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The emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling

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Abstract

In models of plant volatile isoprenoid emissions, the instantaneous compound emission rate typically scales with the plant's emission capacity under specified environmental conditions, also defined as the emission factor, E_S . In the most widely employed plant isoprenoid emission models, the algorithms developed by Guenther and colleagues (1991, 1993), instantaneous variation of the steady-state emission rate is described as the product of E_S and light and temperature response functions. When these models are employed in the atmospheric chemistry modeling community, species-specific E_S values and parameter values defining the instantaneous response curves are typically considered as constant. In the current review, we argue that E_S is largely a modeling concept, importantly depending on our understanding of which environmental factors affect isoprenoid emissions, and consequently need standardization during E_S determination. In particular, there is now increasing consensus that variations in atmospheric CO_2 concentration, in addition to variations in light and temperature, need to be included in the emission models. Furthermore, we demonstrate that for less volatile isoprenoids, mono- and sesquiterpenes, the emissions are often jointly controlled by the compound synthesis and volatility, and because of these combined biochemical and physico-chemical properties, specification of E_S as a constant value is incapable of describing instantaneous emissions within the sole assumptions of fluctuating light and temperature, as are used in the standard algorithms. The definition of E_S also varies depending on the degree of aggregation of E_S values in different parameterization schemes (leaf- vs. canopy- or region-level, species vs. plant functional type level), and various aggregated E_S schemes are not compatible for different integration models. The summarized information collectively emphasizes the need to update model algorithms by including missing environmental and physico-chemical controls, and always to define E_S within the proper context of model structure and spatial and temporal resolution.

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1 Introduction

Volatile organic compounds (VOC) are major determinants of atmospheric oxidative capacity and play important roles in formation of secondary organic aerosols and cloud condensation nuclei with important implications for the Earth's climate (Chameides et al., 1988; Claeys et al., 2004; Engelhart et al., 2008; Fuentes et al., 2000; Kiendler-Scharr et al., 2009; Kulmala et al., 2004; Mentel et al., 2009; Peñuelas and Staudt, 2010; Spracklen et al., 2008; Tunved et al., 2006). VOC emissions from plants are particularly relevant for these atmospheric processes as worldwide emissions from vegetation exceed anthropogenic emissions by more than an order of magnitude (e.g., Guenther et al., 1995). Only in highly industrialized areas, human-produced VOC may exceed the contribution from vegetation, but even there, biogenic emissions peak when high temperatures and levels of radiation foster photochemical reactions, and thus, biogenic emissions do significantly contribute to air photochemistry in urban areas as well (Chameides et al., 1988; Karlik and Winer, 1999, 2001).

Among plant-released compounds, volatile isoprenoids, isoprene and methylbutenol (C₅), monoterpenes (C₁₀) and sesquiterpenes (C₁₅), deserve special attention because of high reactivity in the atmosphere and their large contribution, often more than 90%, to total plant emissions. Atmospheric chemistry and transport and chemistry-climate models require accurate estimation of volatile isoprenoid emission rates with satisfactory spatial and temporal resolution. For biome to global-scale predictions of air chemistry and climate, BVOC emission estimates with a spatial resolution of 100–10000 km², depending on the process studied, can be satisfactory, but for regional air quality, the emission estimates need to be of very high temporal (~ 1 h) and spatial (1–50 km²) resolution to appropriately account for the source variability (Eder et al., 1993; Fiore et al., 2003; Logan, 1989; Loughner et al., 2007). Such high resolution data are obtained using predictive models that require climatic forcing variables, information on plant leaf area, architecture of plant stands, species composition and isoprenoid emission potentials as input data and provide instantaneous emission rates as model output.

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In these models, the key characteristic determining the emission capacity of vegetation is the emission factor (E_S), separately determined for different classes of volatile isoprenoids, isoprene, monoterpenes and sesquiterpenes. As originally defined (Guenther et al., 1991, 1993), E_S is the steady-state emission rate standardized for instantaneous variations in environmental drivers. In the initial form of the models, E_S was standardized for leaf temperature (commonly and arbitrarily taken as $T_L = 30^\circ\text{C}$) and light intensity (commonly and arbitrarily taken as $Q = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$). Such a definition allowed for convenient simulation of volatile isoprenoid fluxes as the product of E_S and the normalized light and temperature functions, so called Guenther et al. algorithms (Guenther et al., 1991, 1993). A similar logic, defining the emission capacity and modifying this by environmental drivers is used in all upcoming emission models, even if including more detailed process-based descriptions of various biochemical steps and resulting environmental dependencies (Martin et al., 2000; Niinemets et al., 1999, 2002c; Zimmer et al., 2000).

At the time of its initial definition, E_S was considered as a species-specific constant and the shapes of light and temperature response functions were considered constant as well (Guenther et al., 1991, 1993). Up to present, the majority of atmospheric modeling exercises continue to be established on the premise of constant E_S and response function shapes. However, over recent years it has become increasingly evident that apart from light and temperature, additional short- and medium-term drivers play an important role in modifying the emission rates (Arneth et al., 2007; Heald et al., 2009; Possell et al., 2005). In some recent efforts, modelers have grappled with ways to include some of these additional factors in their simulations (Arneth et al., 2007; Heald et al., 2009; Possell et al., 2005), while others have retained the simpler structure of the original models. As a result, the concept of E_S has become conceptually “opaque” and variable.

In particular, CO_2 concentration response functions have been developed (Arneth et al., 2007; Possell et al., 2005; Wilkinson et al., 2009), and it has been suggested that CO_2 concentrations also need standardization in defining E_S (Wilkinson et al.,

2009). In addition, it has been demonstrated that the standardized emission rates as well as the shape of the temperature response curve can vary depending on the rate of temperature change (e.g., fast vs. slow temperature response curves, Singaas et al., 1999; Singaas and Sharkey, 2000). Furthermore, for less volatile mono- and sesquiterpenes, it has been shown that the steady-state assumption underlying E_S and environmental response curves is often not satisfied due to simultaneous controls of emissions by the rate of synthesis and volatility (Grote and Niinemets, 2008; Niinemets and Reichstein, 2002; Noe et al., 2006, 2010; Schurgers et al., 2009a). This evidence collectively suggests that E_S is a modeling concept that depends on the understanding of the biological, environmental and physico-chemical factors limiting isoprenoid emission and, thus, varies in dependence on the model structure.

Of course, every model is incomplete in its representation of true biochemical and physico-chemical processes, and E_S is differently defined depending on the assumptions carried in each model. This recognition should compel us to continually assess missing processes and their importance to the uncertainties contained in model predictions, as well as to identify strategies for model improvement. It is within this spirit that we have undertaken the current analysis as a means to evaluate the current state-of-affairs of isoprenoid emission models and definitions of E_S . In this synthesis, we will begin by reviewing the traditional “Guenther” algorithms that have been so widely used in the modeling of plant isoprenoid emissions. We will attempt to define these algorithms within the context of our knowledge about biochemical processes, thus establishing a mechanistic justification for their use. We also review the way the species-specific leaf-level E_S values are aggregated in higher scale emission models, and the potential for aggregation errors during the scaling of emission estimates from the leaf- to landscape-scales. Apart from strong biological sources of variation, definitions of E_S differ depending on the underlying model algorithms and degree of aggregation, and can be a chief reason for large between-model discrepancies of simulated emission totals (e.g., Arneth et al., 2008 for a compilation of respective global extrapolation exercises).

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We use the overall analysis to emphasize that E_S as a modeling concept should always correspond to the structure, time-step and spatial resolution of the model used, and to highlight the prime areas for future experimental work needed for model improvement and application in highly variable field environments. In this analysis, we focus on instantaneous environmental responses, and consider acclimation of isoprenoid emission to environmental conditions as much as this is needed to understand the variability in the shape of environmental response curves and development of novel models (induced emissions). For acclimation, developmental and stress responses in E_S we refer to the accompanying paper (Niinemets et al., 2010).

2 Models and definitions of E_S

The definition of E_S , the emission rate under arbitrarily chosen standard conditions, largely depends on an understanding of the rapid emission controls and on the form of the specific emission model that is used. In the past, it has been considered safe to fix only light intensity and leaf temperature to derive E_S values for isoprene, a compound that is rapidly synthesized from a small carbon pool in chloroplasts. Moreover, it was considered sufficient to fix only temperature for monoterpenes emitted from a large pool in specialized storage tissues such as resin ducts and resin blisters in conifers (Guenther et al., 1991, 1993; Tingey et al., 1980). Later, it was observed that in several species lacking specialized storage tissues, monoterpene emissions depend on light availability, in a manner similar to isoprene (Loreto et al., 1996c; Staudt and Seufert, 1995). It was further found that in species with large monoterpene reservoirs in storage tissues, light-dependent monoterpene emissions can also occur (e.g., Staudt et al., 1997).

Discovery of the light-dependent emissions in both the non-storing and storing species caused us to re-assess the definition of E_S for monoterpene emissions, and made clear that light, in addition to temperature, must be fixed in determining monoterpene E_S . To complicate matters even further, it was discovered that species lacking

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specialized storage tissues, can exhibit light-dependent and light-independent emissions, which can potentially interfere with each other (Kahl et al., 1999; Loreto et al., 1996a; Niinemets and Reichstein, 2002; Schuh et al., 1997). Thus, we were forced to develop mixed models or dynamic models for prediction of E_S , especially for the emission of isoprenoids with higher molecular mass (Niinemets and Reichstein, 2002; Schuh et al., 1997).

Apart from light and temperature, isoprene emissions also vary in response to changes in CO₂ concentration (Jones and Rasmussen, 1975; Loreto and Sharkey, 1990; Mgalobilishvili et al., 1978; Monson and Fall, 1989). This physiological evidence has been neglected so far, and only recently, the importance of standardization of CO₂ concentration inside the leaf for determination of E_S values has been recognized (Wilkinson et al., 2009).

The above discussion emphasizes that the definition of E_S depends on what environmental factors are considered as operative in altering the emission rate and thus needing standardization during the emission measurements. The definition of E_S is also different when the emissions come from a large pool of preformed compounds, or are immediately synthesized, or when they come simultaneously from both large existing pools and from de novo synthesis. Thus, the choice of the emission model used can crucially alter E_S estimations. In the following sections, various model approaches are summarized and model-specific sources of variation in emission rates are analyzed.

