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Emission of monoterpenes from European beech (*Fagus sylvatica* L.) as a function of light and temperature

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Abstract

Using a dynamic branch enclosure technique European beech (*Fagus sylvatica* L.) was characterised as a strong emitter of monoterpenes, with sabinene being the predominant compound released. Since monoterpenene emission was demonstrated to be a function of light and temperature, application of light and temperature dependent algorithms resulted in reasonable agreement with the measured data. Furthermore, during high temperature periods the depression of net CO₂ exchange during midday (midday depression) was accompanied by a depression of monoterpenene emission on one occasion. The species dependent standard emission factor and the light and temperature regulated release of monoterpenes is of crucial importance for European VOC emissions. All measurements were performed within the framework of the ECHO project (Emission and CHemical transformation of biogenic volatile Organic compounds) during two intensive field campaigns in the summers of 2002 and 2003.

1. Introduction

The release of biogenic volatile organic compounds (VOCs) represents a substantial input of reactive trace gases into the atmosphere and influences atmospheric chemistry and physics (Andreae and Crutzen, 1997; Atkinson, 2000; Fehsenfeld et al., 1992; Went, 1960). Furthermore, VOC may represent a substantial loss of carbon for the biosphere (Guenther, 2002; Kesselmeier et al., 2002). The exchange (emission and deposition) of volatile organic compounds, involved in the oxidant cycle, aerosol production and carbon budget estimates, plays a crucial role in climate forcing but is poorly understood in view of the high number of different VOC species and their exchange regulations. The emission of isoprenoids, the dominating biogenic VOC fraction consisting mainly of isoprene and monoterpenes, has been investigated intensively during the last decades. However, our knowledge still is full of gaps. Until a decade ago a clear difference between the emission of isoprene and that of monoterpenes was
postulated. Isoprene emission was regarded as dependent on light and temperature, whereas monoterpenes were thought to be produced as storage compounds and to be emitted as a function of temperature only. However, within the course of the EU-project “BEMA, Biogenic Emissions in the Mediterranean Area” (for an overview see Seufert et al., 1997), it became obvious that monoterpenes can be released in the same manner as isoprene (see Kesselmeier and Staudt, 1999), an observation which has recently been confirmed for the tropical rainforest (Kuhn et al., 2002b; Rinne et al., 2002). Meanwhile the release of monoterpenes from storage pools as a function of temperature only is discussed rather as a special case (Kesselmeier, 2004). Light dependence of monoterpene emission is in full agreement with the recent knowledge of biosynthesis of isoprenoids and the close relation between photosynthesis and isoprene/monoterpene production within chloroplasts (see Lichtenthaler, 1999). This knowledge has resulted in a substantial number of new questions concerning ecology and evolution (Lerdau and Gray, 2003), regulation and controls of production and emission (Niinemets and Reichstein, 2003; Peñuelas and Llusia, 2001; Wolfertz et al., 2003), as well as what the contribution of different carbon sources to isoprenoid biosynthesis are in order to understand production, accumulation and emission (Schnitzler et al., 2004). Several plant species of high importance for regional or global estimations have not been sufficiently investigated yet but are nevertheless included in budget calculations just by assigning emission rates based on plant family relationship (Karlik and Winer, 2001). Finally, the seasonal development of VOC emission capacity plays a significant role (Kesselmeier et al., 2003; Kuhn et al., 2004) and neglecting environmental effects and plant adaptations may lead to a significant under/overestimation of isoprenoid emission. Within the framework of the German ECHO project (Emission and CHemical transformation of biogenic volatile Organic compounds, AFO, 2000) we performed enclosure measurements during two intensive field campaigns in the summers of 2002 and 2003 in order to investigate the primary emission of volatile organic compounds from naturally growing >100 years old European beech (Fagus sylvatica L.). Until now this tree species has been regarded as a non-isoprene, but low emitter of
monoterpenes (see Kesselmeier and Staudt, 1999). As *Fagus sylvatica* L. is one of the dominant deciduous tree species occurring in Europe, the two years of measurements should help to clarify the significance of beech trees for regional and global budgets of VOCs.

2. **Experimental**

2.1. Site description

The measurement site was located in an urban area near the small city of Jülich, Germany. All experiments were carried out in a deciduous forest stand of about 3.5 km² size, partially located on the premises of the Research Centre Jülich. The location is characterised by moderate climatic conditions, with a mean annual precipitation of 685 mm and an average annual temperature of 10°C. Enclosure measurements were performed on top of a 24 m scaffold tower located at 50°54.321’ N, 006°25.130’ E. The predominant soil type of this forest area is luvic stagnosol that provides a moderate supply of nutrients for the growing plants. The area nearby the tower site was dominated by ~160 year old European beech trees of up to 28 m in height. The leaf area index (LAI) at this tower site showed a maximum density of 4.7 at ground level, quite typical for a European beech stand. A detailed overview of the measurement site is given by Auburn et al. (2005).

2.2. Enclosure measurements and plant material

Enclosure measurements for monoterpane emission from European beech (*Fagus sylvatica* L., plant family: *Fagaceae*) were carried out during two intensive field campaigns.

