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Atmospheric Chemistry and Physics

Process-based estimates of terrestrial ecosystem isoprene emissions: incorporating the effects of a direct CO_2-isoprene interaction

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Abstract. In recent years evidence has emerged that the amount of isoprene emitted from a leaf is affected by the CO_2 growth environment. Many – though not all – laboratory experiments indicate that emissions increase significantly at below-ambient CO_2 concentrations and decrease when concentrations are raised to above-ambient. A small number of process-based leaf isoprene emission models can reproduce this CO_2 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 for incorporation into a dynamic vegetation model framework, LPJ-GUESS, yielding a tool that allows the interactive effects of climate and increasing CO_2 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 CO_2 concentration can be assessed. We show here for five model test sites that the suggested CO_2-inhibition of leaf-isoprene metabolism can be large enough to offset increases in emissions due to CO_2-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 CO_2-isoprene inhibition may have the potential to significantly dampen the expected steep increase of ecosystem isoprene emission in a future, warmer atmosphere with higher CO_2 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; Lerdau 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

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

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, although, at standardised measurement conditions, the potential of a leaf to emit varies greatly from zero to values $>100\,\mu g_C\ g_{leaf}^{-1}\ h^{-1}$ (Kesselmeier and Staudt, 1999; Wiedinmyer et al., 2004). It is difficult to relate the potential for isoprene emission to plant taxonomic affinity, although some plant families or genera encompass several emitting species (Benjamin et al., 1996; Kesselmeier and Staudt, 1999). Global estimates of the amount of carbon emitted by terrestrial biota in the form of isoprene appear to converge around $c.$ 500 $Tg_C a^{-1}$, 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., 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 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 (Henze and Seinfeld, 2006).

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 (c.f. Appendix A; 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; Lathière 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; Lathière 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 CO_2 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 CO_2 concentration ($[CO_2]$) may have on leaf isoprene production. An increasing number of experiments indicate that leaf emission generally increases in plants grown at below-ambient $[CO_2]$ and decreases in a high-CO_2 environment, with only very few studies reporting the opposite (c.f. Sect. 2). If these effects are taken into account, isoprene emission estimates for past and future environments may have to be revised, since they offset, at least partially, the interactions of CO_2 concentration with plant leaf production (Arneth et al., 2007[1]).

Some leaf isoprene models have sought to link production rates explicitly to the chloroplastic biochemistry of isoprene precursors (c.f. Sect. 3; Niinemets et al., 1999; Martin et al., 2000; Zimmer et al., 2000; Bäck et al., 2005), thus including a direct interaction of carbon assimilation with isoprene emission. Since terrestrial carbon cycle and dynamic vegetation models generally have at their core 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. This approach would have the advantage of permitting the assessment of not only the combined effects of temperature, vegetation distribution and productivity on terrestrial isoprene emissions, but also emissions directly related to CO_2. In what follows, we briefly summarise observations of direct CO_2-isoprene interactions, review the existing mechanistic leaf-level isoprene models that seek to incorporate these effects, and compare the potential of the models to predict the emission response to light, temperature and CO_2, as well as their applicability in global models.

[1]Arneth, A., Miller, P. M., Scholze, M., et al.: CO_2 inhibition of leaf isoprene metabolism offsets effect of increasing temperature and GPP fertilisation on global terrestrial emissions, in preparation, 2007.

Table 2. Effects of increasing atmospheric CO_2 concentration on emissions of isoprene. Arrows indicate the direction of the response ("↓" = decreasing isoprene emissions as CO_2 concentration increases; "–" indicates no trend) in plants growing along a CO_2 gradient in the vicinity of CO_2 springs, or grown in chamber or FACE experiments with CO_2 either varying between sub-ambient and ambient, or ambient and elevated levels. Exposure to non-ambient CO_2 concentration in the experimental treatments varied from a few weeks to several years.

Plant species	Single leaf level	Branch or canopy level	Source
Arundo donax	– (trend to ↓[(1)])	– (trend to ↓)	Possell et al. (2005)
Mucuna pruriens	↓[(1)]	– (trend to ↓)	Possell et al. (2005)
Phragmites australis	↓		Scholefield et al. (2004)
Populus deltoides[(2)]	↓	↓	Rosenstiel et al. (2003)
P. deltoides[(2)]		↓	Pegoraro et al. (2005)
P. X euro-americana	↓	–[(3)]	Centritto et al. (2004)
P. tremuloides	↓		Sharkey et al. (1991)
Quercus rubra	↑		Sharkey et al. (1991)
Q.chapmanii	–		Buckley (2001)
Q. pubescens	[(4)]	–	Rapparini et al. (2004)
Q. pubescens	↑		Tognetti et al. (1998)
Q. robur	↓		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 CO_2.

We incorporate one such model into the dynamic vegetation model framework LPJ-GUESS (Smith et al., 2001; Sitch et al., 2003) and test the 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 [CO_2].

2 The response of leaf isoprene emission to changes in atmospheric CO_2 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. 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 CO_2-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 than that of photosynthesis, and isoprene emission appears inhibited at elevated [CO_2] (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 used for isoprene production are still not fully resolved.

Short-term exposure to increasing [CO_2] inhibits leaf isoprene emissions whereas exposure to decreasing [CO_2] has the opposite effect, unless [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 with 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 with 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 and canopy levels. Of the twelve datasets summarised in the table, seven show decreasing leaf isoprene emissions with increasing [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 concentration on isoprene emission was observed, and only two studies show an increase. Hence, the majority of studies to date that investigate effects of growth-CO_2 environment on isoprene emissions support observations made from the short-term variation of CO_2 concentration around the leaf.