2.1 Modeling standardized responses of volatile isoprenoids to key environmental factors in steady-state conditions

Since the early 1990's, two prominent models, the so-called "Guenther et al., algorithms", have been used to simulate the responses of isoprene emissions to incident quantum flux density (Q , light intensity) and leaf temperature (T_L) and the release of monoterpenes from storage tissues with regard to dependence on temperature (Guenther, 1991, 1993, 1995, 1999, 1996c). In the case of isoprene, the emission algorithm was constructed on the premise that the emissions are driven by the combined

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coupling of isoprenoid biosynthesis to photosynthetic processes and the temperature-dependence of enzyme activity, while the monoterpene release model was based on monoterpene vaporization and diffusion out of the storage tissues, i.e., on physical processes (see Guenther, 1999; Guenther et al., 1991, 1993, 1995, 1996c). Later, the isoprene emission algorithm was also employed to simulate methylbutenol (Harley et al., 1998; Schade et al., 2000) and light-dependent monoterpene emissions in species lacking specialized monoterpene storage tissues (Bertin et al., 1997; Ciccioli et al., 1997b; Dindorf et al., 2006; Kesselmeier et al., 1997; Kuhn et al., 2002; Steinbrecher et al., 1997). Additionally, CO₂ response functions have recently been added to the Guenther et al. algorithms (Wilkinson et al., 2009), as well as to emission models that seek to link isoprenoid production directly to photosynthetic metabolism (Arneeth et al., 2007; Schurgers et al., 2009a).

According to the Guenther et al. type of models, the volatile isoprenoid emission rate, E , is a product of the standardized emission rate, E_S , and non-dimensional light $f(Q)$ and leaf temperature $f(T_L)$ and CO₂ $f(C_i)$ functions:

$$E = E_S f(Q) f(T_L) f(C_i). \quad (1)$$

The functions $f(Q)$, $f(T_L)$ and $f(C_i)$ are normalized to 1.0 at standardized conditions used for E_S determination. For monoterpene emissions from storage compartments, $f(Q) = f(C_i) = 1$ in all cases.

2.1.1 The light dependence ($f(Q)$ function)

The dependence of isoprenoid emissions on incident quantum flux density (Q) was originally described by a model similar to that used to simulate the net CO₂ assimilation rate and its dependence on incident quantum flux density (Guenther et al., 1991), the so-called Smith's function (Smith, 1937; Tenhunen et al., 1976). This response function represents a classic rectangular hyperbola, with the emission rate approaching

an asymptote as Q approaches infinity:

$$f(Q) = \frac{C_{L1}\alpha Q}{\sqrt{1 + \alpha^2 Q^2}}, \quad (2)$$

where α is the apparent (standardized) quantum yield of isoprenoid emission and C_{L1} is the scaling constant to force the function to 1.0 at the standardized value of Q (commonly taken as $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$).

The metabolic basis for the $f(Q)$ function is not well understood. It is known that the 2-C-methyl-D-erythritol 4-phosphate (MEP) pathway that leads to the synthesis of both isoprene and monoterpenes occurs in the chloroplasts, and is dependent on ATP and NADPH produced in the light-dependent reactions of photosynthesis (e.g., Lichtenthaler et al., 1997; Schwender et al., 1997). Additionally, the rate of production of glyceraldehyde 3-phosphate (G3P), a primary product of photosynthesis, and a primary substrate of isoprene and monoterpene biosynthesis, is dependent on light intensity in rectangular hyperbolic fashion (Magel et al., 2006; Rasulov et al., 2009). Thus, there is good reason to believe that the rectangular hyperbolic shape of the $f(Q)$ function truly reflects a shape similar to that of the photosynthetic light response function.

In the initial model parameterization, values of $\alpha = 0.0027$ and $C_{L1} = 1.066$ were used for isoprene (Guenther et al., 1991), and these values have been used in unmodified form in the majority of subsequent modeling studies that have employed the Guenther et al. (1991, 1993) algorithms. However, there is evidence of significant variation in the shape of the light response curve, in particular among species (Fig. 1a, b), and within leaves from different canopy positions (Fig. 1a, b). Acclimation to low light conditions increases the apparent quantum yield for an incident light, α , implying that the light function saturates at lower light intensities. Enhanced α in leaves from lower canopy likely reflects more efficient light harvesting in these leaves, compatible with greater foliage chlorophyll contents in low light (Niinemets, 2007 for a review).

In addition, analysis of light dependencies of methylbutenol (Harley et al., 1998; Schade et al., 2000) and light-dependent monoterpene emissions (Schuh et al., 1997;

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Staudt et al., 2003) also simulated by the same algorithm demonstrates that the shape of the response curves can be different for these volatile isoprenoids than the response shape for isoprene (Sect. 2.2.2). Taken together, this evidence strongly suggests that using constant parameters of the light response function, α and C_{L1} , in large-scale simulation analyses, has no empirical justification. In BVOC emission models, more effort should be devoted to gaining adequate parameterizations for the light response functions. Although quantitative relationships with integrated canopy light environment or canopy leaf area index have not been developed, variations in α have been occasionally included in emission models, varying its value with cumulative leaf area index from canopy top to bottom (Guenther et al., 1999).

2.1.2 The temperature dependence ($f(T_L)$ function) for de-novo synthesized isoprenoids

In the Guenther et al. (1991, 1993) algorithms, an Arrhenius type response was used for the temperature function, $f(T_L)$, of isoprene emission. This function describes a curve with an optimum at T_m :

$$f(T_L) = \frac{\exp\left[\frac{C_{T1}(T_L - T_S)}{RT_S T_L}\right]}{1 + \exp\left[\frac{C_{T2}(T_L - T_m)}{RT_S T_L}\right]}, \quad (3)$$

where C_{T1} and C_{T2} are the parameters (J mol^{-1}) characterizing the activation and de-activation energy of the emission, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T_L is the absolute leaf temperature and T_S is the standard temperature (typically 303.16 K) at which $f(T_L) = 1$. In initial temperature response function parameterization (Guenther et al., 1991, 1993), the values used were $C_{T1} = 95000 \text{ J mol}^{-1}$, $C_{T2} = 230000 \text{ J mol}^{-1}$ and $T_m = 314 \text{ K}$. Later, an additional non-dimensional empirical parameter C_{T3} has been

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added (Guenther, 1997):

$$f(T_L) = \frac{\exp\left[\frac{C_{T1}(T_L - T_S)}{RT_S T_L}\right]}{C_{T3} + \exp\left[\frac{C_{T2}(T_L - T_m)}{RT_S T_L}\right]} \quad (4)$$

C_{T3} as originally introduced was taken as 0.961 (Guenther, 1997) to account for the circumstance that the original parameterization proposed in Guenther et al. (1993) did not yield $f(T_L) = 1.0$ at 30°C. However, we note that combinations of C_{T1} , C_{T2} and T_m can be found that satisfy the criterion $f(T_S) = 1.0$ without the need for an additional parameter.

In the atmospheric modeling community, the temperature response function is often used as originally developed, even using the initial default parameterization of Guenther et al. (1991, 1993). This approach does not consider that the temperature response of isoprene emission is variable due to reasons not yet fully understood. The mechanistic basis for the temperature response function (Eq. 3) stems from enzyme kinetics, and Eq. 3 can be successfully parameterized to fit the in vitro temperature response of the isoprene synthase enzyme reaction (Lehning et al., 1999; Monson et al., 1992; Niinemets et al., 1999). Although the shapes of temperature responses of isoprene emission and isoprene synthase are similar, there are several important differences. In particular, isoprene synthase has a higher optimum temperature than isoprene emission and the “standard” isoprene emission curve by Guenther et al. (1991, 1993) lies well below that for isoprene synthase (Fig. 2, Lehning et al., 1999; Monson et al., 1992), (s. also Niinemets et al., 1999 for the comparison of isoprene emission responses and synthase activity). In addition, the observed temperature dependence of isoprene emission differs depending on how measurements are made. When measurements are carried out fast, waiting no more than 3–4 min. at each temperature step, the temperature response curve of isoprene emission has a higher optimum than if measurements are conducted slowly, waiting until an apparent steady-state (30 min. and more) is reached (Singsaas et al., 1999; Singsaas and Sharkey, 2000).

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The discrepancy from isoprene synthase enzyme kinetics and rapid time-dependent changes in temperature response curves (Niinemets et al., 2010 for longer-term acclimation-type changes) suggest that the temperature response of isoprene emission does not solely reflect enzyme kinetics, but also changes in the immediate isoprene precursor, dimethylallyldiphosphate, DMADP, pool size (Niinemets et al., 1999). It is likely that with increasing temperature, isoprene synthase activity increases up to temperatures close to the point of irreversible thermal damage of chloroplasts (Fig. 2), while the DMADP pool size starts to decrease already under mild heat stress conditions that are inhibitory for photosynthetic CO₂ uptake (production of glyceraldehyde 3-phosphate) and photosynthetic electron transport that are both needed for DMADP formation (Niinemets et al., 1999). Thus, the discrepancy between isoprene synthase and DMADP pool size becomes larger the longer the leaf stays at supraoptimal temperatures (Fig. 2 for the comparison of fast vs. slow temperature responses of isoprene emission and Singaas et al., 1999; Singaas and Sharkey, 2000).

Apart from the time-dependent effects, the temperature optimum can also be affected by physiological acclimation to growth temperature regime. Plants of the deciduous vine *Mucuna pruriens* have been shown to have lower temperature optima of isoprene emission when the growth temperature was decreased (Monson et al., 1992). The shape of the temperature response curve has also been shown to vary among the leaves from the top and bottom of tree canopies (Harley et al., 1996, 1997). This evidence collectively demonstrates that the shape of the isoprene temperature response function cannot be taken as constant, but it varies with the rate of change in leaf temperature and can also be modified upon acclimation to different environmental conditions (e.g., Mayrhofer et al., 2005; Wiberley et al., 2005). Modifications in the optimum temperature of isoprene emission in dependence on past temperature environment have been embedded in MEGAN (Guenther et al., 2006), but the quantitative data for parameterization of such relationships are very limited (Pétron et al., 2001).

