

UC Berkeley

UC Berkeley Previously Published Works

Title

A fully integrated isoprenoid emissions model coupling emissions to photosynthetic characteristics

Permalink

<https://escholarship.org/uc/item/4xc4w06p>

Journal

Plant Cell & Environment, 37(8)

ISSN

0140-7791

Authors

GROTE, RÜDIGER

MORFOPOULOS, CATHERINE

NIINEMETS, ÜLO

et al.

Publication Date

2014-08-01

DOI

10.1111/pce.12326

Peer reviewed

Published in final edited form as:

Plant Cell Environ. 2014 August ; 37(8): 1965–1980. doi:10.1111/pce.12326.

A fully integrated isoprenoid emissions model coupling emissions to photosynthetic characteristics

Rüdiger Grote^{1,2}, Catherine Morfopoulos³, Ülo Niinemets⁴, Zhihong Sun⁴, Trevor Keenan⁵, Federica Pacifico⁶, and Tim Butler¹

¹Institute for Advanced Sustainability Studies (IASS), Berliner Str. 130, 14467 Potsdam, Germany

²Karlsruhe Institute for Technology, Institute for Meteorology and Climate Research (IMK-IFU), Kreuzeckbahnstraße 19, 82467 Garmisch-Partenkirchen, Germany

³Department of Life Sciences, Imperial College, Silwood Park, Ascot SL5 7PY, UK

⁴Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 1, Tartu 51014, Estonia,

⁵Department of Biological Sciences, E8C Building Room 270, Macquarie University, Sydney, Australia

⁶University of Exeter College of Engineering, Mathematics and Physical Sciences Harrison, Building, North Park Road Exeter, EX4 4QF, UK

Abstract

Recently, a biogenic isoprene emission model with improved CO₂ dependency was developed for global change applications (Morfopoulos et al., 2013). The model is based on the mechanistic linkage between isoprene emission and the availability of reducing power. Here, we advance the model formulation by introducing an explicit link between the electron transport (supply-constraint) and enzyme activity (capacity-constraint). We furthermore investigate the sensitivity of the model to variations in photosynthetic and emission-specific parameters. By comparing species-specific simulations with experimental data, we demonstrate that differences in photosynthetic characteristics can well explain inter-species differences in emissions. Interestingly, also the seasonal development emissions could be explained to some degree by the change of energy supply from photosynthesis throughout the season. In addition, we show that the principal responses are not limited to isoprene but can be formulated to describe the emission of all light-dependent volatile species. Thus, the model is a good candidate to be implemented in regional and global models that already provide species-specific photosynthesis estimates.

Keywords

Isoprenoid emission; biogenic emission modeling; photosynthetic electron transport; environmental sensitivity; model evaluation

Introduction

Volatile organic compounds (VOCs) constitute an important component of air chemistry at all spatial and temporal scales. They encompass a rather large group of compounds, almost all of which contribute to air chemistry, for example through radical removal or ozone formation. Due to their effect on the concentration of ozone, the lifetime of methane, and the formation of secondary aerosols they also have a considerable indirect impact on climate (Aksoyoglu et al., 2012; Atkinson, 2000; Kulmala et al., 2013; Pike and Young, 2009).

Globally, it is estimated that about 90 % of VOC emission is attributed to vegetation (biogenic VOCs or BVOCs) (Guenther et al., 2012; Piccot et al., 1992). The components and emission pathways are diverse but they are dominated by isoprenoids that are either emitted from specific storage structures or from production sites in the leaf cells. The latter group includes constitutively produced molecules (i.e. products of the methyl-erythritol phosphate (MEP) pathway such as isoprene, monoterpenes, and methyl-butenol) as well as those that are only apparent under stress (i.e. sesquiterpenes and lipoxygenase (LOX) products, but also several stress-induced monoterpenes and homoterpenes (Li and Sharkey, 2013b; Niinemets et al., 2013)). However, some of these apparently induced molecules are likely to be produced at low level also during periods intervening stress events (Niinemets et al., 2013).

The amount of BVOCs emitted under future climate changes is of major concern (Arneth et al., 2010; Fowler et al., 2009; Laothawornkitkul et al., 2009; Park et al., 2013). BVOC emissions not only affect climate but they depend on climate and atmospheric chemistry conditions that are likely to change in the future: 1) BVOC emissions are exponentially linked to temperature over the physiological temperature range although at least isoprene has been found to be negatively correlated to CO₂ concentration (Grote et al., 2013; Li and Sharkey, 2013b). Thus, the impact of climate warming on BVOC emissions is potentially large but rather uncertain (Arneth et al., 2011; Keenan et al., 2009b; Monson et al., 2007); 2) Land-use change is supposed to shift species composition to higher emitters (Hardacre et al., 2013; Niinemets and Monson, 2013; Owen et al., 2013), in particular many plant species used for bioenergy production are known to be high BVOC emitters (Ashworth et al., 2013b; Owen et al., 2013; Porter et al., 2012); 3) Emission control strategies will probably lead to a complex change in air chemical composition that may modify the impact of BVOCs on climate but may also directly affect plant physiology and thus BVOC emissions (Calfapietra et al., 2013; Hogrefe et al., 2011).

