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Process-based estimates of terrestrial ecosystem isoprene emissions

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In recent years evidence has emerged that the amount of isoprene emitted from a leaf is affected by the CO₂ growth environment. Many – though not all – laboratory experiments indicate that emissions increase significantly at below-ambient CO₂ concentrations and decrease when concentrations are raised to above ambient levels. A small number of process-based leaf isoprene emission models can reproduce this CO₂-stimulation and -inhibition. These models are briefly reviewed, and their performance in standard conditions compared with each other and to an empirical algorithm. One of the models was judged particularly useful to be incorporated into a dynamic vegetation model framework, LPJ-GUESS, aiming to develop a tool that allows the interactive effects of climate and increasing CO₂ concentration on vegetation distribution, productivity, and leaf and ecosystem isoprene emissions to be explored. The coupled vegetation dynamics-isoprene model is described and used here in a mode particularly suited for the ecosystem scale, but it can be employed at the global level as well.

Annual and/or daily isoprene emissions simulated by the model were evaluated against flux measurements (or model estimates that had previously been evaluated with flux data) from a wide range of environments, and agreement between modelled and simulated values was generally good. By using a dynamic vegetation model, effects of canopy composition, disturbance history, or trends in CO₂ concentration can be assessed. We show here for five model test sites that the suggested CO₂-inhibition of leaf-isoprene metabolism can be large enough to offset increases in emissions due to CO₂-stimulation of vegetation productivity and leaf area growth. When effects of climate change are considered atop the effects of atmospheric composition the interactions between the relevant processes will become even more complex. The CO₂-isoprene inhibition may have the potential to significantly dampen the expected step increase of ecosystem isoprene emission in a future warmer atmosphere with higher CO₂ levels; this effect raises important questions for projections of future atmospheric chemistry and its connection to the terrestrial vegetation and carbon cycle.

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1 Introduction

Among the wide range of volatile organic carbon compounds (VOC) produced by plants, isoprene (2-methyl-1,3-butadiene) is the single-most abundant chemical species (Rasmussen, 1970; Kesselmeier and Staudt, 1999; Fuentes et al., 2000; Ler-
5 dau and Gray, 2003). The chief pathway for its formation is via 1-deoxy-D-xylulose-5-phosphate (DOXP) synthesised in the chloroplast, which is reduced to the immediate isoprene precursor Dimethylallyl-diphosphate (DMAPP) in a series of energy and reductive equivalent-requiring reactions (Eisenreich et al., 2001; Rohdich et al., 2001; Wolff et al., 2003; Niinemets, 2004). Not all plant species produce isoprene though,
10 at standardised measurement conditions, the potential of a leaf to emit varies greatly from zero to values $>100 \mu\text{g}_C \text{g}_{\text{leaf}}^{-1} \text{h}^{-1}$ (Kesselmeier and Staudt, 1999; Wiedinmyer et al., 2004). It is difficult to associate the potential for isoprene emission with plant taxonomic classifications although some plant families or genera subsume a notable number of emitting species (Benjamin et al., 1996; Kesselmeier and Staudt, 1999).
15 Global estimates of the amount of carbon emitted by terrestrial biota in the form of isoprene appear to converge around $c. 500 \text{Tg}_C \text{a}^{-1}$, which exceeds carbon emitted as methane from biogenic sources by a factor of two to three. The uncertainties associated with these calculations, however, are large, and independent constraints of a global isoprene budget from observations are presently not available (Guenther et al.,
20 1995; Wang and Shallcross, 2000; Abbot et al., 2003; Levis et al., 2003; Sanderson et al., 2003; Gedney et al., 2004; Naik et al., 2004; Shindell et al., 2004; Lathiere et al., 2005; Guenther et al., 2006).

For those plants that do produce isoprene its function is still unclear. However, its significance in the climate system is well established. Isoprene reacts readily with the hydroxyl radical and is a key constraint of the tropospheric oxidation capacity and atmospheric lifetime of methane (Poisson et al., 2000; Monson and Holland, 2001; Valdes et al., 2005). Depending on the level of NO_x , isoprene emissions contribute to the production of tropospheric ozone (Atkinson, 2000; Atkinson and Arey, 2003; Sanderson

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et al., 2003), which is not only a greenhouse gas but also toxic in high concentrations. Recently, oxidation products of isoprene have been discovered to contribute to the growth of biogenic particles (Claeys et al., 2004; Kourtchev et al., 2005). Although mass yields are low these reactions may potentially contribute significantly to global secondary aerosol formation because of the large amount of isoprene emitted (Matsunaga et al., 2005).

Global and regional isoprene emission estimates are based on algorithms developed in the early to mid 1990s. These describe the light and temperature response of leaf-emissions and can be up-scaled to the canopy (cf., Appendix; Guenther et al., 1993, 1995; Geron et al., 1994; Guenther, 1997). In a number of recent model experiments these empirical algorithms have also been linked to dynamic global vegetation models to investigate the impact of changing vegetation cover on global atmospheric emissions and atmospheric chemistry (Levis et al., 2003; Sanderson et al., 2003; Naik et al., 2004; Lathièrè et al., 2005). From these, emission rates are predicted to decrease for past environments and possibly increase markedly in the future (Sanderson et al., 2003; Naik et al., 2004; Lathièrè et al., 2005; Valdes et al., 2005). These results are to some extent caused by the strong temperature sensitivity of emission rates. They also reflect the CO₂ fertilisation of vegetation, stimulating gross primary productivity and leaf growth – and in that way the amount of isoprene emitting biomass. However, these studies do not account for possible direct effects atmospheric CO₂ concentration may have on leaf isoprene production. An increasing number of experiments indicate that leaf emission increases in plants grown at below-ambient CO₂ concentrations and decreases in a high CO₂ environment, with only very few studies reporting the opposite (cf., Sect. 2). If these effects are taken into account past and future isoprene emission estimates may have to be revised since they offset, at least partially, the interactions of CO₂ concentration and plant leaf production (Arneth et al., 2006¹).

¹Arneth, A., Miller, P. M., Scholze, M., et al.: CO₂ inhibition of leaf isoprene metabolisms offsets effect of increasing temperature and GPP fertilisation on global terrestrial emissions., in preparation, 2006.

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Some leaf isoprene models have sought to link production rates explicitly to the chloroplastic biochemistry of isoprene precursors (cf., Sect. 3; Niinemets et al., 1999; Martin et al., 2000; Zimmer et al., 2000; Bäck et al., 2005), in that way including a direct interaction of carbon assimilation and isoprene emission. Since terrestrial carbon cycle and dynamic vegetation models generally evolve around a mechanistic model for leaf photosynthesis (e.g., Farquhar et al., 1980; Collatz et al., 1991) a process-based leaf isoprene model could, in principle, be relatively easily incorporated into these large-scale models. A possibly advantageous approach, that would permit to assess not only the combined effects of temperature, vegetation distribution and productivity on terrestrial isoprene emissions, but also those attributed to CO₂ directly. In what follows we briefly summarise observations of direct CO₂-isoprene interactions, review the existing mechanistic leaf level isoprene models that seek to incorporate these effects, and compare the models' potential to predict the emission response to light, temperature and CO₂, as well as their applicability in global models. We incorporate one of these into the dynamic vegetation model framework LPJ-GUESS (Smith et al., 2001; Sitch et al., 2003) and test model output against isoprene flux measurements at a range of sites representing different biomes. Finally, we assess the sensitivity of the calculations to canopy disturbance and changes in atmospheric CO₂ concentration.

2 The response of leaf isoprene emission to changes in atmospheric CO₂ concentration

DOXP, the eponym of the chief isoprene synthesis pathway, is a reaction product of Glyceraldehyde-3-phosphate (G3P, Table 1) and Pyruvate, in a reaction that is catalysed by DOXP-synthase. Since G3P is a chief metabolite of carbon assimilation, experimental evidence linking variation in leaf isoprene emission to photosynthetic carbon metabolism is to be expected (Monson and Fall, 1989b; Loreto and Sharkey, 1990; Kesselmeier et al., 2002). What is more, the redox-equivalents (NADPH) and ATP required to reduce the initial sugars to isoprene originate from chloroplastic electron flow.

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Yet, although some studies have provided compelling evidence for strong links between leaf isoprene emission and photosynthesis rates e.g., by linear correlations with gross photosynthetic capacity or by high retrieval rates of ^{13}C labelled $\text{CO}_2\text{-C}$ in isoprene (Sharkey et al., 1991a; Delwiche and Sharkey, 1993; Kuhn et al., 2004; Possell et al., 2004), others have identified discrepancies between the two. The primary carbon source may not always originate from recently assimilated photosynthate (Monson and Fall, 1989a; Affek and Yakir, 2003), the temperature optimum of isoprene emission is often notably higher, compared to that of photosynthesis, and isoprene emission appears inhibited at elevated CO_2 concentration (Table 2). While it is therefore clear, in principle, that isoprene synthesis is linked to assimilation via availability of substrate, enzyme activation and/or redox-status (Lichtenthaler, 1999; Sharkey and Yeh, 2001; Wolfertz et al., 2003) such observations emphasize that the leaf-internal control mechanisms determining the amount of carbon to be used for isoprene production are still not fully resolved.

Short-term exposure to increasing CO_2 concentration ($[\text{CO}_2]$) inhibits leaf isoprene emissions whereas exposure to decreasing $[\text{CO}_2]$ has the opposite effect, unless $[\text{CO}_2]$ is zero (Tingey et al., 1981; Monson and Fall, 1989a; Loreto and Sharkey, 1990; Rapparini et al., 2004). The longer-term response of leaf, branch or canopy isoprene emissions from plants grown in variable CO_2 environments has been investigated in a handful of studies over recent years. Measurements were carried out at plants grown over their lifetime in the vicinity of natural CO_2 springs (Tognetti et al., 1998; Rapparini et al., 2004; Scholefield et al., 2004), or plants grown over a limited time-period in high (Sharkey et al., 1991b; Buckley, 2001; Rosenstiel et al., 2003; Centritto et al., 2004; Possell et al., 2004; Pegoraro et al., 2005a) or low (Possell et al., 2005) CO_2 environment. Table 2 provides an illustrative, non-quantitative overview over the direction of the observed response on leaf and/or branch, plant or canopy level. From the twelve data-sets summarised in the table, seven show decreasing leaf isoprene emissions with increasing $[\text{CO}_2]$ (including one study where the trend was not statistically significant, Possell et al., 2005, *Arundo donax*), in one study no effect of CO_2 concen-

tration on isoprene emission was observed and only two show an increase. Hence, the majority of studies to date that investigate effects of growth-CO₂ environment on isoprene emissions support observations made from the short-term variation of CO₂ concentration around the leaf.

Substantially declining isoprene emissions as [CO₂] increases were observed even though rates of photosynthesis often were stimulated in elevated growth CO₂. For instance, isoprene emissions from *A. donax* and *Mucuna pruriensis* grown in growth chambers at 180 ppm CO₂ exceeded emissions at ambient CO₂ by a factor two to three, when expressed on leaf area basis (Possell et al., 2005). Along a CO₂ gradient in the vicinity of a natural CO₂ spring, leaf emission rates from *Phragmites* decreased five-fold with decreasing distance to the CO₂ source (c. 400 to 900 ppm) when either expressed on leaf area or mass basis (Scholefield et al., 2004). Ecosystem emissions decreased by 21 and 41%, respectively, in the 800 and 1200 ppm CO₂ growth-environment of the Biosphere-II facility, somewhat less when compared to effects on leaf level (c. -35 and -65%; Rosenstiel et al., 2003). This weakening of the CO₂-induced inhibition of isoprene emissions per unit branch or canopy area, compared with observations from the leaf is a common observation, although the number of studies that investigated CO₂ effects on a range of scales within the canopy are limited (Centritto et al., 2004; Rapparini et al., 2004; Possell et al., 2005). The growth CO₂ environment can affect leaf anatomy or simply the total number of leaves per branch or plant in some cases to a degree that it annihilates the leaf isoprene effect completely. In FACE-grown poplar clones leaf isoprene emissions in ambient CO₂ exceeded those of plants in elevated CO₂ by more than 30% but this effect was completely counteracted by the larger number of leaves in the trees in the elevated treatment (Centritto et al., 2004). These observations clearly point to the importance of treating direct and indirect CO₂ effects simultaneously, when modelling terrestrial isoprene emissions, since a number of effects may counterbalance each other.

