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Process-based modelling of biogenic monoterpene emissions combining production and release from storage

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Abstract. Monoterpenes, primarily emitted by terrestrial vegetation, can influence atmospheric ozone chemistry, and can form precursors for secondary organic aerosol. The short-term emissions of monoterpenes have been well studied and understood, but their long-term variability, which is particularly important for atmospheric chemistry, has not. This understanding is crucial for the understanding of future changes.

In this study, two algorithms of terrestrial biogenic monoterpene emissions, the first one based on the short-term volatilization of monoterpenes, as commonly used for temperature-dependent emissions, and the second one based on long-term production of monoterpenes (linked to photosynthesis) combined with emissions from storage, were compared and evaluated with measurements from a Ponderosa pine plantation (Blodgett Forest, California). The measurements were used to parameterize the long-term storage of monoterpenes, which takes place in specific storage organs and which determines the temporal distribution of the emissions over the year. The difference in assumptions between the first (emission-based) method and the second (production-based) method, which causes a difference in upscaling from instantaneous to daily emissions, requires roughly a doubling of emission capacities to bridge the gap to production capacities. The sensitivities to changes in temperature and light were tested for the new methods, the temperature sensitivity was slightly higher than that of the short-term temperature dependent algorithm.

Applied on a global scale, the first algorithm resulted in annual total emissions of 29.6 Tg C a^{-1}, the second algorithm resulted in 31.8 Tg C a^{-1} when applying the correction factor 2 between emission capacities and production capacities. However, the exact magnitude of such a correction is spatially varying and hard to determine as a global average.

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1 Introduction

Biogenic emissions of monoterpenes influence atmospheric composition and air quality, especially on a regional scale. Monoterpene oxidation in the atmosphere contributes to production of ozone (O_3) in the presence of nitrogen oxides (NO_x) (Jenkin and Clemitshaw, 2000). Monoterpenes also react directly with O_3, forming low volatility oxidation products that are important sources for secondary organic aerosol (SOA) formation and growth (Hoffmann et al., 1997; Aumont et al., 2000; Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003; Simpson et al., 2007). SOA yield from monoterpene ozonolysis is considered relatively large, although knowledge on many of the processes involved is still scarce (Tsigaridis and Kanakidou, 2003). Since the annual global SOA production from terrestrial biogenic volatile organics might exceed SOA production from anthropogenic VOC by more than a factor of ten, and could be of same order of magnitude as the production of sulphate particles (Tsigaridis and Kanakidou, 2003), the role of monoterpenes for radiative transfer and cloud properties is probably significant. However, at the same time their regional and global emission patterns are not very well known, and effects of

changing climate, atmospheric CO_2 concentration or human land cover and land use change are uncertain. The incorporation of process understanding related to their cellular production in global vegetation models can help to investigate these effects, as these models are applicable to a wider range of environmental conditions, including global change related questions.

Monoterpene emissions from plants have a variety of crucial ecological functions. They aid in defense against herbivory, either by their toxicity to herbivores or by signalling to predators (Litvak and Monson, 1998). Signalling is used for other purposes as well, e.g. to attract pollinators (Dudareva et al., 2004), and monoterpenes might also function as an antioxidant in reaction to elevated levels of ozone (Loreto et al., 2004). Monoterpenes are produced along the chloroplastic DXP pathway, in a reaction chain that is, except for the final steps, similar to the formation of isoprene (Lichtenthaler et al., 1997). This metabolic pathway is closely linked to photosynthesis through one of the chief precursors, glyceraldehyde-3-phosphate, originating from the chloroplastic Calvin cycle, and the requirement of energy for the reduction of the precursor carbohydrates (Lichtenthaler et al., 1997). Unlike isoprene, monoterpenes and other less volatile compounds can be stored in leaves, either as nonspecific storage (Niinemets and Reichstein, 2002) in cellular liquid or as specific storage in storage organs, such as glandular trichomes (e.g. Gershenzon et al., 1989; Turner et al., 2000), resin canals, or resin ducts (e.g. Franceschi et al., 2005). Non-specific storage has been observed both in conifers (e.g. in *Pinus pinea*, Staudt et al., 2000) and in broadleaf trees (e.g. in *Quercus ilex*, Loreto et al., 1996), and release from this storage is relatively fast (minutes to hours). The specific storage of monoterpenes within a leaf in storage organs is built up during leaf development (Gershenzon et al., 2000; McConkey et al., 2000; Turner et al., 2000), and is mainly observed in conifers. Specific storage can last much longer than the non-specific storage (days to months).

The release of stored monoterpenes is mainly driven by changes in monoterpene vapour pressure, which is primarily determined by temperature (Dement et al., 1975; Tingey et al., 1980). This temperature-driven release from storage has led to the development of an algorithm for emission of monoterpenes (Tingey et al., 1980; Guenther et al., 1993), which has been successfully applied to interpret measurements on leaf or canopy scale (e.g. Ruuskanen et al., 2005; Holzinger et al., 2006), and is generally used for estimates of global monoterpene emissions (e.g. Guenther et al., 1995; Naik et al., 2004; Lathière et al., 2006).

Although monoterpene emissions of many species have been shown to depend primarily on temperature on a relatively short time scale of hours to days, the seasonal variation in monoterpene emissions cannot be explained by temperature response alone (Yokouchi et al., 1984; Staudt et al., 2000; Holzinger et al., 2006). Long-term (∼annual) changes in emissions were so far represented by seasonally varying emission capacities on a local scale (Staudt et al., 2000), although it is not clear whether the observed seasonal variation is related to the dynamics of the monoterpene storage or to the rate of production. On a global scale such changes are ignored, and the temperature-dependent algorithm was used for annual emission estimates so far (e.g. Naik et al., 2004; Lathière et al., 2005). What is more, over recent years an increasing number of studies have identified monoterpene emissions, particularly in broadleaf species, to respond to temperature and light in a pattern similar to that found for isoprene, e.g. for *Quercus ilex* (Staudt and Seufert, 1995; Bertin et al., 1997; Ciccioli et al., 1997; Staudt and Bertin, 1998), *Fagus sylvatica* (Schuh et al., 1997; Dindorf et al., 2006), *Helianthus annuus* (Schuh et al., 1997), several mediterranean species (Owen et al., 2002), *Apeiba tibourbou* (Kuhn et al., 2004), *Hevea brasiliensis* (Wang et al., 2007) and other tropical plant species or land cover types (Greenberg et al., 2003; Otter et al., 2003). In these species, emission takes place directly after production, without intermediate storage within the leaf, in a pattern similar to that observed for isoprene. The observed dependencies reflect those of monoterpene synthesis, which is closely linked to photosynthesis. These findings suggest that modelling of monoterpene emissions for some regions will have to be revised, which will likely affect global emission estimates as well.

A limited number of studies have attempted to express monoterpene production explicitly, linking it to processes of carbon assimilation in the chloroplast (Niinemets et al., 2002; Bäck et al., 2005; Grote et al., 2006), and hence being dependent on both temperature and light. Storage of monoterpenes can then be included as an additional feature to account for the observed short-term temperature dependence of monoterpene emissions (Niinemets and Reichstein, 2002; Bäck et al., 2005). The release from storage can modulate emissions over periods of days to months: Mihaliak et al. (1991) showed that monoterpenes in intact plants of *Mentha×piperita* are stored in a stable pool for several weeks, and Gershenzon et al. (1993) found for several monoterpene-storing species no significant amount of labelled monoterpenes to be released for 8 to 12 days after a pulse of $^{14}CO_2$. These long-term (∼annual) changes in emissions originating from changes in the specific storage (e.g. glands or resin ducts) have not been included in modelling studies so far.

Our chief objective here is to investigate the effects of an explicit representation of chloroplastic and leaf processes on seasonal to annual monoterpene emission patterns. We develop a model for light- and temperature-dependent monoterpene emissions by combining a process-based description of monoterpene production and a temperature-dependent residence in specific storage organs within the plant. The model is implemented in the dynamic global vegetation model (DGVM) framework LPJ-GUESS (Smith et al., 2001; Sitch et al., 2003) to investigate the sensitivity of emissions to temperature and light and the use of monoterpene storage as

a measure to distinguish between production and emission of monoterpenes. The goal is to create a tool that builds on process understanding and that can be used to investigate interactions of climate change, vegetation dynamics, vegetation productivity and trace gas emissions over periods from years to millennia within a consistent modelling framework. In this study, we concentrate on model parameterization and evaluation using observations of monoterpene emissions from a Ponderosa pine plantation. Model sensitivities for this site and implications for application on global scale will be discussed.