Despite the importance of the issue, current models simulating BVOC emission, in particular those BVOCs emitted directly after production (e.g. isoprene), still suffer deficiencies that bring into question their suitability for application in integrated climate-atmosphere models. What are these deficiencies?

One striking issue is that the many environmental controls on BVOCs emission (temperature, light, CO₂, drought, etc.) are assumed to act separately and independently. However, it is well known that light-dependent BVOC emissions are closely connected to photosynthesis (Grote et al., 2013; Grote and Niinemets, 2008; Monson et al., 2012;

Niinemets et al., 2002a; Niinemets et al., 1999), and an interdependency between CO₂ and light control (Sun et al., 2012), as well as CO₂ and temperature control (Rasulov et al., 2010; Sun et al., 2013) has been demonstrated. Thus it is apparent that BVOC emissions reflect to some degree environmental responses of the photosynthesis apparatus in addition to specific properties of the biochemical pathway involved, i.e. the MEP pathway (Li and Sharkey, 2013a; Li and Sharkey, 2013b; Magel et al., 2006; Rasulov et al., 2009; Velikova et al., 2011). Importantly, the relation between those two controls may change with changing environmental conditions, requiring the inclusion of an explicit mechanistic description of both process chains in BVOCs models.

Some models provide such an explicit description (Martin et al., 2000; Niinemets et al., 2002b; Niinemets et al., 1999; Zimmer et al., 2000). However, in coupled climate/chemistry simulations, BVOC emissions are mostly calculated with empirical relations linking emissions to a multitude of environmental conditions, but are independent of photosynthetic performance (Ashworth et al., 2013a; Guenther, 2013; Guenther et al., 2012; Kulmala et al., 2013; Poupkou et al., 2010; Simpson et al., 2012). There are two exceptions known to the authors (Pacifico et al., 2012; Unger et al., 2013) that use a modified version of the Niinemets model (Niinemets et al., 1999) linking isoprene emissions to photosynthesis by energy supply but nevertheless applying additional empirical functions, i.e. to account for CO₂, drought, and seasonal variation. Using such modifiers, however, may cause responses inconsistent with those of photosynthesis, in particular under unprecedented combinations of environmental conditions.

Given these important limitations, we argue that a generally applicable combined photosynthesis – emission model that consistently responds to various environmental conditions without the use of additional empirical response functions is needed. An outline for this approach has already been proposed (Harrison et al., 2013) and a model that calculates isoprene emissions based on a consistent linkage between photosynthesis and emission has been developed (Morfopoulos et al., 2013). Here, we advance this model in order to incorporate it into large-scale coupled climate / chemistry models, providing the first mechanistic isoprene emission model for global application based on the photosynthetic dependency of emissions.

Model Description

The model of Morfopoulos et al. (2013) is based on energy-limited photosynthesis and energetic status. It particularly considers the available energy for secondary metabolism processes, i.e. the difference between the amount of energy that is provided by photosystem II (the protein complex in leaves that captures photons of light to provide the chemical energy needed for further synthesis) and that is used for carbon fixation. This information is provided by Farquhar-type photosynthesis models (Farquhar et al., 1980) although not all variants calculate all the necessary components explicitly. Here we use the simplified photosynthesis model of Collatz et al. (Collatz et al., 1991; Collatz et al., 1992) that is described in the appendix and is widely used in dynamic global vegetation models, for example in CLM (Dai et al., 2004), JULES (Clark et al., 2011), BETHY (also JSBACH) (Knorr and Heimann, 2001) and CTEM (Arora, 2003).

This model differs from the one suggested in Morfopoulos et al. (2013) in the way it considers the fraction of electron engaged in the MEP pathway due to photosynthesis (γ_{ph}) and enzyme activity (γ_{en}) which are calculated separately from the electron transport rate and temperature responses. These parameters are further normalized to standard conditions (of 30 °C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ photosynthetically active quantum flux density) to be scaled with the standard emission factor (emission under standard conditions) available for many species and plant functional types. The model can be formally stated as:

$$\text{emission} = \text{RER} \times EF \quad (\text{Eq. 1a})$$

$$\text{RER} = \gamma_{ph} / \gamma_{ph_norm} \times \gamma_{en} / \gamma_{en_norm} \quad (\text{Eq. 1b})$$

γ_{ph_norm}	photosynthetic emission potential normalized to standard conditions
γ_{en_norm}	enzymatic emission potential normalized to standard conditions
EF	emission under standard conditions (30 °C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ light, 365 ppm CO_2 air concentration) ($\mu\text{g g}^{-1} \text{DW h}^{-1}$)
RER	relative emission response (-)

$$\gamma_{ph} = [c_1 + c_2 \times \max(-\Delta J_{MAX}, J - J_v)] \times J \times \min(1, C_i / \Gamma^*) \quad (\text{Eq. 2})$$

