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The emission factor of volatile isoprenoids: stress, acclimation, and developmental responses

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Abstract

Volatile isoprenoid emission rate from plants is driven by plant emission capacity under specified environmental conditions (E_S, the emission factor) and by responsiveness of the emissions to instantaneous variations in environment. In models of isoprenoid emission, E_S has been often considered as intrinsic species-specific constant invariable in time and space. Here we analyze the variations in species-specific values of E_S under field conditions focusing on biotic and abiotic stresses, past environmental conditions and developmental processes. The reviewed studies highlight strong stress-driven (effects of abiotic and biotic stresses), adaptive (previous temperature and light environment and growth CO_2 concentration) and developmental (leaf age) variations in E_S values. These biological factors can alter species-specific E_S values by more than an order of magnitude. Recent models are including some of these biological sources of variation to some degree, while the majority of models based on early concepts still ignore these important sources of variation. This analysis emphasizes the need to include more biological realism in the isoprenoid emission models and also highlights the gaps in knowledge that require further experimental work for mechanistic consideration of E_S variation in models.

1 Introduction

Accurate prediction of emissions of the very reactive plant-generated volatile organic compound class – volatile isoprenoids – is highly relevant for reliable simulation of a number of atmospheric properties, including chemical reactivity and clearness (secondary organic aerosols, cloudiness) (Claeys et al., 2004; Curci et al., 2009; Fowler et al., 2009; Heald et al., 2008; Kanakidou et al., 2005; Kulmala et al., 2004; Mentel et al., 2009; Peñuelas and Staudt, 2010; Spracklen et al., 2008). The prediction of volatile isoprenoid emission fluxes is achieved by a variety of emission models applied at scales ranging from leaf to globe. These models are based either on Guenther

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et al. (1991, 1993) pivotal algorithms that phenomenologically described the instantaneous responses of isoprenoid emissions to key environmental drivers, light and temperature, or on process-based algorithms trying to link the emissions directly to enzyme kinetics and carbon metabolism (Arneth et al., 2007b; Martin et al., 2000; Niinemets et al., 1999, 2002b; Zimmer et al., 2000).

In all the existing emission models, predicted emission rates critically depend on the emission capacity that characterizes the plant potential for volatile isoprenoid formation under defined environmental conditions. In Guenther et al. (1991, 1993) type of models, the emission capacity is the emission rate under standardized environmental conditions (typically leaf temperature of 30 °C and quantum flux density of 1000 µmol m^{-2} s^{-1}), also called the emission factor (E_S). In the process-based models, the emission capacity typically reflects the maximum activity of limiting enzymes such as isoprene and monoterpene synthases under given temperature (Martin et al., 2000; Niinemets et al., 1999, 2002b; Zimmer et al., 2000). In the latter type of models, the estimates of emission capacity can be obtained from available E_S data under certain assumptions (e.g., Arneth et al., 2007b; Niinemets et al., 1999, 2002b).

Given the importance of E_S, many screening studies all over the world have been conducted to obtain E_S values for model parameterizations. Once reported, E_S estimates have been considered as constant in subsequent model estimates of plant isoprenoid emission fluxes (Guenther et al., 1994, 1995; Lamb et al., 1993; Simpson et al., 1995, 1999). However, many of the existing E_S estimates may not be wholly correct and can be misleading for a variety of reasons including conceptual, analytical and biological issues.

As demonstrated in the accompanying paper (Niinemets et al., 2010b), definition of E_S is dependent on the shape and stability, hence representativeness, of the assumed response curves, and therefore, E_S is largely a modeling concept defined within the given model framework. While E_S is defined in a relatively straightforward manner for isoprene, non-specific storage and induced emissions complicate the definition of the emission factor for mono- and sesquiterpenes (Niinemets et al., 2010b). Among

analytical problems, E_S estimation can critically depend on the enclosure and sampling techniques altering leaf environment during the measurements as well as on the efficiency of volatile sampling and detection (for analytical issues in determination of E_S values see) (Ortega and Helmig, 2008; Ortega et al., 2008). Apart from the conceptual and analytical difficulties, vegetation has huge developmental and adaptive capacity, resulting in strong temporal and spatial variations in E_S. In particular, it has been observed that E_S is affected by leaf age and ontogeny (Monson et al., 1994), climatic conditions preceding the emission measurements (Blanch et al., 2010; Geron et al., 2000; Gray et al., 2006; Pétron et al., 2001; Sharkey et al., 1999; Staudt et al., 2003), environmental stress (Fang et al., 1996; Lavoir et al., 2009; Niinemets, 2010; Peñuelas and Staudt, 2010), growth CO_2 concentration (Possell et al., 2005; Rosenstiel et al., 2003; Wilkinson et al., 2009) and acclimation of foliage to canopy light environment (Harley et al., 1996, 1997). While some recent models have attempted to include some of these factors (Ekberg et al., 2009; Guenther, 1999, 2006; Keenan et al., 2009), many modeling exercises still do not consider vegetation as an adaptive system, leading to large uncertainties in emission inventories using static algorithms.

In this review, we analyze the alterations in constitutive isoprenoid emissions in response to biological factors and the implications for E_S determinations and isoprenoid emission model construction. In particular, we focus on environmental factors that influence longer-term responses of emissions from days to weeks and seasons, including the effects of stress, canopy environment, weather influences and dynamics in the atmospheric CO_2 concentration, as these sources of variability are largely missing from current emission models. We believe that biological limitations in the determination and definition of E_S values that are associated with changes in the leaf physiological status driven by the leaf environment in the hours, days and weeks prior to the measurements can introduce at least as much variability in E_S values as limitations associated with conceptual and analytical problems (Niinemets et al., 2010b for an overview of conceptual issues). The analysis also serves to highlight the key areas for future research, making it possible to include more biological realism in future model analyses.

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2 Biological sources of variability in emission inventories

Most widely used volatile isoprenoid emission algorithms defined by Guenther et al. (1991, 1993) as modified by Wilkinson et al. (2009) describe the isoprenoid emission rate, E, as the product of standardized emission rate, E_S, and the instantaneous responses of isoprenoid emissions to light, $f(Q)$, leaf temperature, $f(T_L)$, and leaf intercellular CO_2 concentration, $f(C_i)$:

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

where the functions $f(Q)$, $f(T_L)$ and $f(C_i)$ are normalized to 1.0 at standardized conditions used for E_S determination. Equation 1 provides a conceptually simple way to separate the emission controls that operate through instantaneous changes in environment and through longer term controls on E_S. Drivers that can modify E_S values in time and space are environmental stress, past environmental conditions, and leaf age and seasonality. Modifications in E_S values due to these sources of variability are not typically considered in the emission models, except for a few cases (Guenther et al., 1999, 2000, 2006; Karl et al., 2009; Keenan et al., 2009; Steinbrecher et al., 2009). As shown in the following, for many of the observed modifications in E_S, we currently lack appropriate models or we lack information of the extent and time-kinetics of the E_S changes. Furthermore, biological sources of variability have been studied in only a few model species, making it difficult to derive parameter estimates for inclusion in large-scale models.