Substantially declining isoprene emissions are, then, commonly observed, even though rates of photosynthesis are often stimulated, at elevated [CO_2]. For instance, isoprene emissions from *A. donax* and *Mucuna pruriensis* grown in growth chambers at 180 ppm CO_2 exceeded emissions at ambient CO_2 by a factor of two to three, when expressed on a leaf area basis (Possell et al., 2005). Along a CO_2 gradient in the vicinity of a natural CO_2 spring, leaf emission rates from *Phragmites* decreased five-fold with proximity to the CO_2 source (*c*. 400 to 900 ppm) whether expressed on a leaf area or a mass basis (Scholefield et al., 2004). Ecosystem emissions decreased by 21 and 41%, respectively, in the 800 and 1200 ppm CO_2 growth-environment of the Biosphere-II facility, which was somewhat less than the leaf level response (*c*. −35 and −65%; Rosenstiel et al., 2003). This weakening of the CO_2-induced inhibition of isoprene emissions per unit branch or canopy area, compared with observations at the leaf level, is a common finding, although the number of studies that have investigated CO_2 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 CO_2 environment can affect leaf anatomy or simply the total number of leaves per branch or plant, in some cases to such a degree that it outweighs the CO_2 effect on leaf isoprene emissions completely. In FACE-grown poplar clones, leaf isoprene emissions in ambient CO_2 exceeded those of plants in elevated CO_2 by more than 30%, but this effect was completely counteracted by the larger number of leaves in the trees in the elevated CO_2 treatment (Centritto et al., 2004). These observations clearly point to the importance of treating direct and indirect CO_2 effects simultaneously, when modelling terrestrial isoprene emissions, since a number of effects may counterbalance each other.

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 μmol $m^{-2}s^{-1}$, which over the course of a day is varied non-linearly in response to changing leaf temperature and radiation at the leaf surface (c.f. Appendix A). 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 the onset of photosynthetic activity and isoprene emission in the spring, or for effects of the 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 adopt a different approach by synthesising current understanding of isoprene metabolism to determine production rates based on enzyme activity and supply of precursors from photosynthesis (c.f. Appendix A for a summary description of the models' main features). Four approaches have been published to date:

1. Martin et al. (2000), who calculates isoprene production as the result of three potentially rate limiting processes: the supply of carbon to isoprene synthesis via pyruvate formed by ribulose1,5bisphosphate (RUBP) carboxylation, the supply of ATP by phosphorylation needed to produce DMAPP from the C-substrate, and the maximum capacity of isoprene-synthase.

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 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 the isoprene synthesis pathway is proportional to the total activity of isoprene synthase in the leaves. As 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.

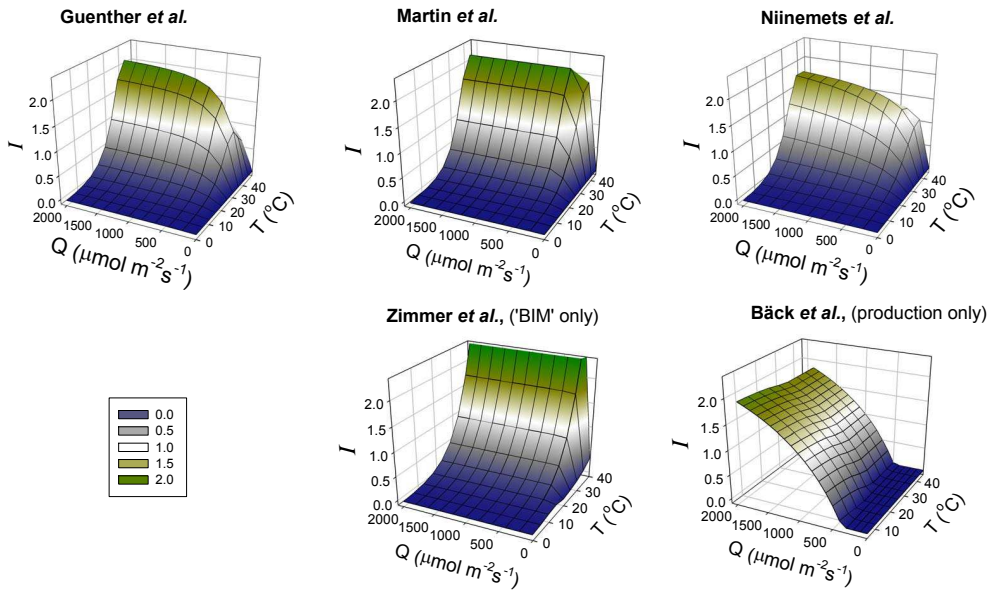

Fig. 1. Responses of leaf isoprene emission rate (I) to variation in temperature (T, °C) and incident quantum flux density (Q, μmol m^{-2}s^{-1}) according to five leaf-level isoprene emission models (Guenther et al., 1995; Niinemets et al., 1999; Martin et al., 2000; Zimmer et al., 2000; Bäck et al., 2005). For the process-based models described in Martin et al. (2000), Niinemets et al. (1999), Bäck et al. (2005) and Zimmer et al. (2000), 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. (2005), 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 $J_{\max}$=130 μmol m^{-2} s^{-1} and $V_{c\,\max}$=70 μmol m^{-2} s^{-1} and a temperature optimum of photosynthesis around 25°C. The responses shown here are for a CO_2 concentration of 370 μmol mol^{-1}. Model output is normalised to be unity at T=30°C and Q=1000 μmol m^{-2} s^{-1}. In the case of Zimmer et al. (2000) and Bäck et al. (2005), only the isoprene production-relevant part of the model was used.

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 (c.f. Appendix A). 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 purposes. Figures 1–4 rather seek to address the relative sensitivity of the models 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 [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. (2000), Zimmer et al. (2000), and Niinemets et al. (1999) models (Appendix A: Sects. A2, A3 and A5), and from Hari and Mäkelä (2003) for the Bäck et al. (2005) model (Sect. 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. (2000) and Niinements et al. models (Fig. 1) – unsurprisingly so, since the isoprene emission responses to Q and T are essentially similar to those of photosynthesis. Both models account for a difference between the T-optimum of carbon assimilation and that of isoprene production; the former depicts a stronger increase with T and a distinct saturation above Q=500 μmol m^{-2} s^{-1}. Furthermore, the inclusion of ν or κ (Eqs. A2b and A4; Fig. 8) in both models leads to isoprene emission declining non-linearly with increasing [CO_2] (Figs. 2–4). In the case of the modified Niinemets et al. (1999), I declines from $C_a > c$. 150 ppm, levelling at around 500 ppm, whereas modelled I from Martin et al. (2000) was not responsive to increasing CO_2 concentration until C_a>400 ppm, and did not level off at high [CO_2] (Figs. 3 and 4). The extent of this emission "plateau" at low to medium [CO_2] depends on the chosen value of Q (Figs. 3 and 4) but also on the assumed temperature of the model experiment (Fig. 4, c.f. also Martin et al., 2000).