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1 Auburn, S., Koppmann, R., Leitl, B., Möllmann-Coers, M., and Schaub, A.: Physical modelling of a complex forest area in a wind tunnel – Comparison with field data, Agricultural and forest Meteorology, submitted, 2005.
in the summers of 2002 and 2003. All experiments were conducted by use of an open, dynamic (flow through) enclosure system, consisting of two identical cuvettes of ~75 l volume each. As proven earlier, the system can be regarded as inert for the relevant volatile organic compounds and allows the investigation of an enclosed branch for several days without visible effect of stress (for a detailed description see Gut et al., 2002; Kesselmeier et al., 1996, 1997, 1998; Kuhn et al., 2002a, b; Schäfer et al., 1992). Enclosure measurements were carried out over a period of 8 days in June 2002 and 16 days in July/August 2003 with the same branch of a ~160 year old beech tree. Leaf samples from the measured branch proved to be “sunlit leaves” by microscopical analysis of the leaf morphology. For measurements, the branch was enclosed in the sample cuvette as shown by Fig. 1, while the other cuvette remained empty as a reference. Leaf area, dry and fresh weight were calculated similar to Kuhn et al. (2002a). An overview of these parameters is given in Table 1. Micrometeorological parameters were recorded by standard sensors. Exchange rates for CO₂ and water vapour were measured by use of an infrared gas analyser (Model Li-7000, Licor, USA). All trace gas exchange rates were calculated by using the difference concentration between the branch enclosing sample cuvette and the empty reference cuvette according to Kuhn et al. (2002a, b). Unless indicated otherwise, leaf gas exchange rates were normalised to leaf dry weight. The stomatal conductance for water vapour was determined according to Pearcy et al. (1989). Uncertainties for gas exchange rates were assessed by conventional Gaussian error propagation. Ambient temperature and rainfall preceding the enclosure measurements were monitored by the meteorological station of the Research Centre Jülich at about 470 m distance from the measurement site on a second scaffolding tower at a height of 20 m.

2.3. Measurement of volatile organic compounds

Measurement of volatile organic compounds was performed by the use of solid adsorbents and subsequent analysis of the sampled compounds by GC-FID and GC-MS. Samples from the reference and branch cuvette, as well as from ambient air, were
collected simultaneously by use of three custom made automatic sampling systems that are described in detail by Kuhn et al. (2005). For GC-FID measurements samples were collected on Silicosteel cartridges (1/4" OD, 89 mm length, Restek, USA) packed with 130 mg Carbograph 1 (90 m² g⁻¹) and 130 mg Carbograph 5 (560 m² g⁻¹) (20–40 mesh each, Lara s.r.l., Italy). Samples were collected for 30 min at flow rates of 150 ml min⁻¹ resulting in a total sampling volume of 4500 ml. Analysis of the samples by GC-FID measurements was performed in the laboratory at the Max Planck Institute in Mainz. Cartridges were desorbed thermally for 10 min by use of a thermal-desorption system (Model ATD400, Perkin Elmer, Germany) at 260°C, that was connected to a GC-FID (Model AutoSystem XL, Perkin Elmer, Germany). Refocussing prior peak separation was accomplished by a small quartz tube packed with 20 mg Carbograph 1 kept at −30°C that was heated rapidly to 280°C. The separation of peaks was achieved by use of a dimethylpolysiloxane column (model HP-1, 100 m length, 0.25 mm ID, film thickness 0.5 µm, [Agilent Technologies, USA]) at a temperature program ranging from −10 to 40°C (20°C min⁻¹), 40 to 145°C (1.5°C min⁻¹) and 145 to 220°C (30°C min⁻¹). In addition to several volatile organics, 10 different monoterpene compounds were evaluated from these analyses: camphene, Δ3-carene, p-cymene, limonene, myrcene, α-pinene, β-pinene, sabinene, α-terpinene, and γ-terpinene. The detection limit for monoterpene samples was calculated to <10 ppt (corresponding to a detection limit of 12 ng g⁻¹ h⁻¹ and 0.9 µg m⁻² h⁻¹ for Fagus sylvatica L.) (for details see Kuhn et al., 2002b). Calibration for this system was accomplished by use of a gaseous standard containing isoprene and several n-alkanes. Unless indicated otherwise, the following paragraphs will report on the total sum of monoterpene compounds measured by GC-FID or GC-MS.

Samples for GC-MS analysis were collected occasionally on glass tubes (6 mm OD, 160 mm length) that were packed sequentially with 118 mg Carbograph 2 (12 m² g⁻¹),

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Kuhn, U., Dindorf, T., Ammann, C., Holzinger, R., Ausma, S., Kenntner, T., Helleis, F., and Kesselmeier, J.: Design and field application of an automated cartridge sampler for VOC concentration and flux measurements, J. Envir. Mon., submitted, 2005
60 mg Carbograph 1, and 115 mg Carbograph 5 (20–40 mesh each, Lara s.r.l., Italy). Analysis of the cartridges was carried out in the laboratory of CNR in Rome, Italy. Monoterpene compounds that were evaluated from these analyses were camphene, Δ3-carene, p-cymene, limonene, myrcene, α-phellandrene, β-phellandrene, α-pinene, β-pinene, sabinene, α-terpinene, γ-terpinene, terpinolene, α-thujene, and tricyclene. A detailed overview of the method used for GC-MS analysis is given by Ciccioli et al. (1992) and Brancaleoni et al. (1999). According to the results of subsequent laboratory tests, it was shown that sabinene partially decomposed to p-cymene, α-phellandrene, β-phellandrene, α-terpinene, γ-terpinene, terpinolene, and α-thujene during the storage time of these cartridges. Thus a correction factor was applied to the relevant compounds.

2.4. Calculation of European VOC emission

To assess the potential implication of monoterpene emissions from *Fagus sylvatica* L. on a European scale, we applied an offline version of the Guenther et al. (1995) VOC emission algorithm, normally applied for global scale studies (Ganzeveld et al., 2002). The algorithm uses the Olson (1992) global ecosystem database, which distinguishes 72 ecosystems at a 0.5×0.5 grid resolution, combined with a 5-year climatology of monthly NDVI (Normalized Differential Vegetation Index) satellite data (Gutman et al., 1995) to infer global surface cover properties. VOC emissions are calculated as a function of ecosystem specific emission factors, surface radiation, temperature, foliar density and its vertical distribution. The latter is required to calculate the within-canopy profiles of photosynthetic active radiation (Weiss and Norman, 1985) and distinguishes four canopy layers based on the sensitivity of the emissions on the vertical resolution (Ganzeveld et al., 2002). Normally, the emission algorithm is applied in the chemistry-climate model ECHAM to calculate the biogenic VOC emissions and their role for atmospheric chemistry online from the model’s surface temperature and net radiation. However, for the offline calculations presented, we have applied the temperature and net radiation output fields of a ECHAM T106 (∼125 km resolution) simulation for the
month of July at 6 h time intervals. For a comparison with the global scale algorithm, we have used a high-resolution dataset that describes the European distribution of *Fagus sylvatica* L. at a 1×1 km grid resolution (Köble and Seufert, 2001) in combination with the measured monoterpane emission factor.