2.1 Effects of stress on E_S

Plants in field environments must frequently sustain stress periods of varying duration and severity. Abiotic and, in particular, biotic stress factors can lead to elicitation of volatile isoprenoid emissions in species non-emitting volatile isoprenoids constitutively, but can also modify the emission profiles in constitutive emitters (for a review see Arneth and Niinemets, 2010). As discussed in the accompanying paper (Niinemets et al.,

2010b), the induced emissions can critically alter the estimates of E_S and also require development of novel emission models.

Apart from the induction of new emissions, stress can also strongly alter the constitutive emissions. So far, the influence of only a few stress factors on constitutive isoprenoid emissions has been studied. Among volatile isoprenoid vs. stress studies, limited water availability has obtained special attention, reflecting the importance of regular drought periods in Mediterranean and tropical dry forests and unpredictable episodic drought in many temperate forests. In addition, heat stress, alone or in combination with drought, often occurs in natural ecosystems (Hall, 1992; Hällgren et al., 1991; Peñuelas and Llusià, 2003). Here we focus on drought and heat stress effects on the constitutive isoprenoid emissions as these two factors have been studied in most systematic manner. To highlight the richness of the stress responses, we also briefly review a number of other stresses and outline ways of considering the stresses in models.

2.1.1 Influence of drought

Drought vs. isoprenoid emission studies have demonstrated that drought effects on isoprenoid emissions crucially depend on the severity of drought (Niinemets, 2010). Mild drought stress does not strongly affect either isoprene (Pegoraro et al., 2004a, 2004b; Sharkey and Loreto, 1993) or monoterpene (Lavoir et al., 2009; Peñuelas et al., 2009; Staudt et al., 2002) emissions. However, both isoprene and monoterpene emissions strongly decrease after prolonged drought (Bertin and Staudt, 1996; Brilli et al., 2007; Grote et al., 2009; Lavoir et al., 2009; Llusià and Peñuelas, 1998; Peñuelas et al., 2009; Sharkey and Loreto, 1993; Staudt et al., 2002, 2008). As photosynthesis rate is significantly reduced already during mild stress due to strong stomatal closure and reduction in intercellular CO_2 concentration (C_i), the proportion of carbon lost as isoprene or monoterpenes increases significantly under conditions of soil moisture deficit (Fang et al., 1996; Llusià and Peñuelas, 1998; Niinemets et al., 2002a; Pegoraro et al., 2004b; Sharkey and Loreto, 1993).

To characterize the isoprene emission responses to changes in within-leaf CO_2 concentration associated with immediate, rapid alterations of CO_2 concentration either because of artificial alteration of ambient CO_2 concentration or due to changes in stomatal openness, Wilkinson et al. (2009) have defined the C_i response function (Eq. 1), $f(C_i)$ as:

$$f(C_i) = E_{max} - \frac{E_{max} C_i^h}{C_*^h + C_i^h}, \quad (2)$$

where E_{max} is the asymptotic value at which further reduction in C_i has an insignificant effect on the isoprene emission rate, and C_* and h are empirical scaling coefficients to calibrate the sigmoidal shape of the relationship between the isoprene emission rate and C_i.

Can this response be used to predict the isoprenoid emission responses to mild and severe drought? At current ambient CO_2 concentration of ca. 385 µmol mol^{-1}, mild drought stress typically results in reduction of C_i values from ca. 250–330 µmol mol^{-1} to 200–250 µmol mol^{-1} (Flexas and Medrano, 2002; Medrano et al., 2002). According to the instantaneous CO_2 response function (Eq. 2), applied over a finite C_i range of ca. 150–330 µmol mol^{-1}, isoprene emission is relatively insensitive over this range or moderately increases at lower C_i (Wilkinson et al., 2009), likely explaining the insensitivity of isoprenoid emissions to (Lavoir et al., 2009; Peñuelas et al., 2009; Sharkey and Loreto, 1993; Staudt et al., 2002) or the moderately increased emissions occasionally observed under mild stress (Bertin and Staudt, 1996; Pegoraro et al., 2005; Staudt et al., 2008; Yani et al., 1993).

In contrast, severe drought results in reductions in C_i down to 100–150 µmol mol^{-1}, C_i occasionally even reaching the photosynthetic compensation point under extreme drought (Flexas and Medrano, 2002; Medrano et al., 2002). Thus, strong reductions in intercellular CO_2 concentration in response to severe drought can explain the massive reduction, up to 10% to that before the stress of isoprene (Sharkey and Loreto, 1993) and monoterpene (Bertin and Staudt, 1996; Llusià and Peñuelas, 1998; Staudt

et al., 2002) emissions. In addition, there is evidence of reduced isoprene synthase activity under severe drought (Brilli et al., 2007). Severe drought also partly uncouples isoprene synthesis from immediate photosynthetic carbon metabolism, implying that droughted plants use stored carbon fixed in periods prior to drought stress (Brilli et al., 2007). This means that the Eq. 2, in which the effects of C_i operate through immediate carbon metabolism, is not adequate in describing the severe drought stress effects.

The situation is further complicated by findings that after severe drought, isoprene and monoterpene emissions are often significantly higher compared to pre-stressed rates (Peñuelas et al., 2009; Sharkey and Loreto, 1993). These observations suggest that instantaneous emission vs. C_i responses can only partly explain the effects of prolonged drought periods on emissions. In addition to physiological short-term responses that can be likely explained by the CO_2 response function (Eq. 2), acclimation in E_S values (emission capacity at any given C_i) and modifications in the carbon sources for isoprenoid production need consideration in prediction of the emissions under prolonged drought and after the drought.

So far, drought effects are mostly not considered in the existing isoprenoid emission models. Recently, the effects of drought were empirically included in MEGAN, assuming hypothetical relationship between soil water content and isoprene emission after a threshold soil water content is reached (Guenther et al., 2006). In other models, effects of drought are included through drought effects on C_i, carbon metabolism and photosynthetic electron transport similarly to the C_i-response function (Arneth et al., 2007b; Grote et al., 2006; Niinemets et al., 2002b; for comparison of approaches to model drought effects on emissions see also Grote et al., 2009, 2010). However, as drought response involves also a longer-term component, an approach linking E_S to integrated drought dose, i.e., time-integrated plant water-status below the stress threshold water status, can provide a proxy to simulate such patterns similar to how past weather effects are included in emission models (Sect. 2.3).