2 Methods

2.1 Short-term monoterpene emission

In those plant species that display a light-independent, temperature-driven monoterpene emission pattern, these emissions usually originate from non-specific (e.g., dissolved in the cytosol) or specific (e.g., glands, resin ducts) storage pools within leaves. The storage pools act as a continuous source of monoterpenes, with emissions driven by changes in monoterpene vapour pressures (Dement et al., 1975; Tingey et al., 1980), hence the clear temperature dependence. Typically, an exponential algorithm as presented by Tingey et al. (1980) and Guenther et al. (1993) is used to simulate these emissions:

$$M = \mathrm{e}^{\beta(T-T_s)} M_s \tag{1}$$

In this equation, M is the monoterpene emission ($\mu g\, g^{-1}\, h^{-1}$), M_s is the emission rate under standard conditions (referred to as emission capacity), β is a constant ($0.09\, K^{-1}$), T is leaf temperature (K), and T_s is the standard temperature (303 K). Simulations with this algorithm were performed for a broad range of species, specifically for many conifers, e.g. for *Pinus elliottii* (Tingey et al., 1980), *P. ponderosa* (Holzinger et al., 2006), and *P. sylvestris* (Ruuskanen et al., 2005). The temperature-dependent algorithm in Eq. (1) is useful for modelling the short-term emission response to temperature, as it reflects the changes in vapour pressure due to temperature, but changes in vapour pressure from changes in the concentrations in the storage pool of monoterpenes are not covered by the algorithm.

2.2 Monoterpene production, storage and emission

The algorithm presented above reflects the short-term dependence of monoterpene emissions from temperature. In order to simulate both the long-term changes and the short-term changes, we split the simulation in two parts: the production of monoterpenes, following a process-based approach based on the energy requirements of monoterpene synthesis, and the emission of monoterpenes, following an approach equivalent to Eq. (1). Between production and emission, monoterpenes can be stored for periods of different length.

Monoterpene production is simulated following Niinemets et al. (2002), who calculate the production of monoterpenes in two *Quercus* species based on the chloroplastic electron transport rate required to drive terpene synthesis:

$$M_{\mathrm{prod}} = \epsilon J \alpha \tag{2}$$

with

$$\epsilon = f_T \epsilon_s \tag{3}$$

In these equations, J is the photosynthetic electron flux ($mol\, m^{-2}\, h^{-1}$), ϵ is the fraction of this flux that is available for monoterpene production, and α converts the electron flux into monoterpenes ($g\, mol^{-1}$). The fraction ϵ depends on temperature and on a species-specific electron fraction ϵ_s, which forms a similar scalar to emissions as the emission capacities or standard emission rates (M_s) that are usually reported for species do. f_T is a temperature factor accounting for the higher temperature optimum of terpene production observed, as was done for isoprene (Arneth et al., 2007). ϵ_s, the fraction of the electron flux under standard conditions, can be derived directly from the emission capacity by calculation of photosynthesis and hence J at standard conditions. This derivation assumes that either there is no storage of monoterpenes, or the storage pool is in a steady state. Although this assumption might be invalid for individual cases on a short timescale, it will hold as an average, particularly when the emission capacity M_s was reported for a longer period of time. Moreover, literature values for M_s are generally obtained from leaf-scale observations. The model does not account for catabolism of monoterpenes within the leaf, and simulates a production that represents observations outside the leaf. Apart from the standard temperature of 30°C, we assume a standard light condition of $1000\, \mu mol\, m^{-2}\, s^{-1}$ PAR (as is standard for isoprene), even though this is not formally determined for monoterpenes that are emitted temperature-dependently.

Produced monoterpenes resulting from the process-based method of Eqs. (2) and (3) can be stored for shorter or longer periods in a specific storage pool with size m (in $g\, m^{-2}$ ground area). This specific storage of monoterpenes within a leaf takes place in storage organs such as glands or resin ducts. We ignore the dynamics of non-specific storage, as it is of minor interest to this study due to its short timescale of up to several hours. Specific storage is represented with a single storage pool, and we assume that the release from specific storage depends on temperature in a similar way as the release from non-specific storage. The size of the storage pool is determined by changes in production M_{prod} and release M_{emis}:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = M_{\mathrm{prod}} - M_{\mathrm{emis}} \tag{4}$$

The concentration of monoterpenes within needles has been shown to affect the emission of monoterpenes from a number of conifer species, e.g. *Pinus ponderosa* (Lerdau et al.,

1994), *Pseudotsuga menziesii* (Lerdau et al., 1995), *Picea mariana* and *Pinus banksiana* (Lerdau et al., 1997). Therefore, the release from the storage pool is simulated depending on the pool size (which is related to monoterpene concentration) with an average residence time τ.

$$M_{\text{emis}} = \frac{m}{\tau} \tag{5}$$

The average residence time τ (in days) is determined under standard temperature T_s and is adjusted for other temperatures with a Q_{10}-relationship:

$$\tau = \frac{\tau_s}{Q_{10}^{(T-T_s)/10}} \tag{6}$$

The short-term temperature response of the monoterpene emission of Eqs. (5) and (6), i.e. the response with negligible changes in m, is adopted from the short-term response in Bäck et al. (2005) for vapourization of α-pinene from the liquid phase. The temperature dependence in their Eq. (8) (Bäck et al., 2005) results in a value for Q_{10} between 1.8 and 2.0 for temperatures between 0 and 30°C. For our modelling exercises we use a constant Q_{10} of 1.9. This is somewhat lower than the temperature response of Eq. (1), which results in a Q_{10}-value of 2.5 (with β=0.09). The value for τ_s was varied in a set of sensitivity tests and will be discussed below.

The presented algorithm thus calculates monoterpene production according to the availability of temperature and light, closely linked to photosynthesis. The produced monoterpenes are then emitted depending on the temperature and on the amount (or concentration) in the leaves. The seasonal cycle of emissions thus differs from the seasonal cycle of production. However, all produced monoterpenes are released after a (varying) period of storage, so averaged over longer periods of time (years), the amount produced and the amount emitted are (nearly) equal.

2.3 Implementation in a dynamic vegetation model framework and experiment setup

For comparative analysis, both the short-term temperature-dependent monoterpene emission algorithm from Eq. (1) and the process-based production and emission from Eqs. (2) to (6) were implemented within the dynamic global vegetation model framework LPJ-GUESS (Smith et al., 2001; Sitch et al., 2003). LPJ-GUESS simulates vegetation distribution as well as the cycles of carbon and water within the vegetation and the soil. The model calculates photosynthesis adopted from Farquhar et al. (1980), applying the daily integration from the optimisation approach presented in Haxeltine and Prentice (1996). The total electron flux J, as required for Eq. (2), is thus calculated on a daily time step as well. LPJ-GUESS can be applied as a gap-model (Smith et al., 2001), where several age cohorts of one species or PFT, which compete for light and water, can occur in one gridcell. In this way, canopy successional dynamics are represented in a realistic manner, and modelling of vegetation dynamics on tree species level is possible (Hickler et al., 2004; Arneth et al., 2008b).

For both methods, the extrapolation from leaf-level to canopy-level within the DGVM is done linearly with the fraction of the radiation absorbed, similar as is done in LPJ-GUESS for the calculation of gross primary productivity (GPP). The storage pool m (Eq. 4) is implemented as a single pool that reflects long-term changes.

LPJ-GUESS with the two algorithms for monoterpene emission incorporated was evaluated against measurements for a Ponderosa pine (*Pinus ponderosa* L.) plantation at Blodgett Forest, California (38.90° N, 120.63° W, elevation 1315 m, Holzinger et al., 2006). Monoterpene emissions were measured between June 2003 and April 2004 using proton-transfer-reaction mass-spectrometry in combination with the eddy covariance method (see Holzinger et al., 2006, for a detailed description of the measurements). Simulations were performed by applying LPJ-GUESS in gap-model mode, averaging 100 repeated calculations for a patch, which is necessary to account for the stochastic nature that is characteristic for some of the processes that underlie vegetation dynamics. To reproduce the plantation's uniform age, seedlings were established in the simulation year representing 1990, and the density was reduced in the simulation year representing 2000 to represent a thinning. The model was spun up with the monthly climate data produced by the Climatic Research Unit of the University of East Anglia (referred to as CRU data, New et al., 2000; Mitchell and Jones, 2005) for the period 1990–2003, corrected with the anomaly between site climate and CRU climate. The spinup was followed by a simulation with observed daily climate data (temperature, precipitation, radiation) at this site for the period from June 2003 until April 2004. The annual atmospheric CO_2 concentration was prescribed following global observations for the spinup and simulation periods.

A set of simulations was performed to study the applicability of temperature-dependent (Eq. 1) and photosynthesis- and storage-dependent (Eqs. 2 and 5) algorithms to reproduce the observed emissions at Blodgett Forest. The parameterization of the release from storage (τ_s in Eq. 6) was varied to determine the value of best fit to the data. The emission capacities (and thus the standard fraction of the electron flux ϵ_s, Eq. 3) were determined from the measurements such that the simulated emissions reproduced the annual average measured emissions on the days of the measurements. The (one-sided) specific leaf area for Ponderosa pine was prescribed to $7.8\,\text{m}^2\,\text{kg}^{-1}\,\text{C}$ following Misson et al. (2005), and the thickness of the model's soil layers was increased to prevent an overestimation of water stress during the growing season.

2.4 Adjustments for global scale modelling

LPJ-GUESS can be applied on a global scale as a DGVM (Sitch et al., 2003). Compared to the gap-mode, it is based

Table 1. Emission capacities for plant species for which a temperature and light limitation was reported. Plant species are grouped in plant functional types.