The Q, T and [CO_2] response of leaf isoprene production calculated from the Bäck et al. (2005) and Zimmer et al. (2000) approaches displayed some unexpected features

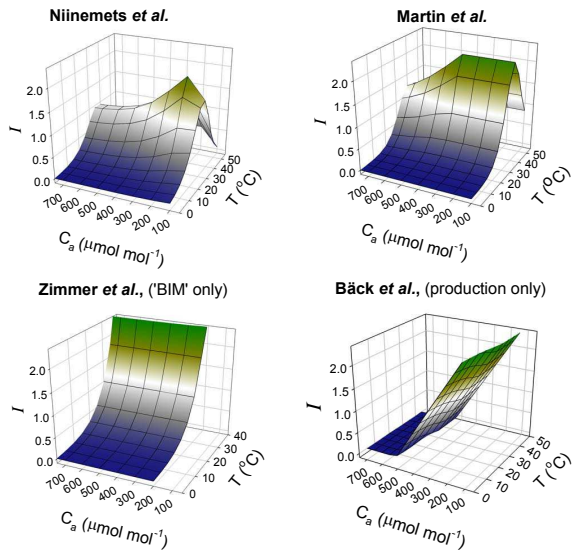

Fig. 2. Simulated leaf isoprene emissions in response to leaf temperature (T, °C) and atmospheric CO_2 concentration (C_a, μmol mol^{-1}) at Q=1000 μmol m^{-2} s^{-1}. Models, parameterizations and colour scale are as in Fig. 1.

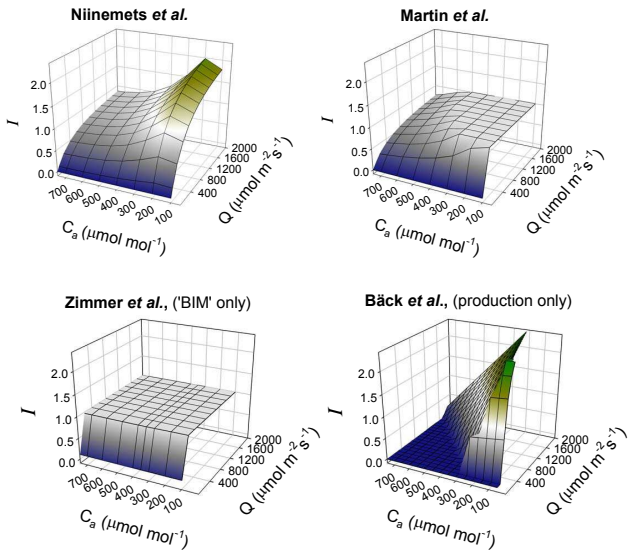

Fig. 3. Response of simulated leaf isoprene emissions to variation in incident quantum flux density (Q, μmol m^{-2} s^{-1}) and atmospheric CO_2 concentration at T=30°C. Models, parameterizations and colour scale are as in Fig. 1.

that require comment. Both are dynamic, non-equilibrium models that do not assume steady-state carbon assimilation. In the case of the former, carbon substrate for isoprene synthesis is supplied by a photosynthesis module that is based on the concept of optimum stomatal control of carbon assimilation (Cowan, 1982; Hari and Mäkelä, 2003). By assuming a steady state, as was done for the calculations shown in the figures, the 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 shown in the figures. This leads to a significant dampening of the dynamic response of the model to transient environmental changes. 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 on which the parameter values of the model are based, the temperature response of photosynthesis is extremely weak, photosynthesis having been observed to commence in early spring, as soon as air temperatures rise above 0°C (P. Hari, pers. obs.). The model therefore reproduced the expected smooth saturation of isoprene emission with increasing light (Fig. 1) but there was only a minor effect of temperature. The evaporation formulation 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 extend its applicability to a wider range, the model would need to be adjusted to account for the difference commonly observed between the temperature responses of carbon assimilation and isoprene production, possibly in a similar way as done in Eq. (A4b). In terms of the CO_2-sensitivity, the model simulates no isoprene synthesis when the mesophyll CO_2 concentration is above ambient CO_2 concentration (of the year 2004). This is clearly seen in Figs. 2–4 as zero emissions at high C_a and thereafter a very steep increase with decreasing intercellular CO_2 concentration, in accordance with the experimental results for the isoprene-CO_2 response (Table 2).

In case of the Zimmer et al. (2000) model, Figs. 1–4 illustrate results from what was termed the "BIM, biochemical isoprenoid biosynthesis"-part of the model. Light saturation of isoprene production was simulated to occur at very low rates (around 200 μmol m^{-2} s^{-1}): the model was originally developed for coupling with a light-fleck model oriented towards plants growing in or beneath dense canopies (Kirschbaum et al., 1998). Modelled isoprene production increased smoothly with temperature up to 40°C; the model is not designed to be applied for temperatures above 42°C, by which 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. (2005) approach, inconsistencies in the isoprene T- or Q-responses are therefore not a shortcoming of the model per se, but purely a numerical consequence of its application in a steady-state environment. However, the model cannot produce a CO_2 response in its present form, as already pointed out by Zimmer and co-authors (Zimmer et al., 2003): while chloroplastic processes are represented mechanistically as a cascade of relevant enzymatically-controlled reactions, the model does not account for the leaf-internal CO_2-dependent competition for carbon, redox- or energy equivalents that

must underlie the observed isoprene-CO_2 response in one way or another. In the Martin et al. (2000), and Niinemets et al. (1999) approach, such leaf-internal competition is introduced semi-mechanistically, while in Bäck et al. (2005), a change in oxygenation vs. carboxylation via Rubisco is calculated explicitly and (as in Eqs. A2b and A4) assumed to be an appropriate surrogate for competition for a range of metabolites.

