of days (21 °C on 24–26/08, 18 °C on 5–6/09, 24 °C on 30/09–01/10).

The emissions were found to be consistently and significantly lower in the morning compared to the afternoon at the same PPFD level, which resulted in a genuine hysteretic behaviour. Note that
The maximal difference between morning and afternoon emissions is found to be much larger than the statistical error on the emissions. A similar behaviour was also observed for the first tree, for which the emissions were measured in July 2007 (data not shown). The hysteresis phenomenon was previously reported in the literature but has not been accounted for in existing BVOC emission algorithms. Dindorf et al. (2005) reported a significant delay in monoterpene emission from a *F. sylvatica* tree in the early morning, which could be better reproduced by the algorithm of Schuh et al. (1997) (S97, Eq. (6)) than by the the G97 algorithm. However, S97 was found to underestimate emission rates in the early evening in their study. The hysteretic behaviour has been described for other monoterpene emitting broadleaf tree species as well, e.g. the evergreen *Q. ilex* (Ciccioli et al., 1997).

The hysteresis might reflect the existence of monoterpene storage pools (Noe et al., 2010) and/or an acclimation to environmental conditions. In any case, it suggests a dependence of the emission rates on past PPFD levels. The S97 algorithm clearly failed to reproduce the diurnal cycle observed in this study, with large underestimations found at low PPFD levels (Fig. 6a). Although the MEGAN model includes a dependence on PPFD history, it also failed to reproduce the observed hysteresis (Fig. 6a). This was due to the choice of the averaging periods in G06, the past PPFD averages $P_{10d}$ and $P_{24d}$, being initially constant in our experimental set-up.

The observed diurnal cycle of emissions can be reproduced only when assuming a dependence of the emissions on past PPFD fluxes averaged over a shorter period ($n = 10–13$ h, see Fig. 6). The averaging period $n$ and the parameters $a_3$ and $a_4$ of the adjustable algorithm, G06a, have been obtained by minimizing the root mean squared deviation between modeled and measured emission rates. The values obtained for $a_4$ (0.0025–0.0038) are 5–8 times larger than in MEGAN, reflecting the significance of the PPFD history effect suggested by the measurements. The values for $a_3$ (1.9 at the start of the experimental period, 5–10 times lower at later stages) are also larger than in MEGAN ($a_3 = 1$), indicating that emission saturation occurs at lower PPFD values compared to MEGAN, as clearly seen on Fig. 6b–c. The increase of $a_3$ during the course of the experimental period is presumably related to senescence and acclimation to low light levels and the associated decrease in emission capacity, as discussed in the previous subsection.

4. Conclusion

The response of monoterpene emissions of two young *F. sylvatica* L. trees to changes in light intensity and temperature has been investigated in controlled growth chamber conditions. The observations show a clear dependence of the emissions on the past light and temperature levels experienced by the trees. In addition, a strong decline of the emission capacity was observed in late August and September, with an e-folding time of 18 days, most probably related to leaf senescence.

The response of the monoterpene emission capacities to temperature variations at a constant daily PPFD pattern could be fairly well described by a modified version of the MEGAN algorithm (Guenther et al., 2006) originally developed for isoprene emissions. The results of our study suggest a much stronger dependence of the emission rates on the past temperature conditions than in previous algorithms (Guenther et al., 2006; Gray et al., 2006), and a typical dependence on the average temperature of the past five days.

The observed diurnal cycle of the emissions confirms the hysteretic behaviour which has been previously described, with lower emissions in the morning than in the afternoon at the same PPFD values. This effect can be parameterized with a modified version of the MEGAN algorithm, through a dependence of the emissions to the average PPFD over the past $10–13$ h. In addition, emission saturation is observed to occur at lower PPFD values compared to MEGAN.

Since the experiments were performed on young trees and at PPFD levels which are typical for shaded conditions, additional enclosure measurements in natural outdoor conditions are required to confirm the strong dependence on past temperature and light observed in this study, and to further refine the adapted version of the MEGAN algorithm developed from our measurements. In particular, the seasonal evolution of the model parameters in response to phenological development will require further investigation. Finally, the applicability of the modified MEGAN algorithm...
to BVOC emissions by other plant species will clearly require a more systematic investigation on the environmental dependence of these emissions.

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References