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2.1.3 The temperature dependence ($f(T_L)$ function) for stored isoprenoids

For species with monoterpenes stored in specialized leaf tissues, only physical evaporation and diffusion were originally suggested to control the emission rate and $f(T_L)$ has been defined as (Guenther et al., 1991, 1993):

$$f(T_L) = \exp[\beta(T_L - T_S)], \quad (5)$$

where β (K^{-1}) is the temperature response coefficient characterizing the exponential increase of monoterpene vapor pressure and velocity of diffusion with temperature. In chemistry and biology, the temperature dependence of processes is often described according to the Q_{10} , the rate at temperature $T + 10^\circ C$ relative to the rate at temperature T . Q_{10} values are then used to characterize the exponential increase in process rates as a function of temperature. Q_{10} and β are related as:

$$Q_{10} = \exp(10\beta), \quad (6)$$

In the original parameterization of the Guenther et al. (1993) algorithms, a value of $\beta = 0.09 K^{-1}$ was employed, corresponding to a Q_{10} value of 2.46.

Again, in many past and contemporary simulation analyses, β has been considered constant. Yet, recent studies have demonstrated significant interspecific and seasonal variation in β values for the sum of total emitted monoterpenes (Komenda and Koppmann, 2002; Llusia and Peñuelas, 2000; Ruuskanen et al., 2007; Tarvainen et al., 2005). Monoterpenes largely differ in volatility (saturated vapor pressure, partitioning between gas, liquid and lipid phases, Sect. 2.2) at given temperature (Table 1, Copolovici and Niinemets, 2005; Niinemets and Reichstein, 2002). Thus, these variations in β values may reflect interspecific and seasonal differences in the composition of emitted monoterpenes (Sect. 2.4). Although quantitative measurements of sesquiterpene volatility are rare, sesquiterpenes are generally characterized by lower volatility than monoterpenes, and large differences in volatility occur among various sesquiterpenes as well (Bowles, 2003; Helmig et al., 2003; Paluch et al., 2009). Varying temperature response coefficients have been reported for mono- and sesquiterpenes emitted

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by the same species (Ruuskanen et al., 2007), and differing β values have been observed for different mono- and sesquiterpenes (Llusià and Peñuelas, 2000; Tarvainen et al., 2005), supporting the association of β values with compound volatility.

Nevertheless, the β values for any given mono- and sesquiterpene have been observed to vary during the season (Peñuelas and Llusià, 1999; Tarvainen et al., 2005), occasionally more than 4-fold for given monoterpene species (Tarvainen et al., 2005). Such changes may reflect modifications in monoterpene diffusion conductance from the site of storage to the ambient atmosphere, but there is currently no experimental data to inform us about such changes. An alternative explanation might be that in field studies, a limited temperature range is available for estimation of β values. In seasonal climates, the range is shifted to lower temperatures in the beginning and end of the growing season and to higher temperatures in mid-season. As the rise of compound vapor pressure with temperature is not strictly exponential, but is typically fitted by a three-parameter Antoine equation (Copolovici and Niinemets, 2005; van Roon et al., 2002), β for a given terpene will somewhat vary over different ranges of temperature. Thus, the variation in β values recovered in seasonal field studies may reflect inadequacy of the single parameter temperature response function.

A further shortcoming of current models of the monoterpene emission temperature responses is that some species, which were traditionally considered to emit monoterpenes only from storage tissues, have now been shown to also emit monoterpenes that have been synthesized from recently-assimilated CO₂. These emissions are predicted to depend on temperature according to Eq. 3 and also depend on light according to Eq. 2. For instance, the temperate evergreen conifer *Pinus sylvestris* has been previously considered to be only a storage emitter (Janson, 1993). However, using stable carbon isotope (¹³C) labeling to distinguish slow and fast turnover pools of monoterpenes, it was found that about 30% of emissions rely on de novo synthesis (fast turnover pools) in this species (Shao et al., 2001, see also the Sect. 2.3 for the light-dependent emissions of induced monoterpenes in other conifers). In such species with the emissions coming from both storage and de novo synthesis, modeling

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the temperature responses of emissions solely by Eq. 5 will be inadequate. β will inevitably have to be defined as a mixed parameter depending on the temperature effects on enzyme activity and physico-chemical properties of specific monoterpenes, including diffusion conductance. In addition, dependence of emissions on light suggests that values of β may also differ among past studies due to lack of standardization for light during measurements of temperature response curves (e.g. measurements in darkness vs. measurements under light). With this new knowledge in hand, further experimental studies are called for to gain insight into causes of variations in β values in emitters with terpene storage tissues.

2.1.4 CO₂ dependence ($f(C_i)$ function)

Apart from light and temperature, within leaf CO₂ concentrations (intercellular CO₂ concentration, C_i) also vary during the day as the result of changes in stomatal conductance (a measure of stomatal openness), especially under low atmospheric humidities and in plants experiencing soil water deficit. These short-term (also called “instantaneous”) influences of C_i are different than the effects of growth CO₂ concentration on E_S (for reviews see Arneth et al., 2007; Niinemets et al., 2010; Young et al., 2009). The instantaneous influences of C_i on isoprenoid emissions likely affect the partitioning of metabolites between the chloroplast and cytosol of plant cells (Rosenstiel et al., 2003), whereas the effect of growth CO₂ concentration likely affects the expression of key enzymes (Loreto et al., 2007; Rosenstiel et al., 2004). The CO₂-dependence function that is used to calculate E in Eq. 1, refers to the instantaneous influence of C_i .

Observations used to support parameterization of $f(C_i)$ demonstrated that isoprene emission rates decrease with increasing CO₂ concentration above the current ambient CO₂ concentrations of ca. 385 $\mu\text{mol mol}^{-1}$, while the emissions increase at sub-ambient CO₂ concentrations (Fig. 3, Loreto and Sharkey, 1990; Monson and Fall, 1989; Monson et al., 1991; Rasulov et al., 2009; Sharkey et al., 1991; Wilkinson et al., 2009). Fewer studies have further demonstrated that after the initial increase of

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isoprene emissions at lower CO_2 , the emissions level off and decrease again at C_i values below $100\text{--}150\ \mu\text{mol mol}^{-1}$ (Fig. 3, Loreto and Sharkey, 1990; Rasulov et al., 2009).

Few studies have looked at the CO_2 responses of higher molecular mass isoprenoid emissions. The immediate CO_2 effects are expected to be small for terpene emissions from storage tissues, but effects similar to isoprene emissions are predicted for emissions of de novo synthesized terpenes. In agreement with this expectation, monoterpene emission rates were not different at 350 and $700\ \mu\text{mol mol}^{-1}$ in terpene-storing species *Rosmarinus officinalis* (Peñuelas and Llusà, 1997). However, contrary to the predictions, monoterpene emission rates from the foliage of evergreen broad-leaved *Quercus ilex* that does not have specialized terpene storage tissues was also not significantly different between 350 and $1500\ \mu\text{mol mol}^{-1}$ in Loreto et al. (1996b) and between 350 and $700\ \mu\text{mol mol}^{-1}$ in Staudt et al. (2001a), although photosynthesis was stimulated by 1.4–1.8-fold by higher CO_2 in these studies. Differently from these two studies, monoterpene emission rate was reduced at $1000\ \mu\text{mol mol}^{-1}$ relative to $350\ \mu\text{mol mol}^{-1}$ in the same species in the study of Rapparini et al. (2004). In addition, in a manner similar to that for isoprene, Loreto et al. (1996b) demonstrated a reduction of monoterpene emission in CO_2 -free air in *Q. ilex*. Clearly more work on instantaneous CO_2 responses of mono- and especially sesquiterpene emissions is needed (Peñuelas and Staudt, 2010).

Definition of $f(C_i)$ in Eq. 1 has been attempted based on biochemical knowledge of isoprene synthesis (Wilkinson et al., 2009). In particular, it has been assumed that isoprene production at different CO_2 concentrations is determined by the partitioning of intermediates for DMADP synthesis between the cytosol and chloroplasts (Wilkinson et al., 2009). At low C_i , $f(C_i)$ was assumed to increase due to enhanced transport of triose phosphates from the cytosol into chloroplasts (Wilkinson et al., 2009), while at high CO_2 concentration, $f(C_i)$ was suggested to decrease due to increased use of phosphoenolpyruvate (PEP) in the cytosol by the enzyme PEP carboxylase, and thus decreased transport of PEP into the chloroplast for use in producing isoprenoid compounds in the

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MEP pathway (Loreto et al., 2007; Monson et al., 2007; Rosenstiel et al., 2003). Thus, as C_i is increased due to increases in stomatal conductance or increases in ambient CO_2 concentration, less substrate is made available for chloroplastic processes, such as DMADP synthesis, and the isoprene emission rate decreases. In contrast, when C_i is decreased, such as during moderate water stress, less PEP will be diverted away from DMADP synthesis, and isoprene biosynthesis rate will increase. Combining the two different processes and simplifying, Wilkinson et al. (2009) proposed the following empirical equation to describe the dependence of isoprene emissions on short-term variation in C_i :

$$f(C_i) = E_{\max} \frac{E_{\max} C_i^h}{C_*^h + C_i^h}, \quad (7)$$

where E_{\max} is the isoprene emission rate normalized to a reference concentration, taken as $400 \mu\text{mol mol}^{-1}$ and h and C_* are empirical coefficients. This function describes data obtained over the C_i range of ca. $150\text{--}1000 \mu\text{mol mol}^{-1}$ reasonably well (Fig. 3). However, the mechanism proposed cannot explain the reduction of isoprene emissions below ca. $150 \mu\text{mol mol}^{-1}$ (Fig. 3). In addition, the shape of the $f(C_i)$ function varies among plants adapted to different atmospheric CO_2 concentrations (Fig. 3, Wilkinson et al., 2009), complicating the use of Eq. 7 for simulation of the CO_2 -response in plants in different CO_2 atmospheres.

Alternative approaches, such as the control of isoprene (Rasulov et al., 2009) and monoterpene (Niinemets et al., 2002c) synthesis by energy supply from photosynthetic electron transport have been suggested to describe the full CO_2 dependence of volatile isoprenoid emission, and semi-empirically included in predictive models (Arnth et al., 2007; Schurgers et al., 2009a). Such an approach can be promising as it allows description of both light and CO_2 responses of isoprene by the same mechanism, although it has not yet been conclusively shown that the CO_2 dependence of isoprene emission is caused by dynamics in photosynthetic electron transport. More experimental work is needed to determine the basis for the exact shape of the CO_2

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responses functions, the biochemical basis for the effect of growth CO₂ concentration on the shape of the response, and the interactions between $f(C_i)$ and $f(Q)$ and $f(T_L)$.