4 Modelling at the 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 combined 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, 2006; Geron et al., 1997; Baldocchi et al., 1999; Huber et al., 1999; Simpson et al., 1999; Lindfors and Laurila, 2000). Since the complexity of the canopy models may not necessarily improve the isoprene model performance when compared to measured emissions (Lamb et al., 1996), the most appropriate method of upscaling 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 [CO_2], climate change and changes in surface vegetation cover in determining isoprene emissions. In a set of initial analyses the Guenther et al. algorithms have been used in Dynamic Global Vegetation Models (DGVMs) to account for interactions between climate and plant cover in determining 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 distributed in the ecosystem. They thereby constitute a suitable platform for investigating the sensitivity of terrestrial isoprene emissions not only to changes in surface plant cover, but also to climate- or CO_2-related changes in gross primary productivity (GPP) or canopy phenology. Studies to date, however, have ignored the possibly significant direct effect [CO_2] may have on leaf level emission (Table 2). Since some of the studies summarised in Table 2 have indicated that such a direct isoprene-CO_2 inhibition can potentially offset effects due to stimulated GPP or leaf growth, and since

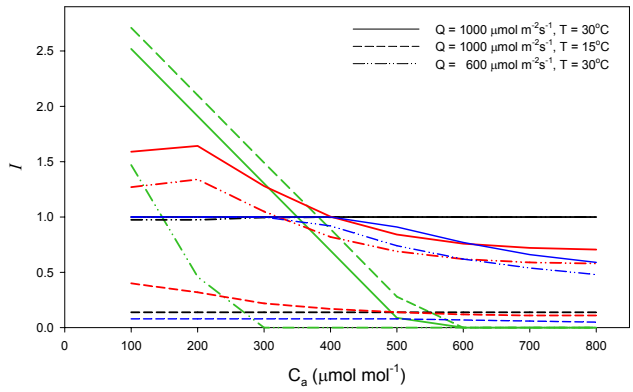

Fig. 4. Model responses to increasing CO_2 concentration, simulated for Q=1000 μmol m^{-2} s^{-1} and T=30 and 15°C (straight and dashed lines, respectively), and for Q=600 μmol m^{-2} s^{-1} and T=30°C (dash – dotted line). Colours are: red – Niinemets et al. (1999), blue – Martin et al. (2000), black – Zimmer et al. (2000), green – Bäck et al. (2005).

increasing [CO_2] go hand-in-hand with increasing temperatures, it seems essential to quantify the possible importance of a direct CO_2 response at ecosystem, regional and global scales.

4.1 Ecosystem model

As summarised in the Appendix A and demonstrated in Figs. 1–4, the Niinemets et al. (1999) formulation is the prime candidate for use in a broader model framework to address this issue: the model's response to Q, T and [CO_2] is in general agreement with current understanding; furthermore, it can be applied without difficulties in a steady-state photosynthesis module of the kind generally adopted by large-scale vegetation and carbon cycle models. It has the advantage over the Martin et al. (2000) model of requiring determination of only one main input parameter (ε, cf., Appendix A) 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 Niinemets et al. (1999) 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 responses of vegetation and soil carbon and water cycling 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 [CO_2]. 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 capacity for resource uptake, carbon sequestration, mortality and/or rate of establishment under the varying environment and stand structure. For large-scale, e.g. global, applications (DGVM mode), the latter processes are

described fairly generally, since on these scales considerable averaging of vertical and horizontal structure is required to keep the model computationally efficient. Vegetation within a gridcell (typically $0.5° \times 0.5°$) is defined by the fractional cover of the average individual of a given PFT that can grow within the cell. For regional or stand-scale applications, the model may be applied in cohort mode (with "patch" vegetation dynamics). In this case, 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 the latter case, PFT sub-groups or even individual species can be defined in terms of resource use syndromes (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. Because demography and community structure in a particular patch is influenced by stochastic processes, the model output is the average over a number of replicate patches.

The physiological process descriptions in LPJ-GUESS, for instance, the coupling of photosynthesis and stomatal conductance, plant and ecosystem carbon and water balance, litter decomposition and soil processes, are identical to those used in LPJ-DGVM (Sitch et al., 2003), including improvements in the hydrology presented by Gerten et al. (2004)[2]. LPJ-DGVM and LPJ-GUESS have both been extensively evaluated with respect to observations of ecosystem functioning and vegetation structure (Hickler et al., 2004; Morales et al., 2005; Sitch et al., 2005). The model has also been shown to reproduce CO_2 effects on primary productivity that have been observed at a number of Free Air CO_2 Enrichment experiments (Gerten et al., 2005). Here we concentrate on the performance of the model when used 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., 2006[1]).

The functional significance of the presence or absence of isoprene production in plant species has not yet been resolved. In order to link isoprene production to the vegetation description provided by LPJ-GUESS, we therefore prescribe a single representative value for ε (Eq. A4a) for each PFT simulated by LPJ-GUESS. The value chosen is one that yields $I = I_s$ at standard T and Q, 370 ppm atmospheric CO_2 concentration, and that is based on the value of J predicted by LPJ-GUESS for the given PFT under these conditions. This approach allows us to draw on the existing data-bases for I_s.

Isoprene emission rates from newly developing leaves are known to be considerably smaller than the maximum capacity reached in fully mature leaves and lag the development of assimilation capacity by several days to a few weeks at 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 the growth environment on the expression of isoprene synthase (Wiberley et al., 2005). This mechanism can explain field observations for which 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

$$\sigma = \exp\left[-e_1((-x_0)/b)^2\right] \tag{1}$$

with e_1=2, x_0=1000 and b=1100 (Fig. 8b) 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 for which the model is run. 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 in warm climates (c.f. 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):

$$\Delta T = (R_n - \lambda E)/(\rho C_p g_a)\,, \tag{2}$$

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 and 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% or more in a wide range of climates (A. Arneth, personal. observation), the difference between daytime temperature and daily temperature was calculated from:

$$\Delta T_b = \sin h' h'^{-1} dtr'\,, \tag{3}$$

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

4.2 Flux data

Measurements of ecosystem-atmosphere exchange of trace gases, in particular that of CO_2 but also water vapour, have become a standard benchmark for the evaluation of terrestrial carbon cycle models (Krinner et al., 2005; Morales et al.,

[2] Except for maximum transpiration from tropical trees, set to 5 mm d^{-1} (Sitch et al., 2003).

Table 3. Plant functional types simulated by LPJ-GUESS to grow at five isoprene flux sites used to test model performance, and their corresponding 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 μmol m^{-2}s^{-1}, T=30°C, CO_2=370 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: [1]Costa Rica, [2]Manaus, [3]Michigan Biological Station (UMBS), [4]Harvard, [5]France.

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

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

2005; Friend et al., 2006). In principle, isoprene flux measurements can be used for the same purpose, since the atmospheric lifetime of isoprene 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 the 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 intensive but brief measurement campaigns lasting from a few days to a 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 only a few studies report daily totals for periods of more than a few days. Longer-term data, preferably spanning at least one growing-dormant period cycle (i.e. one year) are ideally required for comparison with daily to monthly output from LPJ-GUESS. 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 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 canadiensis* (Goldstein et al., 1998).