J	electron transport rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
J_v	electron flux required to support Rubisco-limited carbon assimilation ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
C_i	intracellular CO_2 (Pa) (see Equation A1 for derivation)
Γ^*	CO_2 compensation point (Pa)
$\Delta J_{MAX} = 30$	maximum amount of electrons that can be supplied from other sources ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
$c_1 = 0.1765$	share of energy used from excess electron transport (nmol isoprene $\mu\text{mol electron}^{-1}$)
$c_2 = 0.0028$	basic fraction of energy supply from photosynthesis (nmol isoprene $\mu\text{mol electron}^{-12}$)

$$\gamma_{en} = \exp(c_0 - \Delta H_{a_en} / (R_G * tc)) / (1 + \exp((\Delta S_{en} * tc - \Delta H_{d_en}) / (R_G * tc))) \quad (\text{Eq. 3})$$

T_c	temperature at the leaf surface (K)
$c_0 = 32.86$	scaling constant (J mol^{-1})
$\Delta H_{a_en} = 83129$	activation energy of emission enzyme (J mol^{-1})
$\Delta H_{d_en} = 284600$	deactivation energy of emission enzyme (J mol^{-1})
$\Delta S_{en} = 887.5$	entropy term of emission enzyme ($\text{J mol}^{-1} \text{K}^{-1}$)
$R_G = 8.314$	($\text{J mol}^{-1} \text{K}^{-1}$)

Parameters c_0 , ΔH_{a_en} , ΔH_{d_en} , and ΔS_{en} are taken from Niinemets et al. (1999). The values for c_1 and c_2 were determined from observations of isoprene emission and photosynthesis of *Populus tremula* x *tremuloides* saplings (Sun et al., 2012). These data were used to:

- 1) evaluate the photosynthesis model with the species-specific parameters (see Table 2) except K_{C25} , and K_{O25} which were measured directly and V_{cmax25} which is estimated

iteratively to approach a simulation/ measurement relationship of 1 for the rubisco limited photosynthesis capacity A_C (see appendix). The resulting relationship between measured and simulated photosynthesis using the Collatz model is shown in Figure 1A;

2) derive emission model parameters from the relation between $J-J_v$ and emission/ J . The variables J and J_v have been calculated using the photosynthesis model described in the appendix with given environmental conditions as well as measured internal CO_2 concentration (C_i) and isoprene emission. The latter relationship gives the share of energy used from excess electron transport (parameter c_2 , slope in Figure 1B) as well as the basic energy supply (parameter c_1 , Y-axis interception in Figure 1B). Due to its dependency on J and J_v we refer to the new model JJv emission model.

More information about the measurements is available in Sun et al. (2012). It should be noted that the regression between emission and $[J-J_v]$ depend on the photosynthetic parameters and model formulation to derive J (including the formulation of J_{MAX} and the parameters E_{aJ} , θ , ΔH_D and ΔS_D).

The sensitivity of the simulated emission to environmental variables is shown in Figure 2. Note that the indication of the ‘original’ Niinemets differs from the formulation in Niinemets et al. (1999) in neglecting the C_i depending term that leads to a continuous rise of emission with increasing CO_2 concentration (Morfopoulos et al., 2013).

Additionally, we assumed that drought stress reduces the saturated rate of carboxylation (V_{cmax}) according to literature (Flexas and Medrano, 2002; Niinemets and Keenan, 2013; StPaul et al., 2012). This is important as V_{cmax} is an intermediate variable calculated to estimate energetic status (see appendix, Equation A9) and energy usage by photosynthesis (Equation B4). As a result of this drought stress dependent decrease in V_{cmax} , the light-dependent emission rate also declines under severe drought stress. A possible implementation of this mechanism has been proposed by (Keenan et al., 2009c; Keenan et al., 2010). This formulation (Equation 4) has been used for the current investigation of emission model sensitivity to environmental conditions. We note that the drought impact on V_{cmax} intentionally includes a parallel reduction of J_{max} (Equation B1), which has been reported on Mediterranean drought adapted species (Limousin et al., 2010; Vaz et al., 2010). However, since these two parameters may not always decrease in parallel, we introduced a specific parameterization for each process. We have also considered that drought affects stomatal conductivity and thus C_i according to the dependence of stomatal conductance on net assimilation rate, leading to an iterative loop between stomatal conductance, net assimilation rate and C_i (Ball et al., 1987). However, the effect of this process on the energy production is minor and is not discussed further. In addition, there may be a further reduction in photosynthesis due to photoinhibition (Werner et al., 2001) that is not considered.

$$V_{cmax'} = V_{cmax} \times \min(1.0, rswc/R_L) \wedge E_{QV} \quad (\text{Eq. 4a})$$

$$J_{max'} = J_{max} \times \min(1.0, rswc/R_L) \wedge E_{QJ} \quad (\text{Eq. 4b})$$

