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Significant light and temperature dependent monoterpene emissions from European beech (*Fagus sylvatica* L.) and their potential impact on the European volatile organic compound budget

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[1] By using a dynamic branch enclosure system the emission of monoterpenes from European beech (*Fagus sylvatica* L.) was investigated during two consecutive summer vegetation periods in the years of 2002 and 2003 in Germany. All measurements were performed under field conditions within the framework of the ECHO project (Emission and Chemical Transformation of Biogenic Volatile Organic Compounds, AFO 2000). European beech was characterized as a substantial emitter of monoterpenes, with sabinene being the predominant compound released. The monoterpene emission from European beech was shown to be a function of light and temperature and agreed well to emission algorithms that consider a light and temperature dependent release of volatile organics. Standard emission factors that were measured from these sunlit leaves of European beech ranged up to 4–13 $\mu g\ g^{-1}\ h^{-1}$ (normalized to 1000 $\mu mol\ m^{-2}\ s^{-1}$, 30°C) in the years of 2003 and 2002, respectively. The nighttime emission of monoterpene compounds was negligible. Also the artificial darkening of the sunlit branch during daylight conditions led to an immediate cessation of monoterpene emission. European beech is the dominating deciduous tree species in Europe. To demonstrate the effect of an updated monoterpene emission factor for European beech in combination with the consideration of a light and temperature dependent monoterpene emission, we applied a species based model simulation on a European scale. With respect to conventional estimates of the European volatile organic compound budget, the latter simulation resulted in relative increases of 16% by taking solely this tree species into account. On local scales these increases exceeded even more than 100% depending on the respective vegetation area coverage of European beech.

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1. Introduction

[2] 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 [*Went*, 1960; *Fehsenfeld et al.*, 1992; *Andreae and Crutzen*, 1997; *Atkinson*, 2000]. The exchange (emission and deposition) of volatile organic compounds plays a crucial role in the oxidant cycle, aerosol production, and in climate forcing but is poorly understood in view of the high number of different VOC species and the environmental factors controlling their exchange. Furthermore, VOC may represent a substantial loss of carbon for the biosphere [*Guenther*, 2002; *Kesselmeier et al.*, 2002].

[3] The emission of isoprenoids, the dominating biogenic VOC fraction consisting mainly of isoprene and monoterpenes, has been investigated intensively during the last decades. 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 only as a function of temperature. 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 that has recently been confirmed for

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the tropical rainforest [*Kuhn et al.*, 2002b; *Rinne et al.*, 2002] and savannah woodland [*Greenberg et al.*, 2003]. Meanwhile, the release of monoterpenes from storage pools that is regulated only by temperature effects is discussed rather as a special case of monoterpene emission [*Kesselmeier*, 2004]. The light dependence of monoterpene emission is also in full agreement with the recent knowledge of the biosynthesis of isoprenoids and the close relation between photosynthesis and the production of isoprene and monoterpenes within the chloroplasts [see *Lichtenthaler*, 1999].

[4] Up to now, several plant species of high importance for regional or global estimations have not been sufficiently investigated but are nevertheless included in budget calculations just by assigning emission rates based on specific ecosystem types or plant family relationship [*Guenther et al.*, 1995; *Karlik and Winer*, 2001]. Furthermore, the seasonal development of VOC emission capacity may play a significant role for global and regional estimates of VOC emissions [*Harley et al.*, 1994; *Monson et al.*, 1994; *Kesselmeier et al.*, 2003; *Kuhn et al.*, 2004; *Holzke et al.*, 2006].

[5] To identify the controlling environmental parameters of monoterpene emission from the predominant deciduous tree species in Europe, we investigated a sunlit branch of European beech (*Fagus sylvatica* L., vegetation area coverage of 7% on a European scale) by means of a dynamic enclosure system. To investigate the potential change of monoterpene emission during two consecutive summer vegetation periods in the years of 2002 and 2003, all measurements were performed under near-natural conditions at a field site within the framework of the ECHO project (Emission and Chemical transformation of biogenic volatile Organic compounds, AFO 2000). To demonstrate the effects of an updated emission factor for European beech in combination with the consideration of a light and temperature controlled monoterpene emission, we applied a species based model simulation on a European scale.

2. Experimental

2.1. Enclosure Studies of European Beech

2.1.1. Site Description

[6] 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 km^2 size that is partially located on the premises of the Research Center Jülich. The location is characterized by moderate climatic conditions, with a mean annual precipitation of 685 mm and an average annual temperature of 10°C. All enclosure measurements were performed at the canopy top by means of a scaffold tower that was 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 the tower site was measured with a plant canopy analyzer (model LAI-2000, Licor, USA) and showed a maximum density of 4.7 at ground level which is quite typical for mid latitude European beech forest (for details, see *Aubrun et al.* [2005

2.1.2. Enclosure Measurements and Plant Material

[7] All enclosure measurements investigating the emission of monoterpenes from European beech (*Fagus sylvatica* L., plant family: *Fagaceae*) were carried out during two intensive field campaigns in the summers of 2002 and 2003. The experiments were conducted by use of an open, dynamic (flow through) enclosure system, that consisted of two identical cuvettes of ~75 l volume each. Each cuvette was made from FEP Teflon foil (Norton, 50 μm thickness, Saint-Gobain Performance Plastics, Germany) that was fully light permeable in the spectral range of 400–700 nm [*Schäfer et al.*, 1992]. Ambient air was filtered from small particles and ozone (Zeflour Teflon filters, 2 μm poresize, Gelman Science, USA and MnO_2 covered copper screens, Ansyco, Germany) and was pumped into the enclosure system by 4 Teflon membrane pumps (model MZ2C/2.4, Vacuubrand, Germany). Flow rates to each cuvette were monitored by flowmeters (model EL-Flow, 50 l min^{-1}, Bronkhorst Hi-Tec, Germany) and were typically adjusted to constant flow rates of 25–35 l min^{-1}, resulting in a total exchange of the enclosure volume every 2 to 3 min. As demonstrated 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 effects of stress (for a detailed description, see *Kesselmeier et al.* [1996, 1997, 1998], *Gut et al.* [2002], and *Kuhn et al.* [2002a, 2002b]).

[8] For the enclosure measurements, the branch was enclosed in the sample cuvette, while the other cuvette remained empty as a reference. Measurements of the empty cuvette system were conducted before or after each experiment, but showed no significant bias between the both enclosures. Monoterpene differences of the empty enclosure system ranged at mixing ratios of 0.0 ± 0.5 ppb in 2002 and at 0.0 ± 0.1 ppb in 2003. Assuming cuvette air flow rates of 35 l min^{-1} these differences correspond to monoterpene exchange rates of 0.00 ± 0.08 μg g^{-1} h^{-1} and 0.01 ± 0.36 μg g^{-1} h^{-1} for European beech investigated in 2002 and 2003, respectively. To prevent the impact of stress effects on the measured VOC exchange, at least ~7 hours of acclimatization time was allowed before the first monoterpene measurements were performed.

[9] The 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 located at the canopy top of a ~160 year old European beech tree. Since the branch was located above the scaffold tower it was sunlit for the whole sunshine period of the day. To demonstrate the light dependence of monoterpene emission from European beech under a daytime temperature regime, the investigated branch was coated by a dark cover during the midday hours of one single measurement day. Leaf samples from the measured branch demonstrated to be sunlit leaves by microscopical and morphological analysis, as well as by investigation of their specific leaf weight (i.e., the investigated leaves were smaller but showed a higher cross section than leaves that were collected from below of the canopy. Therefore the specific leaf weight of the investigated leaves exceeded the specific leaf weight of leaves that were located below the canopy). Leaf area, as well as the dry and fresh weight of the investigated leaves was determined directly after the enclosure experiments that were performed in 2002

and 2003. Leaves of the investigated tree were harvested directly from the measurement branch (experiments performed in 2003) or from a second branch located next to the investigated one (experiments performed in 2002, in the following referred to as reference leaves or branch). In either case, the leaf area (single side plus petiole) was copied or drawn from the enclosed leaves and was calculated by use if a calibrated scanner system (ScanJet IIX with DeskScan II, Hewlett Packard, USA and the Software SIZE, Mueller, Germany). Fresh and dry weight of the original or reference leaves was determined by a microbalance (PM 400, Mettler-Toledo, Germany) before and after drying in an oven (Heraeus, Germany) at 70°C for several days. Thus fresh and dry weight of the measurement branch was determined either directly or was calculated by use of the specific leaf weight of the reference branch (see Table 1).