2.2 Key differences between the emission algorithms of highly volatile isoprene and less volatile mono- and sesquiterpenes emitted in light-dependent manner

As noted in Sect. 2.1, several species have specialized storage tissues such as resin ducts, oil glands, and glandular trichomes for terpene storage. In such species, large compound storage pools are generally in equilibrium with the compound concentration in the leaf gas-phase, and emissions are predicted by simplified models based on temperature effects on compound vaporization and diffusion out of storage pools (Eq. 5). After the detection of the light-dependence of monoterpene emissions in broad-leaved species lacking specialized storage tissues (Loreto et al., 1996c; Staudt and Seufert, 1995), and analogous findings for sesquiterpenes (Hansen and Seufert, 2003), the isoprene emission algorithm (Eqs. 1–3) has been applied to simulate light- and temperature dependent emission of these other compounds (e.g., Bertin et al., 1997; Ciccioli et al., 1997b; Dindorf et al., 2006; Kesselmeier et al., 1997; Kuhn et al., 2002; Pio et al., 2005). However, monoterpenes and sesquiterpenes have lower volatility than isoprene, and the crucial question is to what extent use of the isoprene emission algorithm is justified.

2.2.1 Non-specific storage of isoprenoids

Volatility is a basic physico-chemical characteristic of any emitted organic compound. Volatility can be characterized by the gas/water partition coefficient (Henry's law constant, H) that describes the partitioning of the compound to the gas phase, and octanol/water (K_{OW}) partition coefficient that characterizes the partitioning of the compound to the lipid phase (Niinemets et al., 2004). The smaller the value of H , the more a compound tends to be stored (concentrated) in the leaf liquid phase, and the

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larger the value of K_{OW} , the more a compound tends to be stored in the leaf lipid phase (Niinemets and Reichstein, 2002; Niinemets and Reichstein, 2003). The ratio K_{OW} to non-dimensional form of Henry's law constant gives the octanol to air partition coefficient K_{OA} (Chen et al., 2003; Copolovici et al., 2005; Meylan and Howard, 2005).

5 For isoprene and monoterpenes, the values of K_{OW} vary by more than two orders of magnitude, the values H by over four orders of magnitude, and the values of K_{OA} by over five orders of magnitude (Table 1). Typically, the values of H and K_{OW} are low for oxygenated water-soluble compounds such as the monoterpene alcohols linalool and α -terpineol, and the values of H and K_{OW} are large for non-oxygenated monoterpenes
10 (Table 1, Copolovici and Niinemets, 2007; Copolovici et al., 2005). In contrast, isoprene has a large H and a low K_{OW} , implying that this compound is preferably partitioned to the gas phase with minor storage capacity in the leaf liquid and lipid phases.

Depending on the specific physico-chemical characteristics, certain monoterpenes can be non-specifically stored within the leaves of species that lack dedicated monoterpene storage tissues (Loreto et al., 1996b; Staudt and Seufert, 1995). Those compounds with low H (e.g., linalool, 1,8-cineole) can be stored in the leaf liquid phase (Niinemets et al., 2002b; Noe et al., 2006). Compounds with high K_{OW} such as non-oxygenated mono- and sesquiterpenes can be stored in the leaf lipid phase consisting of lipid bilayers in various membrane structures and other leaf hydrophobic regions
20 (cuticle, lignified cell wall regions) (Niinemets and Reichstein, 2002; Noe et al., 2006, 2008). Such a non-specific storage of monoterpenes inside leaves can be important in modifying the time-dependent kinetics of emissions, implying that control over emissions is shared between monoterpene synthesis and volatility. While monoterpene synthesis in these species is believed to be rapidly modified by temperature and light,
25 non-specific storage induces time-lags between compound synthesis and emission. The presence of a foliar pool of "old" monoterpenes synthesized previously is supported empirically by labeling experiments that switch between $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ and concomitant monitoring of changes in the fractions of ^{12}C - and ^{13}C -labelled monoterpenes (Loreto et al., 1996a; Noe et al., 2006, 2010). All these experiments demonstrate

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important time-lags from hours to tens of hours between the start of ^{13}C -labelling and attainment of a steady-state ^{13}C -labelled monoterpene emission rate (Fig. 4).

The presence of non-specific storage also implies that emissions do not respond immediately to modifications in environmental variables (Fig. 4). For instance, due to non-specific storage, emissions may increase slower than predicted by a steady-state light-response function (Eq. 2), and emissions may continue for more than half an hour into the dark period (Fig. 4, Niinemets et al., 2002a; Peñuelas et al., 2009). This type of pattern is in marked contrast with the isoprene emission model that predicts an instant response of emissions to light (Eqs. 1–2). In addition, as different emitted monoterpenes have different volatilities (Table 1), the time-lags induced due to non-specific storage are different for different terpenes (Niinemets and Reichstein, 2002; Noe et al., 2006). This leads to time-dependent modifications in the fractional composition of emitted monoterpenes under non-steady state conditions (Niinemets and Reichstein, 2002).

Niinemets and Reichstein (2002) and Noe et al. (2006) have developed a dynamic model to consider the effects of non-specific storage on monoterpene emission kinetics. At least two pools, S_1 (nmol m^{-2}) and S_2 (nmol m^{-2}) with varying time-kinetics (time constant k_1 and k_2 , s^{-1}) were needed to simulate monoterpene emission rate at time t (Niinemets and Reichstein, 2002; Noe et al., 2006):

$$E(t) = k_1 S_1(t) + k_2 S_2(t), \quad (8)$$

where the pool kinetics are given as:

$$\frac{dS_1(t)}{dt} = \eta I - k_1 S_1(t) \quad (9)$$

$$\frac{dS_2(t)}{dt} = (1 - \eta) I - k_2 S_2(t). \quad (10)$$

Analytical solution of the model is provided in Niinemets and Reichstein (2002). In these equations, η is the fraction of monoterpenes going to pool S_1 , and $1 - \eta$ is the

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fraction going to pool S_2 . The rate of compound synthesis, I , can be simulated by the standard Guenther et al. (1991, 1993) model (Eq. 1), with corresponding instantaneous light- (Eq. 2), temperature- (Eq. 3) and CO_2 - (Eq. 7) response functions. The pool S_1 was presumed to exist in the leaf liquid phase and S_2 in the lipid phase. The half-time of non-specific storage varies from minutes (pool S_1) to hours (pool S_2), depending on the monoterpene physico-chemical characteristics, indicating that non-specific storage effects need consideration in simulating monoterpene emissions in species lacking specialized storage. Overall, employing the non-specific storage model provides a good fit to the data (Fig. 4).

2.2.2 Implications of non-specific storage on E_S and the shape of the light and temperature response functions

In addition to the above mentioned factors driving variability in light (2.1.1) and temperature (2.1.2) responses of isoprene emission, non-specific partitioning of monoterpenes into internal leaf tissues can alter both the temperature and light-responses of monoterpene emission rate, and such effects are particularly significant for modeling the dynamics of monoterpene emissions. Studies on the light-dependence of monoterpene emissions in species lacking specialized storage tissues have demonstrated that the light response of emissions has a different shape than the rectangular hyperbola produced by the isoprene response function (Schuh et al., 1997; Staudt et al., 2003). In particular, the initial part of the monoterpene emission response to light is often sigmoidal (Fig. 5). To parameterize the sigmoidal rise of the emissions as light intensity increases, it has been suggested to modify the Guenther et al. algorithm (Eq. 2) as (Schuh et al., 1997):

$$f(Q) = C_{L1m} \left(\frac{\alpha_m Q}{\sqrt{1 + \alpha_m^2 Q^2}} \right)^2, \quad (11)$$

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where C_{L1m} and α_m are the modified light response function parameters. This function has been shown to fit light-dependent monoterpene emissions better than the original isoprene emission algorithm (Fig. 5a, Dindorf et al., 2006; Schuh et al., 1997; Staudt et al., 2003). However, the sigmoidal shape of the light-response of monoterpene emissions likely results from non-specific monoterpene storage (Fig. 5b). Reaching a steady-state emission rate at any given light intensity can be time-consuming, taking tens of minutes (see e.g., Fig. 4a). In leaves with empty non-specific storage pools, the emission rate is initially less than the synthesis rate. In typical measurements of light response curves, starting from low light with a gradual increase of light, non-specific storage leads to apparent sigmoidal shape of the light response curve (Fig. 5b).

Although the sigmoidal light response curves can be parameterized with the modified equation (Eq. 11), the subsequent model would not be effective in describing time-lags between changes in light intensity and monoterpene emission rate that occur, for example, during the course of a day (Fig. 4). To parameterize such patterns, a dynamic model (Eq. 8) is needed. In fact, such time-lags can be successfully simulated by deploying a simplified lag factor in the models rather than applying sigmoidal light-response functions.

To further account for monoterpene release in darkness and better parameterize the temperature dependence of existing models (e.g., Fig. 4a), it has been suggested to combine the light-dependent emission model (emission rate E_L) and the model developed for species with specialized storage tissues (emission rate E_S) (Schuh et al., 1997):

$$E = E_L + E_S. \quad (12)$$

In this mixed algorithm used to simulate emissions in broad-leaved deciduous tree species *Fagus sylvatica* and herb species *Helianthus annuus*, emission from the non-specific storage pool, E_S , was exponentially dependent on temperature similar to Eq. 5, while E_L was described as dependent on light according to Eq. 11 and on temperature according to Eq. 3, and separate emission factors were used for E_L and E_S . Thus,

under given conditions, this mixed model predicts that E_S adds a constant factor to the total flux. However, the size of the non-specific storage pool very much depends on the previous conditions, implying, for instance, that the emission rate in darkness decreases in time and that the response of the emission to given increase or decrease in light level depends on how long the leaf has been under given conditions (Fig. 4a, Loreto et al., 1996a; Niinemets et al., 2002a). Such effects can only be simulated by a model based on dynamic pools (Eq. 8).