V_{CMAX}' and J_{MAX}'	altered V_{cmax} and J_{max} under water stress conditions
R_{swc}	relative available soil water holding capacity (–)
$R_L = 0.6$	limit value of relative soil water content below which V_{CMAX} is affected (–), average of the range indicated by (Keenan et al., 2009a)
$E_{\text{QV}} = 0.4$	parameter to account for non-linear decline of V_{CMAX} with drought increase, average of the range indicated by (Keenan et al., 2009a)
$E_{\text{QJ}} = \leq 0.4$	parameter to account for non-linear decline of J_{MAX} with drought increase

Simulations

Model sensitivity to photosynthesis parameters

The proposed emission model is directly derived from foliage photosynthetic characteristics, and therefore, we expect the variations in the emission rate to reflect variations in photosynthetic parameters. Overall 13 parameters are used in the photosynthesis model and all of these are potentially species-dependent (Table 1, for equations see appendix). In many cases, only few investigations have determined these parameters experimentally, implying that the actual uncertainty range cannot be currently determined. However, the sensitivity of the electron transport chain – and thus BVOC emission – to variations of these parameters can be assessed by varying them across the observed range.

We analyzed simulated emissions under a range of values for 10 of these parameters with ranges defined by literature values (see Table 1). The remaining parameters (three Q10 dependencies of carboxylation, oxygenation and electron transport on temperature) are specific for the Collatz-model and assumed to be fixed. The analysis revealed that the most influential parameters on temperature, light and CO_2 sensitivity of emission are: Rubisco activity at 25 °C ($V_{\text{cmax}25}$) and the ratio between deactivation energy (ΔH_D), and entropy (ΔS) (Fig. 3). In addition temperature, light and CO_2 responses were also sensitive to activation energy (E_{aJ}), to the curvature parameter used to define the light dependency of electron production θ , and to the ratio between the potential rate of electron transport $J_{\text{max}25}$ and $V_{\text{cmax}25}$ at standard temperature (Q_{JV}) respectively.

It should be noted that the parameters affect the shape of the response curves in different ways. While the magnitude of the temperature response is determined by $V_{\text{cmax}25}$ and E_{aJ} , optimum temperature shifts with $\Delta H_D/\Delta S$. The slope of the light response curve is affected by all the parameters mentioned above, but the start of emissions based on electron excess – which is apparent by the onset of a steeper slope – particularly depends on $V_{\text{cmax}25}$. Regarding the CO_2 response of emission, all parameters affect the steepness of the decline although in different directions. For example a small $V_{\text{cmax}25}$ might be counterbalanced by a high $J_{\text{max}25}$.

Model sensitivity to emission parameters

The current parameterization of the parameters c_1 and c_2 is based on one dataset. As we cannot say how general or species-specific these parameters actually are, it is necessary to explore the sensitivity of the emission model to variations in these parameters. It should be noted that in Equation 1, the parameters c_1 and c_2 are used in fixed relation to each other, as:

$$\frac{\{[c_1 + c_2 \times (J - J_v)] \times J\}}{\{[1 + rc \times (J - J_v)] \times J\}} / \frac{\{[c_1 + c_2 (J_{30} - J_{v30})] \times J_{30}\}}{\{[1 + rc (J_{30} - J_{v30})] \times J_{30}\}} \quad (\text{Eq.5})$$

$$rc = c_2/c_1$$

J_{30} electron transport rate for standard conditions ($\mu\text{mol m}^{-2} \text{s}^{-1}$)

J_{v30} fraction of J_j used for photosynthesis for standard conditions ($\mu\text{mol m}^{-2} \text{s}^{-1}$)

Thus, we test the sensitivity of the model to this relation, rather than varying the absolute values.

From the very few datasets available in the literature, we analyzed a preliminary dataset from Morfopoulos et al. (submitted) examining emissions from *Populus nigra* seedlings and other from *Acacia nigrescens* (Possell and Hewitt, 2009). This resulted in c_2 ranging between 0.000004 and 0.003 and c_1 ranging between 0.003 and 0.18. Thus, values of rc ranging between 0.001 and approximately 0.02 were included in the sensitivity analysis.

Within the range of values tested, responses to light and temperature are not very sensitive to the selected parameters (Fig. 4). However, a wider range between the two parameters delays the light response of emissions similarly to high $V_{\text{cmax}25}$ values, but retains the steep slope of the response. This indicates that a wider range than that tested should not be selected. In contrast, the response to increased atmospheric CO_2 concentration is quite sensitive to the shift in parameters, making it a suitable candidate for fine-tuning CO_2 responses when coordinated measurements of photosynthesis and emission are missing.