[10] Micrometeorological parameters were recorded by standard sensors. Photosynthetic active radiation (PAR) was measured outside of the enclosure by the use of two quantum sensors (model SB 190, Licor, USA) that were mounted in horizontal arrangement on top of the branch cuvette but not shading the leaves (one sensor in 2003). Enclosure temperatures of the reference and branch cuvette, as well as ambient temperatures were monitored by Teflon covered thermocouples (0.005″, Chromel-Constantan, Omega, UK). Leaf temperatures were measured on two representative leaves inside of the branch enclosure on the respective upper and lower side of each leaf by application of the same type of thermocouples. All leaf temperatures reported here are given as the average of these four temperature sensors. Exchange rates for CO_2 and water vapor were measured by use of an infrared gas analyzer operated in differential mode (model Li-7000, Licor, USA). To prevent condensation of water vapor within the sampling lines, all tubings downstream of the cuvettes were heated slightly above ambient temperatures. 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, 2002b]. Unless indicated otherwise, the leaf gas exchange rates were normalized to leaf dry weight. The uncertainties for gas exchange rates were assessed by conventional Gaussian error propagation. Environmental parameters preceding the enclosure measurements were monitored by the meteorological station of the Research Center Jülich at about 470 m distance from the measurement site on a second scaffolding tower at a height of 20 m.

2.1.3. Measurement of Volatile Organic Compounds

[11] The 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. VOC samples from the reference and branch cuvette were collected simultaneously in 1–2 hour intervals by the use of three custom made automatic sampling systems that are described in detail by *Kuhn et al.* [2005].

[12] For GC-FID measurements, the samples were collected on Silicosteel cartridges (1/4″ OD, 89 mm length, Restek, USA) that were packed with 130 mg Carbograph 1 (90 m^2 g^{-1}) and 130 mg Carbograph 5 (560 m^2 g^{-1}, 20–40 mesh each, Lara s.r.l., Italy). VOC samples were collected for 30 min at flow rates of 150 ml min^{-1} resulting in a total sampling vo of 4500 ml. Analysis of the samples by GC-FID was performed at the laboratory of the Max Planck Institute for Chemistry 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). Refocusing in advance of the separation of VOC species was accomplished by a small quartz tube packed with 20 mg Carbograph 1 that was kept at −30°C. After its desorption by rapid heating to 280°C, the GC separation 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 total, 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 an exchange rate of 12 ng g^{-1} 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 mixture containing isoprene and several n-alkanes. Unless indicated otherwise, the following paragraphs will report on the total sum of these monoterpene compounds that were measured by GC-FID.

Table 1. Leaf Area, Fresh, and Dry Weight of the Investigated Sunlit European Beech Leaves[a]

	Measurement Period	
	June 2002	July/August 2003
Number of enclosed leaves	117	87
Enclosed leaf area, m^2	0.17[b]	0.14[b]
Enclosed fresh weight, g	32.62[c]	21.33[b]
Enclosed dry weight, g	18.35[c]	10.73[b]
Water content of enclosed leaves, %	44[c]	50[b]
Enclosed leaf dry mass per area, g m^{-2}	108	77

[a]All leaves were harvested directly after the enclosure experiments performed in June 2002 and July/August 2003.
[b]Determined from originally enclosed leaves.
[c]Calculated by use of the specific leaf weight that was measured from a reference branch located next to the investigated one.

[13] VOC 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 m^2 g^{-1}), 60 mg Carbograph 1, and 115 mg Carbograph 5 (20–40 mesh each, Lara s.r.l., Italy). Analysis of these cartridges was carried out in the laboratory of CNR in Rome, Italy. The 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 that was used for GC-MS analysis is given by *Ciccioli et al.* [1992] and *Brancaleoni et al.* [1999].

[14] 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 the GC-MS cartridges. Sabinene decomposition followed a saturation trend, yielding 55% of the initial sabinene amount after a storage time of 7 days. Since the

increase of the above specified decomposition products accounted completely for the observed sabinene decrease, the total sum of the measured monoterpene compounds was not affected by this decomposition. To specify the composition of monoterpene compounds that are emitted from European beech, a correction factor was applied to the relevant compounds taking a cartridge storage time of more than 7 days into account. In contrast, previous experiments performed for the GC-FID cartridges did not indicate a similar decomposition of sabinene on the respective VOC samples. However, during the present study some of the potential decomposition products were not investigated by the GC-FID analysis and assuming a similar decomposition process as observed for the GC-MS cartridges may therefore lead to an underestimation of the total sum of monoterpenes measured by GC-FID of up to 20%.

2.1.4. Emission Algorithms

[15] The emission of monoterpenes from European beech was simulated by two different light and temperature dependent algorithms. The first algorithm applied (in the following referred to as G97) was developed for isoprene emission by *Guenther et al.* [1993, 1995] and *Guenther* [1997]. In previous studies, isoprene emission has been shown to be triggered by light as a result of the close link between its emission and production from photosynthetic precursor compounds. However, several authors demonstrated that the latter algorithm may also be used to calculate the emission of monoterpenes that are released directly upon their production [e.g., see *Kesselmeier et al.*, 1996; *BEMA-Project*, 1997; *Ciccioli et al.*, 1997; *Kuhn et al.*, 2002b; *Kuhn et al.*, 2004].

[16] The G97 algorithm assumes a hyperbolic increase of VOC emissions to light intensity, leading to a saturation effect. With respect to leaf temperature the algorithm assumes enzymatic processes leading to a temperature optimum of the VOC emission at temperatures of 39°C. Within the algorithm, the light dependent term of the G97 function (in the following referred to as C_L) is specified by Formula 1. The temperature dependent term (in the following referred to as C_T) is specified by Formula 2. To calculate the actual VOC emission, both factors (C_L and C_T) are linked by multiplication with a standard emission factor (in the following referred to as SEF) that describes the basal VOC emission at standard light and standard temperature conditions (1000 μmol m^{-2} s^{-1}, 30°C, see Formula 3).

(1) Light dependent term of the G97 function:

$$C_L = \frac{\alpha \cdot C_{L1} \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}}$$

(2) Temperature dependent term of the G97 function:

$$C_T = \frac{\exp\left(\frac{C_{T1} \cdot (T - T_S)}{R \cdot T_S \cdot T}\right)}{C_{T3} + \exp\left(\frac{C_{T2} \cdot (T - T_M)}{R \cdot T_S \cdot T}\right)}$$

(3) Calculation of the actual VOC emission by the G97 function:

$$\text{VOC emission} = \text{SEF} \cdot C_L \cdot C_T$$

(α = 0.0027, C_{L1} = 1.066, C_L = light dependent term of the G97 function, C_T = temperature dependent term of the G97 function, C_{T1} = 95,000 J mol^{-1}, C_{T2} = 230,000 J mol^{-1}, C_{T3} = 0.961, L = actual light intensity (μmol m^{-2} s^{-1}), R = universal gas constant (8.314 J K^{-1} mol^{-1}), SEF = standard emission factor, T = leaf temperature (°K), T_M = 314°K, T_S = 303°K).

[17] The second algorithm (in the following referred to as S97) that was applied to the present data set was developed to describe the emission of monoterpenes from sunflower and European beech as a function of light and temperature by *Schuh et al.* [1997]. In comparison to the G97 function the S97 algorithm assumes also a saturation effect of VOC emission at high light intensities. However, in contrast to the G97 simulation which assumes a hyperbolic increase of VOC emission, the S97 algorithm assumes an allosteric enzyme regulation leading to a sigmoid increase of VOC emission at lower light intensities. This light dependent term (in the following referred to as $C_{L(S)}$) of the S97 algorithm is described by Formula 4. The temperature dependent term, describing the instantaneous emission of monoterpenes, is identical to the G97 function (see C_T, Formula 2). In addition to the instantaneous emission of monoterpenes, the original S97 function assumes also a release of VOCs from unspecific storage pools (Formula not shown). However, in the present study a release of monoterpenes from unspecific storage pools was not detectable. Therefore the storage pool term of the S97 algorithm was neglected, as recommended for sabinene emission from European beech by *Schuh et al.* [1997]. To calculate the actual VOC emission by the S97 function, the respective terms were linked by multiplication with a standard emission factor (in the following referred to as Φ_{LT}) as described by Formula 5, yielding a modified form of the original S97 algorithm that neglects a monoterpene release from storage pools.