3. Results and discussion

3.1. Diurnal course of plant physiology and monoterpane emission

Figure 2 shows the evolution of micrometeorological and physiological parameters that were measured during the enclosure of *Fagus sylvatica* L. in June 2002 and July/August 2003. Regarding the course of net CO$_2$ assimilation, transpiration, and stomatal conductance, all parameters exhibited pronounced diurnal characteristics following photosynthetic active radiation (PAR) and leaf temperature. Irradiation and leaf temperatures increased particularly during the course of the measurement period in June 2002 as a result of a short high ambient temperature period. Only a few days were cloudy during both campaigns and saturation of photosynthesis was reached for most of the days. Leaf temperature reached maximum readings of 44°C during the experiments in June 2002 and July/August 2003 and was several times above the temperature optimum of net CO$_2$ assimilation (see Fig. 3). In close relation to the course of PAR and leaf temperature, monoterpane emission from European beech exhibited pronounced diurnal characteristics during both years. As shown in Fig. 2 monoterpane exchange was measured typically in 1–2 h intervals during three and six days in June 2002 and July/August 2003, respectively. Daytime monoterpane emission for the sum of 10 individual monoterpane compounds, reached maximum exchange rates of up to 33.2 µg g$^{-1}$ h$^{-1}$ in June 2002 and 9.6 µg g$^{-1}$ h$^{-1}$ in July/August 2003. Night time monoterpane emission was always close to the detection limit (emission ≤80 ng g$^{-1}$ h$^{-1}$ for both experiments).
3.2. Monoterpene emission as a function of light and temperature

According to the diurnal characteristics of monoterpene emission from European beech a correlation of monoterpene exchange to micrometeorological parameters is evident. Night time exchange rates near the detection limit eliminate an exclusive role of leaf temperature as reported for monoterpene emission from coniferous trees. In analogy to the monoterpene emission pattern that was observed for other tree species of the plant family *Fagaceae* (e.g. BEMA-Project, 1997; Bertin and Staudt, 1996; Ciccioli et al., 1997; Loreto et al., 1996; Niinemets et al., 2002a; Owen et al., 2002; Staudt and Seufert, 1995; Staudt and Bertin, 1998), and the laboratory experiments conducted on European beech by Schuh et al. (1997), net CO$_2$ assimilation and monoterpene emission from *Fagus sylvatica* L. were correlated to PAR and leaf temperature for both years (Fig. 3). While in 2002 the small dataset was limiting, in 2003 both net CO$_2$ assimilation and monoterpene emission revealed similar saturation effects when correlated to light intensity (saturation trend at light intensities of more than 400 µmol m$^{-2}$ s$^{-1}$). A temperature optimum of net CO$_2$ assimilation was found between leaf temperatures of 25 to 27°C. Monoterpene emission did not exhibit a temperature optimum and increased exponentially with leaf temperature up to a maximum of 43°C during both campaigns. According to the laboratory experiments conducted by Fischbach et al. (2000, 2002) temperature optima for monoterpene synthase from *Quercus ilex* L. ranged between 30 to 40°C (in vitro) and enzyme activity was measurable up to 60°C. Staudt and Bertin (1998) reported in vivo optima at 42°C for a variety of monoterpene compounds that were emitted by *Quercus ilex* L.. Similar optima (∼40°C) were obtained by Niinemets et al. (2002b) with *Quercus ilex* L. and *Quercus coccifera* L. (in vivo), who demonstrated that the shape of in vitro and in vivo temperature dependencies differed. They concluded that monoterpene synthase activity was influenced by the chloroplastic (stromal) pH. As a decrease in photosynthetic activity at temperatures above the optimum of photosynthesis lead to acidification of the stromal pH, a decrease in photosynthesis should favour monoterpene emission since pH
Scattering in the present dataset (including morning and afternoon exchange rates) does not allow clear conclusions as to whether the increase of monoterpene emission with light intensity was hyperbolic or sigmoid. However, emission in the absence of light was near detection limit. Thus, the storage pool term of the S97 algorithm was
neglected as recommended for sabinene emission by Schuh et al. (1997), extracting the term from biosynthesis directly prior to emission ($\Phi_B$) only. Figure 4 shows the linear correlation of monoterpene emission to the product of light and temperature terms from the G97 and S97 models. Outliers from this correlation were often caused by temperature effects (e.g. midday depression (see Sect. 3.5.)). Standard emission factors ($SEF$, G97) that were calculated from the linear correlation for the sum of monoterpenes ranged between $13.1 \, \mu g \, g^{-1} \, h^{-1}$ for the experiments performed in June 2002 and $4.4 \, \mu g \, g^{-1} \, h^{-1}$ for the experiments performed in July/August 2003. Application of the S97 model resulted in emission factors ($\Phi_{BS}$) of $14.1 \, \mu g \, g^{-1} \, h^{-1}$ and $4.6 \, \mu g \, g^{-1} \, h^{-1}$ for the campaigns of 2002 and 2003, respectively. Although standard emission differed by a factor of 3 between both years, differences observed for individual days during one growing season were smaller. Table 2 gives an overview of minimum, maximum, and average standard emission factors that were calculated for single days of the respective year by application of the G97 algorithm. Consistent with the results obtained by the enclosure measurements, ambient monoterpene concentrations (measured at the canopy top) ranged up to 1.8 ppb in June 2002 and up to 1.1 ppb in July/August 2003. This result is indicative of the strong influence of beech trees on atmospheric gases in the vicinity of the tower site.