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3 Leaf level isoprenoid production algorithms

By far the most widely used algorithms to describe isoprene emissions from leaves have been developed by Guenther and colleagues (Guenther et al., 1993; Geron et al., 1994; Guenther et al., 1995; Guenther, 1997). The production of isoprene is calculated from a plant species-specific standardised emission factor (I_s), the rate determined at a leaf temperature (T) of 30°C and a photon flux density (Q) of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$, which over the course of a day is varied non-linearly in response to changing leaf temperature and radiation at the leaf surface (cf., Appendix). Upscaling to the canopy level may be done using light transfer and canopy characteristics (e.g., foliar density, or leaf specific weight; e.g., Lamb et al., 1996; Baldocchi et al., 1999; Huber et al., 1999). Recently, the use of a net-canopy emission factor was suggested to replace the leaf-level I_s (Guenther et al., 2006). The emission factor, sometimes also called the basal rate, can be varied seasonally to account for the observed time-lag between leaf development and onset of photosynthetic activity and spring isoprene emission, or for effects of light-environment on leaf development and the investment into isoprenoid enzymatic machinery (Kuzma and Fall, 1993; Monson et al., 1995; Fuentes and Wang, 1999; Fuentes et al., 1999; Geron et al., 2000; Hanson and Sharkey, 2001).

A small number of leaf models have sought to pursue a different approach by synthesising current understanding of isoprene metabolism to calculate production rates based on enzyme activity and supply of precursors from photosynthesis (cf., Appendix for a summary description of the models' main features). Four approaches have been published to date:

1. Martin et al. (2000), which calculates isoprene production as the result from three potentially rate limiting processes: the supply of carbon to isoprene synthesis via pyruvate formed by Ribulose 1,5-bisphosphate (RUBP) carboxylation, the supply of ATP by phosphorylation needed to produce the isoprene precursor dimethylallyl-diphosphate (DMAPP) from the carbon substrate, and the maximum capacity of isoprene-synthase.

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2. Zimmer et al. (2000), where isoprene production is described by a set of reactions that account for the transient changes in pool sizes along the pathway from the C-3 precursors to isoprene, each controlled by Michaelis-Menten kinetics with specific reaction velocities. The C-3 precursors are provided by the dynamic photosynthesis model by Kirschbaum et al. (1998).
3. Bäck et al. (2005), a model originally designed for monoterpene emissions that can also be adopted for isoprene. The chief constraint for isoprene production is the availability of G3P, which is derived from the rate of photosynthesis or photorespiration, depending on the difference between ambient (C_a) and internal (C_i) CO_2 concentrations.
4. Niinemets et al. (1999), where the supply of DMAPP for isoprene synthesis and isoprene synthase activity are considered to be the primary control processes. Photosynthetic electron transport rate supplies the required ATP and NADPH for carbon reduction to isoprene; it is assumed that a certain fraction of electrons, ε , is available for isoprene synthesis and that the competitive metabolic strength of isoprene synthesis pathway is proportional to the total activity of isoprene synthase in the leaves. Described in detail in the appendix, we use here a modification of the model that specifically accounts for the effects of atmospheric CO_2 concentration on isoprene synthesis.

3.1 Common features

While these leaf-level models endeavour to link isoprene production to carbon assimilation in a mechanistic way they all nonetheless require some empirical, plant species-specific parameterisations to compensate for the insufficient understanding of the cellular regulation of isoprene production (cf., Appendix). Since it is not our chief concern to assess and compare absolute leaf isoprene emission rates calculated by the models these can be largely neglected for our purpose. Figures 1–3 rather seek to address

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the models' relative sensitivity to changes in environmental conditions, and their applicability in terrestrial carbon cycle and dynamic vegetation models for estimates of past, current and future isoprene emissions. To do so, we compare the normalised model response to variation in either Q , T or $[\text{CO}_2]$, while keeping the other variables constant. We derive the information related to carbon assimilation, required as input for the calculation of isoprene production rates, from Farquhar et al. (1980) in case of the Martin et al., Zimmer et al., and Niinemets et al. models (Appendix: A2, A3 and A5), and from Hari and Mäkelä (2003) for the Bäck et al. model (A4).

In the short-term, leaf isoprene emissions increase hyperbolically with light and in an Arrhenius-type fashion with temperature with, for many plant species, an optimum well above 30°C . These commonly observed relationships that are empirically described by Eq. (A1a) are also reproduced well by the Martin et al. and Niinemets et al. models (Fig. 1) – unsurprisingly so, since the isoprene emission responses to Q and T are essentially similar to those of photosynthesis. The former depicts a stronger increase with T and a distinct saturation above $Q=500 \mu\text{mol m}^{-2} \text{s}^{-1}$; both models account for a difference between the T -optimum of carbon assimilation and that of isoprene production. Furthermore, the inclusion of κ (Eqs. A2b, A4; Fig. 7) in both models leads to isoprene emission declining non-linearly with increasing atmospheric CO_2 concentration (Figs. 2, 3). In case of the modified Niinemets et al., I declines from $C_a > c. 150$ ppm, levelling at around 500 ppm, whereas modelled I from Martin et al. was not responsive to increasing CO_2 concentration until $C_a > 400$ ppm, and it did not level off until $c. 700$ ppm. The extend of this emission “plateau” at low to medium CO_2 concentrations depends on the chosen value of Q (Fig. 3) but also on the assumed temperature of the model experiment (not shown, cf. Martin et al., 2000).

The Q , T and $[\text{CO}_2]$ response of leaf isoprene production calculated from the Bäck et al., and Zimmer et al. approaches displayed some unexpected features that require commenting. Both are dynamic, non-equilibrium models that are not designed to be coupled to steady-state carbon assimilation. In case of the former, carbon substrate for isoprene synthesis is supplied by a photosynthesis module that is based on the

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concept of optimum stomata control of carbon assimilation (Cowan, 1982; Hari and Mäkelä, 2003). By assuming steady state, as done for the calculations shown in the Figures, the value of a model parameter λ , the marginal cost of plant carbon gain, is set to a value that results in open stomata over the entire range of conditions used in the Figures. This leads to the dynamic response of the model to transient environmental changes being dampened significantly. Moreover, calculation of isoprene synthesis does not include a specific temperature dependence (Eq. A3b) but depends on the temperature response of carbon supply from the assimilation module. In Scots pine, the species this module is adjusted to, the temperature response of photosynthesis is extremely weak, photosynthesis has been observed to occur already in early spring, as soon as air temperatures are above 0°C (P. Hari, personal observation). The model therefore reproduced the expected smooth saturation of isoprene emission with increasing light (Fig. 1) but there was no temperature response. The evaporation process in the original version of the model includes a strong temperature response for monoterpene emissions, and results in diurnal variation as observed under field conditions. To expand its applicability for a wider range of plant species, the model would need to be adjusted to account for the difference commonly observed between the temperature response of carbon assimilation and isoprene production, possibly in a similar way as done in Eq. (A4b). In terms of the CO₂-sensitivity, the model simulates no isoprene synthesis when the mesophyll CO₂ concentration is above ambient CO₂ concentration (of the year 2004). This is clearly seen in Figs. 2 and 3 as zero emissions at high C_a, and thereafter a very steep increase with decreasing intercellular CO₂ concentration, in accordance with the experimental results of isoprene-CO₂ response (Table 2).

In case of the Zimmer et al. model, Figs. 1–3 illustrate results from what had been termed the “BIM, biochemical isoprenoid biosynthesis”-part of the model. Light saturation of isoprene production was simulated already at very low rates (around 200 μmol m⁻² s⁻¹) reverberating the model’s original interface with a light-fleck model that by its nature has a strong focus on plants growing in or underneath dense canopies

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(Kirschbaum et al., 1998). Modelled isoprene production increased smoothly with temperature until 40°C; the model is not designed to run with temperatures above 42°C when the triosephosphate pool runs empty. Clearly, most of the emission dynamics were accounted for in the “seasonal isoprene synthesis model, SIM” part of the originally coupled version, and similarly to what was shown for the Bäck et al. approach, inconsistencies in the isoprene T - or Q - responses are therefore not a shortcoming of the model per se, but purely a numerical consequence when placed in a steady-state model environment. Even so, the model cannot produce a CO₂ response in its present form as was pointed out already by Zimmer and co-authors (Zimmer et al., 2003). Not surprisingly so: while chloroplastic processes are represented in a mechanistic way by including a cascade of relevant enzymatically controlled reactions, the model does not calculate a leaf-internal CO₂-dependent competition for carbon, redox or energy equivalents that underlies the observed isoprene-CO₂ response in one way or another. In the Martin et al., and Niinemets et al. such leaf-internal competition is subsumed semi-mechanistically in κ , while in Bäck et al. (2005) a change in oxygenation vs. carboxylation via Rubisco is calculated explicitly and (as in κ) assumed to be an appropriate surrogate for competition for a range of metabolites.

4 Modelling at ecosystem scale

A wide range of studies have used the Guenther et al. algorithms to estimate isoprene (or BVOC in general) emissions from a canopy, a region or from the global terrestrial biosphere. Expanding beyond the leaf-scale requires the leaf-level algorithms to be joined with a land surface description that accounts for the canopy structure and phenology, canopy micro-climate and the canopy species composition – input that can be provided, e.g., from surface cover observations, a complex, multi-layer canopy model, a terrestrial biogeochemistry model, surface cover information derived from remote sensing, or a combination of these (e.g., Guenther et al., 1996; Geron et al., 1997; Baldocchi et al., 1999; Huber et al., 1999; Simpson et al., 1999; Lindfors and Laurila,

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2000; Guenther et al., 2006). Since the complexity in the canopy models may not necessarily improve model performance when compared to measured isoprene emissions (Lamb et al., 1996), the way the upscaling is performed depends on the specific scientific question, the spatial scale to be considered, and on the time period the simulation is performed for.

The increasing awareness of important bi-directional exchange processes between terrestrial surfaces and the atmosphere that affect the physical as well as chemical characteristics of the latter has stimulated interest in the interactions between atmospheric CO₂ concentration, climate change and changes in surface vegetation cover on isoprene emissions. In a set of initial analyses the Guenther et al. algorithms were used in Dynamic Global Vegetation Models (DGVM) to account for interactions between climate and plant cover on simulated emissions (Levis et al., 2003; Sanderson et al., 2003; Naik et al., 2004; Lathiere et al., 2005). DGVMs simulate vegetation cover dynamics based on plant bioclimatic limits, carbon uptake by the vegetation, and the way carbon is allocated in the ecosystem. They can thus be applied to investigate the sensitivity of terrestrial isoprene emissions not only to changes in surface plant cover, but also to climate- or CO₂-related changes in gross primary productivity (GPP) or canopy phenology. Yet, the possibly significant direct effect atmospheric CO₂ concentration may have on leaf level emission (Table 2) has so far been ignored in the simulations. Since some of the studies summarised in Table 2 have indicated that such a direct isoprene-CO₂ inhibition can potentially offset effects due to stimulated GPP or leaf growth, and since increasing atmospheric CO₂ concentration goes hand-in-hand with increasing temperatures it seems essential to quantify its possible importance on ecosystem, regional or global scale.

