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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 $\mu g\ g_{DW}^{-1}\ h^{-1}$ 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 (Arneth 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 monoterpene emission rates are only ~15% of isoprene emission rates, a recent NMVOC inventory predicts equal isoprene and monoterpene 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 (O_3) 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 monoterpene 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

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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 (MBO) (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 (Copolovici 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) monoterpene 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, monoterpene emissions are expected to depend on past environmental conditions during the previous minutes or hours, due to the existence of transient storage pools, as suggested for instance by the observed temporal dynamics of ^{13}C incorporation into newly synthesized monoterpenoid emissions (Noe et al., 2006, 2010). The time-lag between monoterpene 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 monoterpene 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 monoterpene 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 m^2 and 0.89 g for the enclosed branch of the first tree and 0.0120 m^2 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 (13–16/07), 19.5 (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 thermistors (type 10k, NTC, Omega, NL). Leaf temperature was measured by an infrared thermocouple (type IRt/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 HIH-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).