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

	Shade tolerant	Intermediate shade tolerant)	Shade intolerant
Growth efficiency threshold for growth suppression mortality ($kg_C m^{-2} a^{-1}$)	0.05	0.1	0.12
Maximum sapling establishment rate (saplings $m^{-2} a^{-1}$)	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 ratio ($m^2 m^{-2}$)	1700 (NE) 3000–3100 (BS, BE)	1700 (NE) 3300–3350 (BS)	3000 (BS)
Maximum expected tree longevity under non-stressed conditions (years)	300 (NE) 430 (BS, BE)	300 (NE) 500 (BS)	220 (BS)

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 were 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 macroloba*, 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 were 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 an isoprene flux measurement campaign was conducted during September 2004 (Karl et al., 2007[3]). 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 approximately two-week long periods in summer 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 the above five sites, LPJ-GUESS was run in cohort mode, which is particularly suitable for the description of vegetation dynamics on the ecosystem scale. Values for ε were assigned in the manner described above to the PFTs that were simulated to grow at each particular site; the simulated vegetation composition in terms of PFTs agreed well with the actual species composition recorded at each site (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 PFTs 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 a few adjustments to represent the composition of the five benchmark forests as closely as possible (Table 4). The adjustments included a reduced sapwood-to-hardwood conversion rate, lower 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 for the period 1900–1998 using climate input data derived from the CRU climate data set (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) canopy LAI and biomass

[3]Karl, T., Guenther, A., Greenberg, J., Yokelson, R., Blake, D., and P. Artaxo: Investigating emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, J. Geophys. Res., in review, 2007.

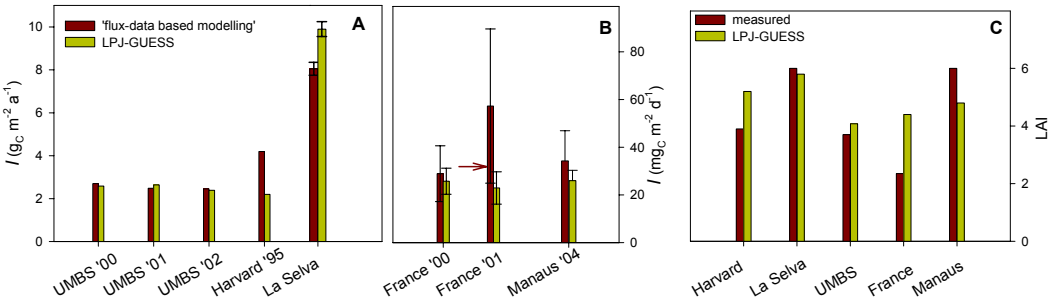

Fig. 5. **(a)** and **(b)**: Annual (panel a) and daily (panel b) simulated canopy isoprene emissions (I) and estimates derived from flux measurements ("flux-data based modelling") from five different forest sites (UMBS, Harvard, La Selva, France, Manaus). Numbers indicate the year of measurements and 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 approximately two-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 as published for the larger area, LAI in the immediate vicinity of the eddy flux tower site is somewhat lower (*c*. 4).

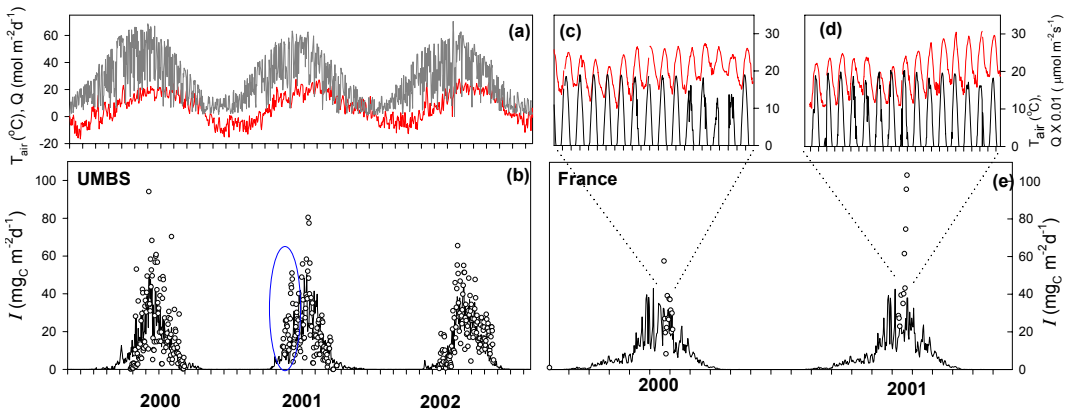

Fig. 6. **(a)** Daily average temperature (T, red line) and total quantum flux density (Q, grey line) at the UMBS site for 2000–2002. **(b)** Measured (circles) and simulated (line) daily isoprene emission rates at UMBS for 2000–2001. **(c)** and **(d)**: Diurnal course of temperature (T, red line) and 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)).

were reset to zero in the appropriate simulation year, initiating succession and producing forests with the approximately correct age structure for the year the isoprene measurements were conducted. Before using the historical climate data, the model was "spun up" for 1000 years to achieve equilibrium in ecosystem carbon pools. The number of patches for averaging model output was set to 90.

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 of representing the correct canopy structure and physiological activity. The model performance in these respects was acceptable for the five model test sites, with the simulated total leaf area index lying, on average, within 10% of measured values (Fig. 5), 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 $g_C\ m^{-2}a^{-1}$ for UMBS, Harvard and La Selva, and 20–30 $mg_C\ m^{-2}d^{-1}$ for the French and Manaus sites (Fig. 5).

Agreement of modelled with measured isoprene production was particularly good for the mixed hardwood forest at the University of Michigan Biological Station, where modelled isoprene production was within 5–10% of measured