4.1 Ecosystem model

The relative simplicity of the Niinemets et al. formulation makes it a prime candidate to be used in a broader model framework to address this issue. As demonstrated above, the model's response to Q , T and $[CO_2]$ is in general agreement with today's under-

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standing; furthermore it requires determination of only one chief input parameter (ε , cf., Appendix) that scales with carbon assimilation rate over its entire range and that can be modified to describe short and longer term emission responses. Here we incorporated the model into LPJ-GUESS, a framework that combines the dynamic global vegetation model LPJ (Sitch et al., 2003) with the “patch”-model GUESS (Smith et al., 2001). LPJ-GUESS simulates the vegetation and soil carbon and water cycle response to variation in weather, as well as changes in productivity, vegetation structure and cover in response to episodic events like fire, or to trends in climate and atmospheric CO₂ concentration. Briefly, the competitive strength of a “plant functional type” (PFT), the modelled unit, is defined by its set bioclimatic limits, its phenology, and by a range of functions describing its ability for resource competition, carbon sequestration, mortality and/or rate of establishment. When using the model on global scale (DGVM mode), the latter processes are described fairly generally; on that scale considerable averaging of vertical or horizontal canopy structure is required to keep the model computationally efficient. Vegetation within a gridcell (typically 0.5° × 0.5°) is defined by the fractional cover of the average individual of a given PFT that can grow within the cell. When run in cohort mode (with “patch” vegetation dynamics), formulations for establishment and mortality, growth, and light and water competition between neighbouring plant individuals within a patch, are taken into account more explicitly. In that way, PFT-sub-groups or even individual species can be defined in terms of their resource use (e.g., their shade tolerance; Smith et al., 2001; Hickler et al., 2004; Koca et al., 2006). The area of a single patch is approximately equal to the area of influence of one large individual; the model output is the average from a number of replicate patch calculations, whereby establishment and mortality is stochastic. The physiological process descriptions in LPJ-GUESS, for instance the coupling of photosynthesis and stomata conductance, plant and ecosystem carbon and water balance, litter decomposition or soil processes are identical to those used in LPJ-DGVM (Sitch et al., 2003) including updates to the model’s hydrology presented by Gerten et al. (2004)². LPJ-DGVM and

²Except for maximum transpiration from tropical trees, set to 5 mm d⁻¹ (Sitch et al., 2003).

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LPJ-GUESS have both been extensively evaluated with respect to ecosystem functioning or vegetation representation (Hickler et al., 2004; Morales et al., 2005; Sitch et al., 2005). The model has also been shown to reproduce CO₂ effects on primary productivity that have been observed at a number of Free Air CO₂ Enrichment experiments (Gerten et al., 2005). Here we concentrate on the model's performance to simulate isoprene emissions from a range of ecosystems, using it in cohort-mode; an assessment of global emission patterns in a changing environment is provided elsewhere (Arneth et al., 2006¹).

The chief link between isoprene production and the vegetation distribution provided from LPJ-GUESS is via ε (Eq. A4), a plant species-specific parameter. For use in LPJ-GUESS it needs to be assigned to each PFT simulated by the model, as the functional significance of the presence or absence of isoprene production in plant species has not yet been resolved. Therefore, ε is currently set to yield I_s at standard T and Q , 370 ppm atmospheric CO₂ concentration, and based on calculated J under these conditions, an approach that allows to draw on the existing data-bases for I_s . The isoprene-CO₂ response that is introduced in the leaf model via κ requires calculation of the rate of photorespiration (Eq. A2b) which is not explicitly included in the modification of the Farquhar et al. scheme that is used in LPJ-GUESS (Farquhar et al., 1980; Haxeltine et al., 1996). The variation of κ with CO₂, shown in Fig. 7a (Appendix) therefore was empirically reproduced by

$$\kappa^{**} = y_0 + b_1 \exp(-b_2 C_a) \quad (1)$$

with $y_0=0.51$; $b_1=5.98$; and $b_2=0.068$ ($r^2=0.99$).

Isoprene emission from newly developing leaves is known to be considerably less than the maximum capacity reached in fully mature leaves and it lags the development of assimilation capacity by several days to few weeks in cool temperatures (Monson et al., 1994; Schnitzler et al., 1997; Sharkey et al., 1999). This delay between the onset of photosynthesis and development of isoprene emission capacity can be explained by effects of growth environment on the expression of isoprene synthase (Wiberley et al.,

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2005). A mechanism that can explain field observations where seasonal variation in isoprene emission capacity could be approximated successfully by using degree-day temperature sums (gdd) following the last spring frost, reaching its maximum between c. 400 and 1000 degree-days (Goldstein et al., 1998; Hakola et al., 1998; Fuentes and Wang, 1999; Geron et al., 2000; Pressley et al., 2005). Here we use the simple function

$$\sigma = \exp[-e_1((\text{gdd} - x_0)/b)^2] \quad (2)$$

with $e_1=2$, $x_0=1000$ and $b=1100$ (Fig. 7b) to describe this seasonal effect, which also accounts for the decline of isoprene emission capacity in autumnal leaves.

LPJ-GUESS runs on a daily time step, using average air temperature, precipitation and insolation as climate input. These can either be provided by gridded climate data (e.g., the CRU climate time series 1901–1998; <http://www.cru.uea.ac.uk/cru/data/hrg.htm>), or from measured, daily climate at a location the model is run for. In case of the gridded CRU data, monthly input is interpolated to quasi-daily values. Because of the strong temperature sensitivity of leaf isoprene emissions, particularly so in warm climate (cf., Eq. A4b), a simplified energy balance scheme was added to LPJ-GUESS that accounts for the difference between leaf and air temperature (ΔT ; Campbell and Norman, 1998):

$$\Delta T = (R_n - \lambda E)/(\rho C_p g_a), \quad (3)$$

where R_n = net radiation, λE = latent heat flux, ρ = air density, C_p = heat capacity of air, g_a = aerodynamic conductance. Values of g_a were set to 0.14 for needle-leaf, 0.04 for broadleaf, and 0.03 mm h^{-1} for C-3 & C-4 herbaceous plant functional types, respectively (Kelliher et al., 1993; Huber et al., 1999). Finally, since the average temperatures during daylight hours typically exceed daily averages by 10% and more in a wide range of climates (A. Arneth, personal observation) the difference between daytime temperature and daily temperature was calculated from

$$\Delta T_b = \sin h' h'^{-1} dt r', \quad (4)$$

where h' = half-day length (in radians) and $dt r'$ = half daily temperature range.

4.2 Flux data

Measurements of ecosystem-atmosphere exchange of trace gases, in particular that of CO₂ but also water vapour, have become one standard set of data to evaluate output of terrestrial carbon cycle model with (Krinner et al., 2005; Morales et al., 2005; Sitch et al., 2005; Friend et al., 2006). In principle, isoprene flux measurements can be used to the same purpose, since its atmospheric lifetime is long enough for fluxes measured above the canopy to be representative for integrated leaf emissions. Additional assumptions to account for fast chemical transformation taking place between emission at leaf level, and measurement above the canopy (Guenther et al., 2006) can therefore be neglected in the first instance. From a DGVM modelling perspective it is thus unfortunate that, with the commendable exception of one long-term data set (Pressley et al., 2005), most isoprene flux studies to date have concentrated on succinct measurement campaigns lasting from few days to few weeks. The lack of robust, fast isoprene sensors that can be operated in the field with reasonable effort on a continuous basis prevents longer-term monitoring in many cases – with the consequence that few studies only report daily totals for periods from more than a few days to months that are ideally required to compare with the daily LPJ-GUESS output. Still, we were able to identify five ecosystems where isoprene flux measurement-based estimates of weekly to seasonal and annual totals are available that were suitable for our purpose (Table 3):

- the southern boreal mixed hardwood forest at the University of Michigan Biological Station (UMBS, 45°33' N, 84°43' W), dominated by *Populus grandidentata*, *P. tremuloides*, *Quercus rubra*, *Fagus grandifolia*, *Acer rubrum*, and *Pinus strobus* (Curtis et al., 2005; Pressley et al., 2005). This is a successional forest regrowing from harvest and fire disturbance that took place until the early 20th century (<http://www.biosci.ohio-state.edu/~pcurtis/UMBS~Flux>); it has a maximum leaf area index of 3.7, a GPP of *c.* 1.2–1.6 kg_C m⁻² a⁻¹, and a net primary productivity (NPP) of *c.* 0.65 kg_C m⁻² a⁻¹ (Curtis et al., 2005). Eddy correlation isoprene flux measurements were performed over the three consecutive growing seasons

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- 2000–2002, covering in each periods of 100–120 days.
- the northern temperate Harvard forest (42°32' N, 72°11' W), with measurements performed in an area dominated by *Quercus rubra*, *Acer rubrum*, *Pinus strobus*, and *Tsuga canadensis* (Goldstein et al., 1998). The forest is regrowing after having been largely destroyed in 1938 by a severe hurricane. Maximum LAI is 3.5–4.0, GPP and NPP vary around 1.2 and 0.6 kg_C m⁻² a⁻¹, respectively (Goldstein et al., 1998; Waring et al., 1998; Curtis et al., 2001). Isoprene flux measurements at the site had been conducted in 1995, using a flux gradient similarity approach (Goldstein et al., 1998).
 - the tropical lowland rainforest La Selva in Costa Rica (10°26' N, 83°59' W; Geron et al., 2002; Karl et al., 2004) dominated by *Pentaclethra maculoba*, an isoprene emitting species. LAI immediately surrounding the tower is 4.2, but *c.* 6.0 in the wider area (Karl et al., 2004). Relaxed eddy accumulation measurements at that site had been conducted during a short campaign in 1999 (Geron et al., 2002). These were used to test output of a model that combined leaf level measurements, information on canopy structure and the Guenther et al. algorithms to calculate annual totals. A second campaign was conducted in the dry season 2003, using disjunct eddy covariance (Karl et al., 2004).
 - the tropical rainforest near Manaus in Brazil where a isoprene flux measurement campaign was conducted during September 2004 (Karl et al., unpublished). Measurements were performed at ZF2 km14 (2.5° S, 60.1° W), LAI of the stand surrounding the tower is *c.* 6. A detailed species description for the site in terms of isoprene emission potentials is not available, information about the larger region can be found in Harley et al. (2004).
 - two Mediterranean *Quercus pubescens* stands in southern France, *c.* 60 km NE of Marseille (43°39' N 6° E). Eddy covariance measurement campaigns were performed with a fast isoprene sensor over *ca.* two-week long periods in summer

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2000 and 2001 in an 18 and 35 year old stand, respectively (Serça, unpublished) that had a LAI of 2.3–2.4.