(4) Light dependent term of the S97 function:

$$C_{L(S)} = C_{L1} \cdot \left(\frac{\alpha \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}}\right)^2$$

(5) Calculation of the actual VOC emission by the S97 function:

$$\text{VOC emission} = \Phi_{LT} \cdot C_{L(S)} \cdot C_T$$

(α = 0.0027, C_{L1} = 1.066, $C_{L(S)}$ = light dependent term of the S97 function, C_T = temperature dependent term of the G97 function, L = actual light intensity (μmol m^{-2} s^{-1}), Φ_{LT} = standard emission factor).

[18] As shown by Formulas 3 and 5, both standard emission factors (SEF or Φ_{LT}) can be calculated from the slope of linear regression of the measured VOC emission to the product of the light and temperature dependent terms of the respective algorithm (note that standard conditions correspond to 1000 μmol m^{-2} s^{-1} and 30°C for both algorithms). Since both algorithms assume a cessation of VOC emission in the dark, a linear regression without bias (y = 0) was used for the calculation of both emission factors.

2.2. Species-Based Model Simulation: Calculation of European VOC Emission

[19] According to *Guenther et al.* [1995], *Guenther* [1997], and *Simpson et al.* [1999], there are two approaches to assign emission factors to an ecosystem scale.

[20] 1. The first method assigns a landscape type to each location within a model domain. An emission potential, derived by micrometeorological measurement techniques or from general assumptions of the species distribution, is then associated with each landscape type.

[21] 2. The second approach requires an estimate of the composition of plant species for each location in the respective 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.

[22] 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. As described by these authors the assignment of ecosystem specific emission factors is particularly effective for areas with high species diversity such as a tropical rainforest. In contrast, for areas with low species diversity a species specific assignment of emission factors is encouraged [*Guenther et al.*, 1995; *Simpson et al.*, 1999]. Accordingly, recent studies that investigated VOC emissions in Europe favored a species based model simulation due to the low species diversity that is present on the European continent [e.g., *Simpson et al.*, 1999; *Lenz et al.*, 2001; *Solmon et al.*, 2004].

[23] 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 (in the following referred to as G95Ols). The G95Ols algorithm is normally applied for global scale studies [*Ganzeveld et al.*, 2002] and uses the *Olson* [1992] global ecosystem database, which distinguishes 72 ecosystems at a 0.5 × 0.5 grid resolution. Global surface cover properties were obtained from a 5-year climatology of monthly NDVI (Normalized Differential Vegetation Index) satellite data [*Gutman et al.*, 1995]. In this simulation VOC emissions are calculated as a function of ecosystem specific emission factors, surface radiation, temperature, as well as from the foliar density and its vertical distribution. To obtain the required meteorological data, we have applied the temperature and net radiation output fields of the atmospheric circulation model ECHAM T106 (~125 km resolution, for details see *Roeckner et al.* [1996]) for the month of July at 6-hour time intervals. The vertical distribution of foliar density 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].

[24] To demonstrate the potential impact of European beech on the monoterpene emission on local and/or European scales 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 an average emission factor. The latter average factor amou o 15 μg g^{-1} h^{-1} and was calculated from the standard emission factors (G97) reported by *Moukhtar et al.* [2005], *Spirig et al.* [2005], and from the present study. Moreover, standard emission factors (S97) specified by *Schuh et al.* [1997] and *Kahl et al.* [1999] were used for the calculation. These latter standard emission factors were normalized to standard conditions of 1000 μmol m^{-2} s^{-1} and 30°C by application of the G97 function. Conversion to a leaf dry weight basis was performed by application of the average specific leaf weight measured during the present study. In this way weighted average fluxes were calculated, specifically taking into consideration the fraction of European beech area coverage in every 0.5 × 0.5 grid of the model simulation. Emission factors of the residual vegetation area coverage were calculated with the default G95Ols ecosystem specific emission factor (e.g., 0.9 μg g^{-1} h^{-1} for temperate forest ecosystems). The relative difference of this species based model simulation (in the following referred to as G95FS simulation) to the default G95Ols model is calculated according to Formula 6 (note that the reference value refers to an average of the G95Ols and G95FS simulation): (6) Relative difference to the G95Ols simulation:

$$100 \times \frac{G95FS - G95Ols}{(G95FS + G95Ols)/2}$$

(G95FS = species based modeling of European monoterpene emissions (calculated only as a function of temperature), G95Ols = default ecosystem based modeling of European monoterpene emissions (calculated only as a function of temperature)).

[25] In both simulations (G95Ols and G95FS) the emission of monoterpenes from European beech was calculated only as a function of temperature. To demonstrate the effect of light on the European monoterpene budget, we introduced radiation intensity as an additional controlling parameter to the G95FS simulation and referred to this simulation in the following as G95FSlight. Relative differences to the default G95Ols assumption were calculated in analogy to Formula 6.

3. Results

3.1. Results of the Enclosure Studies

3.1.1. Diurnal Course of Monoterpene Emission and Plant Physiology

[26] Figure 1 shows the course of micrometeorological and physiological parameters that were measured during the enclosure of European beech in June 2002 and July/August 2003. Regarding the course of net CO_2 assimilation, transpiration, and stomatal conductance (data not shown), 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 episode. Only a few days were cloudy during both campaigns and saturation of photosynthesis (at light intensities >400–500 μmol m^{-2} s^{-1}, data not shown) was reached for most of the days. Leaf temperature reached maximum readings of 44°C during the complete measurement period of June 2002 and July/August 2003 and was several times above the temperature optimum of the net CO_2 assimilation (at about 25°C, data not shown).