2.1.2 Effects of heat stress

High temperature is another key stress under natural conditions that may become especially severe in combination with drought when transpiratory water loss is reduced and leaf temperature rises significantly above the ambient air temperature. Sometimes leaf temperatures can exceed the ambient air temperatures even by more than 10 °C (Hamerlynck and Knapp, 1994; Sharkey et al., 1996; Singsaas et al., 1999; Valladares and Niinemets, 2007). The way the emissions respond to temperature depends on the duration of heat exposure. While short-term heat pulses, up to a few minutes, result in amplified emissions that can be explained by temperature-dependent increases in isoprene synthase (Fig. 1a), longer heat stress lasting between tens of minutes to hours results in gradual reduction of the emission capacity, E_S (Fig. 1a, Singsaas and Sharkey, 2000). Analogous responses have also been observed for monoterpene emissions (Fig. 1b, Loreto et al., 1998; Staudt and Bertin, 1998).

Currently, there is not enough physiological information to parameterize such time-dependent modifications in isoprenoid emission rates, and emission rates are predicted using static emission response curves that are based on immediate effects on emissions to temperature, e.g., the rapid increase of isoprene emissions just after the increase of leaf temperature from 30 °C to 40 °C in Fig. 1a. On the other hand, isoprenoid emission capacity increases during recovery after prolonged heat periods lasting from a day to several days (e.g., Pétron et al., 2001; Sharkey et al., 1999). Such longer term effects have been successfully simulated using past temperature variations (Sect. 2.3).

2.1.3 Other abiotic and biotic stresses and outlook

Apart from these two key stresses, constitutive isoprenoid emissions are affected by many other stress factors including air pollutants such as ozone (e.g., Fares et al., 2006; Llusià et al., 2002; Loreto et al., 2004; Loreto and Velikova, 2001; Velikova et al., 2005), wounding (e.g., Funk et al., 1999; Loreto et al., 2000, 2006; Loreto and Sharkey, 1993), insect feeding (e.g., Brilli et al., 2009; Peñuelas et al., 2005; Staudt

and Lhoutellier, 2007) and fungal infection (e.g., Anderson et al., 2000; Steindel et al., 2005). In general, these studies demonstrate a reduction in constitutive isoprenoid emission rates in species lacking specialized storage tissues, but the plant response strongly depends on stress severity and duration (Niinemets, 2010 for a review), and increased emissions have been demonstrated in some cases, for instance in response to wounding (e.g., Loreto et al., 2006) or insect feeding (e.g., Peñuelas et al., 2005). In contrast, enhanced emissions due to wounding or herbivory are observed in species with specialized storage tissues as the result of breakage and exposure of the contents of storage tissues (Chen et al., 2009; Juuti et al., 1990; Kim, 2001; Litvak and Monson, 1998; Loreto et al., 2000; Priemé et al., 2000; Schade and Goldstein, 2003). Although such stress effects are currently ignored in the emission models, under natural conditions, plants essentially always suffer from chronic biotic stresses. Furthermore, as discussed in the accompanying paper (Niinemets et al., 2010b), biotic stress generally results in induced isoprenoid emissions that are sometimes difficult to separate from the constitutive emissions (Litvak and Monson, 1998).

Overall, this evidence suggests that stress effects can prominently modify E_S values. Ignoring abiotic and biotic stress effects on E_S measurements as is common in field studies, especially in large screening programs, introduces large uncertainties in species-specific estimates of E_S. So far, information of many stress effects is rudimentary, and consequently, process-based models cannot yet be derived. However, information about the regulatory elements of key limiting enzymes such as isoprene synthase is gradually becoming available (Cinege et al., 2009; Loivamäki et al., 2007), implying that mechanistic models might be possible to develop in the near future.

2.2 E_S in relation to long-term variations in environment

Many environmental drivers such as light and nutrient availability strongly vary in and among plant communities. There can be further important interactions among environmental drivers (Niinemets and Valladares, 2008 for a review). Effects of a variety of such environmental modifications on isoprenoid emissions have been studied (e.g.,

Peñuelas and Staudt, 2010). Here we analyze in detail the variations in isoprenoid emissions in response to variation in growth CO_2 concentrations and in within-canopy environment to exemplify the potential magnitude of long-term environmental modifications on isoprenoid emissions. Both these sources of variation in emission rates are highly relevant to consider in emission models. Inclusion of the CO_2 effects is important to modeling that aims to understand how CO_2 concentrations that have varied in the geological past, and those that are currently increasing with a rate of ca. 1.5–2.5 ppm/yr (www.esrl.noaa.gov/gmd/ccgg/trends), influence isoprenoid emissions. On the other hand, as light gradients always occur in plant canopies, consideration of acclimation of isoprenoid emission potentials to within-canopy light environment is needed for accurate integration of canopy emission fluxes.

We further note that for simulation of emissions in natural ecosystems, it is important to consider also the soil nutrient effects on E_S. So far, the majority of studies report a positive effect of N-fertilization on E_S (or a positive correlation with foliar nitrogen). We refer to Peñuelas and Staudt (2010) for a recent in-depth review of nutrient effects.

2.2.1 Effects of growth CO_2 in species without isoprenoid storage

Apart from the instantaneous CO_2 responses of isoprene emission (Eq. 2), an increasing number of studies have demonstrated acclimation of E_S to the long-term CO_2 growth environment, evident in modified emission rates when assessed at the same intercellular CO_2 concentration (Fig. 2). Acclimation responses of plant carbon gain to ambient CO_2 concentration are becoming routinely included in modeling earth carbon balance (e.g., Gutschick, 2007; McMurtrie and Comins, 1996; Reynolds et al., 1996), but have so far implicitly been considered in very few models simulating volatile isoprenoid emissions under global change (Arneth et al., 2007a; Heald et al., 2009; Young et al., 2009).

For isoprene emissions, most studies indicate a significant decline in emissions for plants grown at higher CO_2 atmospheres, while a strong increase is observed in plants grown under below-ambient CO_2 concentrations (Fig. 2, for overviews see Arneth et al.,

2007b; Peñuelas and Staudt, 2010; Young et al., 2009). For monoterpene emissions in species without specialized storage tissues, the response of E_S to CO_2 has been studied much less, but the available evidence also demonstrates a reduction of E_S in plants grown under higher CO_2 (Baraldi et al., 2004; Llorens et al., 2009; Loreto et al., 2001; Rapparini et al., 2004), although not always (Llorens et al., 2009; Loreto et al., 2001; Staudt et al., 2001). One study has further reported the increase in monoterpene emissions in plants grown at CO_2 concentrations below the ambient (Baraldi et al., 2004). Such similarity with the majority of isoprene studies is expected given the same chloroplastic MEP pathway responsible for isoprene and monoterpene production.