Species	M_s ($\mu g\, g^{-1}\, h^{-1}$)	
Tropical broadleaved raingreen		
Apeiba tibourbou, RBJ, Rondônia, Brazil [a]	2.1	**
Colophospermum mopane, HOORC site, Botswana [b]	22.0	
Acacia erioloba, HOORC site, Botswana [b, c]	8.5	*,***
Hevea brasiliensis, dry season, XTBG, China [d]	2.0	*
Hevea brasiliensis, wet season, XTBG, China [d]	94.0	*
Temperate broadleaved evergreen		
Quercus sp., greenhouse experiment [e]	68.1	
Quercus ilex, Viols en Laval, France [f]	18.0	**
Quercus ilex, Castelporziano, Italy [f]	19.5	**,***
Quercus ilex, Castelporziano, Italy [g]	21.7	*,**,***
Quercus ilex, Castelporziano, Italy [h]	23.8	**,***
Quercus ilex, Montpellier, France [i]	15.5	**,***
Temperate broadleaved summergreen		
Fagus sylvatica, Jülich, Germany [j]	15.0	**

* Emission capacity measured under standard conditions; ** Emission capacity extrapolated from field measurements; *** Range of values reported, average is given here. [a] Kuhn et al. (2004); [b] Greenberg et al. (2003); [c] Otter et al. (2002); [d] Wang et al. (2007); [e] Owen et al. (2002);[f] Ciccioli et al. (1997); [g] Bertin et al. (1997); [h] Street et al. (1997); [i] Kesselmeier et al. (1998); [j] Dindorf et al. (2006).

on simplified vegetation dynamics of the growth and development of an average individual. The vegetation is represented by ten plant functional types. Within such a global framework, a standard fraction of the electron flux used for monoterpene production ϵ_s (Eq. 3) needs to be assigned as an average value to each PFT. Similar as in Arneth et al. (2007) for isoprene, ϵ_s is set in a way that the emission rate obtained at standard conditions (303 K and 1000 $\mu mol\, m^{-2}\, s^{-1}$ PAR) equals the emission capacity M_s. These emission capacities are applied as average value to each PFT (e.g. Naik et al., 2004; Lathière et al., 2006), based on recommendations given in Guenther et al. (1995).

Values for the standard emissions for monoterpenes are highly uncertain, probably even more so than for isoprene: Leaf measurements, that are the basis for recommended values of M_s, were mostly analysed using the temperature dependence in Eq. (1) which implies that emissions take place both day and night, independent of light conditions (and hence independent of the occurrence or absence of monoterpene production in the chloroplast) or of storage pool size (which may vary seasonally). For emissions from storage, the assumption of a constant emission factor is applicable for a short period only. Due to changes in the concentrations of monoterpenes in the storage organs, partial pressures will differ throughout the year, and will thereby influence volatilization and emission, and hence the measured M_s. Several studies on monoterpenes report changes in emission capacities for different dates or seasons (e.g. Staudt et al., 1997; Komenda and Koppmann, 2002; Pressley et al., 2004; Hakola et al., 2006), which might be partially assigned to this storage effect. A seasonally changing production rate that was intended to reflect variations in enzyme activity, similar to what has been included in the isoprene model by Arneth et al. (2007), might be important to explain these changes (Bertin et al., 1997; Fischbach et al., 2002). We note that this might be an important process, but in our view the current state of knowledge does not allow for a clear description of such an effect on global scale.

The commonly reported emission capacity M_s, expressed at a standard temperature, is not necessarily equivalent to the production capacity under similar standard conditions, because the latter is a light-dependent process that takes place during daytime only. Therefore, in plants where a storage pool exists, to maintain this pool over a period of one day or longer, production during daylight hours must be sufficient to support release from storage over 24 h. Or in other words: a (daytime) production-derived value for M_s must exceed an emission-derived M_s (that would cover daytime as well as nighttime emissions) notably. Of interest in this context is that emission capacities for monoterpene-emitting broadleaf species that do not store monoterpenes, taken from studies that applied a temperature and light dependent algorithm, range from 2 to 70 $\mu g\, g^{-1}\, h^{-1}$ (Table 1), and are in general on the upper end of reported monoterpene emissions when compared to emissions that are released solely temperature-driven from storage (Kesselmeier and Staudt, 1999). These observations may indeed indicate a larger rate of production of monoterpenes taking place also in species where this

Table 2. Presence or absence of long-term monoterpene storage organs (+ indicates monoterpene storing PFT, − indicates non-storing), and emission capacities for the plant functional types used for the global simulation as adopted from Naik et al. (2004).

PFT	Monoterpene storage	M_s ($\mu g\, g^{-1}\, h^{-1}$)
Tropical broadleaved evergreen	−	0.4
Tropical broadleaved raingreen	−	1.2
Temperate needleleaved evergreen	+	2.4
Temperate broadleaved evergreen	−	0.8
Temperate broadleaved summergreen	−	0.8
Boreal needleleaved evergreen	+	2.4
Boreal needleleaved summergreen	+	2.4
Boreal broadleaved summergreen	−	0.8
Temperate herbaceous	+	0.8
Tropical herbaceous	+	1.2

production rate cannot be observed directly, because of the storage acting as a buffer between production and emission.

In the model, leaf production of monoterpenes is similar for all plants, independent of presence or absence of storage. For the application of storage (Eq. 4) the produced monoterpenes can be transferred into storage, depending on the plant functional type (PFT). To do so, the group of PFTs was separated as in Table 2: all broadleaved trees are considered to be non-storing, while the conifers and herbs are considered to be storing monoterpenes. Such a simplification is unavoidable in DGVMs and is based on current observations: an isoprene-like release of monoterpenes was mostly found in broadleaved species, whereas conifers tend to have monoterpene storage (Kesselmeier and Staudt, 1999). Large amount of stored monoterpenes are also observed in many herbacious species.

Two global simulations were performed using the vegetation dynamics of LPJ-GUESS in DVGM mode, applying both the short-term temperature-dependent algorithm, and the production and storage algorithm. The CRU climate data for the years 1901–2000 were used to force the model with a spinup of 300 years, using the atmospheric CO_2 concentration for 1901 (290 ppm) and a detrended series of data for 1901–1950. This was followed by 100 years of simulation representing the 20th century, using the CRU data and CO2 concentrations from ice cores and from observations. Simulations were performed at a horizontal resolution of $0.5° \times 0.5°$, the average of the last 20 years of this run (1981–2000) was used for the analysis. The effects of the two different algorithms on global monoterpene emissions were compared. For both simulations, the emission capacities as in Naik et al. (2004) were adopted (Table 2). The first simulation assumes all monoterpenes to be released with the short-term temperature algorithm (Eq. 1), changes in the amount of monoterpene storage are not considered. This assumption also underlies all global scale estimates to date (see overview in Arneth et al., 2008a). The second simulation calculates production of monoterpenes from electron transport (Eq. 2). Monoterpenes are emitted either directly, or from a storage pool (conifers and herbs, Eq. 5). For this simulation, emission capacities M_s (and thus the values of ϵ_s) are adjusted as described above with a factor 2 to reflect the difference between the production (taking place only during sunlight hours) and the need to refill the storage (with emissions taking place the entire day).

3 Results and discussion

3.1 Simulated monoterpene emissions

A prerequisite for reliable simulation of BVOC fluxes with vegetation models is the reproduction of important growth characteristics. For the Blodgett Forest site, simulated LAI (one-sided) was 2.6 for 2003 and 2.8 for 2004 (not shown), which compares well to the observed variation of 2 to 3 for the study period (Holzinger et al., 2006). Simulated gross primary productivity (GPP, Fig. 1b) also agreed well with observations (Misson et al., 2006), except for a short period in late July 2003, for which the simulated daily GPP was approximately reduced by 25% compared to the values derived from eddy flux data, likely due to an overestimation of drought stress in the model during that period. Measurements from other years indicate that Blodgett Forest experiences drought stress during summer, but the extent is less than in other Ponderosa pine forests with comparable climatic circumstances (Panek, 2004; Misson et al., 2004).