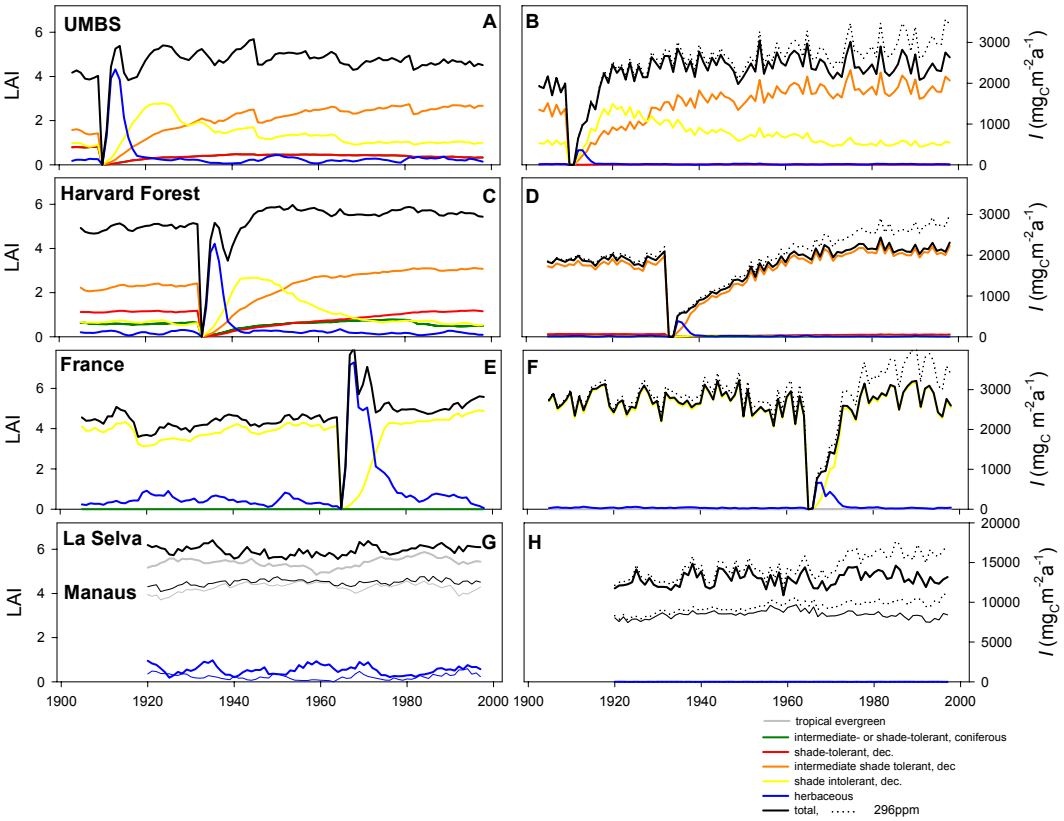

Fig. 7. 20th century time series of simulated canopy leaf area indices (LAI, left hand panels) and isoprene emissions (I, right hand panels) at the model test sites, separated by PFT class. Panels are: **(a)** and **(b)**: LAI and I at UMBS. **(c)** and **(d)**: LAI and I at Harvard Forest. **(e)** and **(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 CO_2 concentration over the course of the 20th century. In a second experiment isoprene-inhibition by $[CO_2]$ was excluded; the dotted line indicates results from a simulation with κ (Eq. A4) calculated for the CO_2 concentration assumed to remain constant at 296 ppm throughout the simulation period (canopy total only).

values for all three years (Fig. 5). The simple growing degree day temperature function (Eq. 1) in the model captured the observed seasonality in emissions well, particularly so in 2002 (Fig. 6). 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. 6). 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.

Viewed side-by-side, the results of simulations for the cool, mixed-hardwood forest at UMBS and the Mediterranean French oak forest (Fig. 6) serve well to illustrate the interactions that take place between species composition (and thus isoprene emission potential) and environmental conditions. Maximum simulated I at the height of the active season was fairly similar in both forests, around 40 $mg_C m^{-2} d^{-1}$, although I_s of the main isoprene emitting *Q. rubra* at UMBS exceed that of *Q. pubescens* by a factor of 2–3 – translating 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. 7), in combination with warmer temperatures, could compensate fully for the hugely dissimilar I_s (and hence ε). 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% of each other (Figs. 5 and 6).

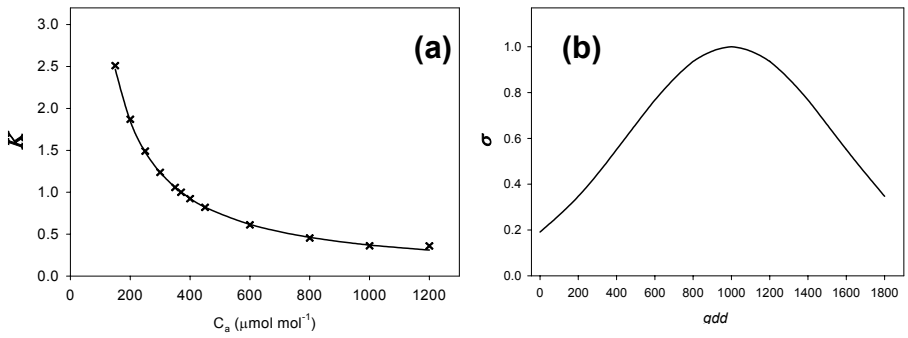

Fig. 8. (a) The effect of changing CO_2 concentration on isoprene emissions as described by κ in Eq. (A4), which is assumed here to represent the change of oxygen and CO_2 concentration in the leaf as the relative rates of carboxylation, photorespiration and respiration change. Points calculated from the empirical relationship presented by Possell et al. (2005, their Fig. 5) are marked with "X"; redrawn here as being unity at 370 ppm for comparison with our approach. **(b)** The simplified seasonal change in leaf isoprene emission potential as a function of growing degree day temperature sum (5°C base) (Eq. 1).

Model runs were completed with canopy ages of 18 and 35 years, respectively, for the two measurement years, 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. 5, arrow). However, during the last few days of the campaign a rather sharp increase of measured fluxes was observed: from 20–40 $mg_C\ m^{-2}\ d^{-1}$ to values well above 60 $mg_C\ m^{-2}\ d^{-1}$. This sudden increase was not reproduced by the model. What may have caused it is still under investigation, but it could evidently not be related to a sudden change in weather conditions (Fig. 6c and 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 a few hours to days preceding a measurement, possibly due to effects on the amount or activity of isoprene synthase (Geron et al., 2000). However, the length of the time period over which such an effect may operate is unknown and most likely to be quite variable, while the underlying mechanisms are far from understood. We therefore did not include it in the current version of the model. Moreover, while possibly helpful for improving model performance on a day-to-day basis, the effect on emissions over the course of a simulation year is presumably small, since omission of the effect will most likely lead to overestimation during certain periods and underestimation during others, depending on variation in the weather. In any case, while the 2000 campaign did not encompass a steady trend of increasing temperatures, maximum air temperatures during both campaigns were reasonably similar (Fig. 6); it is unclear whether a cumulative temperature effect indeed could explain the observed doubling of isoprene fluxes from one day to the next. During the 2001 campaign average maximum surface ozone concentrations were 71 ppbv on the days with high isoprene fluxes, compared to 63 during the preceding days (and 56 ppbv during the campaign in 2000). Further, the daily amplitude increased from 38 to 55 ppbv in those two periods. An alternative (or additional) explanation might therefore lie in a hypothesised plant protection mechanism against high tropospheric O_3 levels; it has been speculated that isoprene may quench reactive oxygen species (Velikova et al., 2005). However, the response of isoprene fluxes to elevated surface O_3 is still unclear.