Contrary to these reports, enhanced isoprene emissions were observed under elevated CO_2 in Tognetti et al. (1998) and Li et al. (2009) and in one out of the two studied species in Sharkey and Loreto (1991). In addition, enhanced monoterpene emissions in plants grown at higher CO_2 environment were found in Staudt et al. (2001) and Llorens et al. (2009). The contrasting observations among the studies are currently not understood. To explain the reduction of isoprenoid emissions under high CO_2 observed in several studies, the same cellular mechanism as for the instantaneous CO_2 response (Eq. 2) has been proposed, i.e., enhanced withdrawal of PEP from chloroplasts and use of the PEP in cytosol by PEP carboxylase (Rosenstiel et al., 2003).

However, not only the literature reports are contrasting, but also the shape of instantaneous response of isoprene emission to CO_2 changes in acclimation to growth CO_2 (Wilkinson et al., 2009). This suggests that factors other than or additional to substrate level controls can be responsible for the observed patterns in E_S under common CO_2. Among these other factors, reduction in isoprene and monoterpene synthase activities may provide partial explanation for the reduction in emission rates. In fact, reduction in monoterpene synthase activity has been observed upon acclimation to elevated CO_2 in the leaves of evergreen sclerophyll *Quercus ilex* (Loreto et al., 2001). Clearly, instantaneous and acclimation responses need to be separately analyzed to simulate responsiveness of isoprenoid emissions to altered CO_2 atmospheres. The situation is analogous to modeling CO_2 effects on carbon gain. While instantaneous

CO_2 responses can be well described by the widely used Farquhar et al. (1980) photosynthesis model, photosynthetic acclimation to elevated CO_2 is much more complex to simulate and requires consideration of additional feedbacks such as nutrient availability etc. (Gutschick, 2007 for a review).

2.2.2 Growth CO_2 effects in terpene-storing species

In species where the emissions mainly rely on a large storage pool such as in conifers, no instantaneous effect of CO_2 is expected, and the effects of altered growth CO_2 concentration can occur through changes in total pool size and modifications in internal diffusion conductance for monoterpenes, e.g., through changes in resin duct to total leaf surface area as well as through changes in resin duct epithelial permeability (Tingey et al., 1991 for a detailed model of monoterpene emission in storing species). Theoretical considerations based on tissue carbon/nitrogen (C/N) ratios predict stronger accumulation of secondary compounds such as monoterpenes when carbon availability is in excess of that required for growth, e.g., under elevated CO_2 concentrations (Lerdau et al., 1994; Litvak et al., 2002; Peñuelas and Estiarte, 1998). This in turn suggests potentially higher emissions under elevated CO_2 (Lerdau et al., 1994; Litvak et al., 2002; Peñuelas and Estiarte, 1998).

So far, some studies have reported a decrease rather than an increase in leaf monoterpene content under elevated CO_2 (Litvak et al., 2002; Räisänen et al., 2008a; Snow et al., 2003), while other studies have reported unaffected monoterpene contents (Constable et al., 1999; Peñuelas and Llusià, 1997), overall not agreeing with theoretical predictions. For the emissions, the studies have found a non-significant effect of elevated CO_2 (Constable et al., 1999; Li et al., 2009; Llorens et al., 2009; Peñuelas and Llusià, 1997) or an increase or decrease under high CO_2, depending on species and time of sampling (Llorens et al., 2009). In Räisänen et al. (2008b), elevated CO_2 alone did not affect the emissions, but a combination of high growth temperature and elevated CO_2 resulted in greater emissions (Räisänen et al., 2008b). Obviously, additional experimental work simultaneously analyzing the alterations in emissions, foliage

anatomy and monoterpene pool sizes is needed to gain conclusive insight into growth CO_2-driven changes in species with specialized terpene storage pools.

2.2.3 Variations in light availability

In plant canopies, there is an inherent variation in light availability, often more than 50-fold between the canopy top and bottom in dense stands (Niinemets, 2007 for a review). In addition, even in less densely vegetated ecosystems such as savanna-type woodlands, foliage is often strongly aggregated in the tree crowns, also bringing about large light availability gradients within the foliated plant parts (Asner et al., 1998). In addition to light, air and leaf temperatures increase with increasing light availability in tree canopies (Baldocchi et al., 2002; Niinemets and Valladares, 2004). Such long-term variations in environmental conditions are reflected in significant increases of isoprene emission rates per unit leaf area ($E_{S,area}$) from the canopy bottom to top (Harley et al., 1996, 1997; Niinemets et al., 1999). Analogous increases in $E_{S,area}$ have been observed for monoterpenes in species without specialized storage tissues (Lenz et al., 1997; Niinemets et al., 2002a).

In general, the within-canopy range in $E_{S,area}$ is more than an order of magnitude (Harley et al., 1996, 1997; Niinemets et al., 1999, 2002a). As $E_{S,area}$ is the product of leaf dry mass per unit area (M_A) and E_S per unit leaf dry mass ($E_{S,mass}$), part of this extensive variation in $E_{S,area}$ reflects modifications in leaf structure, i.e., increases in M_A with increasing light availability. Typically, M_A increases 2–4-fold along the canopy light gradients (Niinemets, 2007 for a review), resulting in accumulation of isoprenoid synthesizing mesophyll cells per unit leaf area. Despite the importance of structural modifications, $E_{S,mass}$ also varies 3–4-fold across the canopy light gradients (Niinemets et al., 2002a), indicating that the isoprenoid synthesis capacity of average leaf cells also increases with increasing light availability within the canopy.

As light and temperature co-vary in plant canopies (Niinemets and Valladares, 2004), the question is whether the long-term variations in light or temperature drive changes in E_S. This question is justified given that growth under higher temperatures also results

in higher isoprene (Hanson and Sharkey, 2001b) and monoterpene emission rates (Staudt et al., 2003). However, studies with plants grown under different incident quantum flux densities in constant temperature environments have also demonstrated positive correlations between light availability and isoprene (Hanson and Sharkey, 2001b; Litvak et al., 1996) and monoterpene (Staudt et al., 2003) emission capacities. This evidence suggests that light alone can drive alterations in isoprenoid emission potential, although the role of temperature in within canopy variation in isoprenoid emission potentials cannot be ruled out.

So far quantitative relationships with light availability or canopy leaf area index have not yet been developed. Nevertheless, within-canopy variation in E_S has been occasionally included in emission models, varying E_S with cumulative leaf area index from the canopy top to the bottom (Guenther et al., 1999).