Simulations were performed with two different algorithms for monoterpene emissions: (1) using the temperature-dependent algorithm (Eq. 1), and (2) using the monoterpene production algorithm (Eq. 2) for direct release (no storage) and for release from storage with time constants up to 160 d. The emission capacities M_s that gave the best fit with each

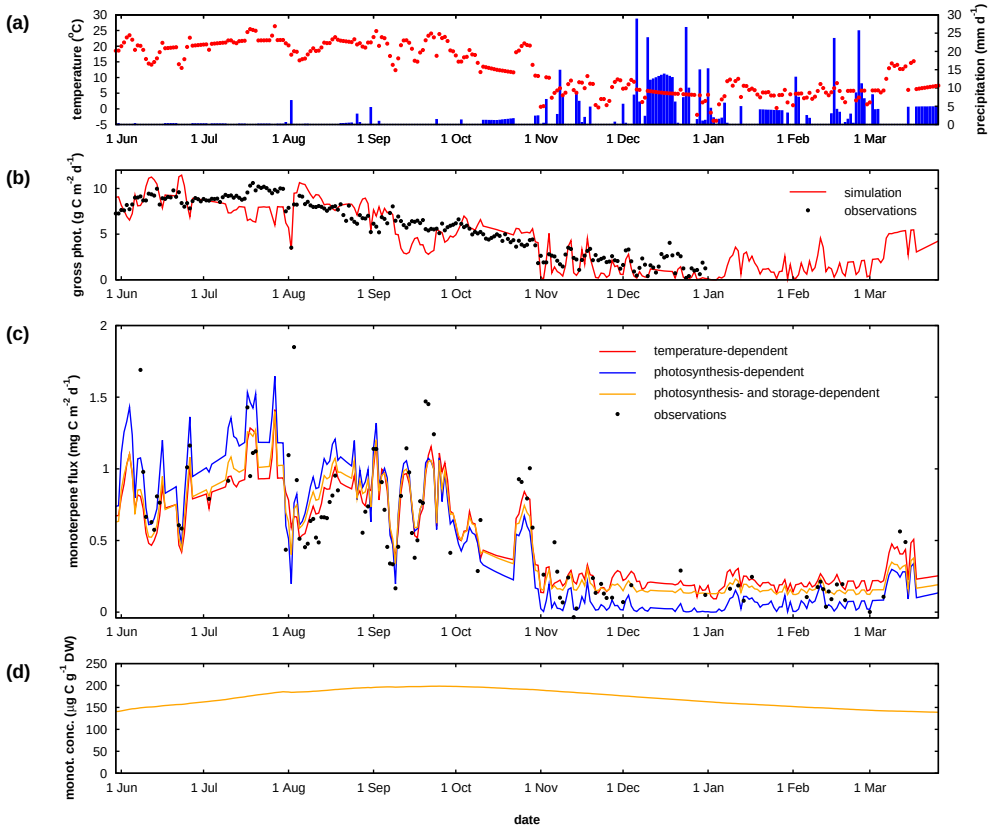

Fig. 1. **(a)** Observed daily average air temperature (in red) and precipitation (in blue) for Blodgett Forest; **(b)** Simulated and measured (2003) photosynthesis rates for Blodgett Forest, California; **(c)** Simulated monoterpene emissions with the temperature-dependent and photosynthesis-dependent algorithms, applying storage of half of the production with τ_s=80 d, and observations for June 2003–April 2004; **(d)** Simulated monoterpene storage in leaves for the simulation with half the production stored applying τ_s=80 d. Emission capacities in (c) were adjusted to match the average of the measured rates (see text).

of the two algorithms (Eq. 1 and Eqs. 2–6 with various storage settings) are of the same order of magnitude (Table 3). Holzinger et al. (2006) report an emission capacity (using Eq. 1 and based on all-sided leaf area) of 1 µmol m^{-2} leaf h^{-1} (or 0.20 µg C g^{-1} h^{-1}), about half of the optimised value for Eq. (1) in this study. Differences between the two studies could be caused by a difference in extrapolation from leaf level to canopy level, as well as by the applied leaf temperature correction in this study.

The simulated seasonality in emissions (Fig. 1c, for clarity only a selection of the simulations summarized in Table 3 is displayed) was very similar in all simulations, irrespective of the presence or absence of storage. This is due to the fact that temperature is always a main contributor to the variability since temperature and radiation normally correlate well, and warm days also have large rates of electron flux and hence monoterpene production. Only at high values for τ_s ($\geq$40 d) the seasonal differences were considerably reduced (not shown). Without storage, the photosynthesis-dependent simulated emissions show a strong day-to-day variability, as was the case with GPP (Fig. 1b), due to the dependence of terpene production on photosynthetic processes. The observed monoterpene emission peaks due to rain events (Fig. 1a and c) as were observed before at the same site (Schade et al., 1999) were not captured by any of the simulation experiments. These peaks in emissions are likely caused by enhanced humidity of the air and a related uptake of water by the leaves (Llusià and Peñuelas, 1999; Schade et al., 1999). Simulated changes in seasonality are caused only by changes in weather conditions and changes in the size of the storage pool, we did not include an explicit change of seasonality of monoterpene production as is often suggested for isoprene production in relation to changes in isoprene synthase activity (Wiberley et al., 2005).

Simulations performed with the photosynthesis-dependent algorithm (Eq. 2) combined with release from storage of monoterpenes (Eq. 5) showed an interesting feature: The best agreement between the fitted parameterization and observations, determined from the average mean error (AME) and the root mean square error (RMSE) between the two, was obtained both with no storage at all and with high residence times in storage (τ_s=80 d, Table 3). However, the ratio

Table 3. Results from simulations for Blodgett Forest: scaled emission capacity M_s, average mean error (AME), root mean square error (RMSE), ratio between summer (JJA) and winter (DJF) emissions for all days (for days with observation available in brackets, n=38 for summer, n=18 for winter).

Simulation		M_s $\mu g\,C\,g^{-1}\,h^{-1}$	AME $mg\,C\,m^{-2}\,d^{-1}$	RMSE $mg\,C\,m^{-2}\,d^{-1}$	$\frac{M_{sum}}{M_{win}}$
Temperature-dependent		0.41	0.154	0.047	4.1 (3.5)
Photosynthesis-dependent		0.42	0.189	0.063	22.1 (13.6)
Photosynthesis- and storage-dependent	τ_s=2.5 d	0.42	0.197	0.069	22.0 (16.3)
Photosynthesis- and storage-dependent	τ_s=5 d	0.42	0.194	0.065	18.1 (15.2)
Photosynthesis- and storage-dependent	τ_s=10 d	0.41	0.191	0.064	11.0 (10.2)
Photosynthesis- and storage-dependent	τ_s=20 d	0.41	0.189	0.064	5.9 (5.6)
Photosynthesis- and storage-dependent	τ_s=40 d	0.43	0.185	0.063	3.7 (3.4)
Photosynthesis- and storage-dependent	τ_s=80 d	0.45	0.185	0.063	2.7 (2.6)
Photosynthesis- and storage-dependent	τ_s=160 d	0.50	0.258	0.108	1.3 (1.3)
Photosynthesis- and storage-dependent	half stored, τ_s=80 d	0.44	0.158	0.049	5.7 (5.0)

between simulated summer and winter emissions decreases with increasing residence times due to the delay caused by the storage. The observed summer to winter emissions ratio of 5.3 was reproduced in the simulations only at values for $\tau_s \geq 40$ d. Although observations for important parts of the simulation period were absent, the reasonably good fits with both low (τ_s=0 d) and high (τ_s=80 d) residence times, combined with the need for long storage to fit the ratio between summer and winter emissions, merits the assumption that part of the produced monoterpenes might be emitted directly, whereas another part is stored for considerable times. Such a mixture of long-term storage and direct emission (or emission from short-term storage, which is ignored in this study) was suggested by Staudt et al. (1997, 2000) for *Pinus pinea*, and was proposed in a more general manner by Kesselmeier and Staudt (1999). A simulation which took this assumption into account (half of the produced monoterpenes was simulated to be emitted directly, the other half was stored with a standard residence time τ_s of 80 d) resulted in lower values for both AME and RMSE, with values close to those obtained with the short-term temperature-dependent algorithm, and in a ratio of summer and winter emissions close to the observed value (5.0 based on the days for which observations were available). Increasing the standardized residence time τ_s caused the concentration of monoterpenes in the leaves to increase to values up to 300 $\mu g\,C\,g^{-1}$ at a τ_s of 160 d (not shown), and the maximum concentration to be delayed until later in the year compared to the simulations with smaller τ_s. Storage also caused the day-to-day variability of emissions to decrease (Fig. 1c), acting as a buffer between production and emission, as is the case for non-specific storage (Niinemets et al., 2004). Observed concentrations of β-pinene in a Ponderosa pine forest in Oregon, US, ranged between 2.8×10^3 and 5.1×10^3 $\mu g\,C\,g^{-1}$ (Lerdau et al., 1994) for September and June, respectively, with emission rates of 0.2 and 1.1 $\mu g\,C\,g^{-1}\,h^{-1}$, which indicates a similar order of magnitude for the residence times as obtained in our simulations.

The simulated seasonality of monoterpene concentrations in the Ponderosa pine plantation for the applied split of the emissions in storage (half) and direct emissions (half) is shown in Fig. 1d. The peak in simulated leaf monoterpene concentrations was reached in autumn. For the range of time coefficients applied (Table 3), the peak in concentrations shifted from summer (τ_s=2.5 d) to late autumn (τ_s=160 d), and the concentrations increased with increasing τ_s (not shown). Measurements of the seasonal cycle of monoterpene concentrations in other species show a wide variety of patterns: A pattern similar to the simulated one, with high concentrations in summer and autumn, was observed for Black spruce (*Picea mariana*) in Canada (Lerdau et al., 1997), but not so for Jack pine (*Pinus banksiana*) in Canada, where concentrations peaked in spring and autumn (Lerdau et al., 1997). Measurements of terpene concentrations in several Mediterranean species indicated low concentrations in summer and high in winter due to higher emissions at high temperatures (Llusià et al., 2006).

Our results did not account for changes in leaf mass over the year, which would affect the maximum storage pool size and could account for some of the variation observed in the timing of peak values and emissions. However, there are likely other factors playing an important role in the timing of emissions that are not considered in our vegetation model. For instance, Bäck et al. (2005) were able to reproduce large spring emissions of monoterpenes in boreal *Pinus sylvestris* by incorporating photorespiration as a carbon source, although the link between terpenoid production and photorespiration is controversial (Hewitt et al., 1990; Peñuelas and

Llusià, 2002). It is also plausible that terpene synthesis could take place during winter, since conifers are able to assimilate, albeit at low rates, during warm winter periods (e.g. Suni et al., 2003).