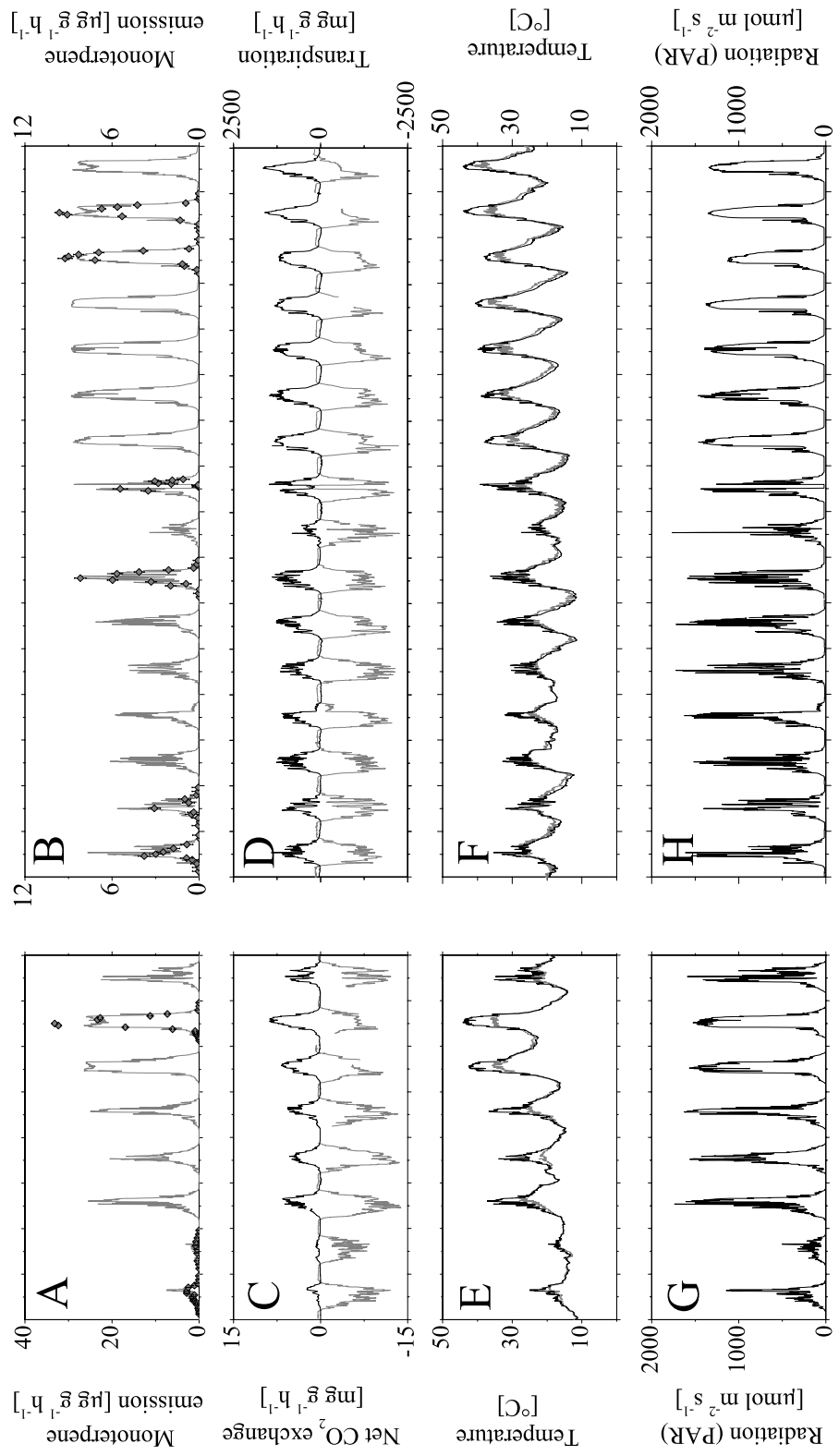

Figure 1. Diurnal course of trace gas exchange of an enclosed branch of European beech and micrometeorological parameters measured during both field experiments in June 2002 (left) and July/August 2003 (right). Positive numbers indicate emission of the respective compound, while negative numbers indicate deposition. (a, b) Monoterpene emission that was measured by GC-FID analysis is indicated by the grey diamonds. Monoterpene emission that was calculated by application of the G97 algorithm (year 2002: average SEF = 13 µg g^{-1} h^{-1}, year 2003: average SEF = 4 µg g^{-1} h^{-1}) is indicated by the grey solid line. The calculated error of monoterpene emission is given by the error bars. If no error bars are visible they reside within the diameter of the plotted symbol. Note the different scales of monoterpene emission measured in 2002 and 2003. (c, d) Diurnal course of net CO_2 exchange (grey solid line) and transpiration (black solid line). (e, f) Ambient temperatures (grey solid line) and leaf temperatures (black solid line). (g, h) Photosynthetic active radiation (black solid line).

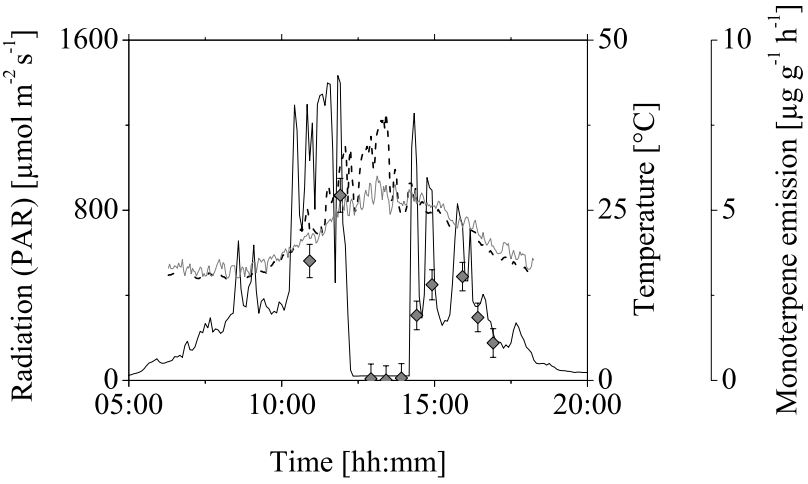

Figure 2. Course of photosynthetic active radiation (black solid line), leaf temperature (black dashed line), and ambient temperature (grey solid line) during the artificial shading of the branch enclosure in July 2003. Monoterpene emission measured before, during and after the artificial darkening is indicated by the grey diamonds. The calculated error of the monoterpene exchange rates is given by the error bars.

As shown in Figure 1, the midday leaf temperatures exceeded ambient temperatures. Ambient temperatures reached maximum values of 36 and 42°C in 2002 and 2003, respectively. Mean daytime differences of these ambient temperatures and leaf temperatures ranged <3°C but amounted up to 12°C in extreme cases. In close relation to the course of PAR and leaf temperature, also monoterpene emission from European beech exhibited pronounced diurnal characteristics during both years. As shown in Figure 1 monoterpene exchange was measured typically in 1–2 hour intervals during 3 and 6 days in June 2002 and July/August 2003, respectively. Daytime monoterpene emission for the sum of 10 individual monoterpene compounds reached maximum exchange rates of 33.2 $\mu g\ g^{-1}\ h^{-1}$ in June 2002 and 9.6 $\mu g\ g^{-1}\ h^{-1}$ in July/August 2003 and could be simulated by the light-dependent G97 algorithm. Nighttime monoterpene emission was always close to the detection limit (emission $\leq 80\ ng\ g^{-1}\ h^{-1}$ for both experiments).

3.1.2. Shading Experiment

[27] To demonstrate the light dependency of monoterpene emission under a daytime temperature regime, an artificial shading experiment was conducted during one measurement day in July 2003 (see Figure 2). Setting up the artificial darkening of the enclosure started at noon and was completed within 30 min (remaining light intensity 20–21 $\mu mol\ m^{-2}\ s^{-1}$). 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 (the maximum difference of leaf temperatures that were measured during the shading period amounted to 13°C, the maximum difference between ambient temperature and leaf temperature amounted to 11°C during the respective period). VOC exchange that was measured before the artificial shading ranged at exchange rates of 3.5 and 5.4 $\mu g\ g^{-1}\ h^{-1}$. Thirty minutes after complete coverage of the cuvette, monoterpene exchange rates dropped to values of $\leq 0.1\ \mu g\ g^{-1}\ h^{-1}$ and remained near zero for the whole time of darkening =). As soon as the artificial cover was removed, monoterpene emission progressed with its conventional diurnal characteristics, yielding exchange rates ranging between 1.9 and 3.0 $\mu g\ g^{-1}\ h^{-1}$.

3.1.3. Monoterpene Emission as a Function of Light and Temperature

[28] According to the diurnal characteristics of monoterpene emission and the results obtained by the artificial shading experiment, the dependency of monoterpene release on irradiation is evident. Moreover, nighttime exchange rates near the detection limit eliminate an exclusive role of leaf temperature as a controlling factor for the release of monoterpenes from European beech. Therefore monoterpene exchange rates were correlated to photosynthetic active radiation and leaf temperature (see Figure 3). The light dependence of monoterpene emission rates (see Figures 3a and 3c) exhibited a similar function as observed for the net CO_2 exchange rates (data not shown), yielding a saturation trend at radiation intensities of >500 $\mu mol\ m^{-2}\ s^{-1}$. With respect to leaf temperatures, monoterpene emission revealed no optimum and increased exponentially with leaf temperature up to 43°C (see Figures 3b and 3d).

[29] As the previous results demonstrated a correlation of monoterpene emission to light and temperature, standard emission factors (SEF) were calculated by application of the G97 algorithm. The calculation of these standard emission factors was obtained from the slope of linear regression of the measured VOC emission versus the product of C_L and C_T. Similarly, a standard emission factor (Φ_{LT}) was calculated by application of the modified version of the S97 function that neglected the storage pool term of the algorithm (see Figure 4).