At the La Selva tropical rainforest site, modelled isoprene production was just below 10 $g_C m^{-2} a^{-1}$ on average for the years 1998–2000, in broad agreement with estimates based on upscaled leaf emissions that were tested against a few days of ecosystem flux data obtained by REA (Fig. 5, 8 $g_C m^{-2} a^{-1}$; Geron et al., 2002). These annual emissions are nearly five times as large as 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 (c.f. Table 3) nor by high daily maximum rates (*c*. 30–60 $mg_C m^{-2} d^{-1}$, not shown), but were rather due to the fact that the modest daily emission rates are sustained for the entire year, as opposed to two to three months in the case of the northern forest sites (Arneth et al., 2007[1]).

LPJ-GUESS and the REA/leaf model-derived estimates for La Selva are both markedly higher than the range suggested by data obtained during a disjunct eddy covariance campaign in 2003 (4.5–6.3 $g_C\ m^{-2} a^{-1}$; 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 their high volatility (Fall and Monson, 1992; Niinemets and Reichstein, 2003). Since isoprene is below its saturation vapour pressure in the substomatal cavity, stomatal closure increases the diffusion gradient, resulting in no 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 markedly; this response indicates that, in addition to the above short-term diffusion effects, isoprene production remains ongoing, stimulated perhaps by a higher leaf-temperature or by lower C_i (Pegoraro et al., 2004; Pegoraro et al., 2005b).

An average I_s to be used as the basis for assigning 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 a 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 $75\,\mu g_C g^{-1} h^{-1}$ 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 to within 25%. The lower model estimates could possibly 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 lower I_s (and thus ε) and the notably lower LAI and GPP (not shown) simulated for Manaus compared to La Selva result in lower annual estimates overall for the former (Fig. 7g and h).

Modelled isoprene production for Harvard forest was nearly identical to rates simulated for the UMBS site. Both sites 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, respectively, 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 somewhat varying proportions of the total LAI (Fig. 7) that was comparable to reported species distributions (Goldstein et al., 1998; Curtis et al., 2001, 2005). Yet, whereas total modelled emission rates at UMBS agreed well with measured rates, modelled values for Harvard were only half as large as the estimate from flux-measurements ($4.2\,g_C m^{-2} a^{-1}$; Goldstein et al., 1998). The reason for this discrepancy remains to be elucidated. Modelled total LAI exceeded actual LAI by approximately 30% (Fig. 5) but modelled gross and net primary productivity were within 10% of reported values (not shown, Waring et al., 1998; Curtis et al., 2001). The latter is, arguably, a more important indicator of the cause of the discrepancy, because of the coupling of isoprene emissions to carbon assimilation. One possible cause for the model-data mismatch could therefore 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 $160\,\mu g_C\ g^{-1}\ h^{-1}$ (Goldstein et al., 1998). For the simulations we initially assumed an average I_s of $100\,\mu g_C\ g^{-1}\ h^{-1}$ to determine ε for the intermediate shade-tolerant PFT (Table 3), and repeating the simulations with an assumed I_s of $160\,\mu g_C\ g^{-1}\ h^{-1} g$ resulted in isoprene emissions of $3.4\,g_C m^{-2} a^{-1}$, which reduced the model-data discrepancy to 20%. These latter calculations draw attention to one notable source of uncertainty in the model calculations: in temperate or boreal ecosystems, where diversity of the dominant species is generally low and where tree growth parameters are relatively well studied, LPJ-GUESS can describe a forest's structure very well (Table 3). Everything else being equal, the emissions calculated for a given PFT will scale directly with I_s, since this value is used to set the value of ε. As the example of *Q. rubra* demonstrates, in such cases the uncertainty in calculated isoprene emissions is dominated by how well one, or a limited number of, species is described in terms of their emission potential. As pointed out elsewhere (Guenther et al., 2006), this uncertainty increases considerably in tropical forests where not only information about the isoprene emission potential is largely lacking, but where a sparsity of information on tree growth and competitive interactions, as well as the extremely high tree species diversity, limits the potential to configure models like LPJ-GUESS to simulate the forest structure, productivity and dynamics in a detailed and realistic way.

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

Figure 7 illustrates the time series of simulated LAI and isoprene production for the 20th century, plotted separately for each plant functional type. These time series provide a vivid illustration of the importance of a correct model representation of canopy 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. Moreover, emissions in the years following a severe disturbance event (e.g. windthrow, harvest) differ markedly compared with the "equilibrium" canopy structure later in succession. Likewise, the rate of "isoprene recovery" following disturbance differs strongly between forests depending on the canopy composition. At Harvard, it took approximately 30 years after an assumed complete and sudden dieback 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 successional stages are strong isoprene emitters (*Populus*), emissions approached pre-disturbance values after only *c*. 10 years. Similar patterns were apparent for 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 CO_2-fertilisation of vegetation productivity due to rising [CO_2]. 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 [CO_2] 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 provide a process-based modelling tool capable of highlighting effects of changing CO_2 concentrations on ecosystem isoprene emission. We therefore repeated the simulations, this time keeping [CO_2] constant at the initial (year 1900) 296 ppm level for the calculation of isoprene production rates (I^{296}), but retaining the observed, annually increasing [CO_2] timeseries for the calculation of GPP and LAI. In other words, κ was kept constant from the beginning of the entire simulation period, which is equivalent to assuming no direct effect of CO_2 on isoprene metabolism. In these simulations, a considerable difference emerged: at the end of the simulation period (1998), canopy I^{296} were approximately 25% higher than I calculated with the "real" scenario. The divergence of simulated isoprene emissions became particularly visible in the second half of the 20th century, reflecting the acceleration in atmospheric CO_2 growth rate and the growing inhibition.