4.3 Modelling protocol

For these five sites, LPJ-GUESS was run in “cohort” mode, which is particularly suitable to describe vegetation dynamics on ecosystem scale. Values for ε were assigned to the PFTs that were simulated to grow at a particular site in the manner described above; the simulated PFTs could be aligned well with the sites’ actual species composition (Table 3). Basic parameter values to describe vegetation dynamics and bioclimatic limits were similar to those used for LPJ-DGVM in Sitch et al. (2003). The modelled tree PFT’s were divided into three sub-groups according to their shade-tolerance (Smith et al., 2001; Hickler et al., 2004; Koca et al., 2006). Parameters to describe the shade tolerance were those used by Smith et al. (2001) and Koca et al. (2006) with few adjustments that aimed to represent composition of the five benchmark forests as closely as possible (Table 4). These included a reduced sapwood to hardwood conversion, slower maximum establishment rate for shade-tolerant and intermediate shade-tolerant trees and modifications of the ratio of leaf area to sapwood cross-sectional area and tree longevity. Model runs were performed over the period 1900–1998 using the CRU climate data (<http://www.cru.uea.ac.uk/cru/data/hrg.htm>), as well as site climate from the periods of the measurement. To reproduce reported disturbances at the Michigan, Harvard and French sites (windthrow, harvest) the canopies’ LAI and biomass was reset to zero in the appropriate simulation year, initiating succession and producing forests with the approximately correct tree age in the year the isoprene measurements were conducted. Before using the historical climate data, the model was spun up for 1000 years to reach equilibrium in ecosystem carbon pools, the number of patches for averaging model output was set to 90.

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5 Model evaluation: isoprene emission from forest ecosystems

When coupled to a dynamic vegetation model, the agreement between measured and modelled isoprene emissions hinges critically not only on the representation of the actual leaf isoprene production, but also on the model's capability to represent the canopy structure and physiological activity. This was the case for the five model test sites where total leaf area index from LPJ-GUESS was on average within 10% of measured values (Fig. 4), while agreement between modelled and measured annual GPP and NPP for the UMBS and Harvard Forest was within 10 to 20% of published values (not shown). Annual ecosystem isoprene production as simulated by LPJ-GUESS ranged from 2 to 10 mg_C m⁻² a⁻¹ for UMBS, Harvard and La Selva, and 20–30 mg_C m⁻² d⁻¹ for the French and Manaus sites (Fig. 4).

Agreement of modelled with measured isoprene production was particularly good for the mixed hardwood forest at the University of Michigan Biological Station, where for all three years modelled isoprene production was within 10% of measured values (Fig. 4). The simple growing degree day temperature function (Eq. 2) in the model captured the observed seasonality in emissions well, particularly so in 2002 (Fig. 5). For years 2000 and 2002, linear regressions between measured and modelled daily values could explain 70 and 50% of the observed daily variation, respectively. However, while the model also captured the average daily variation and annual sum in 2001 very well, agreement on a day-to-day basis was very poor. This was in part caused by a period very early in the growing season when measured fluxes were 10–60 mg_C m⁻² d⁻¹ (encircled in the Figure) whereas modelled rates did not exceed 10–20 mg_C m⁻² d⁻¹ (Fig. 5). During this period maximum temperatures increased rapidly by about 10°C, and as discussed below for the measurements at the French site, the effect of accumulating, rapid temperature changes may have affected canopy isoprene production rates.

When placed side-by-side, the simulations for the cool, mixed-hardwood forest at UMBS and the Mediterranean French oak forest (Fig. 5) serve well to illustrate the in-

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teractions that take place between species composition (and thus isoprene emission potential) and environmental conditions. Maximum simulated I at the height of the active season were fairly similar in both forests, around $40 \text{ mg}_C \text{ m}^{-2} \text{ d}^{-1}$, although I_s of the main isoprene emitting *Q. rubra* at UMBS exceed that of *Q. pubescens* by a factor of 2–3 – which renders into a higher fraction of electrons used for isoprene production in our process-based model (Table 3). Evidently, a higher relative contribution of the main isoprene emitting PFT to the total LAI at the French site (Table 3, Fig. 6) in combination with warmer temperatures could compensate fully for the hugely dissimilar I_s . Overall model performance for the *Q. pubescens* forests was good, particularly when compared with measurements from the campaign in 2000, when average modelled and measured daily values were within 10% (Figs. 5, 6). Model runs were completed with canopy ages of 18 and 35 years, respectively, and the effects of this age difference on the simulated canopy composition, LAI or isoprene emissions proved to be insignificant. In 2001, daily emission rates during the first part of the campaign were rather similar to those measured in the previous year, and 30% higher than model values (Fig. 4, arrow). However, during the last few days of the campaign a rather sharp increase of measured fluxes was observed: from $20\text{--}40 \text{ mg}_C \text{ m}^{-2} \text{ d}^{-1}$ to values well above $60 \text{ mg}_C \text{ m}^{-2} \text{ d}^{-1}$. This sudden increase was not reproduced by the model. What may have caused it is still under investigation, it evidently could not be related to a sudden change in weather conditions (Figs. 5 c, d). The 2001 campaign captured a period when air temperatures steadily increased to maxima around 30°C . It has been demonstrated that leaf isoprene emission rates can be affected by the cumulative meteorological conditions over a period of few hours to days preceding a measurement, possibly due to effects on amount or activity of isoprene synthase (Geron et al., 2000). Yet, the length of the time period that may influence emissions that way is unknown and likely quite variable, and the underlying mechanisms are far from understood. We therefore do not include it into the current version of the model. What is more, while possibly helpful to improve model output on a day-to-day basis, over the course of a year the effect on simulated emissions is presumably small, since its omission will lead

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to over- as well as underestimation during certain periods, depending on the weather history. In any case, while the 2000 campaign did not cover a steady trend of increasing temperatures, maximum air temperatures during both campaigns were not dissimilar (Fig. 5); it is unclear whether a cumulative temperature effect indeed could explain a doubling of isoprene fluxes from one day to the next. An alternative (or additional) culprit could well be protection against high tropospheric O_3 levels since it was speculated that isoprene may quench reactive oxygen species (Velikova et al., 2005).

At the La Selva tropical rainforest site, modelled isoprene production was just below $10 \text{ g}_C \text{ m}^{-2} \text{ a}^{-1}$ on average for the years 1998-2000, not far off from estimates that were based on upscaled leaf emissions that had been tested against a few days of ecosystem flux data obtained by REA (Fig. 4, $8 \text{ g}_C \text{ m}^{-2} \text{ a}^{-1}$; Geron et al., 2002). These annual emissions are nearly five times those modelled or measured at UMBS or Harvard Forest (see below). The mixed hardwood forests of the eastern USA contain a substantial number of significant isoprene emitters (e.g., *Liquidambar styraciflua*, *Quercus* ssp., *Populus* ssp.) and regional monthly emissions during the northern hemisphere summer have been estimated to be equal to, or higher, than those from tropical forests (Geron et al., 2001; Guenther et al., 2006). Our model results support this view, the high annual emissions at La Selva were neither caused by high I_s (cf., Table 3) nor by high daily maximum rates (ca. $30\text{--}60 \text{ mg}_C \text{ m}^{-2} \text{ d}^{-1}$, not shown), but were rather due to the fact, that emission rates are sustained for the entire year – and not just for two to three months as is the case for the northern forest sites (Arneth et al., 2006¹).

LPJ-GUESS and the REA/leaf model derived estimates for La Selva are both notably higher than the range suggested from data obtained during a disjunct eddy covariance campaign in 2003 ($4.5\text{--}6.3 \text{ g}_C \text{ m}^{-2} \text{ a}^{-1}$; Karl et al. (2004), based on their Table 1). The latter data were obtained during a particularly dry period but it remains to be evaluated whether the measured fluxes were reduced in comparison to the wetter periods of the year. Isoprene emissions are fairly unaffected by short-term closure of stomata, largely due to its high volatility (Fall and Monson, 1992; Niinemets and Reichstein, 2003). Since isoprene is below its saturation vapour pressure in the substomata cavity,

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stomata closure results in increased diffusion gradient, resulting in a net-change in the flux from the leaf. Even under periods of prolonged soil water deficit, isoprene emissions can remain relatively unaffected, or even increase, even though assimilation rates might be declining notably; this response indicates that in addition to the above short-term diffusion effects, isoprene production remains ongoing (Pegoraro et al., 2004; Pegoraro et al., 2005b).

An average I_s to be used as the basis for assigning an average canopy ε for the Manaus site simulation is hugely uncertain. The larger forest area around Manaus is dominated by species belonging to the Lecythidaceae and Sapotaceae, and to lesser degree to the Papilionaceae, Burseraceae or Moraceae families. With the exception of the Sapotaceae, these families include some notable isoprene emitting species (Harley et al., 2004). Based on a range of leaf-level isoprene measurements and forest census data, Harley et al. (2004) suggested a mean emission capacity of $75 \mu\text{g}_C \text{g}^{-1} \text{h}^{-1}$ for the emitting species in the Manaus area forests. This average value was also adopted for our simulations (Table 3) and resulted – perhaps fortuitously so – in an agreement of modelled and measured average daily values within 30%. The lower model estimates could easily be explained by the somewhat lower model LAI (4.8 vs. 6) but without more information on the potential isoprene emission capacity of the tower site it seems futile to discuss this in more detail. Still, the slightly less I_s (and thus ε) and the notably lower LAI simulated for Manaus compared to La Selva result in overall lower annual estimates for the former (Fig. 6g).

Modelled isoprene production for Harvard forest was nearly identical to rates simulated for the UMBS site. Both represent mixed-hardwood forests of the north-eastern USA, regrowing after disturbance. At UMBS, the significant isoprene emitters are *Q. rubra* and *Populus* ssp., which in LPJ-GUESS corresponded to the intermediate shade-tolerant and shade-intolerant broadleaved summergreen PFTs, with ε set to match their respective leaf level I_s (Table 3). At Harvard forest, canopy isoprene emission originates mostly from *Q. rubra*; the shade-intolerant species at that site (mostly birch) are non-emitters. LPJ-GUESS reproduced a PFT mix at both sites with a some-

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what varying proportion to the total LAI (Fig. 6) that was comparable to reported species distributions (Goldstein et al., 1998; Curtis et al., 2001; Curtis et al., 2005). Yet, whereas total modelled emission rates at UMBS agreed well with measured rates, were modelled values at Harvard only half of the estimate from flux-measurements $4.2 \text{ g}_C \text{ m}^{-2} \text{ a}^{-1}$; Goldstein et al., 1998). The reason for this discrepancy remains to be elucidated, since modelled total leaf area index exceeded the actual one by ca. 30% (Fig. 4) although modelled gross and net primary productivity were within 10% of reported values (not shown, Waring et al., 1998; Curtis et al., 2001). The latter arguably are important indicators for overall model performance because of the coupling of isoprene emissions to carbon assimilation. One possible cause for the model-data mismatch therefore could lie in ε being set too low for Harvard Forest. It is well established that basal isoprene emission rates can vary greatly for a single plant species, measured peak I_s for *Q. rubra* ranged from 70 to $160 \mu \text{ g}_C \text{ g}^{-1} \text{ h}^{-1}$ (Goldstein et al., 1998). For the simulations we initially assumed an average I_s of $100 \mu \text{ g}_C \text{ g}^{-1} \text{ h}^{-1}$ to determine ε for the intermediate shade-tolerant PFT (Table 3) and repeating the simulations with an assumed I_s of $160 \mu \text{ g}_C \text{ g}^{-1} \text{ h}^{-1}$ resulted in isoprene emissions of $3.4 \text{ g}_C \text{ m}^{-2} \text{ a}^{-1}$, which reduced the model-data discrepancy to 20%.