[30] The standard emission factors that were obtained for monoterpene emission measured by GC-FID ranged at 12.9 and 4.1 $\mu g\ g^{-1}\ h^{-1}$ in 2002 and 2003 by application of the G97 function. Utilization of the leaf area as a reference of monoterpene emission even increased the difference between the standard emission factors of 2002 and 2003. This was induced by differences of the leaf mass per area index that was measured in both years (see Table 1). Nevertheless, the standard emission factors that were calculated for

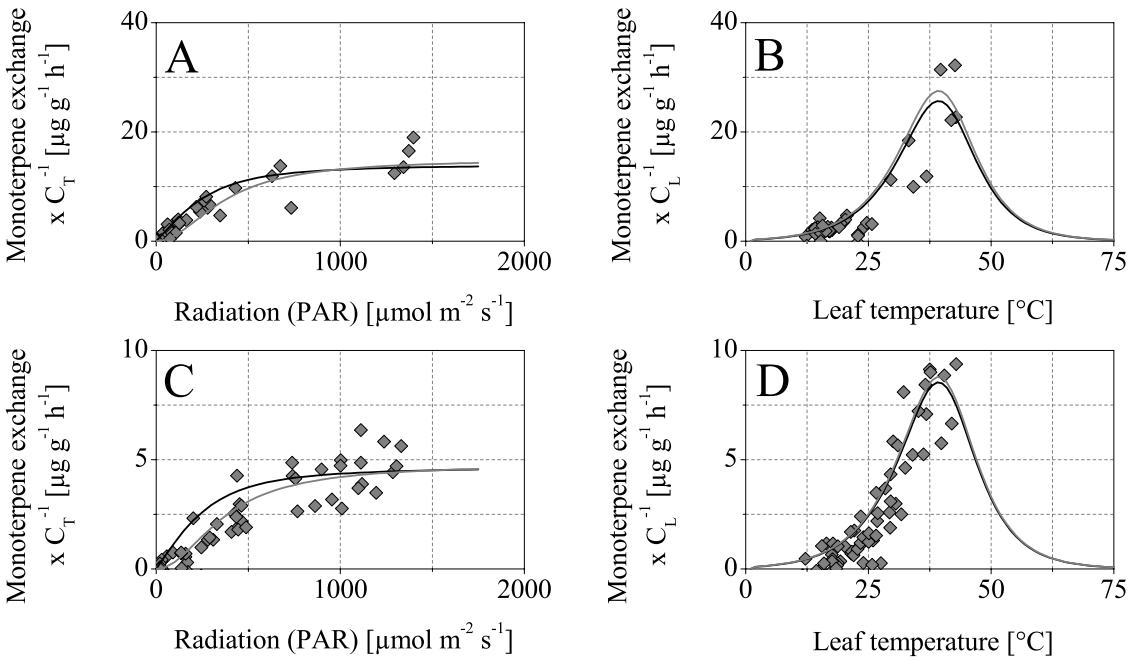

Figure 3. Light (left) and temperature dependence (right) of the monoterpene emission by *Fagus sylvatica* L.. (a, b) Monoterpene emission measured in June 2002 and (c, d) in July/August 2003. Monoterpene emission measured by GC-FID analysis is indicated by the grey diamonds. Note that the respective exchange rates are normalized with the relevant function of the G97 algorithm (i.e., the light dependence of VOC emission is normalized with the temperature function and vice versa) The respective function of the G97 algorithm is given by the black line. The respective function of the modified S97 algorithm is given by the grey line.

individual measurement days within one growing season were consistent with each other. Differences between these individual factors are much smaller than the differences observed between 2002 and 2003 (see Table 2). Application of the S97 function resulted in similar integrated standard emission factors for both measurement years (i.e., 14.1 µg g^{-1} h^{-1} in 2002 and 4.5 µg g^{-1} h^{-1} in 2003) than application of the G97 function. As observed for individual measurement days, the difference between the G97 and S97 standard emission factors can become substantial only in case of low radiation intensities.

[31] As shown by Figure 4, the correlation coefficients that were obtained from the linear fit of VOC emission versus the S97 function showed slightly better results, than the correlation to the G97 function. The latter effect was induced by the diurnal progression of monoterpene emission that is shown in detail by Figure 5. As demonstrated by this Figure the light and temperature dependency of monoterpene emission was observed for all analyzed compounds with exception of tricyclene that scattered at exchange rates <1 ng g^{-1} h^{-1}. Sabinene was shown to be the predominant monoterpene compound emitted from European beech. As shown by Figure 5, the monoterpene emission calculated by the G97 function fitted well to the measured midday and afternoon monoterpene exchange rates, but the morning and evening exchange rates were generally lower than calculated by the latter algorithm. Application of a sigmoid increase with light intensity (as assumed by the S97 function) resulted in a better reproducibility of the observed data in the early morning hours (<1100 LT) due to a small time lag phase in the onset of monoterpe ission. However, the monoterpene emission measured in the early evening was slightly underestimated by the S97 function.

3.2. Results of the Species-Based Model Simulation

[32] In the global model of *Guenther et al.* [1995] distinct emission factors have been assigned to various ecosystem types. In this simulation the current monoterpene emission factors that are assigned to temperate mixed forests or temperate deciduous forest ecosystems amounted to 0.9 µg g^{-1} h^{-1}. Consequently, the mean European monoterpene emission flux (domain 10°W–30°E and 35°N–60°N, grid resolution 0.5 × 0.5) that is calculated for the month of July by the latter approach (in the following referred to as G95Ols simulation) reached carbon amounts of 695 Gg month^{-1} in total.

[33] Figure 6a shows the relative increase of monthly mean monoterpene emission in relation to the latter G95Ols assumption if the spatial distribution of *Fagus sylvatica* L. is specifically considered. The obtained flux is calculated from the flux using the default emission factor of the G95Ols assumption (i.e., 0.9 µg g^{-1} h^{-1}) and the flux based on an updated average monoterpene emission factor for European beech (i.e., 15 µg g^{-1} h^{-1}), yielding a weighted average emission factor that considers the respective vegetation area coverage of European beech in every 0.5 × 0.5 grid of the model simulation. As shown by Figure 6a, consideration of this weighted average emission factor for the month of July resulted in a significant increase of the European monoterpene emission. With the latter simulation (in the following referred to as G95FS simulation) carbon fluxes of 1067 Gg month^{-1} were obtained for the European

Table 2. Standard Emission Factors (1000 μmol m^{-2} s^{-1}; 30°C) Calculated for Monoterpene Emission From European Beech[a]

Measurement	SEF, μg g^{-1} h^{-1}	Φ_{LT}, μg g^{-1} h^{-1}	Maximum PAR, μmol m^{-2} s^{-1}	Maximum Leaf Temperature, °C
12 Jun 2002	12.7	17.4	674	21
13 Jun 2002	9.7	26.9	164	17
18 Jun 2002	12.9	14.1	1398	43
23 Jul 2003	3.1	3.5	1286	31
24 Jul 2003	2.9	3.4	955	30
29 Jul 2003	5.3	5.8	1237	32
5 Jul 2003	4.4 (5.7)	4.8 (6.2)	1119	38
6 Jul 2003	3.8	4.2	1331	43

[a]Standard emission factors were calculated by application of the G97 (SEF) and S97 (Φ_{LT}) function integrating all VOC samples that were collected during the respective measurement days. The emission factors were calculated from the sum of 10 individual monoterpene compounds measured by GC-FID analysis or GC-MS analysis (data in parenthesis). The maximum values of photosynthetic active radiation (PAR) and leaf temperature are given as 30 min average values for each measurement day.

domain, yielding an increase of the European monoterpene emission by 54% in relation to the default G95Ols simulation. On a local scale, the consideration of the weighted average emission factor resulted in significant increases of >100% if relative differences of the European monoterpene emission were calculated according to Formula 6.

[34] However, in both simulations (G95Ols and G95FS) the monoterpene emission was only calculated as a function of temperature. By also considering the role of light as a controlling parameter of monoterpene emission from European beech the total amount of monoterpene release is reduced significantly. In the latter assumption (in the following referred to as G95FSlight, see Figure 6b) the total European carbon flux for the month of July amounted to 809 Gg $month^{-1}$, representing an increase of the European monoterpene emission by 16% in relation to the default G95Ols simulation. Nevertheless, as shown by Figure 6b, relative increases >100% were observed on a local scale, if relative differences of the European monoterpene emission were calculated in analogy to Formula 6.

4. Discussion

4.1. Enclosure Studies of European Beech

4.1.1. Monoterpene Emission as a Function of Light and Temperature

[35] In analogy to the monoterpene emission pattern that was observed for other tree species of the plant family *Fagaceae* [e.g., *Staudt and Seufert*, 1995; *Bertin and Staudt*, 1996; *Kesselmeier et al.*, 1996; *Loreto et al.*, 1996; *BEMA-Project*, 1997; *Ciccioli et al.*, 1997; *Staudt and Bertin*, 1998; *Niinemets et al.*, 2002a; *Owen et al.*, 2002] and the laboratory experiments conducted by *Schuh et al.* [1997], monoterpene emission from European beech was shown to be a function of light and temperature.