Although the mixed model (Eq. 12) predicts a stronger temperature response than the standard Guenther et al. (1991) model, it cannot predict bursts of emission following short-term increases in temperature such as occur during a single day (Fig. 6) and for hot days that follow cold days (e.g., Niinemets et al., 2002a). Such phenomena reflect the circumstance that when ambient temperatures are low, monoterpenes are non-specifically stored in leaf liquid- and aqueous pools, and released with faster rates than the rate of synthesis that is predicted by the increase in leaf temperature alone. Unlike the case for isoprene emission (Fig. 2), monoterpene emissions are characterized by large apparent Q_{10} (emission rate at the temperature $T + 10^\circ\text{C}$ relative to the rate at T), even larger than those for monoterpene synthase activity (Fig. 6). Again, this large Q_{10} value may reflect filling of the monoterpene pools under low temperature when compound volatility limits the emission rate, and transient emptying of these pools at higher temperature (Fig. 6). Parameterization and simulation of such hysteresis effects in the temperature response is possible only with a dynamic model such as Eq. 8.

From the evidence we have presented, it is clear that light-dependent monoterpene emissions reflect the contribution of both de novo monoterpene synthesis and emission of monoterpenes from storage. The value of E_S will approach the rate of monoterpene synthesis, I , as a steady state is approached. It is important to recognize the difference between the standardized emission rates when directly applying the Guenther et al. (1991, 1993) isoprene emission model and when using a dynamic model. In the dynamic model approach, the appropriate E_S needed is $E_S = I$. For the steady-state model, even the best estimate of E_S yielding the smallest sum of error squares (min S_S)

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between the predictions (E_{pred}) simulated by Eq. 1 and observations (E_{obs}) during the day (where n is the number of measurements conducted during the day),

$$\min S_S = \sum_{i=1}^{i=n} (E_{\text{pred},i} - E_{\text{obs},i})^2, \quad (13)$$

will overestimate the emissions under some conditions, e.g., after induction of synthesis in the morning hours when light increases, and underestimate the emissions under other conditions, e.g., after reduction of synthesis in the afternoon when light decreases. Furthermore, the value of E_S that best fits the daily time-course of emissions with a steady-state model does not necessarily coincide with the value of E_S measured under standardized conditions of 30 °C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$. This conceptual difficulty further underscores that E_S is a modeling concept, depending on what model is used and even how the model is parameterized, e.g. measuring E_S values under standardized conditions or deriving E_S from Eq. 13 as the best fit value from field measured time-courses ($E_{\text{pred}} = f(E_S)$, Eq. 1).

This evidence collectively demonstrates that the use of steady-state temperature- and light dependencies developed for isoprene emission (e.g., the Guenther algorithms) in simulating the emissions of higher molecular mass compounds is likely to carry significant uncertainties and errors in the estimation of emissions from vegetation experiencing diurnal fluctuations in leaf temperature and light intensity. This is clearly an area that should receive high priority in future research.

2.3 Towards the construction of models for induced emissions

In the previous section, we focused on constitutive emissions present only in certain species. Yet, emissions of volatile compounds can be triggered by various biotic and abiotic stress factors in essentially all plant species (Arimura et al., 2009; Brillì et al., 2009; Niinemets, 2010; Wu and Baldwin, 2009). Furthermore, foliage sesquiterpene emissions are mostly associated with stress (Duhl et al., 2008; Hakola et al., 2006), and

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emissions of homoterpenes, C₁₁ compound DMNT (4,8-dimethylnona-1,3,7-triene) and C₁₆ compound TMTT (4,8,12-trimethyltrideca-1,3,7,11-tetraene) are exclusively associated with stress, in particular, with biotic stress (Arimura et al., 2009; Herde et al., 2008; Vuorinen et al., 2007; Wu and Baldwin, 2009). The stress-driven monoterpene emissions are often dominated by specific stress-marker compounds such as the oxygenated monoterpenes linalool and non-oxygenated ocimenes (Blande et al., 2005; Cardoza et al., 2002; Martin et al., 2003; Pinto et al., 2007; Staudt and Bertin, 1998; Staudt et al., 2003). In addition to these specific compounds, a blend of monoterpenes can often be elicited that resembles the emissions in constitutive emitters such as emissions of α - and β -pinene, limonene etc. (Brilli et al., 2009; Huber et al., 2005; Paré and Tumlinson, 1998). To further complicate matters, such typical monoterpene emissions can be triggered in species emitting these compounds constitutively (Huber et al., 2005; Staudt and Lhoutellier, 2007). Clearly, stress-induced emissions cannot always be separated from the modulation of constitutive emissions by environment and physiology and also because the stressors are not always directly visible (e.g., small sap-sucking herbivores such as spider mites).

An important implication of induced emissions is that standardized emission factors (E_S) can vary widely depending on whether plants have been exposed to or are suffering from certain biotic or abiotic stresses. The presence of induced emissions can explain why species found to be non-emitters in some studies, are subsequently observed to be strong emitters in other studies. For example, temperate deciduous broad-leaved *Betula* spp. have been found to be low mono- and sesquiterpene emitters in some studies and during certain times of the year, with emission rates in standardized conditions only on the order of 0.1–0.4 $\mu\text{g g}^{-1} \text{hr}^{-1}$ (Hakola et al., 1998, 2001; König et al., 1995). In other studies and at other times of the year, they have been found to be moderately strong emitters, with E_S values on the order of 1.5–8 $\mu\text{g g}^{-1} \text{hr}^{-1}$ and the emissions dominated by the monoterpenes linalool and ocimenes, and by sesquiterpenes (Hakola et al., 1998, 2001; König et al., 1995; Owen et al., 2003; Steinbrecher et al., 1999). In analogous manner, a large variability, more than 80-fold, is present in E_S values

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in the Mediterranean evergreen conifer *Pinus pinea* (Fig. 7). In this species, emissions during the wet and cool season are dominated by the monoterpene limonene (constitutive emissions), while the emissions in the hot dry season are dominated by the monoterpenes linalool and *trans*- β -ocimene (induced emissions) (Niinemets et al., 2002b; Staudt et al., 1997, 2000). Importantly, even in the constitutive emitters, the induced emissions can by several-fold exceed constitutive emissions (Fig. 7).

Currently, the variation in E_S values due to induced emissions cannot be considered in simulation models. There is encouraging evidence that stress dose versus induced emission relationships can be derived (Beauchamp et al., 2005; Karl et al., 2008; Niinemets, 2010), making it possible to include induced emissions in future models. Despite this evidence, there is currently limited information on the stress thresholds leading to elicitation of induced emissions and also on how the stress thresholds vary with species constitutive and induced tolerance to given environmental driver and biotic stress (Niinemets, 2010). Evidently, much more experimental work is needed for quantitative incorporation of induced emissions into large scale predictive models.

The other important issue with induced emissions is that the induced monoterpenes (Brilli et al., 2009; Niinemets et al., 2002b; Ortega et al., 2007; Staudt et al., 1997), DMNT (Staudt and Lhoutellier, 2007), and sesquiterpenes (Hansen and Seufert, 2003; Staudt and Lhoutellier, 2007) are often emitted in light-dependent manner. For constitutive emitters, the presence of parallel induced emissions can greatly complicate efforts to characterize E_S . For instance in *Pinus pinea*, low-level constitutive emissions dominated by limonene are only dependent on temperature (Staudt et al., 1997, 2000) and can be simulated by Eq. 5. In contrast, the induced emissions dominated by linalool and *trans*- β -ocimene depend both on light and temperature (Niinemets et al., 2002b; Staudt et al., 1997) and are better simulated by Eqs. 2 and 3. Thus, the total emission rate (induced and constitutive) can be simulated using the mixed model (Eq. 12). In reality, this situation is rendered even more complex due to physico-chemical effects resulting from the non-specific storage of induced monoterpenes (Niinemets et al., 2002b; Noe et al., 2006), requiring the use of a dynamic model (Eqs. 8–10). Thus, in

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conifer species where the emissions are typically assumed to be simulated by only one simple temperature-dependent equation (Eq. 5), parameterization of daily time-courses may necessitate the use of a complex array of models. Given the fundamentally different controls on constitutive and induced emissions, it is important to separately define the emission potentials for constitutive (standardized emission rate in the absence of induced emissions) and induced (standardized emission rate in the absence of constitutive emissions) emissions.

2.4 Consideration of alterations in mono- and sesquiterpene compositions in models

Terpene-emitting species release simultaneously many different compounds. This reflects the presence of several different terpene synthases in plant foliage as well as production of several terpenes by the same terpene synthases (Alonso and Croteau, 1993 for a review). For instance, monoterpene emitting species can release more than 20 different monoterpenes (Niinemets et al., 2002c) (for a review of monoterpenes released from the foliage of *Quercus ilex*). In isoprenoid emission and modeling studies, E_S for monoterpenes is generally taken as a sum of all monoterpenes emitted and E_S for sesquiterpenes as a sum of all sesquiterpenes. Because the reactivity of different terpenes with OH radicals and ozone differs several orders of magnitude (Atkinson and Arey, 2003b; Atkinson and Arey, 2003a; Calogirou et al., 1999), for reliable air quality simulations, it is highly relevant to consider the variations in the composition of emitted terpene blends as well. There are multiple factors that can affect the composition of the emitted compounds, and we provide here only a brief overview of the key determinants.

In terpene-storing species, it is well-known that different genotypes have varying foliage terpene compositions (e.g., Canard et al., 1997; Hayashi and Komae, 1974; Tobolski and Hanover, 1971). In non-storing species, it has also been demonstrated that genotype affects the emission compositions, reflecting differences in the expression of various terpene synthases. For instance, in Mediterranean evergreen sclerophyll *Quercus ilex*, monoterpene emissions of some populations are dominated by α -pinene and

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β -pinene, while in other populations by limonene (Niinemets et al., 2002c; Staudt et al., 2001b). Analogous observations have been made for another Mediterranean sclerophyll *Quercus suber* (Staudt et al., 2004). Apart from the strong genetic component, there is evidence of environmental effects such as water, nutrient and light availabilities on terpene composition in terpene-storing species (Firmage, 1981; Letchamo et al., 1994; Merk et al., 1988; Schiller, 1993; Voirin et al., 1990).

Leaf age and seasonality have also been shown to affect the composition of stored terpenes (Hall and Langenheim, 1986; Rohloff, 1999). In addition, variation in the composition of emissions during the season has been demonstrated for terpene storing and non-storing species (Bertin et al., 1997; He et al., 2000; Kuhn et al., 2004; Llusà and Peñuelas, 2000; Sabillón and Cremades, 2001; Staudt et al., 1997, 2000). Interestingly, in constitutive isoprene emitters, young leaves that do not yet have developed the capacity for isoprene emission may be significant monoterpene emitters (Brilli et al., 2009; Kuhn et al., 2004). With development of isoprene emission capacity, monoterpene emissions decrease and cease in fully mature non-stressed leaves (Brilli et al., 2009; Kuhn et al., 2004).