6 Effects of site disturbance history and increasing atmospheric CO_2 concentration on forest isoprene emission

Figure 6 illustrates the time series of simulated leaf area indices and isoprene production for the 20th century, plotted separately for each plant functional type. These time series provide vivid examples for the importance of providing a correct representation of a canopies' composition and disturbance history for isoprene estimates, since the relative contribution of a species (or PFT, or PFT sub-class) to the total LAI is by no means necessarily equivalent to its relative contribution to total isoprene emissions. This becomes obvious from the Harvard Forest simulation where nearly all emission originates from the intermediate shade-tolerant PFT (*Q. rubra*, Table 3) that contributes

only about 50% to the total LAI. What is more, emissions in the years following a severe disturbance event (e.g., windthrow, harvest) differ from a canopy in equilibrium notably and the rate of “isoprene recovery” following disturbance differs strongly between forests depending on the canopy composition. At Harvard, approximately 30 years passed after an assumed complete and sudden die-back of the forest until emission equilibrated, at a level somewhat above the pre-disturbance level. By contrast, at UMBS where the shade-intolerant deciduous trees that dominate the early succession stages are strong isoprene emitters (*Populus*) emissions approached pre-disturbance values already after c. 10 years. Similarly so at the French site, where the canopy is more or less dominated by one isoprene emitting species (*Q. pubescens*). Post-disturbance LAI exceeded pre-disturbance values to some degree, a result of forest regrowth as well as some CO₂-fertilisation of vegetation productivity due to rising atmospheric CO₂ concentration. In terms of isoprene, total emissions were thus 10 to 20% above the pre-disturbance rates at the end of the simulation period.

The simulations shown in the Figures were performed using a time series of gradually increasing atmospheric CO₂ concentration that is derived from observations at atmospheric stations or measurements of air trapped in ice-cores (Sitch et al., 2003). One of our chief objectives is to present a modelling tool to highlight effects of changing CO₂ concentration on ecosystem isoprene emission by means of process-based modelling. We therefore re-run the calculations, but this time keeping [CO₂] constant at the 296 ppm level for the calculation of isoprene production rates (I^{296}), but not so for the calculation of GPP and LAI. In other words, κ (or its surrogate κ^{**}) was kept constant from the beginning of the entire simulation period, which is equivalent to assuming no direct effect of CO₂ on isoprene metabolism. In that way a considerable difference emerged – at the end of the simulation period (1998), canopy I^{296} were approximately one quarter higher compared with the “real” scenario of increasing [CO₂] for the calculation of both, I and GPP. The divergence of simulated isoprene emissions became particularly visible in the second half of the 20th century, reflecting the acceleration in atmospheric CO₂ growth rate and the growing inhibition.

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Thus, from a modelling perspective and taking the early 20th century as reference, our simulations indicate a notable difference emerging between a time series of isoprene emissions that is based on forest physiological activity and climate alone vs. estimates that take into account the direct CO₂-isoprene interaction. The implications this may have for past and future projections of emissions and its effects on atmospheric oxidation capacity are evident. Studies to date have suggested significantly lower isoprene emissions in the past, caused by lower GPP in cooler climate and/or an atmosphere with lower CO₂ concentration (Lathière et al., 2005; Valdes et al., 2005). By contrast, projections of future isoprene emissions have always projected substantial increases (Sanderson et al., 2003; Lathière et al., 2005). These projections combine two postulated mechanisms: enhanced leaf growth and total LAI stimulated by CO₂ fertilisation of GPP, and increasing leaf isoprene emissions due to rising temperatures caused by the CO₂ increase. But this picture may have to be revised to take into account the observed direct CO₂-inhibition of leaf isoprene production.

7 Concluding remarks

Process based leaf-isoprene models are capable to not only match the well-known light and temperature response of emissions but they can also reproduce a CO₂ – induced inhibition of emissions. Incorporated into large-scale vegetation models the calculated emissions compare well with data from ecosystem-atmosphere flux measurements. When used over a longer time period, including a measurable change of the atmospheric CO₂ concentration, our initial model calculations imply that a CO₂ – inhibition of leaf isoprene metabolism may reduce the expected isoprene increase due to CO₂ fertilisation of vegetation productivity. However, we did not consider here the additional effects of climate change on our isoprene calculations that accompany changes in [CO₂], and these climate-CO₂ interactions may complicate the picture even further. The high temperature sensitivity, and high temperature optimum of isoprene synthase cause emissions to respond significantly to warmer temperatures; warmer

temperatures may also stimulate GPP – or inhibit productivity, if they go hand-in-hand with drier conditions. These interactions are currently being analysed (Arneth et al., 2006¹)

It should be emphasised that laboratory studies do not agree unanimously on the direction of medium to long term isoprene-CO₂ interactions. Lacking a full understanding of the underlying processes our analysis is best understood as a sensitivity study to quantify a possible isoprene-inhibition by [CO₂], postulating this effect as given until proven otherwise. Since this inhibition indeed may be significant, but has been studied to date only in a relatively small number of experiments, one hopes to see it verified -or perhaps refuted- by results from a much larger number of plants. Similarly, a larger number of seasonal or longer isoprene flux measurements will help to evaluate DGVM-based isoprene estimates over a wider range of ecosystems, thus improving confidence of spatial or temporal extrapolations.

Appendix A

Leaf level isoprenoid production algorithms: model description

A1 Guenther et al.

This most widely used set of algorithms to predict the effects of changing environmental conditions on the production of BVOC from plant leaves uses a species-specific emission rate, I_s , determined under standardised conditions (also called basal rate or emission factor). As a rule, I_s is estimated at a leaf temperature (T) of 30°C and at an incident quantum flux density (Q) of 1000 $\mu\text{mol m}^{-2}\text{s}^{-1}$. As T and Q vary during the day, actual emissions (I) are calculated from the basal rate and empirical correction functions summarized by γ (for review see, e.g., Guenther, 1997):

$$I = I_s \gamma \tag{A1}$$

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For isoprene,

$$\gamma = \frac{\alpha C_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}} \frac{\exp \frac{C_{T1}(T-T_s)}{RT_s T}}{C_{T3} + \exp \frac{C_{T2}(T-T_m)}{RT_s T}} \quad (A1a)$$

T (K) is leaf temperature at ambient and T_s (K) at standard conditions, R is the gas constant ($\text{JK}^{-1} \text{mol}^{-1}$) and C_{T1} , C_{T2} , C_{T3} and T_m are empirical coefficients. In general, these are kept constant at $C_{T1} = 95\,000$, $C_{T2} = 230\,000 \text{ J mol}^{-1}$, $C_{T3} = 0.961$ and $T_m = 314 \text{ K}$, reproducing the T -response across a wide range of species. α and C_{L1} characterize the shape of the light-response of isoprene emission, and are also generally kept constant at 0.027 and 1.066, respectively, for all isoprene-emitting species (Guenther, 1997).

In principle, Eq. (A1) can be used to investigate the short-term response to current environmental conditions for a range of BVOC – as long as a value for I_s is assigned, and γ is varied depending on whether the emissions are controlled by volatilisation from storage pools or by immediate metabolic responses (Wiedinmyer et al., 2004). Additional multipliers may be introduced into Eq. (A1) to account for seasonal changes in leaf structure or the observed seasonality of isoprene emissions; a comprehensive description of the most up-to-date developments is provided by Guenther et al. (2006).

The algorithm presented in Eq. (A1a) emulates the Arrhenius-temperature dependency of the enzymes involved in isoprene synthesis and the production of precursors of isoprene during carbon assimilation with its well-known, hyperbolic light-dependence (Fig. 1). Impressively extensive data-bases of I_s exist, particularly for plants grown in (sub)tropical and temperate environments (Hewitt and Street, 1992; Kesselmeier and Staudt, 1999; Wiedinmyer et al., 2004; <http://bvoc.acd.ucar.edu>; <http://www.es.lancs.ac.uk/cnhgroup/download.html>). The applicability of emission factors measured at 30°C is somewhat debatable for plants growing in boreal or (sub)arctic environments. There, temperatures around 30°C are encountered rarely, if ever, and determination of I_s thus requires either artificial measurement conditions or the math-

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emational extrapolation of measured emissions to “standard” temperature. Moreover, while the activation energy describing the temperature response of isoprene emission indeed appears to be fairly constant, this is not necessarily the case for its temperature optimum which can vary between species or in response to growth environment (Niinemets et al., 1999; Singsaas et al., 1999; Hanson and Sharkey, 2001).

A2 Martin et al.

Ribulose-1,5-bisphosphate (RUBP) carboxylase/oxygenase (Rubisco) is the main photosynthetic enzyme that catalyzes RUBP carboxylation or oxygenation. In case of the carboxylation reaction ($\text{RUBP} + \text{CO}_2$) two molecules of 3-phosphoglycerate (3-PGA) are formed, while oxygenation ($\text{RUBP} + \text{O}_2$) yields one molecule of phosphoglycolate and one molecule of 3-PGA. According to early studies on Rubisco, RUBP carboxylation yields also a small amount of pyruvate, ca. 1% of total sugar phosphates (Andrews and Kane, 1991). Pyruvate is needed for isoprene formation, but the chloroplastic sources of pyruvate are still unclear (Sharkey et al., 1991a; Rosenstiel et al., 2004).

The hypothesis of pyruvate formation in the chloroplast via RUBP carboxylation, although not yet unequivocally proven, was employed in the isoprene emission model by Martin et al. (2000). In this model, leaf isoprene production is calculated as the minimum of three potentially rate-limiting processes:

1. the rate of supply of carbon to isoprene synthesis pathway via pyruvate formed in chloroplasts in RUBP carboxylation (W_{isoco});
2. the rate of supply of ATP by phosphorylation needed to produce the isoprene precursor dimethylallyl-diphosphate (DMAPP) from the carbon substrate (W_{isop});
3. maximum capacity of isoprene-synthase (V_{isomax}).

Defining σ_s as a species-specific fraction of maximum isoprene flux,

$$I = (\sigma_s \min \{W_{\text{isoco}}, W_{\text{isop}}, V_{\text{isomax}}\} 10^3) / 5, \quad (\text{A2})$$

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and

$$W_{\text{isoco}} = \eta F_{\text{PYR}} \quad (\text{A2a})$$

$$W_{\text{isop}} = \eta(V_C + 1.5V_{pr} - R_d)\kappa, \text{ where } \kappa = [(O_i + V_C)/(C_i + V_{pr} + R_d)] \quad (\text{A2b})$$

The parameter η describes the fraction of assimilated carbon lost as isoprene, which increases exponentially with temperature, and F_{pyr} is the rate of pyruvate formation from RUBP carboxylation. V_C , V_{pr} and R_d are the rates of carboxylation, photorespiration and leaf dark respiration, respectively, C_i is the CO_2 , and O_i the oxygen concentration in the leaf.

The maximum activity of isoprene synthase, V_{isomax} , depends on temperature according to an Arrhenius-type response function:

$$V_{\text{isomax}} = [\exp(c - \Delta H_A/(RT))]/[1 + \exp(\Delta S/R - \Delta H_D/(RT))], \quad (\text{A2c})$$

where c is a scaling constant, ΔH_A (kJ mol^{-1}) is the activation energy, ΔH_D (kJ mol^{-1}) is the deactivation energy and ΔS ($\text{kJ mol}^{-1} \text{K}^{-1}$) is the entropy change. (Eq. A2c) is a slight modification of the temperature dependence of V_{isomax} used in Martin et al. (2000), to be compatible with the analogous expression in the model of Niinemets et al. (1999; cf., Sect. A5). Eq. (A2) provides a direct coupling of isoprene production to leaf carbon assimilation via V_C , V_{pr} , R_d and F_{pyr} , which can be calculated e.g. using the model by Farquhar et al., or an appropriate modification (Farquhar, 1989; Long, 1991; Harley et al., 1992). In case of leaf level or ecosystem models that do not explicitly include the rate of photorespiration required for the calculation of κ an empirical surrogate can be used (cf., Sect. 4.1., Ecosystem model)

The model was originally tested against isoprene emission measurements from leaves of *Populus tremuloides*, *Eucalyptus globulus*, *Quercus rubra* and *Mucuna pruriensis*, and showed good agreement between measured and modelled variation of leaf isoprene production under a range of environmental conditions. However, the absolute values of measured and modelled maximum I differed in several cases considerably (Martin et al., 2000). One possible explanation for this mismatch may be

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that isoprene production scales with carbon assimilation via (Eq. A2a) and (Eq. A2b) only, but not via (Eq. A2c). This limits the model's applicability to calculate emissions from a range of plants with widely varying rates of photosynthesis. In such a case, V_{isomax} eventually becomes under all environmental conditions either lower or higher than rates calculated from (Eq. A2a) and (Eq. A2b), and I is no longer determined as the minimum of all three contributing processes (Eq. A2). Therefore, V_{isomax} would also need to be adjusted for each plant species, which may be achieved by varying c if the temperature dependence of isoprene synthase is expressed in the form shown in (Eq. A2c).