2.3 E_S in relation to short-term variations in environment

Apart from the effects of long-term within-canopy variation in environment, light and temperature strongly fluctuate among consecutive days or groups of days. Abrupt alterations in environmental conditions such as suddenly improved light conditions after canopy gap formation in the understory or heat waves associated with synoptic weather systems also occur in nature. Experimental data demonstrate that E_S at any given location within the canopy is capable of acclimating to such environmental fluctuations (Funk et al., 2003; Hanson and Sharkey, 2001a; Sharkey et al., 1999). In fact, circadian and light-dependent regulatory elements have been observed for isoprene synthase, implying that the expression of isoprene synthase has the potential to respond to short-term stimuli (Cinege et al., 2009; Loivamäki et al., 2007; Wilkinson et al., 2006). Weather-dependent variation in isoprene emission capacity over periods of one to few days was best predicted by average temperature or light conditions of 12–48 h preceding the measurements (Ekberg et al., 2009; Funk et al., 2003; Geron et al., 2000; Sharkey et al., 1999; Simon et al., 2005; Wiedinmyer et al., 2005). Analogous

relatively rapid acclimation responses have been reported for methylbutenol (Gray et al., 2006) and monoterpenes (Porcar-Castell et al., 2009; Staudt et al., 2003).

In addition to short-term responses to fluctuating light and temperature conditions, full acclimation to any given environmental modification can take much longer, especially for profound alterations in environment. For isoprene emissions, 4–6 days are needed to fully respond to a step change in environmental conditions (Hanson and Sharkey, 2001a; Pétron et al., 2001). For monoterpene emission, it has further been demonstrated that the response kinetics differ for the increase (Fig. 3a) and decrease (Fig. 3b) of light intensity and temperature (Staudt et al., 2003). While full acclimation to the increased light and temperature took ca. 10 days (Fig. 3a), the response to reduced light and temperature took almost 40 days (Fig. 3b). Such asymmetric responses mean that the use of simple correlations of E_S with average values of temperature from the preceding few days are likely in error. In fact, the correlations observed with past environmental drivers are often scattered (Funk et al., 2003; Geron et al., 2000), possibly reflecting the different time kinetics for the rise and reduction of emission capacities in response to environment.

Although using an average value of E_S during a certain time period may realistically estimate the average emission rate during this time period, such an approach will overestimate the emissions during some periods of the simulation and underestimate during other periods, with the magnitude of the errors depending on the degree of fluctuation of environment. So far, the influence of preceding environmental conditions is included in only very few models. In MEGAN (Guenther et al., 2006), the temperature response function used in Eq. 1 is modified in dependence on the average temperature of past 24 h and past 10 days to consider longer-term acclimation responses (s. seasonality in Sect. 2.6). In this new model formulation (Guenther et al., 2006), the temperature response function, $f(T_L)$, modified this way, does generally not equal 1.0 under typical standard temperature of $T_L = 30^{\circ}C$. Apart from temperature response function, the light response function is also modified in dependence on past 24 h and 240 h light environment (Guenther et al., 2006). Ekberg et al. (2009), recently

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proposed an empirical relationship between 48 h average temperature and E_S to simulate the modifications of past weather influences on isoprene emission (Ekberg et al., 2009, Fig. 4), implicitly arguing that with field observations it is not possible to separate effects of past temperature and light conditions since these strongly co-vary. The simulations of the influences of temperature history on temporal dynamics with both models demonstrate significant effects of past weather conditions on the emissions, but also that the function used to describe the past weather can alter the predicted emission fluxes (Fig. 4).

Apart from the need for consensus description of past climate effects on emissions, there are other difficulties associated with the existing models. First, the speed of acclimation and response curve shapes can vary between species of the same biome (Ekberg et al., 2009) and possibly between different biomes. So far, the models use a constant past climate function for ecosystems as divergent as tropics and tundra (Ekberg et al., 2009; Guenther et al., 2006). In addition, past environmental effects in large scale models are only considered for isoprene. Yet, the temporal kinetics can be different for isoprene (Funk et al., 2003; Geron et al., 2000; Hanson and Sharkey, 2001a; Sharkey et al., 1999) and monoterpenes (Porcar-Castell et al., 2009; Staudt et al., 2003). Clearly more experimental work is needed to gain insight into the variations of past weather vs. isoprene and monoterpene emission responses.

2.4 Seasonal and age-dependent variations in E_S

Short-term environmental fluctuations between the days are superimposed on longer-term seasonal and developmental variations. Because environmental conditions vary during the season, in principle, the same mechanisms responsible for shorter-term changes can be considered operational (Sect. 2.3), e.g., seasonal variations in E_S are associated with seasonal changes in temperature (Mayrhofer et al., 2005; Wiberley et al., 2005).

Apart from immediate environmental effects operating on fully mature non-senescent leaves in seasonal climates, the physiological activity of foliage varies in dependence on leaf ontogenetic stage, increasing rapidly in developing leaves and decreasing in senescing leaves undergoing programmed cell death (e.g., Niinemets et al., 2010a; Shesták et al., 1985). Isoprene synthase activity increases gradually until full leaf maturation and decreases thereafter with the onset of leaf senescence (Schnitzler et al., 1997). Analogous developmental modifications have been observed for monoterpene synthase activity in species without specialized storage (Fischbach et al., 2002). The changes in limiting enzyme activity are accompanied by strong seasonal modifications in isoprene and monoterpene emissions with a maximum during the active growth period, and decline in senescing leaves (Fig. 5, Boissard et al., 2001; Ciccioli et al., 2001; Fischbach et al., 2002; Fuentes and Wang, 1999; Geron et al., 2000; Keenan et al., 2009; Kuhn et al., 2004; Sabillón and Cremades, 2001; Schnitzler et al., 1997). These reports collectively demonstrate the inadequacy of using a single standard emission factor for the entire seasonal cycle.

As isoprene synthase is not expressed in very young leaves, the leaves achieve photosynthetic competence earlier than the capacity for isoprene emission (Grinspoon et al., 1991). The lag between the onset of photosynthesis, and the capacity of the leaves to emit isoprene is a few days in hot tropical environments where the temperature environment is relatively stable (Kuhn et al., 2004). The lag increases to weeks in cooler seasonal temperate environments where leaf developmental periods are associated with strong increases in temperature (Monson et al., 1994; Schnitzler et al., 1997; Wiberley et al., 2005).

A further complication with developmental modifications in isoprenoid emission capacity is that M_A also varies during the season, strongly increasing in developing leaves, and decreasing somewhat in senescing leaves (Grassi and Magnani, 2005; Niinemets et al., 2004; Wilson et al., 2001). Thus, part of the seasonal variation in $E_{S,area}$ is structural rather than entirely associated with alterations in enzyme activity of single cells.