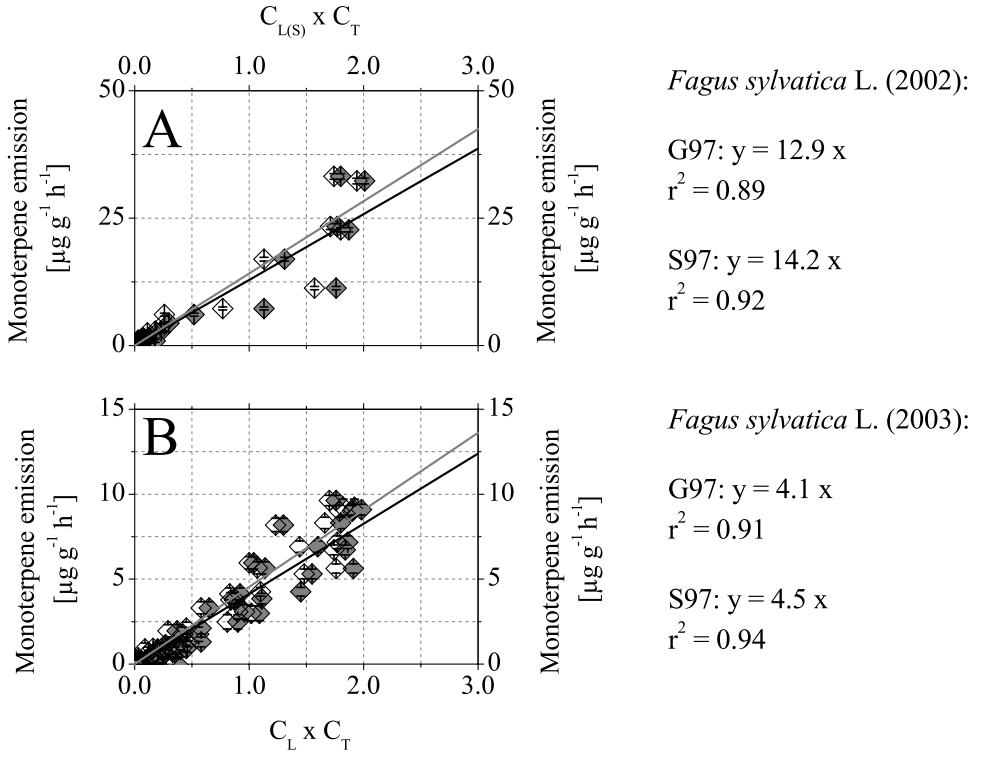

Figure 4. Monoterpene emission as a function of the G97 and the modified S97 algorithm. (a) Monoterpene emission from *Fagus sylvatica* L. measured in 2002 and (b) in 2003. Grey solid diamonds indicate the regression of monoterpene emission versus the product of the light and temperature function of the G97 algorithm (bottom x-axis ($C_L \times C_T$)). The black line gives the linear fit of the respective regression. Hollow diamonds indicate the regression of monoterpene emission versus the light and temperature function of the modified S97 algorithm (top x-axis ($C_{L(S)} \times C_T$)). The grey line indicates the linear fit of th ssion. The respective functions of the linear fit are given on the right panel.

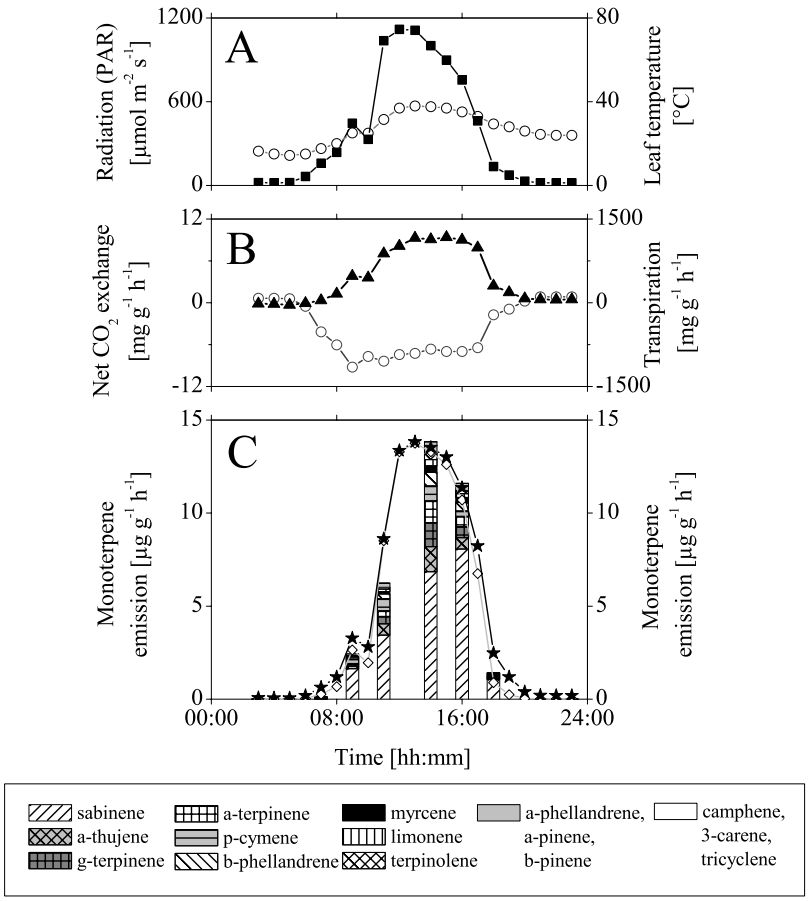

Figure 5. Course of micrometeorological and physiological parameters as well as monoterpene emission measured during one single day in August 2003. (a) Course of PAR (black squares plus black line) and leaf temperature (hollow circles plus grey line). (b) Diurnal course of net CO_2 exchange (hollow circles plus dark grey line) and transpiration (black solid triangles plus black line). Note that negative values indicate deposition of the respective compound and that micrometeorological and physiological data show the appropriate 30 min average corresponding to the VOC sampling time. (c) Diurnal course and composition of monoterpene emission. The data show the monoterpene emission that was measured by GC-MS analysis (stacked bars, for caption see graph), the respective emission calculated by the G97 algorithm (black stars plus black line, SEF = 7.1 µg g^{-1} h^{-1}), and the modified S97 function (hollow diamonds plus grey line, Φ_{LT} = 7.4 µg g^{-1} h^{-1}). Note that the monoterpene emission measured by GC-MS analysis represents the sum and apportionment of 15 different monoterpene compounds, yielding higher standard emission factors than for the GC-FID analysis that represents the sum of only 10 different monoterpene compounds (see Table 2 for a comparison of both methods).

Regarding the correlation of monoterpene emission with light intensity, a saturation trend was observed at radiation intensities of >500 µmol m^{-2} s^{-1} in both years. The results are in good agreement to previous studies that demonstrated that monoterpene emission from *Quercus ilex* L. was also a function of radiation intensity [see, e.g., *BEMA-Project*, 1997].

[36] A temperature optimum was not reached in the present study and monoterpene emission increased exponentially with leaf temperature up to a maximum temperature 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 leads to an acidification of the stromal pH, a decrease in photosynthesis could favor the emission of monoterpenes since the pH optima of monoterpene synthases range between pH values of 6 and 7 [*Bohlmann et al.*, 1998; *Fischbach et al.*, 2000; *Niinemets et al.*, 2002b].