3.2 Sensitivity to changes in temperature and light

The sensitivities of the leaf emissions calculated with the new algorithm were tested by varying the temperature and radiation input data to the model, but keeping the other settings as in the experiments described above. Temperature changes between −5 K and +5 K and radiation changes between −100% and +100% were added over the whole year to the forcing of the models for all days in spinup and simulation period. The responses shown are thus reflecting those of the canopy, including effects on canopy properties (e.g. LAI). The long-term sensitivity to temperature, reflecting the sensitivity of monoterpene production, that resulted from this was compared with the short-term (instantaneous) sensitivities of vapourization-related emissions from storage, both for the 'classical' algorithm in Eq. (1) and for the short-term release implemented in the new algorithm (Eqs. 5 and 6).

GPP varied roughly 40% over the prescribed 10 K range, Fig. 2c), with changes in LAI of 30% (not shown). GPP showed a gradual increase up to its maximum at 3 K above ambient values, and a gradual decay from 3 K onwards, reflecting increasingly enhanced evaporation and stomatal closure as temperature increases in response to a soil water deficit (not shown). Due to the higher temperature optimum of terpene production combined with the relatively small changes in electron flux (and GPP) caused by the temperature difference, the long-term temperature sensitivity of monoterpene emissions (reflecting the sensitivity of production) is dominated by an exponential increase at low temperature, which levels off slightly at higher temperature due to the decreasing electron flux related to the decay in GPP (Fig. 2a). Relative changes in monoterpene production were much higher than for GPP for the same range of temperature changes. Due to the temperature optimum for GPP, relatively lower rates of GPP can coincide with either low or high rates of monoterpene emissions, depending on the temperature (Fig. 2b).

Next to the response of monoterpene production, Fig. 2a illustrates the short-term response of emissions from storage, both from Eq. (1) and from Eqs. (5) and (6). Both short-term sensitivities show an exponential increase with temperature; the difference in steepness of the two short-term curves is the result of the difference in Q_{10} values that result from the two methods. The short-term sensitivities were slightly smaller than the long-term response, although the reaction to more extreme changes differs: because of the exponential nature of the short-term functions, it tends to cause larger peaks in emissions for short periods with high temperatures, whereas the long-term sensitivity showed a levelling off at high temperatures. This difference between production

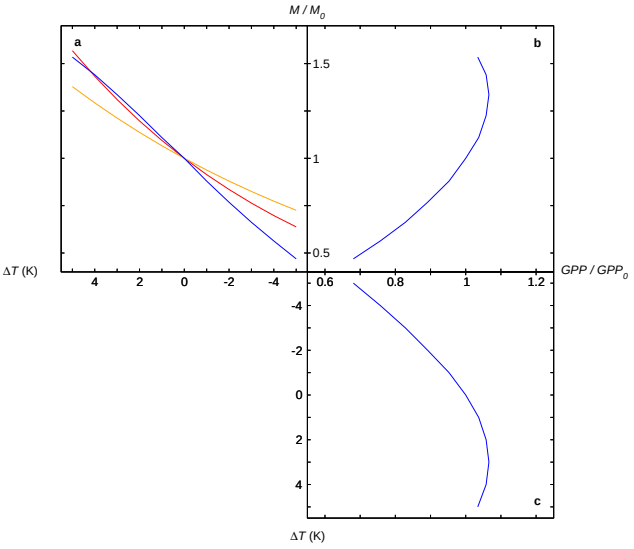

Fig. 2. Sensitivity of GPP and monoterpene emissions to temperature changes: **(a)** Long-term change (in blue) of monoterpene emissions following Eq. (2) (reflecting the sensitivity of monoterpene production), compared to the short-term sensitivities (reflecting those of instantenous emissions from storage) of the "classical" temperature-dependent release from Guenther et al. (1993) (Eq. 1, in red) and of the storage release implemented in the photosynthesis-dependent algorithm (Eqs. 5 and 6, in orange); **(b)** Resulting relation between GPP and monoterpene emissions; **(c)** Change in GPP with temperature. GPP and monoterpene emissions are given relative to the standard case in which there is no temperature change.

and emission at high temperatures was suggested as well by Kesselmeier and Staudt (1999).

Emission response to prescribed changes in radiation are shown in Fig. 3. GPP shows a logistic increase with increasing light levels from 25% of the current level onwards (Fig. 3c), below that radiation level photosynthesis over the year is too low to sustain the vegetation. LAI varied between 0 and 5.9 for the prescribed range in radiation levels (not shown). The logistic increase in GPP reflects the expected saturation for light, that is dominating larger parts of the year with increasing light levels. For monoterpene production, the relation is more linear, and the relative changes in monoterpene production were larger than those in GPP (Fig. 3a). This was caused by a small heating of the leaf by enhanced radiation levels, causing the temperature dependence discussed above to play a minor indirect role as well.

4 Implications for global simulations of monoterpene emissions

For the global simulations, the determination of the standard fraction of the electron flux ϵ_s from the usually reported standard emission capacities M_s emphasises some critical

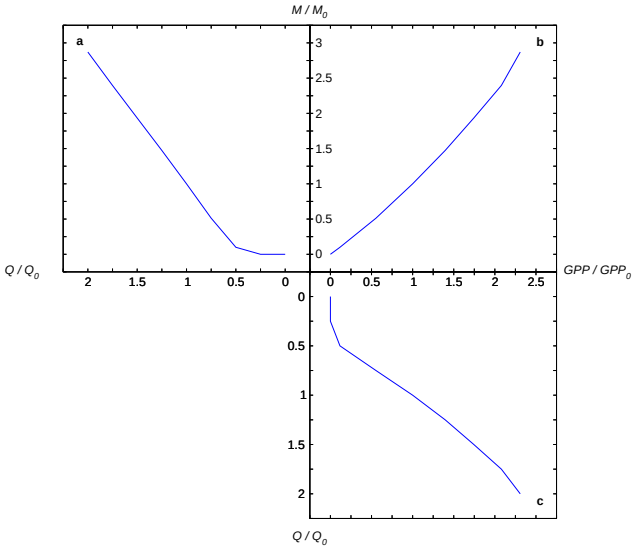

Fig. 3. Sensitivity of GPP and monoterpene emissions to changes in radiation: **(a)** Change in monoterpene emissions with light; **(b)** Resulting relation between GPP and monoterpene emissions; **(c)** Change in GPP with light. Radiation level, GPP and monoterpene emissions are given relative to the standard case in which there is no radiation change.

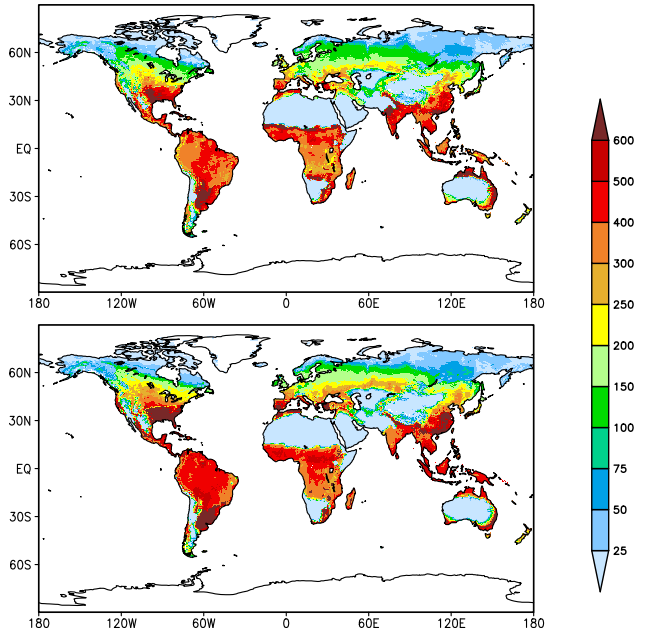

Fig. 4. (a) Global monoterpene emissions (mg C m^{-2} a^{-1}) as simulated with the temperature-dependent short-term emission algorithm (Eq. 1), and **(b)** global monoterpene emissions as simulated with the new photosynthesis-dependent algorithm (Eq. 2). Shown are averages for 1981–2000.

uncertainties in understanding the processes that determine seasonal and annual emission patterns. The difference between an emission-based and a production-based value of M_s, as discussed in Sect. 2.4, was estimated to be approximately a factor of two, which reflects the difference between daylight hours and 24 h as well as the additional light limitation of the production and thus emissions. Incidentally, measured emission capacities of broadleaved trees where emissions are light-dependent, and the standardized rates hence represent the monoterpene production, also tend to be substantial (Table 1), supporting the view that the leaf production of monoterpenes during daylight hours is larger than seen when emissions are measured from storage pool release. M_s was therefore doubled compared to the simulations using Eq. (1).