3.3. Artificial shading experiment

A variety of physiological functions is influenced by diurnal rhythms of the plant. Whereas endogenous (circadian) rhythms are characterised mainly by the fact that they obtain periodicity even if environmental factors remain constant, exogenous rhythms are triggered by ambient conditions. Monoterpene emission for European beech was shown to have a diurnal periodicity that correlates to light and temperature (see context above and Schuh et al., 1997). However, since light intensity and temperature exhibited a coupled diurnal periodicity by themselves, a pseudo correlation of monoterpene emission to both factors might be possible. To exclude this and to prove the light dependency of monoterpene emission under a daytime temperature regime, an artificial
shading experiment was conducted in 2003 (see Fig. 5). The artificial darkening of the enclosure started at noon and was completed within 30 min (remaining light intensity 20–21 µmol m\(^{-2}\) s\(^{-1}\)). Two hours later the artificial plant cover was removed again and irradiation progressed in a conventional daily pattern. When the plant cuvette was coated by a dark cover, cuvette temperature (and as a consequence leaf temperature) decreased after darkening but increased again in the course of the shading period (max. difference in leaf temperature during shading 13\(^{\circ}\)C). VOC exchange measured 30 min after complete coverage of the cuvette showed no emission of monoterpane compounds. As soon as the artificial darkening was removed, monoterpane emission progressed with its conventional diurnal characteristics. Assuming the existence of unspecific storage pools for monoterpenes in European beech as reported by Schuh et al. (1997), storage pools must have been emptied after darkening in a time period of 30 min. This is not consistent with the analysis performed by Niinemets and Reichstein (2002) which proved that the decrease in monoterpane emission from storage pools follows a double exponential function. Other authors have also reported a persistence of monoterpane emission from unspecific storage pools of Quercus sp., for several hours to days (Ciccioli et al., 1997; Loreto et al., 1996, 2000; Niinemets et al., 2002a). However, if storage pools would have existed for European beech and were not depleted by the time the cover was removed, a typical burst of monoterpane emission as reported earlier for Quercus ilex L. (Loreto et al., 2000) should have been observed for European beech as well (which was not the case). Furthermore, a rapid depletion of potential storage pools would explain the lack of night time emission in the present study, since time resolution of monoterpane measurement was typically 1–2 h. However, the darkening experiment clearly showed the obligatory role of light for monoterpane emission from beech and that emission from storage pools may also be neglected under a high temperature regime.
3.4. Composition of emitted monoterpene species

Figure 6 shows the diurnal course of individual monoterpene emission measured by GC-MS for one of the measurement days in August 2003. Light and temperature dependency of monoterpene emission was observed for all analysed compounds with exception of tricyclene that scattered at exchange rates below 1 ng g\(^{-1}\) h\(^{-1}\). Sabinene was the predominant monoterpene compound emitted (max. 8.1 µg g\(^{-1}\) h\(^{-1}\)). Standard emission factors that were calculated for the sum of all monoterpenes for this respective day reached 7.1 µg g\(^{-1}\) h\(^{-1}\) (G97, sum of 15 individual monoterpene compounds) and 5.9 µg g\(^{-1}\) h\(^{-1}\) (G97, sum of 10 individual monoterpene compounds, see GC-FID). Monoterpene emission calculated by the G97 algorithm fitted well to midday and afternoon values but morning and evening monoterpene emission was much lower than calculated. Thus integration of measured and calculated emission for the respective day resulted in an overestimation of +13% by the calculated data. Application of a sigmoidal increase of monoterpene emission with light intensity (as assumed by the S97 algorithm, Φ\(^B\) only) resulted in a better reproducibility of the observed data in the morning hours. However, both algorithms still overestimated monoterpene emission in the morning and underestimated midday and afternoon emission to a various extent. In order to determine the contribution of different monoterpene species to the sum of monoterpene emission, the fraction of standard emission factors for different monoterpene compounds were calculated as shown in Table 3. Correlation of different monoterpene species to each other resulted in good results for the majority of compounds with the exception of tricyclene. Our results are consistent with most previous studies which report sabinene as being the predominant monoterpene compound released from European beech (see Kahl et al., 1999; Schuh et al., 1997; Tollsten and Müller, 1996). Moreover, reasonable agreement was obtained for the emission of myrcene and limonene. In contrast to these results, the apportionment of other monoterpene compounds was much more inconsistent between the different studies mentioned above. This particularly affects the emission of α-pinene, that was reported
to be released to a major (Kahl et al., 1999; Schuh et al., 1997), moderate (König et al., 1995), or minor (this study and Tollsten and Müller, 1996) extent by European beech. Similar contradictory results were obtained for the emission of β-pinene that was reported to be released as a major (König et al., 1995) or minor (this study and Tollsten and Müller, 1996) compound. As discussed by König et al. (1995) temperature effects can be an important factor for the apportionment of monoterpene emission from European beech, resulting in the dominance of different compounds at different enclosure temperatures. Hence, inconsistencies between the different studies mentioned above might not be surprising, since most of them were conducted at different temperatures.