A3 Zimmer et al.

This isoprene synthesis model (Zimmer et al., 2000; Lehning et al., 2001; Zimmer et al., 2003) combines the dynamic photosynthesis model by Kirschbaum et al. (1998) to predict the pool sizes of precursors, and intermediate compounds in isoprene synthesis pathway and maximum capacities and kinetic properties of enzymes at terminal steps of isoprene synthesis.

The model distinguishes three chief processes:

1. The seasonal temperature and light dependence of isoprene synthase activity
2. Transient changes in pool sizes along the pathway from the C-3 precursors to isoprene, described by a set of reactions that are each controlled by Michaelis-Menten kinetics with specific reaction velocities
3. Initial concentrations of isoprene precursors, as provided by a photosynthesis model

Carbon input provided from the dynamic, non-steady state photosynthesis model is passed to a set of consecutive differential equations that describe the chief successive reaction steps in the isoprene synthesis pathway. Each reaction is characterized

by its corresponding maximum reaction velocity and Michaelis-Menten constants that have been established from leaf extracts for *Quercus robur* and *Q. petraea* (Lehning et al., 2001; Brüggemann and Schnitzler, 2002). In its coupled mode (seasonal isoprene synthase model–biochemical isoprenoid biosynthesis model, SIM-BIM), bud-break and leaf senescence, and day-to-day changes of isoprene synthase activity enter the calculation as a function of light and/or temperature (Lehning et al., 2001).

A4 Bäck et al.

This model was originally designed for analysis of VOC emissions in the field when the dynamics of internal VOC pools determine the diurnal variation of emissions. It was described and tested for monoterpene emissions from Scots pine needles, and includes five steps: substrate production, biosynthesis, storage, transport within the leaf, and emission (Bäck et al., 2005). Since the chloroplastic pathway for the production of DMAPP is similar for isoprene and monoterpene synthesis, and since storage in the leaf is negligible in case of isoprene the model can be adopted to represent isoprene synthesis. In terms of substrate availability, ATP and NADPH in the model are delivered from leaf photochemistry and available energy does not restrict the synthesis of isoprene or monoterpenes. The chief regulatory mechanism is the availability of G3P. Two alternative possible pathways of G3P production were postulated and parameterized. In the first approach, corresponding to a situation when a major part of RUBP is carboxylated (high internal CO₂ concentration), G3P was directly linked to the rate of photosynthesis:

$$I_1 = \alpha_1 A(Q, T, D, C_a), \quad (\text{A3a})$$

while in the second approach, corresponding to a situation when the difference between ambient (C_a) and internal (C_i) CO₂ concentrations is large, G3P was assumed to arise from photorespiratory metabolism:

$$I_2 = \max\{0, \alpha_2(C_a^{2004} - C_i(Q, T, D, C_a))\}, \quad (\text{A3b})$$

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In these equations, α_1 and α_2 represent the efficiency for synthesis, the amount of isoprene (or monoterpene) produced per CO_2 assimilated. They were estimated from measured VOC emission data from Scots pine branches. Since the specificity of Ru-bisco to carbon dioxide does not change with atmospheric CO_2 , the ambient CO_2 concentration in the synthesis of isoprene was assumed to be the concentration in the year 2004 (C_a^{2004}). C_i was calculated from the optimum photosynthesis model by Hari and Mäkelä (2003). For seasonal monoterpene emissions, the mechanisms postulated in (Eq. A3b) provided a better agreement between the simulated and measured monoterpene emissions in *Pinus sylvestris* (Bäck et al., 2005).

A5 Niinemets et al.

In this model, the supply of DMAPP for isoprene synthesis and isoprene synthase activity exert the primary control on production (Niinemets et al., 1999). DMAPP levels are affected by photosynthetic electron transport rate which supplies the required ATP and NADPH for carbon reduction from CO_2 to isoprene. Two major assumptions underlie this approach, namely that (i) a certain fraction of electrons, ε , is available for isoprene synthesis and (ii) the competitive metabolic strength of isoprene synthesis pathway is proportional to the total activity of isoprene synthase in the leaves. Here we present a modification to the model that also accounts for the effects of atmospheric CO_2 concentration on isoprene synthesis. In its original form, isoprene emission rate is calculated as

$$I = \varepsilon J \alpha, \text{ where } \alpha = \frac{(C_i - \Gamma^*)}{6(4.67C_i + 9.33\Gamma^*)}, \quad (\text{A4a})$$

where ε is the fraction of electrons available for isoprene production, J is the rate of electron transport, and α a temperature- and CO_2 - dependent parameter that converts the electrons to isoprene equivalents. Γ^* denotes the hypothetical CO_2 compensation point in the absence of non-photorespiratory respiration (Farquhar et al., 1980). The model assumes that the production of isoprene requires relatively more NADPH

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than ATP, and that isoprene production should scale positively with electron transport. The link to carbon assimilation and its mathematical representation is thus provided via J and C_i (Farquhar et al., 1980). The competitive strength of isoprene synthesis, which is proportional to the total activity of isoprene synthase is defined through the value assigned to ε . The model was tested for leaf isoprene emissions of *Liquidambar styraciflua* and *Quercus* sp. and described the instantaneous responses of I to temperature, Q , and high saturation deficit well. With ε it contains only one species-dependent coefficient that may also be varied to reproduce longer-term effects associated, e.g., with changing CO_2 concentration (see below) or leaf developmental state although the competitive ability of isoprene synthase, or indeed the leaf-internal regulation loops in these cases are not yet fully understood.

The temperature maximum of isoprene synthase in vitro is close to 45°C and is the chief reason for the generally high temperature optima of leaf isoprene emissions (Monson et al., 1992). In vivo, the T -optimum of leaf isoprene emission is generally lower, in some cases considerably so, and varies plastically in response to growth temperatures – likely related to adjustments in synthase activity (Monson et al., 1992; Sharkey and Loreto, 1993; Niinemets et al., 1999; Hanson and Sharkey, 2001; Pétron et al., 2001). At high temperature the break-down of electron transport rate severely inhibits the energy requiring processes in the chloroplast. Therefore, leaf isoprene emission should depend not only on the T -dependence of isoprene synthase but also that of J (Niinemets et al., 1999). Due to Arrhenius kinetics with different (de)activation energies and entropy terms in the temperature response of J and I this will result in an exponential increase of ε with T , which may reach a threshold level as J collapses (e.g., 37°C ; Martin, 1997; Niinemets et al., 1999). This theoretical consideration is supported by ecosystem-atmosphere flux observations that reported an exponential increase of the proportion of GPP released as isoprene with T (Goldstein et al., 1998). The postulated exponential temperature dependency of ε can be reproduced via

$$\tau = \exp[a_\tau(T - T_{\text{ref}})], \quad (\text{A4b})$$

where T_{ref} is 30°C and a_{τ} a scaling parameter that was set to 0.1 to mimic the response reported in Niinemets et al. (1999).

In its original version, the model does not account for limitation of substrate for isoprene synthesis (e.g., the chloroplastic G3P pool size, availability of pyruvate, or availability of inorganic phosphate (P_i) for phosphorylation reactions) which may underlie the observed CO_2 inhibition on isoprene production. Thus (Eq. A4a) suggests a positive scaling of I with C_i . Under conditions when supply by chloroplastic C-3 sugars is non-limiting, changes in I are strongly correlated with ATP content (Monson and Fall, 1989a; Loreto and Sharkey, 1993). But under photosynthesis feedback-limited conditions, a range of metabolic reactions may be inhibited by sluggish recycling of P_i from phosphorylated intermediates (Stitt, 1991; Stitt and Krapp, 1999). High atmospheric CO_2 concentration could also foster cytosolic reactions requiring pyruvate, reducing pyruvate transport into the chloroplast and its availability for isoprene synthesis (Rosenstiel et al., 2003). In the absence of fully mechanistic understanding, a CO_2 -dependence of ε thus may be included in (Eq. A4a) in an equivalent way to what has been proposed by Martin et al. via κ (Eq. A2b). Hence, the model is used here in a modified form as

$$I = \varepsilon \xi J \alpha \quad (\text{A4})$$

where $\xi = \kappa \tau$ with κ as defined in (2b), and κ and τ being both unity at 30°C and $Q = 1000 \mu \text{mol m}^{-2} \text{s}^{-1}$. The changing C_i : O_i calculated via κ can be understood as a surrogate for the reversal of the sensitivity of photosynthesis and isoprene synthesis to intercellular concentrations of CO_2 and O_2 which expresses non-matching requirements for pyruvate or P_i (Martin et al., 2000). The consequence is an exponential decrease of κ with CO_2 (Fig. 7) at a rate that is nearly identical to the empirical isoprene emission – CO_2 relationship that was drawn through data from a range of species grown and measured between 180 and $1200 \mu \text{mol mol}^{-1} \text{CO}_2$ (Possell et al., 2005, their Fig. 5a), which supports this semi-mechanistic approach.

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Table 1. Frequently used abbreviations.

C_i	Chloroplastic CO ₂ concentration
[CO ₂]	CO ₂ concentration in the atmosphere
DMAPP	Dimethylallyl-diphosphate
DOXP	1-deoxy-D-xylulose-5-phosphate
ε	Fraction of electrons available for isoprene synthesis
G3P	Glyceraldehyde-3-phosphate
GPP	Gross primary productivity
I_s	Leaf isoprene emissions at standard conditions
3-PGA	3-phosphoglycerate
RUBP	Ribulose-1,5-bisphosphate
T	Temperature
Q	Quantum flux density

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Table 2. Effects of increasing atmospheric CO₂ concentration on emissions of isoprene. Arrows indicate the direction of the response (“↓” = decreasing isoprene emissions as CO₂ concentration increases; “—” indicates no trend) in plants growing along a CO₂ gradient in the vicinity of CO₂ springs, or grown in chamber or FACE experiments with CO₂ either varying between sub-ambient and ambient, or ambient and elevated levels. Exposure to non-ambient CO₂ concentration in the experimental treatments varied from few weeks to several years.

Plant species	Single leaf level	Branch or canopy level	Source
<i>Arundo donax</i>	— (trend to ↓) ¹⁾	— (trend to ↓)	Possell et al. (2005)
<i>Mucuna pruriens</i>	↓ ¹⁾	— (trend to ↓)	Possell et al. (2005)
<i>Phragmites australis</i>	↓		Scholefield et al. (2004)
<i>Populus deltoides</i> ²⁾	↓	↓	Rosenstiel et al. (2003)
<i>Pop. deltoides</i> ²⁾		↓	Pegoraro et al. (2005)
<i>Populus X euro-americana</i>	↓	— ³⁾	Centritto et al. (2004)
<i>Populus tremuloides</i>	↓		Sharkey et al. (1991)
<i>Quercus rubra</i>	↑		Sharkey et al. (1991)
<i>Q. chapmanii</i>	—		Buckley (2001)
<i>Q. pubescens</i>	4)	—	Rapparini et al. (2004)
<i>Q. pubescens</i>	↑		Tognetti et al. (1998)
<i>Q. robur</i>	↓		Possell et al. (2004)

¹⁾ Re-expressed from measurements on full plants using information on leaf dry weight and area.