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To include the seasonal modifications in large-scale models, several approaches have been proposed. Schnitzler et al. (1997) included an additional modifier in Eq. 1, the seasonality function. In such an approach, E_S is defined as the maximum emission rate in standardized conditions observed during the season. While first parameterized empirically (Schnitzler et al., 1997), the seasonality function was later related to leaf phenology, temperature sum and light intensity (Lehning et al., 2001). Arneth et al. (2008) applied a seasonally varying E_S (expressed as a fraction of electrons used for isoprene production, Niinemets et al., 1999) as a function of growing degree temperature sums, and linked E_S to modeled canopy phenology in spring and autumn. In MEGAN (Guenther et al., 2006), the seasonality in isoprenoid emission rates mainly results from two factors: leaf age and average temperature and light intensity of the last 10 days. Leaf age effect is parameterized assigning different emission capacities for four different leaf age classes – new (emissions not yet induced significantly), growing (emissions below the peak rates), mature (peak emissions) and senescing (emissions below the peak rates) leaves (Guenther et al., 1999, 2000, 2006). On top of the leaf age effects, seasonality also results from temporal changes in average temperature that is used to modify the temperature response function (as stated in Eq. 1) as explained in Sect. 2.3. (Guenther et al., 2006). Both the leaf age and leaf temperature function may obtain values above 1 (Guenther et al., 2006), and thus, E_S is differently defined in this model than in the previous Guenther et al. (1991, 1993) algorithms, and is basically a modeled variable, which cannot be experimentally assessed in field conditions.

Alternatively, variation in the seasonality of emissions can be directly ascribed to set changes in E_S (Geron et al., 2000; Keenan et al., 2009; Staudt et al., 2000). In such an approach, variation in a measured quantity, the emission rate standardized for immediate variation in environmental drivers (Eq. 1), can be either linked to observed patterns in leaf phenology, and variations in light availability and temperature during the season (Geron et al., 2000) or seasonal variations in E_S can be empirically fitted (Fig. 6, Keenan et al., 2009; Staudt et al., 2000). Although mechanistic or semi-mechanistic descriptions linking variation in E_S to leaf developmental status and seasonal variation

in environmental drivers are promising, there is large species-specific variability in leaf phenology (Augsburger and Bartlett, 2003; Lechowicz, 1984) and in responsiveness of E_S to seasonal climate (Ekberg et al., 2009), and probably also to stress events during the season. In addition to the environmental drivers so far included in the models, there is evidence that the history of drought may affect the seasonal E_S responses (Fig. 6). Such variations likely explain significant interspecific variability in seasonal responses of emissions (Keenan et al., 2009).

To our knowledge, different parameterization schemes have been compared only in the study of Keenan et al. (2009) who compared the seasonal variations predicted by MEGAN (Guenther et al., 2006), i.e., a generalized past weather-dependent response function for temperature combined with a discrete four-level leaf age classification, and by a model using empirical parameterization fitted to the seasonal E_S data (Fig. 5). This model comparison exercise indicated that the MEGAN parameterization predicted weaker seasonality of the emissions than was actually observed (Keenan et al., 2009). Given the importance of seasonality in shaping the annual time-courses of isoprenoid emissions, clearly more experimental information is needed on the species-specific rates of leaf development and senescence, and on the sensitivity of E_S to seasonal variations in temperature, light and water availability. As leaf-level seasonal variation studies may be tedious and difficult to replicate, canopy-level flux measurements routinely carried out during the full year may provide an important vehicle for obtaining seasonal variation data (e.g., Ciccioli et al., 2003; Fuentes et al., 1999).

2.5 Philosophy of consideration of biological factors in models

We note that contrasting approaches are currently used to include the biological aspects in the isoprenoid emission models. Guenther et al. (1999, 2000, 2006) have considered E_S at a canopy level as a constant value, and used age-, previous climate and stress dependent multipliers in Eq. 1 to describe the biological effects on the emissions. According to this approach, E_S will be a pure modeling concept, as

it is essentially impossible to simultaneously standardize leaf previous environment, leaf age, and stress status to determine a single species-specific value of E_S. Problematic is also, that at least under field conditions, cumulative weather history, leaf age or "seasonality" factors are often correlated, and care has to be taken to avoid double-accounting by adding ever more empirical multipliers into the Guenther-type algorithms.

In contrast, other studies have considered that E_S, the emission rate under standardized conditions, varies in dependence on climatic conditions, leaf age and physiological status and growth CO_2 environment (Funk et al., 2003; Geron et al., 2000; Gray et al., 2005, 2006; Keenan et al., 2009; Possell et al., 2005; Sharkey et al., 1999). In the latter approach, any measurement under standardized light and temperature conditions will by definition be the "emission factor", and thus, E_S vs. past temperature (T_{past}), light intensity (Q_{past}) and CO_2 concentration (C_{past}) and leaf age (Λ) relationships are developed for isoprenoid emission modeling purposes:

$$E_S = f(T_{past}, Q_{past}, C_{past}, \Lambda), \quad (3)$$

whereas T_{past}, Q_{past} and C_{past} each can operate at several time frames to capture day-to-day to seasonal variations and variations during the foliage development (e.g., within-canopy gradients, growth CO_2). Additional response functions may be needed to consider the effects of various abiotic and biotic stress on constitutive emissions and predict stress-induced novel emissions (Niinemets et al., 2010b). As the "variable E_S" approach separates between the instantaneous effects of light, temperature and internal CO_2 concentration on the emission rate (Eq. 1) and the leaf-specific capacity for isoprenoid formation (E_S) that depends on longer term factors, we encourage the use of this modeling tactic. Furthermore, this is analogous to widely used models of carbon gain, where short term responses of photosynthesis to environmental drivers are simulated using process-based models, as a rule, Farquhar et al. (1980) photosynthesis model, while modifications in the capacities of the partial processes are studied using acclimation models (Harley and Baldocchi, 1995; Kull, 2002; Niinemets and Anten, 2009; Wilson et al., 2000a, b). However, under field conditions, it can be difficult

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to separate leaf age from environmental variation and light and temperature effects (Sect. 2.3 and 2.4). Thus, as with the Guenther et al. (2006) approach, care has to be taken not to double-account the effect of various factors in predicting E_S according to Eq. 3.

3 Conclusions and outlook

A plethora of recent experimental studies has demonstrated that a large number of processes shape variation in E_S on timescales from days to decades, overall indicating that the constancy of values used from study to study is illusion. These major biological sources of variation in E_S values need consideration when examining past experimental and model studies, and the novel information of biological sources of variation in E_S needs to be included more efficiently in the emission models. Here, we have synthesized the existing knowledge about dynamics in E_S, and attempted to chart a path forward for including E_S as a dynamic term in future modeling efforts. We admit that all of these effects cannot be included in a straightforward way into large scale models, partially due to our lack of process understanding, partially because this would lead to over-parameterization of such models. Clearly, inclusion of new response functions into existing large-scale predictive models must go hand-in-hand with experimental work testing the importance of specific biological responses and verifying the more complex models under typical natural settings. While studies on surface-atmosphere interactions have to rely on state-of-the art source/sink distribution of isoprenoid emissions, they also need to progress on some of the known weaknesses regarding their atmospheric oxidation patterns. In chemistry-climate feedback analyses even the best emission model will be of little value if the chemical reaction pathways are insufficiently described. Separation of first and second-order effects should therefore be a research priority, by quantifying sensitivities of isoprenoid emission model response to increasing complexity of process description in the emission models themselves, as well as quantifying effects on atmospheric composition.