3.5. Midday depression of net CO$_2$ assimilation and monoterpene emission

The clear light dependence of monoterpene release reflects the close link of emission and production, which is closely coupled to net CO$_2$ assimilation. A plant’s primary productivity depends on several factors, with water availability being of essential importance. Increasing leaf temperature and water vapour pressure deficit have a severe effect on the water loss of the leaf epidermis which is an important factor for stomatal aperture (for a detailed overview see Schulze, 1986). According to Backes and Leuschner (2000) *Fagus sylvatica* L. evolved a very sensitive stomatal regulation that allows maintenance of leaf turgor during dry, high temperature conditions. Consequently, on days with high ambient temperature European beech, due to its sensitive stomatal regulation, exhibited a distinct midday depression of net CO$_2$ assimilation as observed two times in June 2002 and five times in July/August 2003. Figure 7 gives an overview of the daily course of leaf temperature, as well as the correlation of stomatal conductance and photosynthesis to PAR during the measurement period in June 2002. As shown, European beech developed a midday depression of photosynthesis when midday leaf temperatures increased to more than 41°C during the 6th and 7th day of measurement (Figs. 7f and 7g). As soon as midday leaf temperatures decreased and were below 28°C the next day, midday depression was not observed and plant stomatal conductance and net CO$_2$ assimilation progressed in a conventional pattern. As
discussed above, monoterpene emission exhibited light saturation. However, during sunny days the correlation revealed a typical hysteretic structure that was observed to be a function of time (lower monoterpene emission in the morning, see Fig. 8, top graph). The hysteresis was attributed to a time lag phase of monoterpene emission in the early morning. Since the morning increase of monoterpene emission with PAR was less pronounced than the decrease in the early evening, the correlation of monoterpene emission to PAR resulted in a hysteresis. In contrast, during hot sunny days, midday depression of net CO$_2$ assimilation and stomatal conductance may lead to a hysteretic course of monoterpene emission that follows the time of day in an opposite direction (lower monoterpene emission in the afternoon). Indeed, this effect was observed once, during the measurement period in June 2002 as monoterpene emission was very high and the plant experienced its first high temperature period of the respective growing season (see Fig. 8, bottom graph). As reported by Loreto et al. (1996) and discussed in detail by Niinemets and Reichstein (2003) monoterpenes are emitted through stomata but are not controlled by stomatal aperture. Thus, other physiological processes such as photosynthesis must have limited monoterpene emission during the respective day. As discussed above, a decrease in photosynthesis and consequently in stromal pH, should favour monoterpene emission (Bohlmann et al., 1998; Fischbach et al., 2000; Niinemets et al., 2002b). However, midday depression of monoterpene emission from Quercus ilex L. has been observed by other studies as well (Bertin et al., 1997; Kesselmeier et al., 1997; Penuelas and Llusia, 1999). The DOXP Pathway with its substrates glycerine-aldehyde-3-phosphate and pyruvate is known to represent the major source for plastidic isoprenoids (Lichtenthaler, 1999). As reported by Parry et al. (2002), drought effects may lead to a down regulation of ribulose-1,5-bisphosphate-carboxylase (RUBISCO) by tight binding inhibitors, a mechanism that was discussed recently as a central effect of midday depression of photosynthesis (Griffith and Parry, 2002). Thus, a restriction of RUBISCO might lead to a substrate limitation under high monoterpene production rates. Experiments performed by Kahl et al. (1999) on European beech indicated that 90% of the total sabinene emission was formed de novo from...
photosynthetic intermediates. Since sabinene was the predominant compound emitted by *Fagus sylvatica* L. (fraction of 57%) a decrease of photosynthetic activity might also lead to a decrease in the emission of monoterpenes. During the midday depression of monoterpene emission the carbon balance (carbon loss in form of monoterpenes per photosynthetic fixed carbon) exceeded the 1% level (up to 1.7%), while under normal environmental conditions the carbon loss was typically below 0.5%. Since midday depression of monoterpene synthesis was observed only during high monoterpene production rates in 2002, we conclude that monoterpene emission was limited by substrate availability in this special case.

3.6. Variability of standard emission factors

Standard emission factors that were calculated by application of the G97 algorithm on a dry weight basis differed by a factor of 3 between both years. However, the relatively low standard emission factors calculated for 2003 were confirmed by canopy scale flux measurements performed by Spirig et al. (2004). The importance of variations in developmental stages, seasonality, growth conditions, and habitat for monoterpene emission from *Quercus ilex* L. has been reported recently (e.g. Bertin et al., 1997; Fischbach et al., 2002; Llusia and Peñuelas, 2000; Niinemets et al., 2002a; Peñuelas and Llusia, 1999; Sabillon and Cremades, 2001; Staudt et al., 2002, 2003; Street et al., 1997). Also, European beech is known to develop ecotypes that are adapted to the climatic conditions of the habitat they live in (Peuke et al., 2002). The location selected for our measurements of European beech is characterised by temperate climatic conditions. However, temperatures can display strong variations as observed during the measurement period of 2002 and 2003. Figure 9 gives an overview of ambient temperature and rainfall that were measured prior and during the enclosure of European beech in the summers of 2002 and 2003. Average ambient temperatures measured 30 days preceding the enclosure measurements ranged from moderate temperatures of 16°C in Mai/June 2002 to higher temperatures of 20°C in June/July 2003. As observed by Staudt et al. (2003), the acclimatisation time of standard emission factors to
previous temperatures was highly variable and ranged between 3 days and 3 weeks for Quercus ilex L.. These experiments are not in agreement with our results from European beech, as higher daytime temperatures were observed in the days preceding the measurements in 2003, when exchange rates were much smaller. Thus, other effects might have dominated the observed variability in standard emission between the experiments in 2002 and 2003. One of these effects might have been a long lasting drought period that preceded the measurements in 2003 and resulted in a reduction of average photosynthesis during the latter campaign. Since a reduction of photosynthesis and transpiration have been reported to be indicators of drought to European beech (Peuke et al., 2002; Thomas, 2000), we can not exclude long term effects of drought in 2003. However, transpiration did not decrease in the latter campaign. Bertin and Staudt (1996) demonstrated that long periods of drought restricted monoterpene emissions from Quercus ilex L. by two orders of magnitude as the daily net carbon balance approached zero. Likewise, Staudt et al. (2002) reported a reduction of photosynthesis and transpiration, paralleled by a reduction of monoterpene emission of at least 25% due to drought effects. As reported by Backes and Leuschner (2000) and Thomas (2000), physiological properties of European beech are much more sensitive to drought than physiological properties of oak trees. Hence, this sensibility provides an explanation for the stronger reduction of monoterpene emission observed during the present study. Moreover, comparing the intensity of photosynthetic active radiation during clear sky days in 2002 and 2003, light intensity was lessened by some percent during the latter campaign. This effect might have been caused by an increase of biomass that surrounded the investigated branch during the vegetation period. However, light intensity was still high and microscopic analysis of leaf morphology pointed to the typical structure of sunlit leaves. Although the lower light intensity might explain the decrease in LMA values in 2003 and might have contributed to the lower standard emission factors investigated. Furthermore, as measurements started in June during the first campaign but were conducted in July/August in 2003, seasonal effects on monoterpene emission have to be taken into account as well. According to Schuh
et al. (1997), monoterpene emission from *Fagus sylvatica* L. decreased by a factor of 16 between spring and autumn. Also König et al. (1995), who investigated beech trees in Austria in late August and early September, reported a decrease of monoterpene emission. For a detailed overview of the seasonal development of monoterpene emission from European beech see Holzke et al. (2005)\(^3\), who monitored monoterpene emission from *Fagus sylvatica* L. for a time period of 2 years. In contrast to most literature data, the present study revealed *Fagus sylvatica* L. as being a strong monoterpene emitter. For the plant family *Fagaceae*, only a few species that have been investigated so far have exhibited substantial monoterpene emission rates (for review see Kesselmeier and Staudt, 1999). Table 4 gives an overview of experiments that were conducted earlier to examine monoterpene emission from European beech. The majority of these experiments reported that *Fagus sylvatica* L. emitted only low amounts of monoterpenes. Regarding the laboratory experiments performed by Hewitt and Street (1992) and Steinbrecher et al. (1993), monoterpene emission from European beech was below or near the detection limit of the analytical system. Also König et al. (1995) and Tollsten and Müller (1996) who examined European beech trees under field conditions in Austria and Switzerland found only low emission of monoterpenes at 0.2 and 0.3 \(\mu g\) g\(^{-1}\) h\(^{-1}\), respectively. Only laboratory experiments conducted by Schuh et al. (1997) and Kahl et al. (1999) revealed substantial monoterpene emission at 414 and 284 \(\mu g\) m\(^{-2}\) h\(^{-1}\) (at 25°C). Monoterpene emissions that were measured during the first year of the present study significantly exceeded these emission rates reported.