Model evaluation

Species specific emission responses

We evaluated the model using isoprene emission data from various sources collected by (Pacífico et al., 2009) for the tree species *Eucalyptus globulus* (eucalypt), *Liquidambar styraciflua* (sweetgum), *Populus tremula* x *P. tremuloides* (hybrid aspen), *Quercus rubra* (red oak) and *Q. robur* (pedunculate oak). Simulations are performed using specific photosynthesis parameters for each of these species with parameter values collected from the literature (Table 2). Note that specific photosynthetic parameters for each individual study as reported in Pacífico et al. (2009) were not available.

In Figure 5, species-specific environmental dependencies are presented together with measurement data of four tree species. Despite the large intra-species variation in the observations, which come from different sources, some basic differences between the species could clearly be explained by photosynthetic characteristics. The higher $V_{\text{cmax}25}$ of sweetgum for example results in a steeper temperature response while its slightly higher temperature optimum can be attributed to its higher $\Delta H_D/\Delta S_D$ relation compared to other species. The relatively small $V_{\text{cmax}25}$ and high θ assumed for poplar is the reason for its higher emission sensitivity to radiation. A steeper decline of emission with increased CO_2 as observed in eucalypt and oak can be traced back to their higher $V_{\text{cmax}25}$ and smaller Q_{JV} parameters.

Emission in different parts of the canopy

In order to investigate how leaf properties that change within the canopy profile affect the light dependent emission rate, we have additionally simulated photosynthesis and emission for the species *Quercus ilex* (holm oak) with two separate parameterizations for sun- and shade leaves. Therefore, we modified the standard parameters first (Table 1) to meet the general photosynthesis response as demonstrated in (Staudt et al., 2003). We used the lower end of values indicated in Table 1 for E_{aJ} , ΔH_D and ΔS_D and then sun and shade values for the parameters V_{cmax25} (sun: 90, shade: 60) and θ (sun: 0.5, shade: 0.7), which are known to vary with canopy depth (Niinemets et al., 2010b).

The comparison of measurements and simulation in Figure 6 shows that despite some deficiencies of the Farquhar/ Collatz model to capture the differences in photosynthetic temperature response for sun leaves (bottom left), the emission responses to temperature and light under sun- and shade conditions are quite well reflected (top panels). Again, the higher V_{cmax25} in sun leaves results in the shift to higher temperature optimum of emissions while the larger light curvature parameter θ in shade leaves is the reason for the steeper light response.

Seasonal emission changes

In addition to the immediate emission responses, the JJv model implicitly also accounts for seasonal dynamics because the amount of energy available for emissions depends on radiation and temperature and thus varies during the year. To demonstrate this, we have calculated monoterpene emissions using the sun-leaf parameters for Holm oak (see previous paragraph) and a constant scaling factor. The weather input is that of the year 2006 on an hourly basis from the EuroFlux eddy-covariance station at Puechabon, South France (Figure 7). At this site, the soil water supply gets very limited in summer. The simulation was run with (natural drought) and without (well watered) considering water limitation as calculated with a soil model specifically developed for this same site (Rambal, 1993). The simulations for the year 2006 have been evaluated with measurements. They decrease to 20 % of maximum soil water storage during summer (Grote et al., 2009). The drought impact on emission was calculated with Eq. 4 using an E_{QV} value of 0.7 for both V_{CMAX} and J_{MAX} modifications.

We compared the outcome with previous estimates of emission dynamics at the site in order to show the potential impact of seasonality and soil drought (Grote et al., 2009). These simulations were done with the SIM-BIM model for monoterpenes emissions which calculates seasonality dynamics considering synthesis and degradation of emission enzymes (Grote et al., 2006). Since it has been evaluated at the site we consider the simulation results of this model as standard here.

Figure 7 demonstrates that the seasonality of emissions is generally well met and the drought impact can be reflected by the proposed impact on photosynthesis. This is due to the cumulative response of electron transport rate (J) increasing in summer due to higher radiation and the immediate temperature response of enzyme activity. Nevertheless, the SIM-BIM model results are still somewhat higher than those obtained by the JJv model

during very warm summer conditions. Under realistic drought conditions, the differences between the two models became negligible.

Discussion

General responses

We presented a modification of a previously suggested emission model that is explicitly linked to photosynthesis by energy supply with a specific emphasis on excess energy. The new model formulation is limited by either the photosynthetic energy supply or by the enzymatic processing capacity. With the enzymatic temperature dependence empirically set, the temperature optimum of the whole emission response is well within the range of observations. The limitation by energy supply ensures a light-limited response under low-light condition and a saturation of emission levels under higher radiation regimes similar to the original Niinemets model (Niinemets et al., 1999). In addition, the newly introduced consideration of electron excess calculated from the supply rate by photosynthesis system II and the energy requirement of carbon assimilation in the Calvin cycle leads to a decreasing emission with increasing carbon assimilation relative to energy supply. Therefore, increasing CO₂ concentration leads to decreasing emission rates as has been frequently observed.