Annual global total terrestrial emissions were 29.6 Tg C a^{-1} for the simulation that assumed monoterpenes to be uniformly emitted from storage (Eq. 1), and 31.8 Tg C a^{-1} for the simulation that was based on production and storage, and that accounted for the frequently observed emissions without storage in broadleaved vegetation (Eq. 2). The spatial distribution of the emissions is surprisingly similar in the two cases (Fig. 4). The production and storage algorithm resulted in larger rates in temperate forest regions in the eastern US, southern Brazil and China. In these areas, the applied correction factor of two is apparently too large compared to the actual reduction by the light dependence. In dry regions in subtropical Africa, Northern India and Australia, where temperatures are high but photosynthesis rates are relatively low, the temperature-dependent algorithm resulted in larger rates.

Our estimates of global annual monoterpene emissions are at the low end of the published global totals. Naik et al. (2004), using the temperature dependence (Guenther et al., 1995) algorithm, reported 33 Tg C a^{-1}, which is comparable to our estimate with the same algorithm. These two experiments are comparable in their experimental design as well: both use potential natural vegetation cover, with similar tree PFTs in both models while Naik et al. (2004) simulated two additional shrub PFTs. However, these estimates are a factor of four lower than the highest published estimates (Guenther et al., 1995 report 127 Tg C a^{-1}, Lathière et al., 2006 report 117 Tg C a^{-1}). This emphasises the large uncertainty in global BVOC emission calculations that can be introduced through use of different basal rates, vegetation cover and phenology, climatology, temporal resolution, and the use of different algorithms (Arneth et al., 2008a).

For the global simulations, storage was applied for the coniferous and herbaceous plant functional types (Table 2), with half of the produced monoterpenes being stored, applying a standard residence time τ_s of 80 d. In the absence of of long-term changes in the storage pool size, the parameterization of the storage equations (Eqs. 5 and 6) affects only the the seasonality of the emissions, but not the annual totals. However, the seasonality of emissions is an important feature of monoterpene emission simulation when it comes to linking these to atmospheric chemistry.

Application of monoterpene storage in the model with the parameters as derived in the local simulations caused significant residence times (averaged for all PFTs) mainly at high latitudes (Fig. 5). Large latitudinal differences between simulations with and without storage occur in spring and autumn at high latitudes. During spring, when environmental conditions allow the onset of photosynthesis and monoterpene production, the storage pool is being built up, thereby moving part of the production into this storage pool and reducing the emitted amount. Moving from pole to equator, the difference between the simulations with and without storage is diminishing due to higher temperatures and the relatively larger contribution of directly emitting PFTs (Table 2).

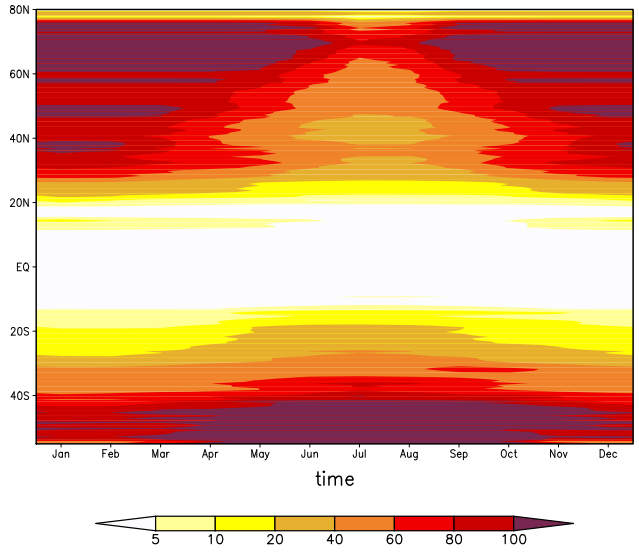

Fig. 5. Annual cycle of the average residence time (in days) of the monoterpenes in the storage pool, shown are zonal means for the period 1981–2000. All PFTs (including the non-storing PFTs) are weighted according to their leaf area index in order to calculate latitudinal averages.

5 Conclusions

We present here an analysis of monoterpene emissions that seeks to investigate the effects of two important processes separately, namely the production in the chloroplast and the ensuing emissions that may or may not be from a storage pool. The analysis aims to provide a basis for better understanding of observed seasonal patterns as well as to take into account the increasing evidence of a direct, production-driven emission pattern in broadleaved vegetation.

The short-term sensitivities to temperature changes for both algorithms were comparable, but also the short-term sensitivity (on volatilization) and the long-term sensitivity (on production) were shown to be remarkably similar, at least as long as small changes in temperature are considered. We did not focus here on how the different monoterpene emission algorithms would be affected in simulations that take into account future climate change. It would seem that algorithms that include solely a response to increasing temperature would be more sensitive under future warming scenarios compared to those that also include a light-limitation, but the overall effects of climate change on other important processes like changes in leaf area index or vegetation cover would also need to be considered. What is more, it is uncertain whether the response of monoterpene production to increasing atmospheric CO_2 concentration follows a similar inhibitory pattern as is shown for isoprene in an increasing number of plants (Constable et al., 1999; Loreto et al., 2001; Staudt et al., 2001; Baraldi et al., 2004), although the similarity in the chloroplastic pathways would suggest a similar response.

It is a general problem of BVOC emission modelling that parameterizations of algorithms that seek to represent observed constraints on emissions can only be based on a very limited number of studies and that true process understanding is often lacking (Guenther et al., 2006; Arneth et al., 2008a). Accounting in a global model for entire plant functional types to have either similar storage residence time or release monoterpenes directly is an inevitable necessity, but it cannot do justice to the natural variation. While most coniferous species that have been studied to date release monoterpenes mostly from storage, there are nonetheless species that emit part of their monoterpenes light-dependently (e.g. *Pinus pinea*, Staudt et al., 1997, 2000). At the same time, some broadleaf monoterpene emitters may also include storage organs (e.g. emissions from *Eucalyptus* spp. have been shown to depend primarily on temperatures, He et al., 2000). New DGVM model developments that – at least on continental scale – are capable of representing actual tree species distribution, rather than PFTs, can be used to assess the uncertainties associated with these globally applied simplified assumptions (e.g. Arneth et al., 2008b). Such a distinction would also allow for a more detailed description of the different types of monoterpenes that are emitted. Current emission inventories do account for a plant species-specific fractionation of different monoterpenes (e.g. Steinbrecher et al., 2009). However, a temporal variation in the composition of monoterpenes, as observed (Staudt et al., 2000) has not been accounted for so far. Additionally, the distinction between monoterpene-storing and non-monoterpene-storing plant functional types has the potential to be extended to monoterpene types that are stored or non-stored. For instance, in *Pinus pinea* several studies (Staudt et al., 1997, 2000) have shown a clear distinction between monoterpenes that are stored and thus have mainly temperature-dependent emission (e.g. limonene, α-pinene), and monoterpenes with emissions that react more directly in response to diurnal patterns of light or to shading, and that do not exhibit long-term storage (e.g. trans-β-ocimene, 1,8-cineole). Such a distinction does not only influence the diurnal course of emissions,

but affects the annual course as well (Staudt et al., 2000). Eventually, such a model setup could also provide the basis for describing emissions that can occur in response to physical damage (e.g. by wind, rain or herbivores, Banchio et al., 2005; Pichersky et al., 2006). Such an analysis would present an important step forward on regional scale when seasonal emission rates are used in atmospheric chemistry simulations.

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References

Arneth, A., Niinemets, U., Pressley, S., Bäck, J., Hari, P., Karl, T., Noe, S., Prentice, I., Serça, D., Hickler, T., Wolf, A., and Smith, B.: Process-based estimates of terrestrial ecosystem isoprene emissions: incorporating the effects of a direct CO_2-isoprene interaction, Atmos. Chem. Phys., 7, 31–53, 2007, http://www.atmos-chem-phys.net/7/31/2007/.

Arneth, A., Monson, R., Schurgers, G., Niinemets, U., and Palmer, P.: Why are estimates of global isoprene emissions so similar (and why is this not so for monoterpenes)?, Atmos. Chem. Phys., 8, 4605–4620, 2008a, http://www.atmos-chem-phys.net/8/4605/2008/.

Arneth, A., Schurgers, G., Hickler, T., and Miller, P.: Effects of species composition, land surface cover, CO_2 concentration and climate on isoprene emissions from European forests, Plant Biology, 10, 150–162, doi:10.1055/s-2007-965247, 2008b.

Aumont, B., Madronich, S., Bey, I., and Tyndall, G. S.: Contribution of secondary VOC to the composition of aqueous atmospheric particles: a modeling approach, J. Atmos. Chem., 35, 59–75, doi:10.1023/A:1006243509840, 2000.

Bäck, J., Hari, P., Hakola, H., Juurola, E., and Kulmala, M.: Dynamics of monoterpene emissions in *Pinus sylvestris* during early spring, Boreal Environ. Res., 10, 409–424, 2005.

Banchio, E., Zygadlo, Y., and Valladares, G. R.: Effects of mechanical wounding on essential oil composition and emission of volatiles from *Minthostachys mollis*, J. Chem. Ecol., 31, 719–727, 2005.

Baraldi, R., Rapparini, F., Oechel, W., Hastings, S., Bryant, P., Cheng, Y., and Miglietta, F.: Monoterpene emission responses to elevated CO_2 in a Mediterranean-type ecosystem, New Phytol., 161, 1–21, 2004.