3.7. Implications for the European budget of monoterpene emission

According to Guenther et al. (1995, 1997), there are two approaches to assign emission factors at an ecosystem scale.

\(^3\)Holzke, C., Dindorf, T., Kuhn, U., Kesselmeier, J., and Koppmann, R.: Terpene emissions from European beech (*Fagus sylvatica* L.): pattern and emission behaviour within two vegetation periods, in preparation, 2005.
1. The first method assigns a landscape type to each location within the model domain. An emission potential, derived by micrometeorological measurement techniques or from general assumptions of species distribution, is associated with each landscape type.

2. The second approach requires an estimate of the composition of plant species for each location in the model domain, as well as a database of specific emission potentials that are derived e.g. by enclosure measurements for each plant species. A landscape average emission potential can then be assigned as the weighted average of all species at each location.

In the global model of Guenther et al. (1995) distinct emission factors have been assigned to various ecosystem types following the first approach described above. Figure 10 shows the mean European monoterpene emission flux (domain 10°W–30°E and 35°N–65°N) for the month of July that was calculated with the default monoterpene emission factors assigned to the Olson ecosystems as described by Guenther et al. (1995, henceforth G95Ols) for a 0.5×0.5 grid resolution. Figure 11 shows the relative increase of monthly mean monoterpene emission in relation to the latter assumption, if the spatial distribution of *Fagus sylvatica* L. is specifically considered (henceforth G95FS). The G95FS flux is calculated from the flux based on the measured monoterpene emission factor (13 µg g⁻¹ h⁻¹, year 2002) and the flux using the default emission factor of the G95Ols algorithm. In this way weighted average fluxes were calculated, specifically taking into consideration the fraction of *Fagus sylvatica* L. area coverage in every 0.5×0.5 grid. The relative difference to the default G95Ols model (see Fig. 11) is calculated according to Eq. (1).

\[
100 \times \frac{G95FS - G95Ols}{(G95FS + G95Ols)/2}. \tag{1}
\]

The spatial distribution of the differences actually reflects the European distribution of *Fagus sylvatica* L., which makes up about 7.1% of the European forest area. Despite
the relatively small area covered by European beech there is a significant increase in the European monoterpene emission in July from about 694 to 1017 t C month$^{-1}$ if the high standard emission factor and the spatial distribution of *Fagus sylvatica* L. are taken into account. However, in both G95Ols and G95FS monoterpene emission was calculated as a function of temperature only. By also considering the role of light as a controlling parameter of monoterpene emission from *Fagus sylvatica* L. (henceforth FSlight), the total amount of monoterpene release is reduced significantly. In the latter assumption the total emission amounts to 792 t C month$^{-1}$. Nevertheless, as shown by Fig. 12, relative increases >100% between the FSlight and the G95Ols were estimated on a local scale, when relative changes are calculated in analogy to Eq. (1). Note that the FSlight results reflect a simulation where only the light and temperature attenuation functions for *Fagus sylvatica* L. are applied, whereas the monoterpene emissions for the remaining fraction in each 0.5×0.5 grid are calculated considering the role of temperature only. However, if generalized for deciduous tree species, a strong light dependence of monoterpene emission would have a strong impact on predicted magnitude and temporal distribution of monoterpenes. Consistent with previous studies that were based on a similar methodology (e.g. Guenther et al., 1997; Lenz et al., 2001; Solmon et al., 2004) it can be concluded that consideration of a more detailed spatial distribution of a specific land cover type, for which measured emission parameters are available, results in significant changes in the local monoterpene emission flux. However, for the European domain the increase is small considering all uncertainties involved such as biomass estimates and using the surface- versus the actual canopy or leaf temperature. In addition, the results reflect the simulations for the month of July with high radiation intensity and temperature using the high emission flux measured in 2002. Consequently, the results reflect an upper range impact of the observed *Fagus sylvatica* L. emission rate and light dependence for the European domain.
4. Conclusions

The experiments performed in the present study clearly indicate that monoterpene emission from European beech is a function of light and temperature. Even though the temperature optimum was not reached up to leaf temperatures of 43°C, monoterpene release that was calculated by application of light and temperature dependent algorithms (G97 and S97), generated reasonable agreement with the measured data. In reference to the default G95Ols model, the consideration of the substantial emission factor and light intensity as a controlling parameter of monoterpene release, generated a relative increase in the European monoterpene emission up to 14%, yielding monoterpene emissions of 792 t C month$^{-1}$. However, long term drought effects might restrict monoterpene emission and might explain the observed interannual and seasonal variability of monoterpene emission. Furthermore, short term drought effects, like midday depression of photosynthesis, can be crucial for daily variations in VOC emission, particularly when rates of monoterpene productivity are high.

Appendix A

Algorithms describing VOC emission as a function of light and temperature.