²⁾ Both measured at the Biosphere II mesocosm.

³⁾ Derived from integrating regressions curves over measurements along the plant profile.

⁴⁾ Basal rate at leaf level was inhibited at short-term exposure to high CO₂.

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Table 3. Plant functional types simulated by LPJ-GUESS to grow at five isoprene flux sites used to test model performance, and their equivalent dominant plant species that grow at each site. The value of ε assigned in LPJ-GUESS to each PFT (Eq. A4) was such that under standard conditions ($1000 \mu\text{mol m}^{-2}\text{s}^{-1}$, $T=30^\circ\text{C}$, $\text{CO}_2=370 \text{ ppm}$) the calculated leaf level isoprene production equals the published I_s for that species (or species-average). The five sites are indicated by numbers as: ¹Costa Rica, ²Manaus, ³Michigan Biological Station (UMBS), ⁴Harvard, ⁵France.

PFT	Representative plant species growing at the site	$I_s \mu\text{gCg}^{-1} \text{h}^{-1}$	Source
Tropical evergreen	¹ Various, dominated by <i>Pentaclethra macroloba</i> ² Various, the larger Manaus area contains significant percentage of isoprene emitters in the Lecythidaceae, and to lesser degree from the Papilionaceae, Burseraceae or Moraceae families.	35 (based on the assumption that 50% of plant species were isoprene emitters) 32 (based on the assumption that 42% of the trees were isoprene emitters, with an average I_s of 75)	Geron et al. (2002) Harley et al. (2004)
Temperate or boreal broadleaf deciduous, shade tolerant	<i>Acer rubrum</i> ^{3,4} , <i>Fagus grandifolia</i> ³	0.1	BEIS
Temperate or boreal broadleaf deciduous, intermediate shade tolerant	<i>Quercus rubra</i> ^{3,4}	100	Goldstein et al. (1998)
Temperate or boreal broadleaf deciduous, shade intolerant	<i>Betula lenta</i> ⁴ <i>Populus ssp</i> ³ <i>Q. pubescens</i> ⁵	0.1 70 38	BEIS BEIS Serça, unpublished
Temperate or boreal needleleaf evergreen, shade tolerant	<i>Tsuga canadensis</i> ⁴	0.1	BEIS
Temperate or boreal needleleaf evergreen, intermediate shade tolerant	<i>Pinus resinosa</i> ⁴ , <i>P. strobus</i> ^{3,4}	0.1	BEIS
C-3 herbaceous vegetation	all sites, herbaceous understory vegetation	16	Guenther et al. (1995)

BEIS: <http://www.epa.gov/asmdnerl/biogen.html>

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Table 4. LPJ-GUESS model parameter settings to describe vegetation dynamics at the sites. Other values are as in (Sitch et al., 2003), (Smith et al., 2001), (Koca et al., 2006). NE: needle-leaf evergreen, BS: broadleaf summergreen, BE: broadleaf evergreen.

	Shade tolerant (sh)	Intermediate shade tolerant (ish)	Shade intolerant (sn)
Growth efficiency threshold for growth suppression mortality ($\text{kg}_C \text{m}^{-2} \text{a}^{-1}$)	0.05	0.1	0.12
Maximum sapling establishment rate (saplings $\text{m}^{-2} \text{a}^{-1}$)	0.03	0.1	0.25
Conversion rate sapwood to hardwood (fraction a^{-1})	0.03	0.03	0.03–0.05
Leaf area to sapwood cross-sectional area ($\text{m}^2 \text{m}^{-2}$)	1700 (NE) 3000–3100 (BS, BE)	1700 (NE) 3300–3350 (BS)	3000 (BS)
Tree longevity under non-stressed conditions (years)	300 (NE) 430 (BS, BE)	300 (NE) 500 (BS)	220 (BS)

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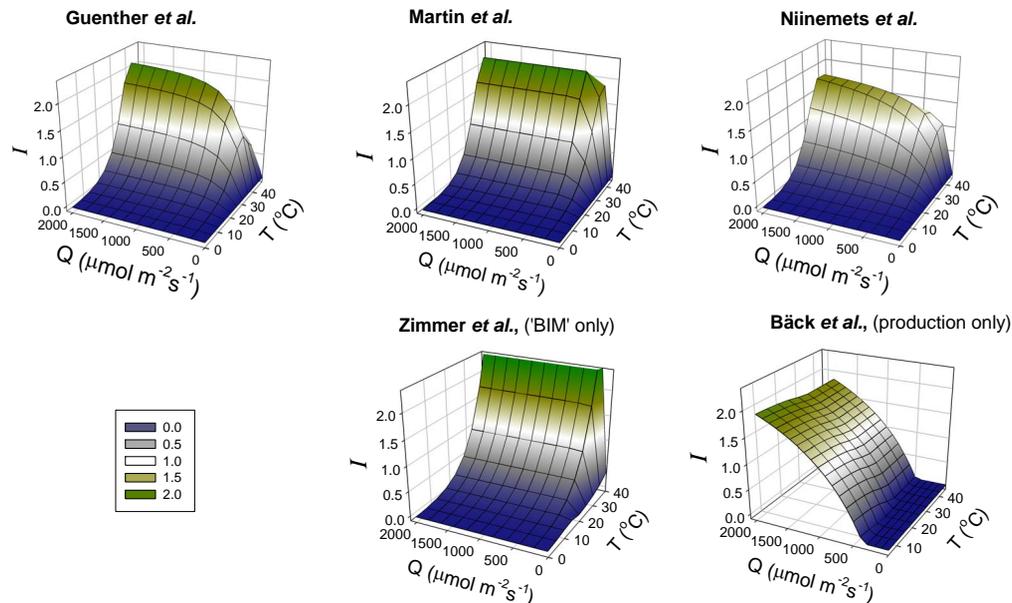


Fig. 1. Responses of leaf isoprene emission rate (I) to variation in temperature (T , °C) and incident quantum flux density (Q , $\mu\text{mol m}^{-2} \text{s}^{-1}$) according to five leaf-level isoprene emission models (Guenther et al., 1995; Niinemets et al., 1999; Martin et al., 2000; Zimmer et al., 2000; Bäck et al., 2005). For the process-based models described in Martin et al., Niinemets et al., Bäck et al. and Zimmer et al. isoprene production was coupled to a photosynthesis model (Farquhar et al., 1980; Hari and Mäkelä, 2003), assuming no limitation by stomatal conductance over the entire range of conditions. In the model of Bäck et al., the photosynthesis model parameters were adopted from Hari and Mäkelä (2003). For the other models, photosynthesis was adjusted to represent a cool-temperate leaf with a $J_{\text{max}}=130 \mu\text{mol m}^{-2} \text{s}^{-1}$ and $V_{\text{cmax}}=70 \mu\text{mol m}^{-2} \text{s}^{-1}$ and a temperature optimum of photosynthesis around 25°C. The responses shown here are for a CO_2 concentration of $370 \mu\text{mol mol}^{-1}$. Model output is normalised to be unity at $T=30^\circ\text{C}$ and $Q=1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. In case of Zimmer et al. and Bäck et al., only the isoprene production-relevant part of the model was used.

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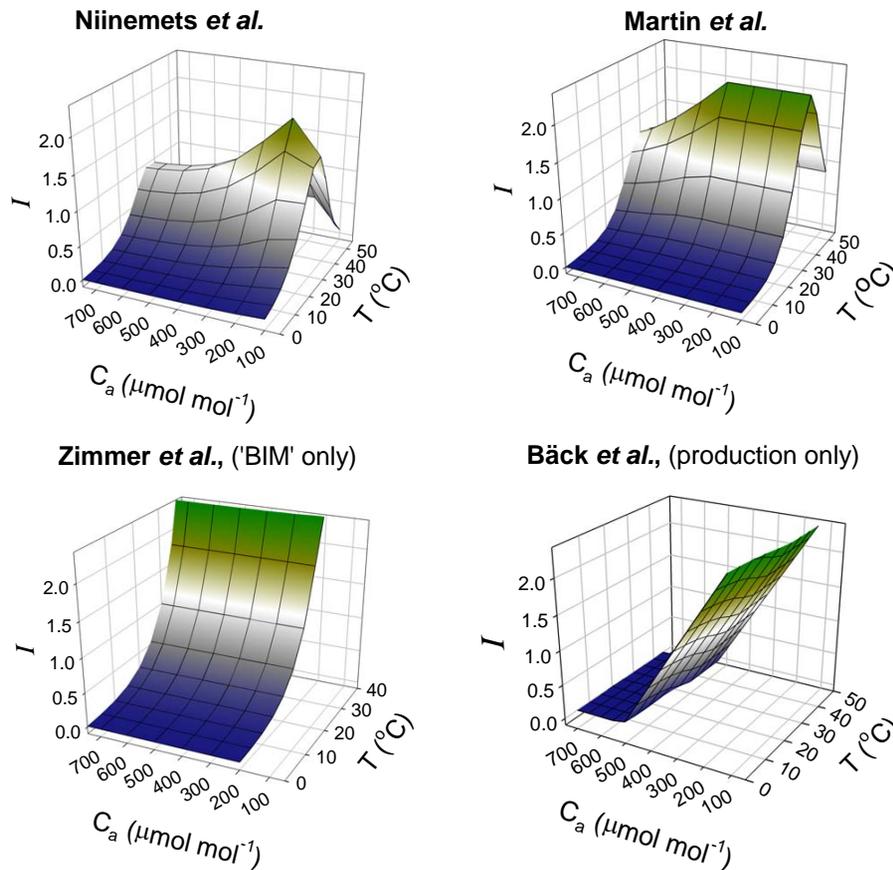


Fig. 2. Simulated leaf isoprene emissions in response to leaf temperature (T , °C) and atmospheric CO_2 concentration (C_a , $\mu\text{mol mol}^{-1}$) at $Q=1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. Models, parameterizations and colour scale are as in Fig. 1.