Bertin, N., Staudt, M., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Fugit, J. L., and Torres, L.: Diurnal and seasonal course of monoterpene emissions from *Quercus ilex* (L.) under natural conditions application of light and temperature algorithms, Atmos. Environ., 31, 135–144, 1997.

Chung, S. H. and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, J. Geophys. Res., 107, 4407, doi:10.1029/2001JD001397, 2002.

Ciccioli, P., Fabozzi, C., Brancaleoni, E., Cecinato, A., Frattoni, M., Loreto, F., Kesselmeier, J., Schäfer, L., Bode, K., Torres, L., and Fugit, J.-L.: Use of the isoprene algorithm for predicting monoterpene emission from the Mediterranean holm oak *Quercus ilex* L.: Performance and limits of this approach, J. Geophys. Res., 102, 23319–23328, 1997.

Constable, J., Litvak, M., Greenberg, J., and Monson, R.: Monoterpene emission from coniferous trees in response to elevated CO_2 concentration and climate warming, Glob. Change Biol., 5, 255–267, 1999.

Dement, W., Tyson, B., and Mooney, H.: Mechanism of monoterpene volatilization in *Salvia mellifera*, Phytochemistry, 14, 2555–2557, 1975.

Dindorf, T., Kuhn, U., Ganzeveld, L., Schebeske, G., Ciccioli, P., Holzke, C., Köble, R., Seufert, G., and Kesselmeier, J.: Significant light and temperature dependent monoterpene emissions from European beech (*Fagus sylvatica* L.) and their potential impact on the European volitile organic compound budget, J. Geophys. Res., 111, D16305, doi:10.1029/2005JD006751, 2006.

Dudareva, N., Pichersky, E., and Gershenzon, J.: Biochemistry of plant volatiles, Plant Physiol., 135, 1893–1902, 2004.

Farquhar, G., Von Caemmerer, S., and Berry, J.: A biochemical model of photosynthetic CO_2 assimilation in leaves of C_3 species, Planta, 149, 78–90, 1980.

Fischbach, R., Staudt, M., Zimmer, I., Rambal, S., and Schnitzler, J.-P.: Seasonal pattern of monoterpene synthase activities in leaves of the evergreen tree *Quercus ilex*, Physiol. Plantarum, 114, 354–360, 2002.

Franceschi, V. R., Krokene, P., Christiansen, E., and Krekling, T.: Anatomical and chemical defenses of conifer bark against bark beetles and other pests, New Phytol., 167, 353–376, doi:10.1111/j.1469-8137.2005.01436.x, 2005.

Gershenzon, J., Maffei, M., and Croteau, R.: Biochemical and histochemical localization of monoterpene biosynthesis in the glandular trichomes of spearmint (*Mentha spicata*), Plant Physiol., 89, 1351–1357, 1989.

Gershenzon, J., Murtagh, G., and Croteau, R.: Absence of rapid terpene turnover in several diverse species of terpene-accumulating plants, Oecologia, 96, 583–592, 1993.

Gershenzon, J., McConkey, M., and Croteau, R.: Regulation of monoterpene accumulation in leaves of Peppermint, Plant Physiol., 122, 205–213, 2000.

Greenberg, J., Guenther, A., Harley, P., Otter, L., Veenendaal, E., Hewitt, C., James, A., and Owen, S.: Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana, J. Geophys. Res., 108, 8466, doi:10.1029/2002JD002317, 2003.

Grote, R., Mayrhofer, S., Fischbach, R., Steinbrecher, R., Staudt, M., and Schnitzler, J.-P.: Process-based modelling of isoprenoid emissions from evergreen leaves of *Quercus ilex* (L.), Atmos. Environ., 40, S152–S165, 2006.

Guenther, A., Zimmerman, P., Harley, P., Monson, R., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, J. Geophys. Res., 98, 12609–12617, 1993.

Guenther, A., Hewitt, C., Erickson, D., Fall, R., Geron, C.,

Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of emissions of gases and aerosols from nature), Atmos. Chem. Phys., 6, 3181–3210, 2006, http://www.atmos-chem-phys.net/6/3181/2006/.

Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J., and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosciences, 3, 93–101, 2006, http://www.biogeosciences.net/3/93/2006/.

Haxeltine, A. and Prentice, I.: A general model for the light-use efficiency of primary production, Funct. Ecol., 10, 551–561, 1996.

He, C., Murray, F., and Lyons, T.: Seasonal variations in monoterpene emissions from *Eucalyptus* species, Chemosphere, 2, 65–76, doi:10.1016/S1465-9972(99)00052-5, 2000.

Hewitt, C., Monson, R., and Fall, R.: Isoprene emissions from the grass *Arundo donax* L. are not linked to photorespiration, Plant Sci., 66, 139–144, 1990.

Hickler, T., Smith, B., Sykes, M., Davis, M., Sugita, S., and Walker, K.: Using a generalized vegetation model to simulate vegetation dynamics in Northeastern USA, Ecology, 85, 519–530, 2004.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C., and Seinfeld, J. H.: Formation of organic aerosols from the oxidation of biogenic hydrocarbons, J. Atmos. Chem., 26, 189–222, 1997.

Holzinger, R., Lee, A., McKay, M., and Goldstein, A. H.: Seasonal variability of monoterpene emission factors for a Ponderosa pine plantation in California, Atmos. Chem. Phys., 6, 1267–1274, 2006, http://www.atmos-chem-phys.net/6/1267/2006/.

Jenkin, M. and Clemitshaw, K.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, Atmos. Environ., 34, 2499–2527, 2000.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology, J. Atmos. Chem., 33, 23–88, 1999.

Kesselmeier, J., Bode, K., Schafer, L., Schebeske, G., Wolf, A., Brancaleoni, E., Cecinato, A., Ciccioli, P., Frattoni, M., Dutaur, L., Fugit, J. L., Simon, V., and Torres, L.: Simultaneous field measurements of terpene and isoprene emissions from two dominant mediterranean oak species in relation to a North American species, Atmos. Environ., 32, 1947–1953, 1998.

Komenda, M. and Koppmann, R.: Monoterpene emissions from Scots pine *Pinus sylvestris*: field studies of emission rate variabilities, J. Geophys. Res., 107, 4161, doi:10.1029/2001JD000691, 2002.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T., and Kesselmeier, J.: Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species, Glob. Change Biol., 10, 663–682, doi:10.1111/j.1529-8817.2003.00771.x, 2004.

Lathière, J., Hauglustaine, D., De Noblet-Ducoudré, N., Krinner, G., and Folberth, G.: Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model, Geophys. Res. Lett., 32, L20818, doi:10.1029/2005GL024164, 2005.

Lathière, J., Hauglustaine, D., Friend, A., De Noblet-Ducoudré, N., Viovy, N., and Folberth, G.: Impact of climate variability and land use changes on global biogenic volatile organic compound emissions, Atmos. Chem. Phys., 6, 2129–2146, 2006, http://www.atmos-chem-phys.net/6/2129/2006/.

Lerdau, M., Dilts, S., Westberg, H., Lamb, B., and Allwine, E.: Monoterpene emission from ponderosa pine, J. Geophys. Res., 99, 16609–16015, 1994.

Lerdau, M., Matson, P., Fall, R., and Monson, R.: Ecological controls over monoterpene emissions from Douglas-fir (*Pseudotsuga menziesii*), Ecology, 76, 2640–2647, 1995.

Lerdau, M., Litvak, M., Palmer, P., and Monson, R.: Controls over monoterpene emissions from boreal forest conifers, Tree Physiol., 17, 563–569, 1997.

Lichtenthaler, H., Rohmer, M., and Schwender, J.: Two independent biochemical pathways for isopentenyl diphosphate and isoprenoid biosynthesis in higher plants, Physiol. Plantarum, 101, 643–652, 1997.

Litvak, M. and Monson, R.: Patterns of induced and constitutive monoterpene production in conifer needles in relation to insect herbivory, Oecologia, 114, 531–540, 1998.

Llusià, J. and Peñuelas, J.: *Pinus halepensis* and *Quercus ilex* terpene emission as affected by temperature and humidity, Biol. Plantarum, 42, 317–320, 1999.

Llusià, J., Peñuelas, J., Alessio, G. A., and Estiarte, M.: Seasonal contrasting changes of foliar concentrations of terpenes and other volatile organic compound in four domiant species of a Mediterranean shrubland submitted to a field experimental drought and warming, Physiol. Plantarum, 127, 632–649, 2006.

Loreto, F., Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., Fabozzi, C., and Tricoli, D.: Evidence of the photosynthetic origin of monoterpenes emitted by *Quercus ilex* L leaves by C-13 labeling, Plant Physiol., 110, 1317–1322, 1996.

Loreto, F., Fischbach, R., Schnitzler, J.-P., Ciccioli, P., Brancaleoni, E., Calfapietra, C., and Seufert, G.: Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak *Quercus ilex* L. grown at elevated CO_2 concentrations, Glob. Change Biol., 7, 709–717, 2001.

Loreto, F., Pinelli, P., Manes, F., and Kollist, H.: Impact of ozone on monoterpene emissions and evidence for an isoprene-like antioxidant action of monoterpenes emitted by *Quercus ilex*, Tree Physiol., 24, 361–367, 2004.