A.1. Algorithm developed by Guenther et al. (1993, 1995, 1997)

$$\Phi = SEF \cdot \left[ \frac{\alpha \cdot C_L \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \right] \cdot \frac{\exp \left( \frac{C_{T1} \cdot (T - T_S)}{R \cdot T_s \cdot T} \right)}{C_{T3} + \exp \left( \frac{C_{T2} \cdot (T - T_M)}{R \cdot T_s \cdot T} \right)}.$$ (A1)
A.2. Algorithm developed by Schuh et al. (1997)

\[
\Phi = \Phi^{P,S} \cdot \exp \left[ \frac{CT_P}{R} \cdot \left( \frac{T - T_S}{T \cdot T_S} \right) \right] + \Phi^{B,S} \cdot C_L \cdot \left[ \frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \right]^2 \cdot \left[ \frac{\exp \left( \frac{C_{T_1}(T - T_S)}{R \cdot T_S} \right)}{1 + \exp \left( \frac{C_{T_2} (T - T_M)}{R \cdot T_S} \right)} \right]. \quad (A2)
\]

A.3. Algorithm developed by Schuh et al. (1997), biosynthesis part, denominator modified according to Guenther et al. (1997)

\[
\Phi^B = \Phi^{B,S} \cdot C_L \cdot \left[ \frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \right]^2 \cdot \left[ \frac{\exp \left( \frac{C_{T_1}(T - T_S)}{R \cdot T_S} \right)}{CT_3 + \exp \left( \frac{C_{T_2} (T - T_M)}{R \cdot T_S} \right)} \right]. \quad (A3)
\]

\[\alpha (\text{empirical coefficient})=0.0027\]
\[C_L (\text{empirical coefficient})=1.066\]
\[C_{T_1} (\text{empirical coefficient} \ [\text{J mol}^{-1}])=95 \ 000\]
\[C_{T_2} (\text{empirical coefficient} \ [\text{J mol}^{-1}])=230 \ 000\]
\[C_{T_3} (\text{empirical coefficient})=0.961\]
\[C_{TP} (\text{empirical coefficient}, \text{e.g.} \ 0 \text{ for sabinene})\]
\[L (\text{photosynthetic active radiation (PAR) [} \mu\text{mol m}^{-2} \text{ s}^{-1}]\]
\[\Phi (\text{actual VOC emission [e.g. } \mu\text{g g}^{-1} \text{ h}^{-1}]\]
\[\Phi^{B,S} (\text{flow from biosynthesis at standard condition [e.g. } \mu\text{g g}^{-1} \text{ h}^{-1}]\]
\[\Phi^{P,S} (\text{flow from pool at standard condition [e.g. } \mu\text{g g}^{-1} \text{ h}^{-1}]\)
\[R (\text{universal gas constant} \ [\text{J K}^{-1} \text{ mol}^{-1}])=8.314\]
\[SEF (\text{standard emission factor [e.g. } \mu\text{g g}^{-1} \text{ h}^{-1}]\]
\[T (\text{leaf temperature [} ^\circ\text{K}]\)
\[T_M (\text{empirical coefficient} \ [^\circ\text{K}])=314\]
\[T_S (\text{leaf temperature at standard condition [} ^\circ\text{K}])=303\]
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Table 1. Reference values for branch enclosures. Abbreviations: (a) from originally enclosed leaves, (b) calculated from reference leaves taken from the same branch.

| Measurement period         | Leaf area (m²) | Fresh weight (g) | Dry weight (g) | Water content (%) | Leaf dry mass per area (g m⁻²) |
|----------------------------|----------------|------------------|----------------|-------------------|--------------------------------|
| June 2002                  | 0.17 (a)       | 32.62 (b)        | 18.35 (b)      | 44 (b)            | 108                            |
| July/August 2003           | 0.14 (a)       | 21.33 (a)        | 10.73 (a)      | 50 (a)            | 77                             |
Table 2. Standard emission factor (G97, monoterpenes, sum of 10 individual compounds) for European Beech as measured during the growing season in the years of 2002 and 2003. Standard temperature 30°C, standard light intensity (PAR) 1000 μmol m⁻² s⁻¹.

| Measurement period          | Standard emission factor (μg g⁻¹ h⁻¹) (μmol m⁻² s⁻¹) | Maximum | Minimum | Average |
|-----------------------------|--------------------------------------------------------|---------|---------|---------|
| June 2002                   |                                                       | 13.5 (3.0) | 9.0 (2.0) | 13.1 (2.9) |
| July/August 2003            |                                                       | 5.6 (0.9)  | 3.1 (0.5)  | 4.4 (0.7)  |
Table 3. Standard emission factors (G97) for 15 monoterpene species measured by GC-MS during one single day in August 2003. Standard temperature 30°C, standard light intensity (PAR) 1000 µmol m⁻² s⁻¹. Abbreviations: (a) partially decomposed, (b) partial decomposition product.

| Monoterpene species | Monoterpene emission, \(SEF\ (\text{ng g}^{-1} \text{h}^{-1})\) | Monoterpene emission, \(SEF\ (%)\) |
|---------------------|-------------------------------------------------|----------------------------------|
| sabinene (a)        | 4036                                            | 56.83                            |
| \(\alpha\)-thujene (b) | 584                                            | 8.22                             |
| \(\gamma\)-terpinene (b) | 541                                            | 7.62                             |
| \(\alpha\)-terpinene (b) | 483                                            | 6.80                             |
| p-cymene (b)        | 365                                             | 5.14                             |
| \(\beta\)-phellandrene (b) | 336                                            | 4.73                             |
| myrcene             | 166                                             | 2.34                             |
| limonene            | 154                                             | 2.17                             |
| terpinolene (b)     | 142                                             | 2.00                             |
| \(\alpha\)-phellandrene (b) | 113                                            | 1.59                             |
| \(\alpha\)-pinene   | 99                                              | 1.39                             |
| \(\beta\)-pinene    | 73                                              | 1.03                             |
| camphene            | 6                                               | 0.08                             |
| \(\Delta\)3-carene  | 3                                               | 0.04                             |
| tricyclene          | 1                                               | 0.01                             |
Table 4. Monoterpene emission from European beech as reported by several authors. Abbreviations: $a$ (age of trees), $bdl$ (below detection limit), $e$ (enclosure), $f$ (field experiment), $l$ (laboratory experiment), $ldm$ (leaf disc method), max. (maximum), — (not specified), PAR (photosynthetic active radiation), $r$ (radiation), $t$ (temperature).