In addition, growth under elevated CO₂ can modify the composition of emissions in non-storing species (Loreto et al., 2001). So far, such variations are imperfectly understood, but may reflect selective expression of different monoterpene synthases in different conditions (Loreto et al., 2001) (for changes in monoterpene synthase activities under elevated CO₂). As discussed in Sect. 2.3, environmental and biotic stress elicits expression of a variety of mono- and sesquiterpenes, and thus, stress-induced emissions typically have different composition than constitutive emissions.

In addition to the biological factors, emission compositions in species without specialized storage can transiently change due to differences in compound physico-chemical characteristics (Eq. 8, Table 1), for instance after dark-light transfers. Due to differences in the capacity for non-specific storage, compounds with lower volatility take longer to reach a steady-state tissue concentration. Thus, after switching on the light, the emissions will be initially dominated by compounds with greater volatility, while after

switching off the light, emissions will be dominated by compounds with lower volatility (Niinemets and Reichstein, 2002). In addition, analogous effects can occur after rapid changes in the rate of monoterpene synthesis such as after light or temperature change. Such physico-chemical effects emphasize the importance of analyzing the emission compositions in steady-state.

These data collectively demonstrate that variation in emission composition occurs among the populations of the same species and can also occur in dependence on environmental drivers and seasonality. We plead that the information of the composition of emitted compounds be published together with the sum of the emissions (E_S).

2.5 Scaling E_S in models

E_S in the emission models have been originally defined as species-specific values on the leaf scale (Guenther et al., 1991, 1993). Further plant functional type specific emission factors (Guenther et al., 1995), and landscape-level (Guenther et al., 1999) emission factors still defined on the basis of leaf area were constructed. Ultimately, average canopy-level integrated emission factors have been defined (Guenther et al., 2006). These canopy-level values were expressed on the basis of ground surface area differently from all previous E_S definitions (Guenther et al., 2006). As the scaled-up values are outcomes of models, the aggregated emission factors are subject to vary with the algorithms used for integration of isoprenoid fluxes. Here we analyze the way E_S values are used and aggregated in different model schemes, potentials and limitations of various scaling routines and the compatibility of aggregated E_S values scaled up in various manner.

2.5.1 Leaf-level emission factors scaled to canopy, landscape and biome

Leaf-scale species-specific estimates of E_S can be directly used to simulate canopy and landscape level BVOC emission fluxes using soil-vegetation-atmosphere transfer (SVAT) models (e.g., Baldocchi and Meyers, 1998; Baldocchi et al., 1999) similar to

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the schemes widely used for simulation of plant carbon gain (Caldwell et al., 1986; Falge et al., 1997; Ryel, 1993). SVAT models are typically 1-D layered models or 3-D models that describe the variation in light, temperature and humidity in dependence on the amount of leaf area and leaf area distribution of the vegetation (e.g., Baldocchi, 1991; Baldocchi et al., 1999; Cescatti and Niinemets, 2004). At the regional scale, species-specific E_S values of dominant species are still typically employed (Guenther et al., 1994, 1996b; Keenan et al., 2009).

In addition to employing appropriate light, temperature and CO_2 response functions (Eqs. 1–7), a series of biological factors such as leaf age, and long- and short-term acclimation responses in E_S are important to consider (Grote, 2007; Niinemets et al., 2010). For accurate integration, distribution of foliage of different emitting species within the canopy is needed. Canopy models with varying complexity can be used in integration schemes, e.g. models including spatial aggregation and 3-D heterogeneity vs. simple Lambert-Beer models with random dispersion of foliage elements (Baldocchi, 1997; Cescatti and Niinemets, 2004). Although E_S is the key predictor of the emission potentials of given vegetation, the structure of the canopy model, as well as the quality of leaf area and canopy architecture data can potentially introduce as much or even more variation in predicted emission fluxes as the prescribed E_S values (Keenan et al., 2010).

At the biome- and global-scales, emission factors are typically determined for plant functional types (PFT), $E_{S,\text{PFT}}$, based on the species-specific E_S estimates obtained from screening studies conducted all across the world (Arneeth et al., 2007; Guenther et al., 1995; Guenther et al., 2006). These functional-type specific E_S estimates significantly simplify the large-scale integration of emission fluxes. However, the accuracy of $E_{S,\text{PFT}}$ values depends on the way the weighted average of species-specific E_S values is obtained. While global average $E_{S,\text{PFT}}$ values can be derived for each PFT, species composition within a given PFT, will significantly affect the predicted emissions. For instance, both deciduous North-American species *Fagus grandifolia* and *Quercus alba* will fall in broad-leaved deciduous PFT, but *F. grandifolia* is an isoprene non-emitter,

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while *Q. alba* is a strong isoprene emitter. Thus, isoprene emissions of areas dominated by *Fagus* will be overestimated by average $E_{S,PFT}$ for broad-leaved forests, while the emissions from areas dominated by *Quercus* will be underestimated. The spatial resolution of emission inventories can be significantly improved by including available vegetation species coverage data (Guenther et al., 2006). In any case, it is important to keep in mind that any PFT-level emission factor is a modeled characteristic that depends both on leaf-level E_S values as well as on species coverage estimates. Errors in species coverage estimates can potentially bias the emission predictions as much as errors in prescription of E_S , and become potentially relevant when vegetation composition changes due to changes in environmental conditions (Schurgers et al., 2009b).

In large-scale emission models, use of layered or 3-D models that specify environmental conditions for each layer or 3-D canopy element, voxel, is complicated by the need for high amount of detailed structural information for model parameterization. Yet, typically only spatial information for integrated traits such as canopy leaf area index and plant functional type is available. As an alternative to the detailed multi-layered models, big-leaf canopy models have been developed that approximate the canopy as a single big leaf (Amthor, 1994; Lloyd et al., 1995). The key limitation of single big leaf models is associated with inherent non-linearity of plant physiological responses to light and temperature. As the result, simple integration that does not consider that under sunny conditions there are sunlit and shaded foliage at any location in the canopy, overestimates the true fluxes: this is a mathematical consequence of Jensen's inequality theorem for concave functions (Niinemets and Anten, 2009 for a review). Such integration problems are partly overcome by development of two big-leaf models, consisting of a sunlit and a shaded big-leaf (Dai et al., 2004; de Pury and Farquhar, 1997).

All big leaf type models assume that the responses of the entire canopy to light and temperature can be approximated with functions similar to those used for single leaves. Certain "optimum" variation in foliage physiological potentials within the canopy is assumed, and thus, only the upper canopy leaf physiological potentials are used for analytical integration of whole canopy responses to above-canopy environmental

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conditions (Amthor, 1994; Dai et al., 2004; de Pury and Farquhar, 1997). In these models, the “optimum” variation is defined as linear decrease of foliage physiological potentials with long-term light availability from top to bottom of the canopy (Amthor, 1994; Dai et al., 2004; de Pury and Farquhar, 1997). With such assumption, the typical E_S values estimated for high-light exposed foliage, and $E_{S,PFT}$ values derived from these, can be used in the area-dependent integration of large-scale fluxes. Such big-leaf approaches have been used in global isoprene and monoterpene simulations with LPJ-GUESS (Arneth et al., 2008; Arneth et al., 2007; Schurgers et al., 2009a). So far, the condition of “optimal” variation of E_S through the canopy still awaits experimental verification, although for photosynthesis, we have learned that the variation is not satisfying the optimality criteria (Friend, 2001; Niinemets and Anten, 2009).

2.5.2 Canopy-level emission factors in integration schemes

In the integration schemes outlined above, E_S values used are still leaf-scale emission factors determined for unshaded foliage. Alternatively, in the recent isoprene emission model MEGAN, canopy-scale isoprene emission factor, E_{can} was defined (Guenther et al., 2006) that is not only standardized for temperature and light as E_S traditionally was, but also for leaf area index and for many biological factors (Niinemets et al., 2010 for a review). The canopy-scale emission factor is a modeled characteristic that is based on available leaf-level E_S estimates for given species that are further combined with a canopy model to yield values of E_{can} (Guenther et al., 2006). PFT-specific values of E_{can} can be further derived combining E_S estimates of species belonging to given plant functional type and linking these again to a canopy model (Guenther et al., 2006). Canopy-level isoprene emission fluxes are then calculated using empirical relationships between above-canopy average incident quantum flux density and temperature (Guenther et al., 2006).

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The potential advantage of the canopy-scale approach is that at this scale, isoprenoid emission fluxes (production of BVOC by vegetation minus decomposition in the ambient atmosphere) can be measured by eddy-covariance techniques (Baldocchi et al., 1999; Fuentes and Wang, 1999; Fuentes et al., 1999; Guenther et al., 1996a; Huber et al., 1999; Rinne et al., 2002; Spirig et al., 2005). Thus, canopy-level estimates of the emission factor, $E_{\text{can,mes}}$, can be directly derived, skipping the tedious leaf to canopy integration step. However, canopy-level emission rates obtained from eddy flux measurements are instantaneous values, while MEGAN runs with average temperature and light conditions. Due to non-linearities inherent to light and temperature responses, use of instantaneous values of $E_{\text{can,mes}}$ derived from the flux measurements would systematically overestimate the predicted emission fluxes using average light and temperature as driving variables (Niinemets and Anten, 2009 for a review of integration problems). In addition, flux measurements, are often not conducted in stands having a “standard” LAI, and converting the values of $E_{\text{can,mes}}$ to a standard LAI again requires a canopy model. Thus, apart from the fact that E_{can} values in MEGAN are derived from leaf-level estimates using a canopy model (Guenther et al., 2006), the values of E_{can} employed in MEGAN are not equivalent to $E_{\text{can,mes}}$ estimates from flux measurements.

In summary, in large-scale integration schemes, it is highly relevant to clearly specify how the emission factor used for scaling emission fluxes is determined. Integration models currently include both emission factors that are directly derived from leaf-level estimates and emission factors that include a great deal of modeling. It is important to consider that these different emission factors cannot be used interchangeably in different models. Particular care should be taken in applying the modeled and aggregated emission factors, e.g., as E_{can} applied in MEGAN (Guenther et al., 2006). Being a modeled variable means that any change in light and temperature response function and their parameterization applied in the emission model, and time-resolution of climatic drivers would require re-computation of E_{can} values.