McConkey, M. E., Gershenzon, J., and Croteau, R. B.: Developmental regulation of monoterpene biosynthesis in the glandular trichomes of peppermint, Plant Physiol., 122, 215–223, 2000.

Mihaliak, C., Gershenzon, J., and Croteau, R.: Lack of rapid monoterpene turnover in rooted plants: implications for theories of plant chemical defense, Oecologia, 87, 373–376, 1991.

Misson, L., Panek, J., and Goldstein, A. H.: A comparison of three approaches to modeling leaf gas exchange in annually drought-stressed ponderosa pine forests, Tree Physiol., 24, 529–541, 2004.

Misson, L., Tang, J. W., Xu, M., McKay, M., and Goldstein, A. H.: Influences of recovery from clear-cut, climate variability, and thinning on the carbon balance of a young ponderosa pine plantation, Agr. Forest Meteorol., 130, 207–222, 2005.

Misson, L., Gershenson, A., Tang, J., McKay, M., Cheng, W., and Goldstein, A. H.: Influences of canopy photosynthesis and summer rain pulses on root dynamics and soil respiration in a young ponderosa pine forest, Tree Physiol., 26, 833–844, 2006.

Mitchell, T. D. and Jones, P. D.: An improved method of constructing a database of monthly climate observations and associated high-resolution grids, Int. J. Climatol., 25, 693–712, 2005.

Naik, V., Delire, C., and Wuebbles, D.: Sensitivity of global biogenic isoprenoid emissions to climate variability and atmospheric CO_2, J. Geophys. Res., 109, D06301, doi:10.1029/2002JD003203, 2004.

New, M., Hulme, M., and Jones, P.: Representing twentieth-century space-time climate variability. Part II: Development of 1901-96 monthly grids of terrestrial surface climate, J. Climate, 13, 2217–2238, 2000.

Niinemets, U. and Reichstein, M.: A model analysis of the effects of nonspecific monoterpenoid storage in leaf tissues on emission kinetics and composition in Mediterranean sclerophyllous *Quercus* species, Global Biogeochem. Cy., 16, 1110, doi:10.1029/2002GB001927, 2002.

Niinemets, U., Seufert, G., Steinbrecher, R., and Tenhunen, J.: A model coupling foliar monoterpene emissions to leaf photosynthetic characteristics in Mediterranean evergreen *Quercus* species, New Phytol., 153, 257–275, 2002.

Niinemets, U., Loreto, F., and Reichstein, M.: Physiological and physicochemical controls on foliar volatile organic compound emissions, Trends Plant Sci., 9, 180–186, 2004.

Otter, L., Guenther, A., Wiedinmyer, C., Fleming, G., Harley, P., and Greenberg, J.: Spatial and temporal variations in biogenic volatile organic compound emissions for Africa south of the equator, J. Geophys. Res., 108, 8505, doi:10.1029/2002JD002609, 2003.

Otter, L. B., Guenther, A., and Greenberg, J.: Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands, Atmos. Environ., 36, 4265–4275, 2002.

Owen, S., Harley, P., Guenther, A., and Hewitt, C.: Light dependency of VOC emissions from selected Mediterranean plants, Atmos. Environ., 36, 3147–3159, 2002.

Panek, J.: Ozone uptake, water loss and carbon exchange dynamics in annually drought-stressed *Pinus ponderosa* forests: measured trends and parameters for uptake modeling, Tree Physiol., 24, 277–290, 2004.

Peñuelas, J. and Llusià, J.: Linking photorespiration, monoterpenes and thermotolerance in *Quercus*, New Phytol., 155, 227–237, doi:10.1046/j.1469-8137.2002.00457.x, 2002.

Pichersky, E., Noel, J. P., and Dudareva, N.: Biosynthesis of plant volatiles: nature's diversity and ingenuity, Science, 311, 808–811, 2006.

Pressley, S., Lamb, B., Westberg, H., Guenther, A., Chen, J., and Allwine, E.: Monoterpene emissions from a Pacific Northwest old-growth forest and impact on regional biogenic VOC emission estimates, Atmos. Environ., 38, 3089–3098, 2004.

Ruuskanen, T. M., Kolari, P., Bäck, J., Kulmala, M., Rinne, J., Hakola, H., Taipale, R., Raivonen, M., Altimir, N., and Hari, P.: On-line field measurements of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry, Boreal Environ. Res., 10, 553–567, 2005.

Schade, G., Goldstein, A. H., and Lamanna, M.: Are monoterpene emissions influenced by humidity?, Geophys. Res. Lett., 26, 2187–2190, 1999.

Schuh, G., Heiden, A. C., Hoffmann, T., Kahl, J., Rockel, P., Rudolph, J., and Wildt, J.: Emissions of volatile organic compounds from sunflower and beech: dependence on temperature and light intensity, J. Atmos. Chem., 27, 291–318, 1997.

Simpson, D., Yttri, K. E., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencser, A., Pio, C., Puxbaum, H., and Legrand, M.: Modeling carbonaceous aerosol over Europe: analysis of the CARBOSOL and EMEP EC/OC campaigns, J. Geophys. Res.-Atmos., 112, D23S14, doi:10.1029/2006JD008158, 2007.

Sitch, S., Smith, B., Prentice, I., Arneth, A., Bondeau, A., Cramer, W., Kaplan, J., Levis, S., Lucht, W., Sykes, M., Thonicke, K., and Venevsky, S.: Evaluation of ecosystem dynamics, plant geography and terrestrial carbon cycling in the LPJ Dynamic Global Vegetation Model, Glob. Change Biol., 9, 161–185, 2003.

Smith, B., Prentice, I., and Sykes, M.: Representation of vegetation dynamics in the modelling of terrestrial ecosystems: comparing two contrasting approaches within European climate space, Global Ecol. Biogeogr., 10, 621–637, 2001.

Staudt, M. and Bertin, N.: Light and temperature dependence of the emission of cyclic and acyclic monoterpenes from holm oak (*Quercus ilex* L.) leaves, Plant Cell Environ., 21, 385–395, 1998.

Staudt, M. and Seufert, G.: Light-dependent emission of monoterpenes by Holm Oak (*Quercus ilex* L.), Naturwissenschaften, 82, 89–92, 1995.

Staudt, M., Bertin, N., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Frenzel, B., and Fugit, J.-L.: Seasonal and diurnal patterns of monoterpene emissions from *Pinus pinea* (L.) under field conditions, Atmos. Environ., 31, 145–156, 1997.

Staudt, M., Bertin, N., Frenzel, B., and Seufert, G.: Seasonal variation in amount and composition of monoterpenes emitted by young *Pinus pinea* trees – implications for emission modeling, J. Atmos. Chem., 35, 77–99, 2000.

Staudt, M., Joffre, R., Rambal, S., and Kesselmeier, J.: Effect of elevated CO_2 on monoterpene emission of young *Quercus ilex* trees and its relation to structural and ecophysiological parameters, Tree Physiol., 21, 437–445, 2001.

Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R., and Curci, G.: Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighbouring countries, Atmos. Environ., 43, 1380–1391, doi:10.1016/j.atmosenv.2008.09.072, 2009.

Street, R., Owen, S., Duckham, S., Boissard, C., and Hewitt, C.: Effect of habitat and age on variations in volatile organic compound (VOC) emissions from *Quercus ilex* and *Pinus pinea*, Atmos. Environ., 31, 89–100, 1997.

Suni, T., Berninger, F., Vesala, T., Markkanen, T., Hari, P., Makela, A., Ilvesniemi, H., Hanninen, H., Nikinmaa, E., Huttula, T., Laurila, T., Aurela, M., Grelle, A., Lindroth, A., Arneth, A., Shibistova, O., and Lloyd, J.: Air temperature triggers the recovery of evergreen boreal forest photosynthesis in spring, Glob. Change Biol., 9, 1410–1426, 2003.

Tingey, D., Manning, M., Grothaus, L., and Burns, W.: Influence of light and temperature on monoterpene emission rates from Slash pine, Plant Physiol., 65, 797–801, 1980.

Tsigaridis, K. and Kanakidou, M.: Global modelling of secondary

organic aerosol in the troposphere: a sensitivity analysis, Atmos. Chem. Phys., 3, 1849–1869, 2003, http://www.atmos-chem-phys.net/3/1849/2003/.

Turner, G. W., Gershenzon, J., and Croteau, R. B.: Development of peltate glandular trichomes of peppermint, Plant Physiol., 124, 665–679, 2000.

Wang, Y.-F., Owen, S. M., Li, Q.-J., and Penuelas, J.: Monoterpene emissions from rubber trees (*Hevea brasiliensis*) in a changing landscape and climate: chemical speciation and environmental control, Glob. Change Biol., 13, 2270–2282, doi:10.1111/j.1365-2486.2007.01441.x, 2007.

Wiberley, A., Linskey, A., Falbel, T., and Sharkey, T.: Development of the capacity for isoprene emission in kudzu, Plant Cell Environ., 28, 898–905, 2005.

Yokouchi, Y., Hijikata, A., and Ambe, Y.: Seasonal variation of monoterpene emission rate in a pine forest, Chemosphere, 13, 255–259, 1984.