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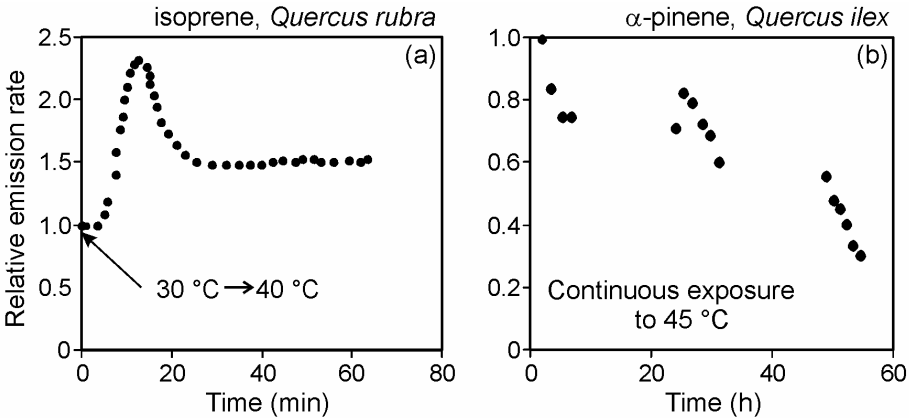

Fig. 1. Illustration of heat stress effects on isoprene **(a)** and monoterpene α-pinene **(b)** emissions. Data in (a) are normalized with respect to the steady-state emission rate at 30 °C, while the data in (b) are normalized with respect to the emission rate before the heat stress. Modified from Singsaas and Sharkey (a) 2000, and (b) Staudt and Bertin 1998.

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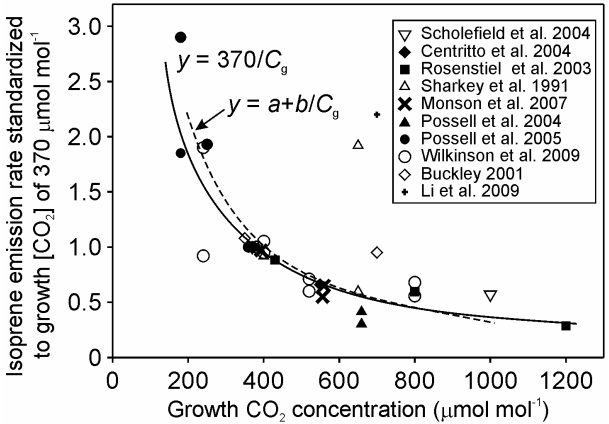

Fig. 2. Review of changes in isoprene emission rate under standardized conditions (leaf temperature of 30 °C, light intensity of 1000 μmol m^{-2} s^{-1} and ambient CO_2 concentration of 370 μmol mol^{-1}) upon acclimation to growth CO_2 concentration (C_g) (modified from Young et al., 2009). The data were expressed relative to the values measured in plants grown at the ambient CO_2 concentration of 370 μmol mol^{-1}. The following species were included in the analysis: *Arundo donax* (Possell et al., 2005), *Ginkgo biloba* (Li et al., 2009), *Eucalyptus globulus* (Wilkinson et al., 2009), *Liquidambar styraciflua* (Monson et al., 2007; Wilkinson et al., 2009), *Mucuna pruriens* (Possell et al., 2005), *Phragmites australis* (Scholefield et al., 2004), *Populus deltoides* (Rosenstiel et al., 2003; Wilkinson et al., 2009), *Populus x euramericana* (Centritto et al., 2004), *Populus tremuloides* (Monson et al., 2007; Sharkey et al., 1991; Wilkinson et al., 2009), *Quercus chapmanii* (Buckley, 2001), *Quercus robur* (Possell et al., 2004), *Quercus rubra* (Sharkey et al., 1991), and *Quercus stellata* (Monson et al., 2007). The solid line denotes $y = 370/C_g$ relationship previously used to simulate elevated CO_2 effects on isoprene emissions (Arneth et al., 2007b), while the dashed line is the best fit relationship fitted to the data after leaving out the outlying observations for *Ginkgo biloba* (Li et al., 2009) and *Quercus rubra* (Sharkey et al., 1991) ($r^2 = 0.78$).

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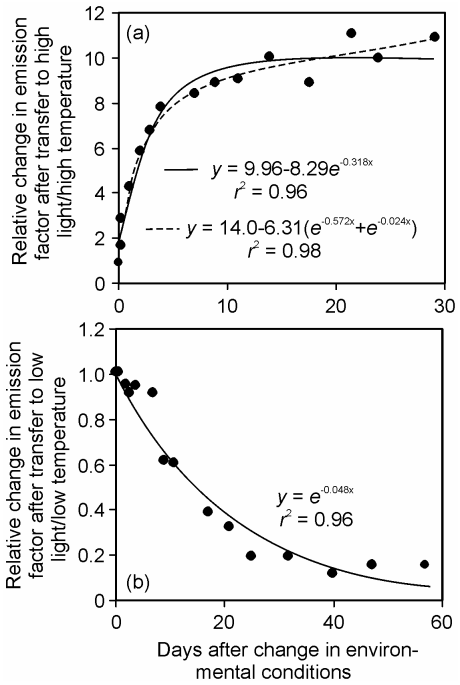

Fig. 3. Example of the acclimation kinetics of the monoterpene emission factor in Mediterranean evergreen sclerophyll *Quercus ilex* after transfer of plants from **(a)** moderate light (Q=300 µmol m^{-2} s^{-1}) and low temperature (10 °C night/20 °C day) to high light (quantum flux density, Q=1100 µmol m^{-2} s^{-1}) and warm temperature (20 °C night/30 °C day), and after an opposite transfer **(b)**. The emission factor was measured at leaf temperature of 25 °C and incident quantum flux density of 900 µmol m^{-2} s^{-1} after reaching the steady state (≥60 min.) under these assay conditions. The data were fitted by exponential decay functions. In (a) double exponential model (dashed line) improved the fit, suggesting that the acclimation consists of several processes with different time-kinetics. The half-time for the response, τ=ln(2)/k, where k is the exponential decay constant. The reduction of the emission factor after transfer to moderate light/low temperature occurs with slower time kinetics τ = 14.4 d than the increase of the emissions after transfer to high light/high temperature (for double-exponential model, shorter τ = 1.21 d, and for single-exponential model τ = 2.18 d). Data modified from Staudt et al. (2003).