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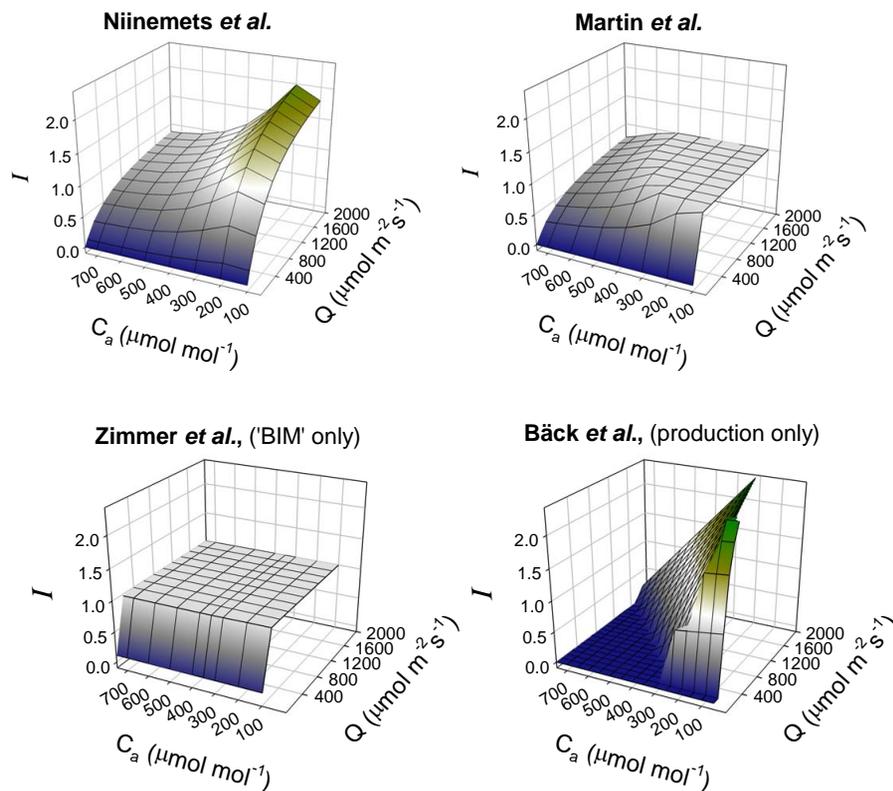


Fig. 3. Response of simulated leaf isoprene emissions to variation in incident quantum flux density (Q , $\mu\text{mol m}^{-2} \text{s}^{-1}$) and atmospheric CO_2 concentration at $T=30^\circ\text{C}$. Models, parameterizations and colour scale are as in Fig. 1.

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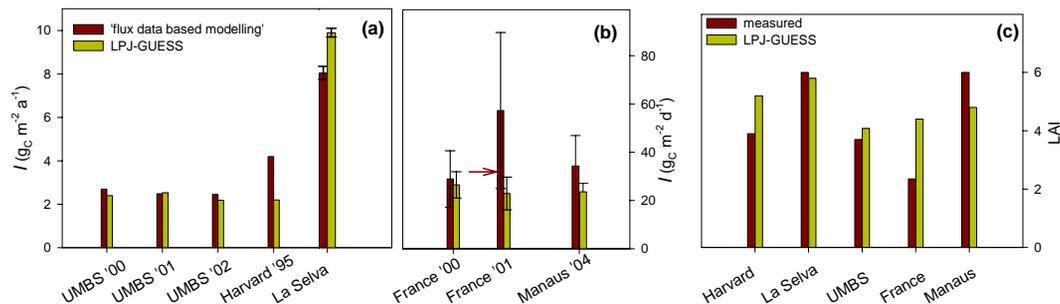


Fig. 4. (a) and (b): Annual (a) and daily (b) simulated canopy isoprene emissions (I) and estimates derived from flux measurements (“flux-data based modelling”) from five different forest sites (UMBS, Harvard, La Selva, France, Manaus). Numbers indicate the year of measurements and simulation. At La Selva the data are average and standard deviation for the period 1998–2000. For the French and Manaus sites, data and model output are average daily emission obtained from ca. 2-week long campaigns. These were performed during June/July 2001 and 2002 in France, and September 2004 at the Manaus tower. An arrow indicates average daily isoprene emissions for the first half of the 2001 measurement campaign in France. A description of the sites and data sets is provided in the text.

(c): Simulated and measured leaf area indices (LAI). LAI for La Selva is the one published for the larger area, LAI immediately at the eddy flux tower site is somewhat lower (c. 4).

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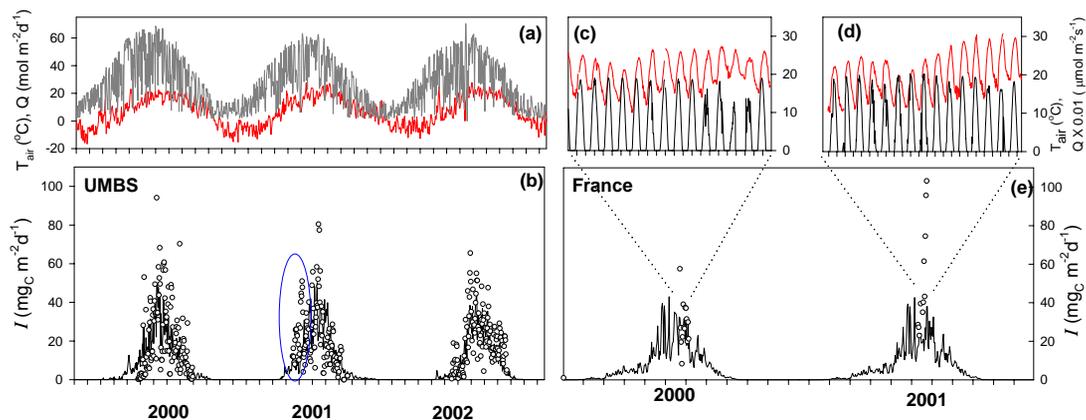


Fig. 5. (a): Daily average temperature (T , red line) and total quantum flux density (Q , grey line) at the UMBS site for 2000–2002.

(b): Measured (circles) and simulated (line) daily isoprene emission rates at UMBS for 2000–2001.

(c) and (d): Diurnal course of temperature (T , red line) and quantum flux density (Q , grey line) at the southern France site for two measurement campaigns (days 173–186 in 2000, and 163–177 in 2001).

(e): Simulated daily isoprene production for 2000 and 2001 (line), and measured isoprene fluxes during the two measurement campaigns (circles, period as in (c) and (d)).

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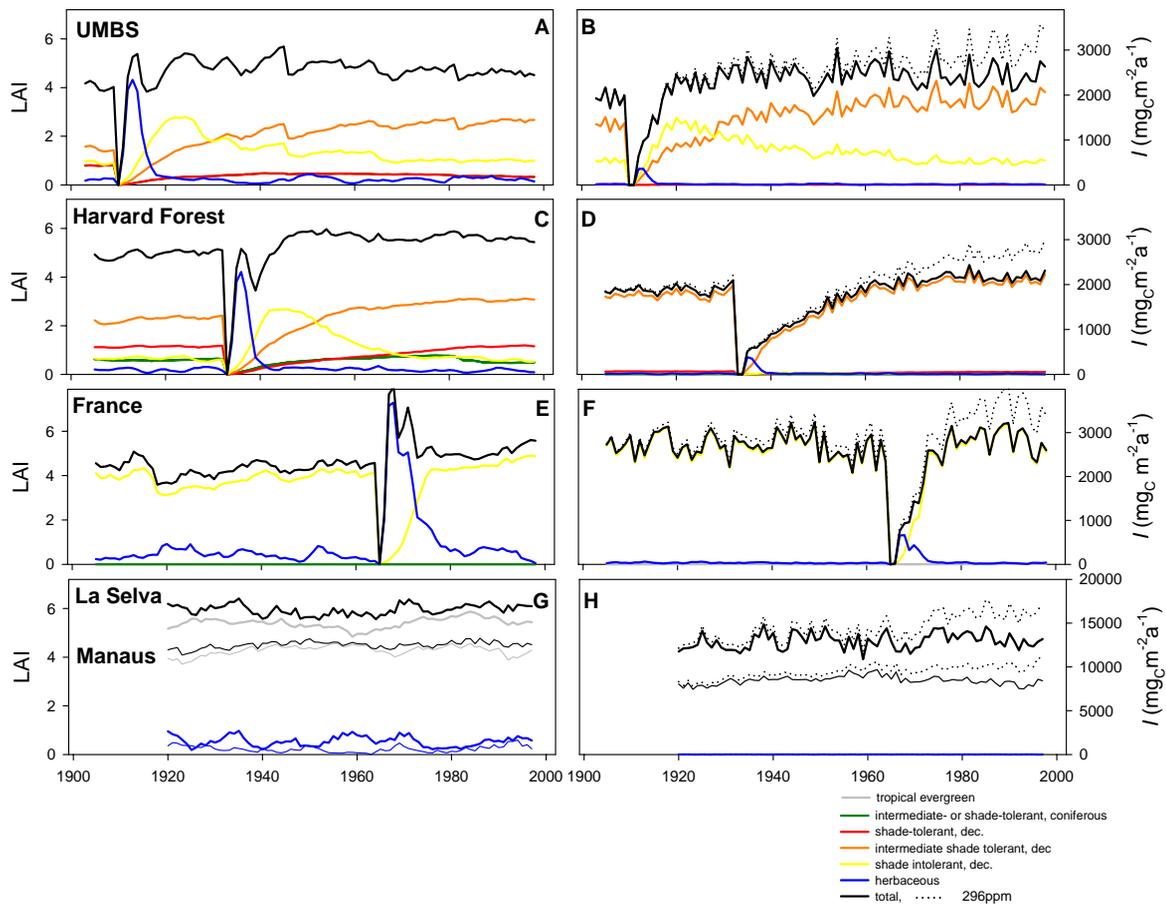


Fig. 6.

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Fig. 6. 20th century time series of simulated canopy leaf area indices (LAI, left hand panels) and isoprene emissions (I , right hand panels) at the model test sites, separated by PFT class. Panels are:

(a) and **(b)**: LAI and I at UMBS

(c) and **(d)**: LAI and I at Harvard Forest

(e) and **(f)**: LAI and I at the southern France site

(g) and **(h)**: LAI and I at the tropical forest sites, La Selva (thick line) and Manaus (thin line)

Simulations were performed using gridded climate input for 1905–1998, in case of the two tropical sites restricted to output from 1920 onwards due to the high uncertainty in climate data for the tropics early in the 20th century. Solid lines represent LAI and isoprene emissions simulated with increasing atmospheric CO₂ concentration over the course of the 20th century. In a second experiment isoprene-inhibition by [CO₂] was excluded; the dotted line indicates results from a simulation with κ (Fig. 7) calculated for the CO₂ concentration assumed to remain throughout the simulation period (canopy total only).

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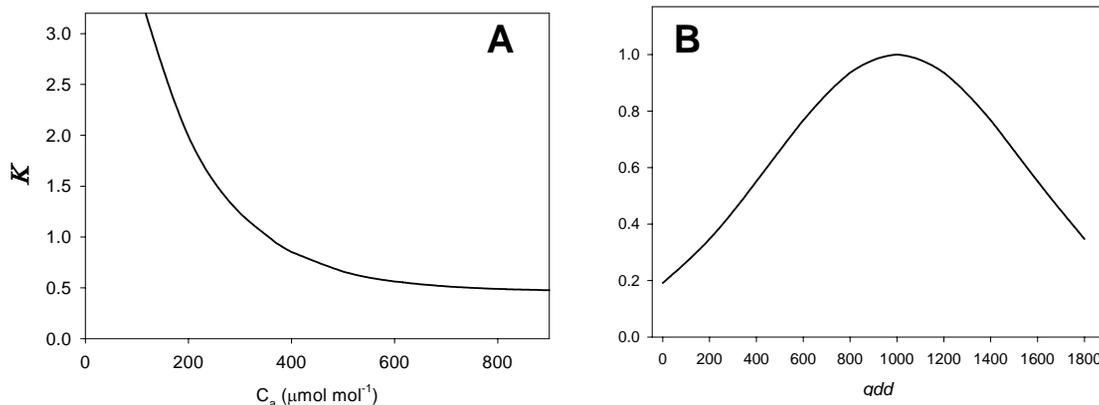


Fig. 7. (a): The effect of changing CO₂ concentration on isoprene emissions as described by κ in Eq. (A2b), which is assumed here to be equivalent to the change of oxygen and CO₂ concentration in the leaf as the relative rates of carboxylation, and photorespiration and respiration change.

(b): The simplified seasonal change in leaf isoprene emission potential as a function of growing degree day temperature sum (Eq. 2).

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