This way, environmental differences that affect photosynthesis also affect emissions in a consistent manner. For example, shade leaves have been shown to have smaller emission capacities than sun leaves which can be seen as a direct result of the photosynthetic adaptation (i.e. smaller V_{cmax25}). Our test with a dataset of (Staudt et al., 2003) indicated that this is the case and that further specification of emission parameters may not be necessary. This is particularly remarkable since this also shows that light-dependent emissions might be treated similarly, independent of the emitted chemical species (i.e. isoprene or monoterpenes).

Similarly, insufficient nutrient or water supply has been shown to affect photosynthesis as well as BVOC emission. However, the relationships are not easily determined. Fertilization and nitrogen supply state has mostly been reported as positively correlated with emission (Funk et al., 2006; Lerdau et al., 1997; Litvak et al., 1996) but also negative impacts have been observed (Ormeno et al., 2007; Van Wassenhove et al., 1990). This might be explained by the positive response of V_{cmax25} to nitrogen, leading to a higher electron supply (positive impact on emission) as well as to a higher electron consumption rate (negative impact on emission). The net impact on emission thus may depend on other species-specific or environmental boundary conditions.

A seasonal development of photosynthesis in the temperature regions is generally connected to the increase and decrease of radiation that determines the electron transport rate. Using this as a major determinant for isoprenoid emissions thus provides a mediating factor that is similar to the shape of empirical curves used to describe emissions empirically (Monson et al., 2012). This mechanism principally offers the possibility of a regionally adapted seasonal emission modification without the need of an additional empirical mechanism. However, it has to be shown, if this mechanism is generally capable to account for the full seasonal

effect. Comparison with other simulations presented here indicate that internal seasonality of enzyme capacity may still be important to consider.

Drought impacts have been observed to increase emission at least for mild drought conditions (Llusia et al., 2010; Šimpraga et al., 2011) and decrease them under more severe conditions (Grote et al., 2009; Wang et al., 2003). The decrease can be described considering a direct drought impact on V_{cmax25} and J_{max25} (Keenan et al., 2010), assuming that both are reduced in parallel. However, if on V_{cMAX} and J_{MAX} are differently affected (in other words Q_{JV} changes with drought) the JJv model offers an explanation for an emission increase with a temporarily increased electron supply. This may happen in the case where V_{cMAX} is temporarily more affected than J_{MAX} so that assimilation is reduced to higher degree than electron transport, leading to higher ‘excess’ energy in the plant cell (Figure 8).

Parameter sensitivity

We have shown that species-specific differences in emission response pattern are explained to a large degree by considering species-specific parameterization of photosynthesis. Particularly, a difference in V_{cmax25} , which is a parameter available for many species and is generally defined in most land-use models, directly influences the shape of the emission response curve for different light and CO₂ conditions. In addition, a species-specific set up of E_{aJ} , ΔH_D , ΔS , and θ – parameters that are often fixed for many if not all species or plant functional types – might have to be considered as species-specific. The suggested mechanism also emphasizes the need to investigate emission and photosynthesis together in order to test the hypothesis that both processes are linked together.

Besides a rigorous test of the linkage between photosynthesis and emission, we hope that the presented model assumptions are spurring research on the allocation of energy within the plant cell – and that this research can lead to further model improvements. The most urgent question in this respect is the generality of the c_1 , c_2 , and ΔJ_{MAX} parameters. From the investigation of another data set from *Populus nigra* (Morfopoulos et al., submitted) we have derived similar parameters but the species is also a similarly high isoprene emitter. In contrast, the parameters c_1 and c_2 were much lower for the low emitting species *Acacia nigrescens* (Possell and Hewitt, 2011). This may imply that mean that the parameters are linked to the emission capacity or to other species traits such as evergreen vs. deciduous. We have also to admit that the share of electron supply for emission is not described fully mechanistically but is directly derived from the data we used. From a physiological perspective the proposed mechanism might reflect the changes in the share of the pathway control between DMADP pool size and isoprene synthase activity, although evidence suggests that this is mainly a DMADP pool-size effect for CO₂ (Rasulov et al., 2010; Rasulov et al., 2011; Rasulov et al., 2009; Sun et al., 2012). From a modeling perspective, it would be more desirable to have a continuous decrease of electron supply when the J-Jv balance gets negative rather than a fixed threshold value. In this way, abrupt changes in the response pattern (i.e. light and CO₂ responses) could be avoided. However, current data do not support any further assumptions.

Outlook

Further developments and test are needed to assess the extent to which the model is effective for spatial and temporal upscaling. Depending on within-canopy responses and the response of whole leaf area growth to elevated $[\text{CO}_2]$ whole-canopy response can significantly differ from single leaf responses (Sun et al., 2013). Applying the model results to the canopy scale requires evaluating whether the “canopy-response” function of isoprene emission can be reproduced (Grote et al., 2013; Niinemets et al., 2010a). Despite a certain degree of inherent seasonality that is linked to the difference in temperature and radiation development, additional consideration of seasonal enzymatic changes will be needed and possible seasonal adjustments of specific time periods such as flowering or senescence (Baghi et al., 2012), as well as induced emissions for example by air pollution (Vitale et al., 2008), are not at all covered. However, having established a physiological linkage between photosynthesis and emission paves the path for further development to implement a possible feedback loop that accounts for air pollution (i.e. ozone) damage and detoxification (Possell and Loreto, 2013; Rasulov et al., 2010).