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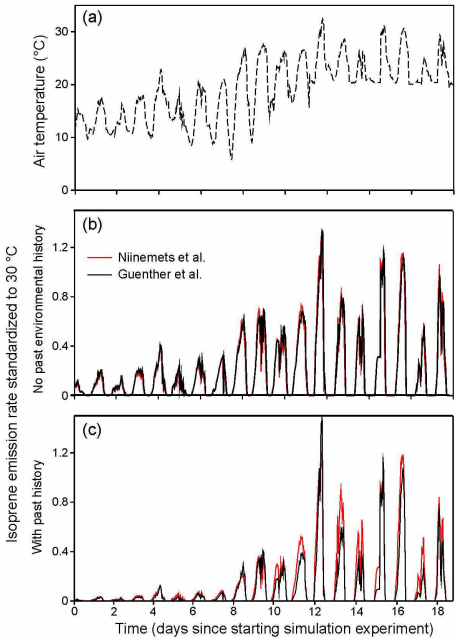

Fig. 4. Simulated temporal variation in isoprene emissions normalized to the rate at 30 °C in response to typical diurnal variations in temperature in continental temperate environments **(a)**. The simulations without temperature history **(b)** were conducted with the algorithms of Guenther et al. (1993, Eqs. 1–3, black line) and Niinemets et al. (1999, red line) that links the isoprene emissions to the rates of photosynthetic electron transport. In the latter simulation, electron flow was provided from the photosynthesis model of Farquhar et al. (1982) and assuming fully open stomata, and adjusting the fraction of electrons going into isoprene synthesis pathway such that the emission rate under standardized conditions equaled that in Guenther et al. (1993). In **(c)**, the emissions were simulated by the same two models, but for Guenther et al. algorithms (1993), the past temperature and radiation history was considered as in Guenther et al. (2006, MEGAN), and the past temperature history for the Niinemets et al. (1999) model as found in Ekberg et al. (2009). The latter was from a study in cool growth environment and the exponential function was re-scaled to same common temperature as used in the MEGAN temperature-history algorithm. In MEGAN, the optimum temperature of the isoprene response function ($f(T)$ in Eq. 1) depends linearly on the previous temperature of the past 240 h, while the standardized emission rate depends exponentially on the temperature of the past 24 and 240 h (Guenther et al., 2006). In Ekberg et al. (2009), the standardized isoprene emission rate depends exponentially on the previous temperature of the past 48 h.

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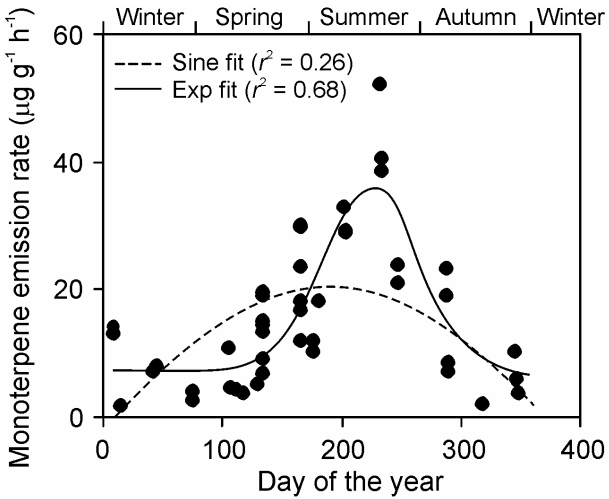

Fig. 5. Seasonal variation in standardized monoterpene emission rate (leaf temperature of 30 °C and light intensity of 1000 µmol m^{-2} s^{-1}) in Mediterranean evergreen sclerophyll *Quercus ilex*. Data (filled symbols) were combined from several independent sources (Bertin et al., 1997; Kesselmeier et al., 1997; Kesselmeier et al., 1998; Llusià and Peñuelas, 2000; Owen et al., 1997; Sabillón and Cremades, 2001; Staudt et al., 2002, 2004; Street et al., 1997) and E_S vs. day of the year relationships were fitted either by a symmetric sine function or an asymmetric exponential function (Keenan et al., 2009). The sine function was defined as $y=a$*sin[$(b+x)$*180/365]+c*sin[$(d+x)$*180/365], where $a-d$ are empirical parameters. The exponential function was defined as $y = a_1 + a_2 e^{\left(-\frac{(x-a_3)^2}{a_4}\right)}$, where $a_1 - a_4$ are empirical parameters; this function allows to parameterize asymmetric seasonal variation patterns (Keenan et al., 2009 for further details). Although the symmetric sine or second order polynomial functions are often used to characterize the seasonal changes (Hargreaves et al., 2000; Stolwijk et al., 1999), the seasonal variation in E_S was clearly asymmetric.

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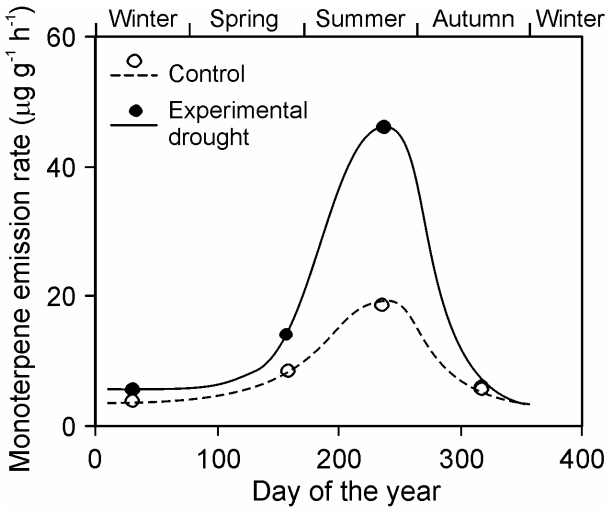

Fig. 6. Interaction of drought stress with seasonal variation in standardized monoterpene emission rate (leaf temperature of 30 °C and light intensity of 1000 µmol m^{-2} s^{-1}) in *Quercus ilex*. The experimental drought treatment in the Mediterranean *Q. ilex* forest included partial rain and runoff exclusions and resulted in a reduction in soil water availability by ca. 25% in all seasons except the summer hot and dry season, where the soil water availability was similar in both control and drought treatments. Thus, drought prior to summer season was responsible for enhanced emission rates in summer in the drought experiment. Average data for the growing seasons 2003 and 2005 were fitted by the exponential asymmetric function as in Fig. 5 (modified from Llusià et al., 2010).

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