3 Conclusions

The emission models used worldwide to simulate volatile isoprenoid emission fluxes from vegetation for further use in atmospheric chemistry models are largely based on Guenther et al. (1991, 1993) algorithms. The strength of these algorithms has been the conceptual simplicity provided to modelers in that they need only the standardized emission factors, E_S , and being able to simulate the emission fluxes using the light and temperature functions specified by Guenther et al. (1991, 1993), for which input data are readily worldwide available. However, our knowledge of the factors influencing E_S , and its application to different scales of consideration, has greatly increased since the original development of the Guenther et al. algorithms. Significant variations in plant responses to environmental drivers light and temperature, and to so far unaccounted environmental drivers such as CO_2 have been highlighted and emission induction by biotic and abiotic stresses and modifications in emission compositions have been demonstrated. Recent studies have also observed important variability in the share of emission controls between compound synthesis and physico-chemical factors. The existence of this knowledge means the days of simple emission source modeling are past. Our purpose in writing this paper is to provide greater depth in the understanding of those who wish to simulate isoprenoid emissions and stimulate the development of novel approaches, such as dynamic emission models, to include the contemporary understanding of emission controls in future emission simulations.

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Table 1. Variation in physico-chemical characteristics of isoprene, non-oxygenated monoterpenes and monoterpene alcohols α -terpineol and linalool at 25 °C.

Compound ¹	Henry's law constant, H_{xy} $\frac{\text{mol/mol air}}{\text{mol/mol water}}$	Octanol/water partition coefficient, K_{OW} $\frac{\text{mol/mol octanol}}{\text{mol/mol water}}$	Octanol/air partition coefficient, K_{OA} $\frac{\text{mol/mol octanol}}{\text{mol/mol air}}$
Isoprene	4266	29.09	0.00682
α -Terpinene	1914	866.5	0.453
α -Pinene	7435	3392	0.456
β -Pinene	3772	4599	1.219
α -Phellandrene	3052	6601	2.163
β -Phellandrene	3052	6684	2.190
S-(–)-Limonene	1577	5537	3.511
R-(+)-Limonene	1563	5490	3.512
Terpinolene	1457	5148	3.532
γ -Terpinene	1433	5354	3.735
Linalool	1.162	104.5	89.90
α -Terpineol	0.1238	105.6	853.1

¹ The compounds were ranked according to increasing values of K_{OA} . Data for isoprene as revised in Niinemets and Reichstein (2003), data for other compounds from Copolovici and Niinemets (2007, 2005). The convention of units as in Staudinger and Roberts (2001).

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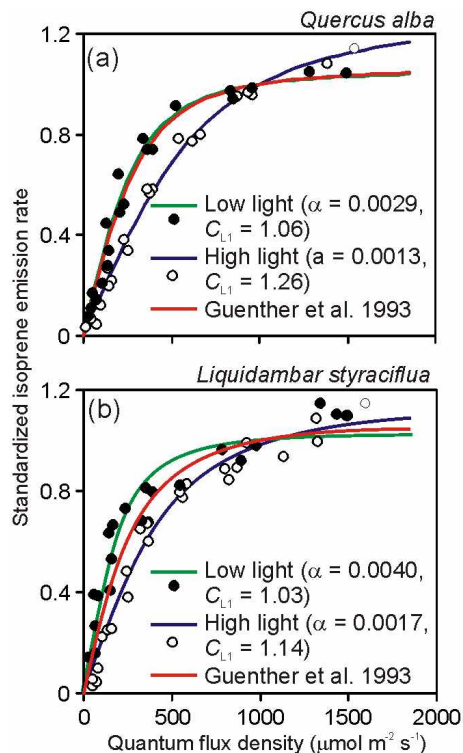


Fig. 1. The rate of isoprene emission in relation to incident quantum flux density (light intensity, Q) in temperate broad-leaved deciduous species *Quercus alba* (a), data modified from Harley et al. (1997) and *Liquidambar styraciflua* (b), data modified from Harley et al. (1996) studied in leaves from the lower and upper canopy. The emission rate was standardized with respect to the rate measured at Q of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ that is the typical light intensity at which the isoprenoid emission factor, E_S , is defined (Guenther et al., 1991, 1993). The light response function (Eq. 2) was fitted to the data and the model parameters, α , the apparent quantum yield, and C_{L1} , the scaling coefficient, are shown for the different responses. In addition, the original light-response function reported by Guenther et al. (1991) is shown in both panels (red lines).

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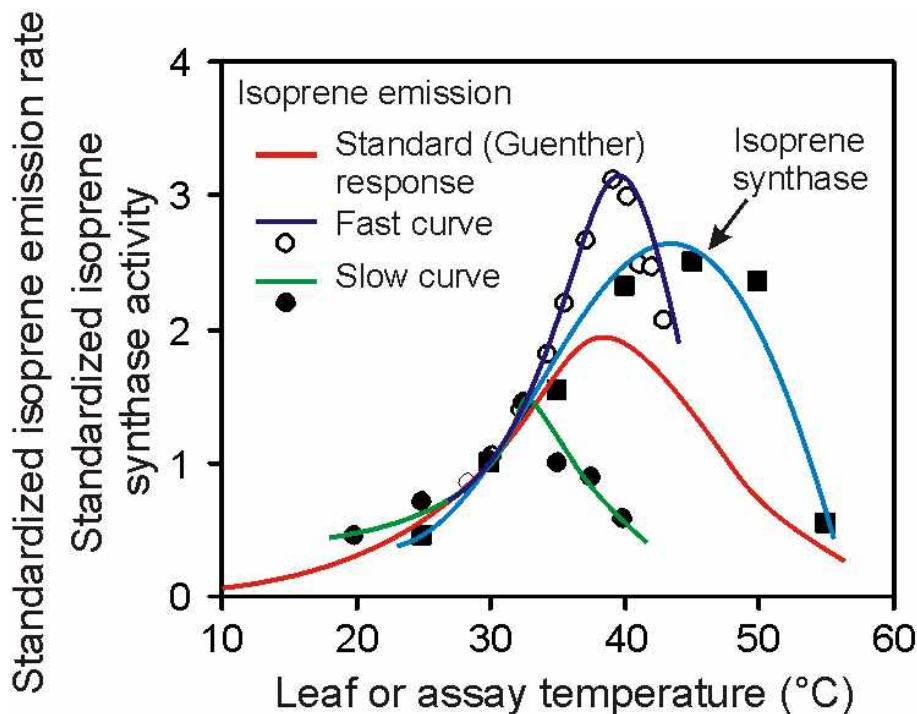


Fig. 2. Comparison of the temperature responses of isoprene synthase activity in *Populus tremuloides* (data from Monson et al., 1992), the “standard” isoprene emission curve by Guenther et al. model (1991, 1993) as reparameterized (1997, Eq. 4) to yield a value of 1.0 at 30 °C, and the measurements of isoprene emission rate in *Quercus rubra* (data from Singaas et al., 1999). These measurements were either conducted rapidly (4 min. at each leaf temperature, fast curve) or slowly (30 min. at each temperature, slow curve). In all cases the data were standardized with respect to the measurements at 30 °C, yielding the temperature response function of isoprene emission.

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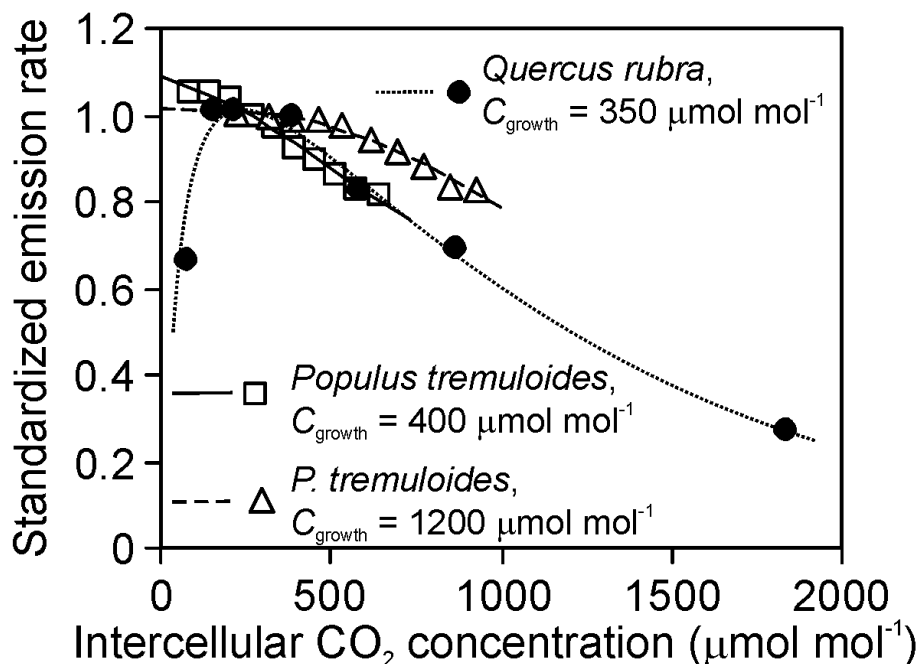


Fig. 3. Isoprene emission rate in relation to intercellular CO_2 concentration (C_i) in *Quercus rubra* plants grown at an ambient CO_2 concentration of $350 \mu\text{mol mol}^{-1}$ (data from Loreto and Sharkey, 1990) and in *Populus tremuloides* plants grown at ambient CO_2 concentrations of 400 and $1200 \mu\text{mol mol}^{-1}$ (data from Wilkinson et al., 2009). Data for *P. tremuloides* were fitted by Eq. 7, while an empirical non-linear relationship with a maximum was used to fit the data for *Q. rubra*.