[37] Several authors discussed also the relevance of unspecific storage pools for the emission of monoterpenes from *Quercus sp*. [*Loreto et al.*, 1996; *Ciccioli et al.*, 1997;

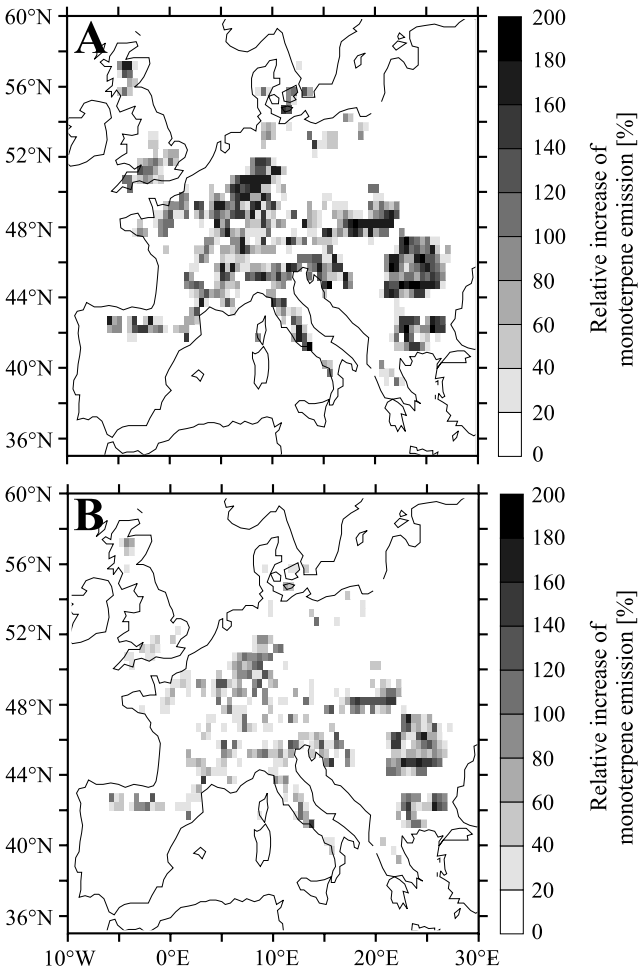

Figure 6. Increase of the mean European monoterpene emission flux for the month of July in relation to the default G95Ols simulation. Note that relative increases of monoterpene emission were calculated in analogy to Formula 6. (a) Relative increase of the mean monoterpene emission if an updated average standard emission factor is considered as a function of temperature and is combined with the spatial distribution of European beech (G95FS simulation). (b) Relative increase of the mean monoterpene emission if an average standard emission factor is considered as a function of light and temperature and is combined with the spatial distribution of European beech (G95FSlight simulation).

Delfine et al., 2000; *Loreto et al.*, 2000; *Niinemets et al.*, 2002b; *Niinemets and Reichstein*, 2002; *Niinemets et al.*, 2004]. We cannot exclude a relevance of such storage pools for the emission of monoterpenes from *Fagus sylvatica* L., particularly since *Schuh et al.* [1997] reported significant night time emission of α-pinene at emission rates of 24.5 $\mu g\ m^{-2}\ h^{-1}$. However, comparable night time emissions should have been detectable in the present study but were not observed. Moreover, the artificial darkening experiment demonstrated a cessation of monoterpene emission in the absence of light. 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 af rkening in a time period of 30 min, although other authors have reported a persistence of monoterpene emission from unspecific storage pools for several hours to days [*Loreto et al.*, 1996; *Ciccioli et al.*, 1997; *Loreto et al.*, 2000; *Niinemets et al.*, 2002a; *Niinemets and Reichstein*, 2002]. A rapid depletion of potential storage pools would explain the lack of night time emission in the present study, since the time resolution of monoterpene measurements was typically 1–2 hours. However, the experiments clearly demonstrated that monoterpene emission from storage pools may be neglected for the investigated branch of European beech.

[38] According to these results, the measured monoterpene emission was compared to the G97 algorithm [*Guenther et al.*, 1993, 1995; *Guenther*, 1997] and to the modified version of the S97 algorithm [*Schuh et al.*, 1997]. Both functions generated a good agreement to the measured monoterpene emission. Correlation coefficients of the measured monoterpene emission to the product of the respective light and temperature dependent terms ranged from 0.89 to 0.94. The slightly better correlation factor obtained for the S97 algorithm was a result of the sigmoid shape of the light dependent term of the S97 function. Regarding the diurnal progression of monoterpene emission under clear sky conditions, a significant delay of monoterpene emission was observable in the early morning (in relation to the onset of photosynthesis), a phenomenon that has previously been described for other monoterpene emitting broad leaf tree species as well [e.g., *Ciccioli et al.*, 1997]. Regarding the correlation of measured monoterpene emission to light intensity for each single measurement day revealed that this effect resulted in lower monoterpene exchange rates in the early morning hours than during the afternoon (at comparable light intensity and leaf temperature) and consequently in a hysteretic structure. Considering the experiments that were performed on European beech during 2002 and 2003 this observation was noticed for 4 measurement days in total and was confirmed also for tropical tree species by the reevaluation of previous datasets (U. Kuhn et al., unpublished data, 2004). According to this dependency of monoterpene emission on the respective time of day, the sigmoid increase of the S97 algorithm resulted in a better reproducibility of monoterpene emissions measured during the early morning hours. However, a sigmoid decrease in the afternoon was not observable by the measured monoterpene emission. Therefore the simulated emission (S97) underestimated the measured monoterpene exchange in the afternoon.

4.1.2. Variability of Standard Emission Factors Observed for the Emission of Monoterpenes From European Beech

[39] A further goal of the present study was to investigate the potential change of monoterpene emission from European beech in the summer season of 2 consecutive years. 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., *Street et al.*, 1997; *Peñuelas and Llusia*, 1999; *Llusia and Peñuelas*, 2000; *Sabillon and Cremades*, 2001; *Fischbach et al.*, 2002; *Niinemets et al.*, 2002a; *Staudt et al.*, 2002; *Staudt et al.*, 2003]. As reported by *Peuke et al.* [2002], also European beech is known to develop ecotype specific species that are adapted to the climatic conditions of

the habitat they live in. To eliminate any tree to tree or branch to branch variability of monoterpene emission, all measurements were conducted on the same single branch of *Fagus sylvatica* L. The measurements were performed as close as possible to natural conditions, although we realize that natural conditions are never matched applying an enclosure system. Within this respect, one of the most important factors might have been an artificial increase in leaf temperatures that may have affected plant physiology as well as monoterpene emission inside of the enclosure system. However, average, maximum and minimum leaf temperatures reached similar values during both experiments performed in June 2002 and July/August 2003.

[40] As shown by Table 2, the differences of the standard emission factors that were observed for individual days during one growing season were much smaller than the differences of the standard emission factors that were observed between both measurement years. Moreover, the standard emission factors obtained with the S97 function reached higher values than the ones obtained from the G97 function. Nevertheless, except for days with only low radiation intensity, both values were comparable with each other.

[41] A statistical analysis revealed that the standard emission factors (G97) that were calculated for single measurement days within one vegetation period exhibited no correlation to the actual minimum, maximum or average leaf-temperature that was observed during the respective measurement day (correlation coefficients <0.36 (2002) and <0.16 (2003)). Regarding the correlation of the standard emission factors to previous ambient temperatures (integrated over 7 days) revealed a good correlation for the measurements performed in 2003 (correlation coefficient 0.83). Here, increasing temperatures resulted in a decrease of monoterpene emission factors. However, this effect was not observed during the measurements performed in 2002.

[42] Although the actual temperature conditions that were measured during the enclosure experiments of June 2002 and July/August 2003 were comparable, the preceding average ambient temperatures differed from each other (measured 30 days prior to the beginning of the respective experiments in 2002 and 2003, i.e., 16°C ± 2°C in Mai/June 2002 and 20°C ± 3°C in June/July 2003). As observed by *Staudt et al.* [2003], the acclimatization time of standard emission factors to previous temperatures was highly variable and ranged between 3 days and 3 weeks for *Quercus ilex* L. However, these experiments can not explain the observed differences between the standard emission factors that were measured in June 2002 (SEF 13 $\mu g\ g^{-1}\ h^{-1}$) and in July/August 2003 (SEF 4 $\mu g\ g^{-1}\ h^{-1}$), since *Staudt et al.* [2003] reported a positive correlation between previous temperatures and SEF. In contrast, during the present study higher daytime temperatures (integrated over 30 days) were observed in the days preceding the measurements performed in 2003, when exchange rates were much smaller. Thus other effects may have dominated the observed variability in standard emission between the experiments conducted in 2002 and 2003.

[43] One of these effects might have been a long lasting drought period that preceded the measurements in 2003 (amount of rainfall preceding the measurement period: 11 mm day^{-1} (May–June 2002) and 1 mm day^{-1} (June–July 2003)) and resu a significant reduction of average photosynthesis during the latter campaign by 9%. Since the reduction of photosynthesis and transpiration have been reported as drought indicators for European beech [*Thomas*, 2000; *Peuke et al.*, 2002], we assume long term effects of drought in 2003. Also *Bertin and Staudt* [1996] and *Staudt et al.* [2002] reported a reduction of monoterpene emission paralleled by a reduction of photosynthesis due to drought effects. However, during the present study transpiration reached significant higher rates in July/August 2003 and increased on average by 48%. Consequently, as the predawn leaf water potential was not recorded during the present study, a potential drought effect on European beech can not be demonstrated clearly.