With this outlook, the JJv model contributes to the discussion about the cause or function of (light dependent) BVOC emissions. It offers an explanation of how the intensively disputed emergency-valve theory (Owen and Peñuelas, 2005), which notes that excess energy is directed to the production of BVOCs, could be linked to evolutionary theories that state BVOCs are produced to detoxify dangerous reactive oxygen species formed under high light and temperature conditions.

Conclusion

We argue that emission models that are expected to explore future conditions need to consider both the adaptation of isoprene emission capacity to elevated atmospheric $[\text{CO}_2]$ and the modification in precursor availability (Sun et al., 2012). It is further important to account for the decrease in $[\text{CO}_2]$ -sensitivity of isoprene emission at higher temperatures (Li and Sharkey, 2013b; Rasulov et al., 2010; Sun et al., 2013). In this regards, the model applied here provides a very useful basis for linking emissions to photosynthesis that already considers the interactive influences of environmental drivers. However, the sensitivity of isoprene emissions to environmental drivers outside of “typical” range requires further exploration. Especially challenging would be to gain insight into isoprene emission responses under heat stress. Under these conditions, the electron transport rate collapses (Hüve et al., 2011), but isoprene is emitted at a high rate, at least over a short term of a few minutes (Niinemets et al., 2010b; Singsaas et al., 1999; Singsaas and Sharkey, 1998; Sun et al., 2013). It is also important to note that heat stress responses of isoprene emission can be considerably altered by acclimation to elevated growth $[\text{CO}_2]$ (Sun et al., 2013).

We suggest implementing the presented model into the land-surface models of regional and global models. As our preliminary analysis implies, this could be done on the basis of the implemented photosynthesis models without the need of additional parameters except emission scaling factors that are already used for specific vegetation types. The advantages would be that photosynthesis and emission would be consistently computed and that environmental responses would no longer depend on a multitude of empirical adjustments. It

can also be expected that emission responses would automatically benefit from a more pronounced differentiation of plant functional types. As BVOC emission capacity can vary more than an order of magnitude within a canopy, i.e. even more than the capacity of photosynthesis (Niinemets et al., 2010b) separate consideration of this variation might be warranted (Grote et al., 2013; Niinemets et al., 2010b). The introduction into Earth System Models of this new, mechanistic approach for the calculation of BVOC emissions can be expected to lead to more realistic simulations of the response of BVOC emissions to changing conditions of temperature, CO₂ concentration, and other environmental stresses expected under multiple future scenarios, and thus to a better representation of Earth System feedback processes involving these emissions.

Acknowledgements

The research has been supported by the Estonian Ministry of Science and Education (institutional grant IUT-8-3), the Estonian Science Foundation (grant 9253), and the European Commission through the European Regional Fund (the Center of Excellence in Environmental Adaptation) and through the Seventh Framework Programme grant 238366 and European Research Council (advanced grant 322603, SIP-VOL+).

Appendix

A) Collatz et al. 1991 photosynthesis model (as implemented in the land-use model CLM, (Oleson et al., 2010), for all species-specific parameter values see Tables 1 and 2

$$C_i = c_{o2} \times 0.7 \quad (\text{Eq. A1})$$

$$I_C = par \times a_L \quad (\text{Eq. A2})$$

$$K_C = K_{C25} \times Q_{10_{KC}}^{((tc - T_{25})/10)} \quad (\text{Eq. A3})$$

$$K_O = K_{O25} \times Q_{10_{KO}}^{((tc - T_{25})/10)} \quad (\text{Eq. A4})$$

$$R_D = 0.015 \times V_{C_{MAX}} \times Q_{10_R}^{((tc - T_{25})/10)} / (1 + \exp(1.3 \times (tc - 308.15))) \quad (\text{Eq. A5})$$

$$f_t = 1 / (1 + \exp((- \Delta H_D + \Delta S_D \times tc) / (R_G \times tc))) \quad (\text{Eq. A6})$$

$$V_{C_{MAX}} = V_{c_{max25}} \times Q_{10_{VC}}^{((tc - T_{25})/10)} \times f_t \quad (\text{Eq. A7})$$

$$\Gamma^* = 0.5 \times K_C \times o_2 \times 0.21 / K_O \quad (\text{Eq. A8})$$

$$A_C = V_{C_{MAX}} \times (C_i - \Gamma^*) / (C_i + K_C \times (1 + o_2 / K_O)) \quad (\text{Eq. A9})$$

$$A_E = I_C \times \alpha \times (C_i - \Gamma^*) / (C_i + 2 \times \Gamma^*) \quad (\text{Eq. A10})$$

$$A_S = 0.5 \times V_{\text{CMAX}} \quad (\text{Eq. A11})$$

$$A_N = \min(A_C, A_E, A_S) - R_D \quad (\text{Eq. A12})$$

t_c = temperature at the leaf surface (K)

par = photosynthetic active radiation ($\mu\text{mol m}^{-2} \text{s}^{-1}$)

co_2 = carbon dioxide concentration ($\mu\text{mol mol}^{-1}$)

o_2 = oxygen concentration (mmol mol^{-1})

aL = radiation absorbance efficiency (see Tab.1)