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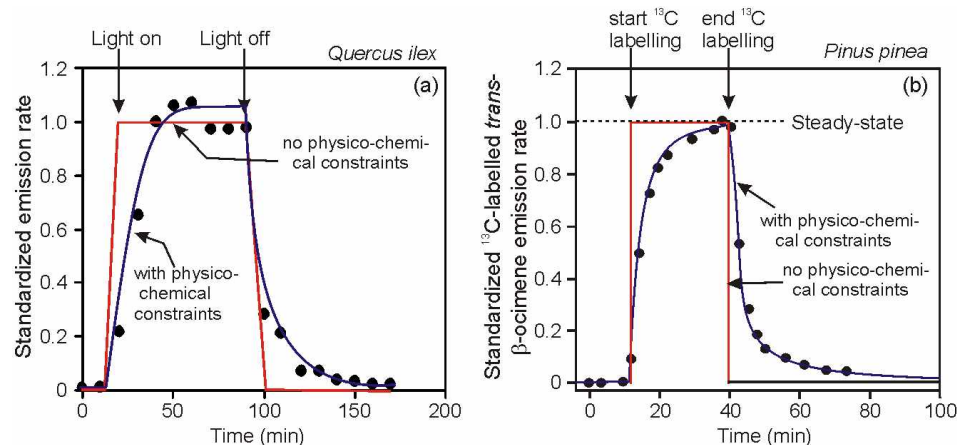


Fig. 4. Interaction of physiological and physico-chemical factors in determining the total light-dependent monoterpene emission rate in the Mediterranean evergreen sclerophyll *Quercus ilex* (a) (modified from Ciccioli et al., 1997b) and light-dependent emissions of monoterpene *trans*- β -ocimene in the Mediterranean conifer *Pinus pinea* (b) (modified from Noe et al., 2006) at a constant temperature of 30 °C. (a) depicts the transient of the emission rates after light-dark changes, while (b) depicts the emissions of ^{13}C -labelled *trans*- β -ocimene following the switch from $^{12}\text{CO}_2$ to $^{13}\text{CO}_2$, and after a steady-state was reached in labeled *trans*- β -ocimene emissions, from $^{13}\text{CO}_2$ to $^{12}\text{CO}_2$. Given that the synthesis of monoterpenes relies on a small chloroplastic carbon pool, application of a simple steady-state model initially developed for isoprene (Guenther et al., 1991) suggests that monoterpene emission rate immediately tracks the altered light intensity (a) and that in all the emitted *trans*- β -ocimene molecules at least one carbon atom is labeled by ^{13}C (b, simulation without the storage pool). In reality, reaching the steady-state is time-consuming due to non-specific monoterpene storage within the leaf liquid and lipid phases (Niinemets and Reichstein, 2002; Noe et al., 2006). This leads to time-lags in reaching the maximum monoterpene emission rates and continued release of monoterpenes from darkened leaves (a), as well as to time-lags in *trans*- β -ocimene labeling with ^{13}C and de-labeling after swapping back to $^{12}\text{CO}_2$. The best fit to the data can be obtained with a model including two leaf monoterpene pools, the faster pool presumably located in the leaf liquid phase and the slower pool presumably located in the leaf lipid phase (Niinemets and Reichstein, 2002; Noe et al., 2006). For (a), the half-time for the faster pool was 0.078 h, while the half-time was 2.05 h for the slower pool (Niinemets and Reichstein, 2002). For (b), the corresponding half-times obtained were 0.03 h for the faster, and 0.26 h for the slower pool (Noe et al., 2006).

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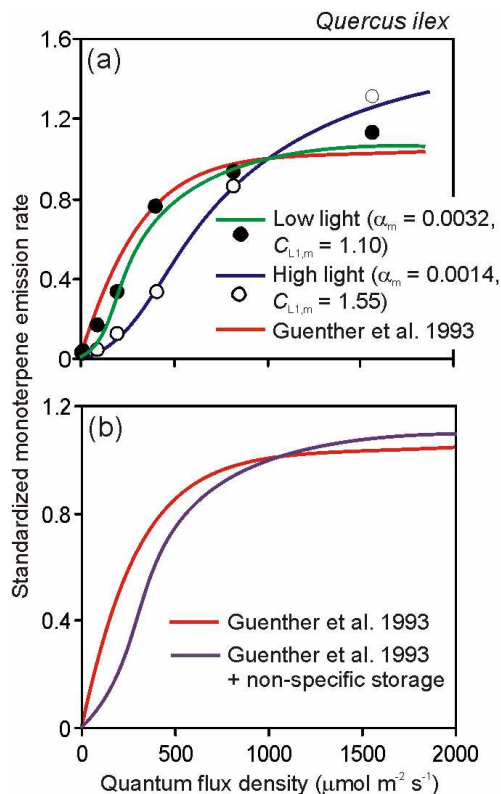


Fig. 5. Light-responses of monoterpane emission rate in the Mediterranean evergreen sclerophyll *Quercus ilex* grown under high and low light and comparison with Guenther et al. (1991) standard emission response (Eq. 2) **(a)** (data from Staudt et al., 2003), and **(b)** simulated responses of monoterpane emissions using a steady-state algorithm (Guenther et al., 1991) and a dynamic algorithm that considers the effect of non-specific storage on monoterpane emissions (Eq. 8, Niinemets and Reichstein, 2002). In the dynamic simulation, the synthesis rate of monoterpane emission at any light intensity was predicted by Guenther et al. (1991) algorithm, and the light level was increased by $50 \mu\text{mol m}^{-2} \text{s}^{-1}$ steps in every 2 min. In (a), the data were fitted by modified light-response function suggested by Schuh et al. (1997, Eq. 10).

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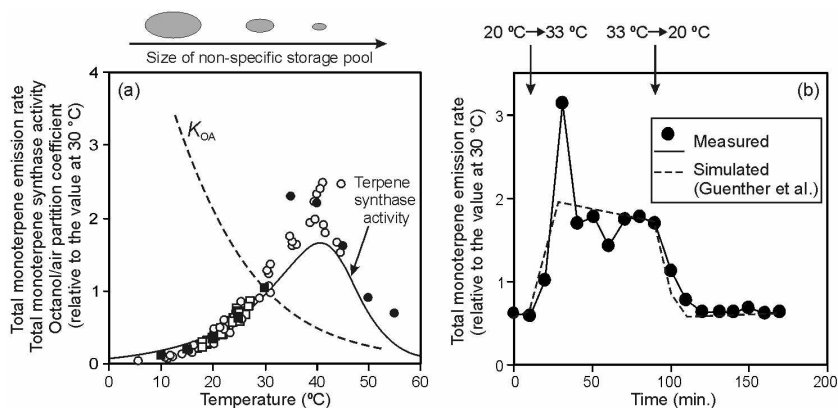


Fig. 6. Temperature effects on monoterpene emission rates from foliage of the broad-leaved evergreen Mediterranean sclerophyll *Quercus ilex* (symbols), on monoterpene synthase activity (solid line) and α -pinene octanol-to-air partition coefficient (K_{OA} , dashed line) that characterizes the equilibrium size of non-specific monoterpene pool in the leaves (a), and time-dependent changes in monoterpene emissions from *Q. ilex* leaves after changes in temperature from 20 °C to 33 °C (b). In all cases, the data were normalized with respect to the value measured at 30 °C. The emission rate data in (a) are from Bertin and Staudt (1996, open squares), Staudt and Seufert (1995, filled squares), Staudt and Bertin (1998, open circles) and Loreto et al. (1998, filled circles) (Niinemets, 2004 for details on data compilation and fitting). The data in (b) are from Ciccioli et al. (1997a). All measurements were conducted at saturating light and cuvette CO_2 concentrations of approximately $350 \mu\text{mol mol}^{-1}$. The measurements of monoterpene synthase activity are from Fischbach et al. (2000) and the K_{OA} estimations from Copolovici et al. (2005, Table 1). Physico-chemical factors likely explain differences between the rates of monoterpene emission and synthesis. As more monoterpenes can be non-specifically stored within the leaves at low temperatures, the emission rates are less than the synthase activity, while at higher temperatures, monoterpenes that have been accumulated at lower temperatures are released. Accordingly, leaves can transiently emit less or more monoterpenes than immediately synthesized. Emission of stored monoterpenes after switching to higher temperature likely explains the monoterpene emission burst in (b).

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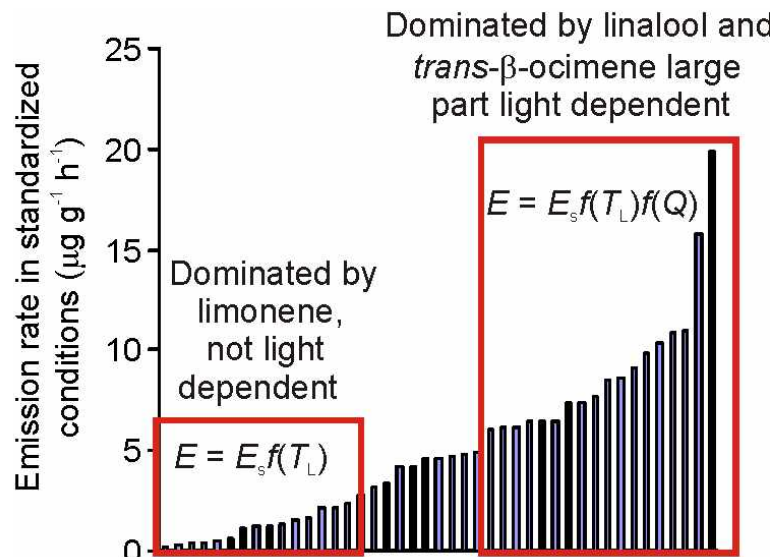


Fig. 7. Estimates of monoterpene emission rate under standardized conditions (leaf temperature, $T_L = 30^\circ\text{C}$, incident quantum flux density, $Q = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$), “the emission factor” (E_S) from the foliage of Mediterranean evergreen conifer *Pinus pinea* (data of Corchnoy et al., 1992; Kesselmeier et al., 1997; Owen et al., 1997, 1998, 2001, 2002; Owen and Hewitt, 2000; Pio et al., 1993; Sabillón and Cremades, 2001; Seufert et al., 1997; Staudt et al., 1997, 2000; Street et al., 1997; Winer et al., 1983). The estimates of E_S ($n = 43$) were ranked from the smallest to the largest. In studies demonstrating low E_S , the emissions were typically dominated by the monoterpene limonene and were not light-dependent (constitutive emissions). High emission rates were typically dominated by the monoterpenes linalool and *trans*- β -ocimene that are considered as typical stress-induced monoterpenes. These emissions were both light- and temperature dependent (e.g., Niinemets et al., 2002b; Staudt et al., 1997). Thus, conceptually, the constitutive emissions can be predicted by Eq. 5, induced emissions by Eq. 1, and total emissions by Eq. 12. However, due to non-specific storage of induced monoterpenes (Noe et al., 2006), a dynamic model is needed to describe these emissions (Eq. 8–10).

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