[44] As measurements started in June during the 2002 campaign but were conducted in July/August in 2003, phenological effects on monoterpene emission may also confer a reasonable explanation for the different emission capacity observed during both years. 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. The results are in agreement to experiments performed by *Holzke et al.* [2006], who investigated European beech trees at the same measurement site like the present study. Also these authors observed a decline of standard emission factors within the course of the vegetation period. However, as observed during the present study, the standard emission factors tend to be higher for the year 2002, than the standard emission factors observed for the year 2003.

[45] In contrast to older literature data, the present study revealed *Fagus sylvatica* L. as being a strong monoterpene emitter. Table 3 gives an overview of experiments that were conducted earlier to examine monoterpene emission from European beech. Several 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. In contrary, 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). Recent flux studies conducted by *Spirig et al.* [2005] in July 2003 at the same forest site as in the present study indicated even higher standard emission factors for *Fagus sylvatica* L.. Finally, *Moukhtar et al.* [2005] reported standard emission factors that exceeded the ones calculated by the present study by a factor of 3. Although seasonal effects may confer an explanation regarding the variations between these different studies, they revealed the wide range of monoterpene standard emission factors that can be assigned to European beech trees.

4.2. Species-Based Model Simulation: Implications for the European Budget of Monoterpene Emission

[46] European beech is known to be the predominant deciduous tree species that is present on a European scale

Table 3. Monoterpene Emission From European Beech As Reported By Several Authors[a]

Reference	Monoterpene Emission		Comment
	$\mu g\ g^{-1}\ h^{-1}$	$\mu g\ m^{-2}\ h^{-1}$	
Hewitt and Street [1992]	bdl	bdl	ldm, a (young/adult), t (−), r (max. 900 $\mu mol\ m^{-2}\ s^{-1}$), s (−)
Steinbrecher et al. [1993]	-	∼0.49	e, l, a (2 years), t (2−14°C), r (max. 600 $\mu mol\ m^{-2}\ s^{-1}$), s (−)
König et al. [1995]	0.19	-	e, f, a (adult), t (20°C), r (−), s (August and September)
Tollsten and Müller [1996]	0.25	-	e, f, a (adult), t(−), r (−), s (May−September)
Schuh et al. [1997]	[8*]	414	e, l, a (−), Φ_{LT} at t (norm. 25°C), r (norm. 1000 $\mu mol\ m^{-2}\ s^{-1}$), s (−)
Kahl et al. [1999]	[8*]	284	e, l, a (6 years), t (norm. 25°C), r (norm. 300 $\mu mol\ m^{-2}\ s^{-1}$), s (−)
Spirig et al. [2005]	10	[930*]	ec, f, a (∼160 years), t (norm. 30°C), r (norm. 1000 $\mu mol\ m^{-2}\ s^{-1}$), s (July)
Moukhtar et al. [2005]	44	[4092*]	e, f, a (∼80 years), t (norm. 30°C), r (norm. 1000 $\mu mol\ m^{-2}\ s^{-1}$), s (May and June)
This study	4−13	334−1415	e, f, a (∼160 years), t (norm. 30°C), r (norm. 1000 $\mu mol\ m^{-2}\ s^{-1}$), s (June/July and August)

[a]Abbreviations: [a] age of tree, [bdl] below detection limit, [e] enclosure, [ec] eddy covariance flux measurement, [f] field experiment, [l] laboratory experiment, [ldm] leaf disc method, [max] maximum, [norm] normalized by the authors to, [r] radiation, [s] season, [t] temperature, [−] not specified, [*] normalized to the average specific leaf weight measured during the present study and by the G97 algorithm to standard conditions of 1000 $\mu mol\ m^{-2}\ s^{-1}$ and 30°C.

(vegetation area coverage 7%, domain 10°W−30°E and 35°N−60°N). Currently monoterpene emission factors that are assigned to beech forest or to temperate forest ecosystems account only to 0.3 to 0.9 $\mu g\ g^{-1}\ h^{-1}$ [see *Olson*, 1992; *Guenther et al.*, 1995; *Simpson et al.*, 1999; *Solmon et al.*, 2004]. Although several studies indicated much higher monoterpene emission factors for European beech [*Schuh et al.*, 1997; *Kahl et al.*, 1999; *Moukhtar et al.*, 2005; *Spirig et al.*, 2005], these factors were not implemented in updated model simulations that calculate the European budget of monoterpenes. Likewise, a light dependent emission of monoterpenes was not considered for European beech. Owing to its broad geographical distribution, the impact of consideration of a higher monoterpene emission factor for European beech on the European monoterpene budget is evident.

[47] While consideration of the default ecosystem emission factors of the G95Ols simulation resulted in European monoterpene emission fluxes of 695 Gg $month^{-1}$, implementation of an updated weighted average emission factor resulted in an increase of 54% with respect to the latter assumption (G95FS simulation: monoterpene emission flux = 1067 Gg $month^{-1}$). Owing to a missing emission of monoterpenes at night, the additional application of light as a controlling parameter of monoterpene emission resulted in an increase of only 16% with respect to the G95Ols simulation (G95FSlight simulation: monoterpene emission flux = 809 Gg $month^{-1}$). Although the default ecosystem emission factors of temperate forest ecosystems (i.e., 0.7 to 0.9 $\mu g\ g^{-1}\ h^{-1}$) that were implemented by the G95Ols and G95FS/G95FSlight simulations, considered also the fraction of monoterpenes that are emitted from European beech, its fraction to the weighted average emission factor that was assigned to the G95FS and G95FSlight simulations may be neglected.

[48] In both simulations (G95FS and G95FSlight) the consideration of the updated weighted average emission factor resulted in significant increases of >100% on a local scale, according to the respective vegetation area coverage of European beech trees. Within this context, it has to be noted that these calculations are still a lower bound estimate, since not the original G95Ols simulation was specified as a reference, but the average of the G95Ols and the G95FS (or G95FSlight) simulation (see Formula 6). Consequently, the consideration of the G95Ols simulation as a reference, would lead to even higher relative increases in the local European monoterpene emission. Moreover, it has to be noted, that in the FSlight simulation, *Fagus sylvatica* L. was the only tree species that was assigned to light dependent monoterpene emissions. Taking into account, that other broad leaf tree species may emit monoterpenes as a function of light and temperature as well, significant higher relative increases should be expected. However, in both simulations the reported increase in the European monoterpene emissions may result from the implementation of the updated average emission factor as well as from the consideration of a more detailed spatial distribution of a specific land cover type as described by several authors [*Guenther*, 1997; *Lenz et al.*, 2001; *Solmon et al.*, 2004].

[49] The results obtained by the various model simulations demonstrated that consideration of the updated average standard emission factor for European beech resulted in a significant increase regarding the European budget of monoterpene emissions. Although the increase in the European budget is small considering all uncertainties involved (e.g., biomass estimates and using the surface- versus the actual canopy or leaf temperature) it is systematic. However, the results reflect the simulations for the month of July with high radiation intensity and temperature. Consequently, regarding a seasonal development of emission factors and climate, they may reflect an upper range impact of the observed *Fagus sylvatica* L. emission rate and light dependence for the European monoterpene budget.

5. Conclusion

[50] The results obtained in the present study clearly demonstrated the light dependence of monoterpene emission from European beech. Consideration of a time lag phase in the onset of monoterpene emission in the early morning (as simulated by the S97 algorithm) resulted in better results than consideration of a hyperbolic increase with light intensity (as assumed by the G97 function). However, both algorithms generated a good agreement with the measured monoterpene emission.

[51] The present study may indicate also the impact of a more detailed spatial distribution of a specific land cover type for the European VOC budget. As European beech is the predominant deciduous tree species in Europe, its broad geographical distribution combined with the high emission factor led to increases in the European monoterpene budget of 16% if monoterpene emission is considered as function

of light and temperature. Considering that a variety of other deciduous tree species may emit monoterpenes as a function of light and temperature as well, would lead to a decrease of the European monoterpene emission in total due to the negligence of monoterpene emissions at low light intensities. Consequently, the relative impact of European beech trees on the European monoterpene budget would be increased. However, the uncertainties regarding the calculation of European VOC budgets are high. Moreover, European beech demonstrated to emit monoterpenes at variable standard emission factors. Within this context, seasonality, drought, and temperature effects may play an important role.

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