| Reference                  | Monoterpene emission $\ (\mu g \ g^{-1} \ h^{-1})$ | Monoterpene emission $\ (\mu g \ m^{-2} \ h^{-1})$ | Comment                                      |
|----------------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------|
| Hewitt and Street (1992)   | $bdl$                                                | $bdl$                                                | $ldm, a$ (young/adult) $t$ ($-$), PAR (max. 900 $\mu$mol m$^{-2}$ s$^{-1}$) |
| Steinbrecher et al. (1993) | —                                                   | $\sim$0.49                                           | $e, l, a$ (2 years) $t$ (2–14°C), PAR (max. 600 $\mu$mol m$^{-2}$ s$^{-1}$) |
| König et al. (1995)        | 0.19                                                | —                                                   | $e, f, a$ (adult), $t$ (20°C), PAR ($-$)     |
| Tollsten and Muller (1996) | 0.25                                                | —                                                   | $e, f, a$ (adult), $t$ ($-$), PAR ($-$)     |
| Schuh et al. (1997)        | —                                                   | 414                                                 | $e, l, a$ ($-$), $\phi^{P+B}$ at $t$ (25°C), PAR (various) |
| Kahl et al. (1999)         | —                                                   | 284                                                 | $e, l, a$ (6 years), $t$ (25°C), $r$ (max. 300 $\mu$mol m$^{-2}$ s$^{-1}$) |
| This study                 | 4–13                                                | 334–1415                                            | $e, f, a$ ($\sim$160 years), $t$ (30°C), PAR (max. 1736 $\mu$mol m$^{-2}$ s$^{-1}$) |
Fig. 1. Enclosure of European Beech (*Fagus sylvatica* L.) during the experiments performed in June 2002.
Fig. 2. Diurnal course of micrometeorological and physiological parameters during both field experiments in June 2002 (left panel) and July/August 2003 (right panel). Top graph: Development of leaf temperatures (red line) and monoterpene emission. Monoterpene emission that was calculated by application of the G97 algorithm is indicated by the grey line, monoterpene emission that was measured by GC-FID analysis is indicated by red circles. Middle graph: Diurnal course of net CO$_2$ assimilation (green line) and transpiration (blue line). Bottom graph: Photosynthetic active radiation (PAR) (black line).
Fig. 3. Light saturation and temperature dependence of net CO$_2$ assimilation and monoterpene emission during both measurement campaigns. Figures A and C indicate measurements performed in the year 2002 (left panel). Figures B and D indicate measurements performed in the year 2003 (right panel). Net CO$_2$ assimilation is indicated by green diamonds. Monoterpene emission was normalised with the respective light and temperature function of the G97 algorithm and is indicated by red circles. Monoterpene emission calculated by the respective term of the G97 algorithm is indicated by the black line.
Fig. 4. Monoterpene emission as a function of the G97 and S97 algorithm for the year 2002 (top graph) and 2003 (bottom graph). Red circles indicate monoterpene emission correlated to the G97 function. Black diamonds indicate monoterpene emission correlated to the S97 ($\Phi^B$) function. Red solid lines represent the linear fit to the G97 function for each dataset. Black solid lines represent the linear fit to the S97 function. The corresponding equation of the linear fit is indicated in the graph.
Fig. 5. Course of photosynthetic active radiation (black solid line) and leaf temperature (red solid line) during the artificial shading of the branch enclosure in July 2003. Monoterpene emission measured prior, during and after the artificial darkening is indicated by red circles.
Fig. 6. Course of photosynthetic active radiation (PAR), leaf temperature, and monoterpene emission measured during one single day in August 2003. Top graph: Diurnal course of PAR (black squares plus dashed line) and leaf temperature (red circles plus dotted line). Data show the appropriate 30 min average during that VOC cartridges were collected. Bottom graph: Diurnal course and composition of monoterpene emission. Data show monoterpene emission measured by GC-MS analysis (stacked bars, for caption see graph), the respective emission calculated by the G97 algorithm (grey stars plus solid line), and the S97 algorithm (emission from biosynthesis only, red diamonds plus dotted line).
Fig. 7. Midday depression of plant physiology in June 2002. Figures A to H show the correlation of net CO$_2$ assimilation (green diamonds) and stomatal conductance (grey stars) to photosynthetic active radiation (PAR) for each single day of the measurement period (12–19 June 2002). The development of the respective daily leaf temperature is indicated by the small graphs as a function of time.
Figure 8. Monoterpene emission as a function of photosynthetic active radiation (PAR) during a typical measurement day in August 2003 (top graph) and during midday depression in June 2002 (bottom graph). Monoterpene emission is indicated by red circles. The respective time of day is indicated for each data point.
Fig. 9. Ambient temperature and rainfall prior and during the enclosure measurements of European beech in the years of 2002 (top graph) and 2003 (bottom graph). Grey areas indicate the respective measurement period of each year. Solid lines represent the daily average temperature. Dashed lines show the daily minima and maxima temperature. Grey bars indicate the respective amount of rainfall. Standard emission factors (SEF) for monoterpene exchange rates were calculated for single measurement days and are indicated by grey stars.
Fig. 10. Mean European monoterpene emission fluxes for the month of July in $\mu$g C g$^{-1}$ h$^{-1}$. Monoterpene emissions were calculated by the default monoterpene emission factors, considering temperature dependence only (G95Ols).
Fig. 11. Relative increase of mean monoterpene emission in % for the month of July if the high standard emission factor and the spatial distribution of European beech are considered as a function of temperature only.
Fig. 12. Relative increase of mean monoterpene emission in % for the month of July if the high standard emission factor and the spatial distribution of European beech are considered as a function of light and temperature.