Thus, from a modelling perspective, and taking the early 20th century as reference, our simulations indicate a notable difference between a time series of isoprene emissions that is based on forest physiological activity and climate alone vs. estimates that also take into account the direct CO_2-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 CO_2 concentrations (Lathière et al., 2005; Valdes et al., 2005). By contrast, projections of future isoprene emissions have always pointed to substantial increases (Sanderson et al., 2003; Lathière et al., 2005). These projections combine two postulated mechanisms: enhanced leaf growth and total LAI stimulated mainly by CO_2 fertilisation of GPP, and increasing leaf isoprene emissions due to rising temperatures caused by the CO_2 increase. This picture may have to be revised to take into account the direct CO_2-inhibition of leaf isoprene production.

7 Conclusions

Process-based leaf isoprene models are capable not only of matching the well-known light and temperature responses of emissions, but also of reproducing a CO_2-induced inhibition of emissions. When incorporated into a large-scale vegetation model, the calculated emissions compare well with data from ecosystem-atmosphere flux measurements. When used over a longer time period, encompassing a measurable change of the atmospheric CO_2 concentration, our initial model calculations imply that a CO_2-inhibition of leaf isoprene metabolism may reduce the expected isoprene increase due to CO_2 fertilisation of vegetation productivity. However, we did not consider here the additional effects of climate change on our isoprene calculations that accompany changes in [CO_2], and these climate-CO_2 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., 2006[1])

It should be highlighted that laboratory studies do not agree unanimously on the direction of medium to long-term isoprene-CO_2 interactions. In the absence of a full understanding of the underlying processes, our analysis is best understood as a sensitivity study to quantify a possible isoprene-inhibition by [CO_2], postulating this effect as given until proven otherwise. Controlled experiments with a strong quantitative focus (e.g. experiments with plants that have different levels of isoprene synthase, combined with high-resolution modelling of key metabolic reactions based on Michaelis-Menten kinetics) are required to test and verify current hypotheses on the cellular mechanisms underlying the inhibitory effect of CO_2 on isoprene. These hypotheses evoke extra-chloroplastic regulation, whereas current photosynthesis models, and the Niinemets et al. (1999) isoprene model, are derived from chloroplastic processes alone. Nevertheless, controlled laboratory high-resolution, enzymatic modelling studies could be used to confirm whether the simplified and conceptual, "semi-mechanistic" isoprene-CO_2 response implemented here is sufficiently accurate, as well as to investigate under what conditions the model may fail to be authentic in its response. Moreover, 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 in 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 μmol m^{-2} 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):

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

For isoprene,

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

T (K) is leaf temperature at ambient and T_s (K) at standard conditions, R is the gas constant (J K^{-1} 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 J mol^{-1}, C_{T3}=0.961 and T_m=314 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 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 mathematical 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 (RUBP+CO_2) two molecules of 3-phosphoglycerate (3-PGA) are formed, while oxygenation (RUBP+O_2) yields one molecule of phosphoglycolate and one molecule of 3-PGA. According to early studies on Rubisco, RUBP carboxylation also yields a small amount of pyruvate, perhaps 1% of total sugar phosphates (Andrews and Kane, 1991). Pyruvate is needed for isoprene formation, but the chloroplastic sources of pyruvate have not been clearly identified (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,

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

and

$$W_{\text{isoco}} = \eta F_{PYR} \tag{A2a}$$

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

The parameter η escribes 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 (kJ mol^{-1} K^{-1}) is the entropy change. Equation (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; c.f. Sect. A5). Equation (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).

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 that isoprene production scales with carbon assimilation via Eqs. (A2a) and (A2b) only, but not via Eq. (A2c). This limits the model's applicability for the calculation of emissions from a range of plants with widely varying rates of photosynthesis. V_{isomax} eventually becomes under all environmental conditions either lower or higher than rates calculated from Eqs. (A2a) and (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, 2003; Lehning et al., 2001) employs the dynamic photosynthesis model of Kirschbaum et al. (1998) to predict the pool sizes of precursors, estimating concentrations of intermediate compounds in the isoprene synthesis pathway and maximum capacities and kinetic properties of enzymes at terminal steps of isoprene synthesis.

The model distinguishes three main 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 the photosynthesis model.

Carbon input provided from the dynamic, non-steady state photosynthesis model is passed to a set of differential equations, each describing a step in the succession of major reaction steps along the isoprene synthesis pathway. Each reaction is characterized by its corresponding maximum reaction velocity and Michaelis Menten constants as established from leaf extracts for *Quercus robur* and *Q. petrea* (Lehning et al., 2001; Brüggemann and Schnitzler, 2002). In the coupled mode of the model (seasonal isoprene synthase model–biochemical isoprenoid biosynthesis model, SIM-BIM), budbreak, leaf senescence, and day-to-day changes in 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 the analysis of VOC emissions in the field where 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 the 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 CO_2 concentration), G3P was directly linked to the rate of photosynthesis:

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

while in the second approach, corresponding to a situation when the difference between ambient (C_a) and internal (C_i) CO_2 concentrations is large, G3P was assumed to arise from photorespiratory metabolism:

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

In these equations, α_x and α_2 represent the efficiency of synthesis, i.e. the amount of isoprene (or monoterpene) produced per CO_2 assimilated. They were estimated from measured VOC emissions data from Scots pine branches. Since the specificity of Rubisco 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 the 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 [CO_2] on isoprene synthesis. In the original form of the model, isoprene emission rate is calculated as

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

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 translates the electron flux into isoprene equivalents. $\Gamma*$ 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 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. The model incorporates, in the paramter ε 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 conditions, 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 – most likely as a result of 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 temperatures, the break-down of the 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 on 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 rationale is supported by ecosystem-atmosphere flux observations that showed 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

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

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 of 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 surrogate for the CO_2-dependence of ε thus may be included in Eq. (A4a) in a conceptually equivalent, but mathematically more coherent, way to what has been proposed by Martin et al. (2000, Eq. A2b). Hence, the model is used here in a modified form as

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

where $\xi = \kappa\tau$ with $\kappa = (O_i : C_i^{-1})/(O_i : C_{i-370}^{-1})$, where c_{i-370} is the leaf internal concentration at ambient [CO_2]

and in the absence of water stress. κ and τ are expressed to unity at 30°C and Q=1000 μmol m^{-2} 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). It results in an exponential decrease of κ with CO_2 (Fig. 8) at a rate that is indistinguishable from the empirical isoprene emission-CO_2 relationship seen in data from a range of species grown and measured at CO_2 concentrations between 180 and 1200 μmol mol^{-1} (Possell et al., 2005, their Fig. 5a). This provides support for this semi-mechanistic approach (Fig. 8).

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