α = quantum efficiency of photosystems (see Tab.1)

$Q10_{KC} = 2.1$	Q10 factor for Rubisco carboxylation reaction (-)
$Q10_{KO} = 1.2$	Q10 factor for Rubisco oxygenation reaction (-)
$Q10_{KC} = 2.4$	Q10 factor for electron transport response (-)
$Q10_R = 2.0$	Q10 factor for photorespiration response (-)
$T_{25} = 298.15$	standard reference temperature (K)
$R_G = 8.314$	general gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
C_i	intracellular CO_2 ($\mu\text{mol mol}^{-1}$)
I_C	absorbed photosynthetic active radiation ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
K_C	Michaelis-Menten constant for carboxylation ($\mu\text{mol mol}^{-1} \text{pbar}^{-1}$)
K_O	Michaelis-Menten constant for oxygenation ($\text{mmol mol}^{-1} \text{pbar}^{-1}$)
F_t	temperature modification term (-)
V_{CMAX}	Rubisco capacity ($\mu\text{mol mg}^{-1} \text{min}^{-1}$)
Γ^*	CO_2 compensation point ($\mu\text{mol mol}^{-1}$)
R_D	photorespiration ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
A_C	Rubisco limited photosynthesis capacity ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
A_E	Rubisco limited photosynthesis capacity ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
A_S	export limited photosynthesis capacity ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
A_N	net photosynthesis ($\mu\text{mol m}^{-2} \text{s}^{-1}$)

B) Electron transport and energy usage by photosynthesis (after von von Caemmerer et al. (2009) and Morfopolous et al. (2013))

$$J_{\text{MAX}} = Q_{JV} \times V_{\text{CMAX}25} \times f_t \times \exp(E_{aJ} + (t_c - T_{25}) / (R_G \times T_{25} \times t_c)) \quad (\text{Eq. B1})$$

$$J = \max \left(0, \left(I_C + J_{\text{MAX}} - ((I_C + J_{\text{MAX}}) \times (I_C + J_{\text{MAX}}) - 4.0 \times \theta \times I_C \times J_{\text{MAX}})^{-0.5} \right) / (2.0 \times \theta) \right) \quad (\text{Eq. B2})$$

$$K_M = K_C \times (1.0 + C_i / K_O) \quad (\text{Eq. B3})$$

$$J_V = 4.0 \times V_{\text{C}_{\text{MAX}}} \times (C_i + 2.0 \times \Gamma^*) / (C_i + K_M) \quad (\text{Eq. B4})$$

J_{MAX}	maximum electron transport rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
J	electron transport rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
J_V	fraction of J used for photosynthesis ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
K_M	Michaelis-Menten coefficient

References

- Aksoyoglu S, Keller J, Oderbolz DC, Barmpadimos I, Prévôt ASH, Baltensperger U. Sensitivity of ozone and aerosols to precursor emissions in Europe. *International Journal of Environment and Pollution*. 2012; 50(1):451–459.
- Arneth A, Harrison SP, Zaehle S, Tsigaridis K, Menon S, Bartlein PJ, Feichter J, Korhola A, Kulmala M, O'Donnell D, Schurgers G, Sorvari S, Vesala T. Terrestrial biogeochemical feedbacks in the climate system. *Nature Geosci*. 2010; 3(8):525–532.
- Arneth A, Schurgers G, Lathiere J, Duhl T, Beerling DJ, Hewitt CN, Martin M, Guenther A. Global terrestrial isoprene emission models: sensitivity to variability in climate and vegetation. *Atmos.Chem.Phys*. 2011; 11(15):8037–8052.
- Arora VK. Simulating energy and carbon fluxes over winter wheat using coupled land surface and terrestrial ecosystem models. *Agricultural and Forest Meteorology*. 2003; 118(1-2):21–47.
- Ashworth, K.; Boissard, C.; Folberth, G.; Lathière, J.; Schurgers, G. Global Modelling of Volatile Organic Compound Emissions. In: Niinemets, Ü.; Monson, RK., editors. *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*. Springer; Netherlands: 2013a. p. 451–487.
- Ashworth K, Wild O, Hewitt CN. Impacts of biofuel cultivation on mortality and crop yields. *Nature Clim.Change*. 2013b; 3(5):492–496.
- Atkinson R. Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment*. 2000; 34(12): 2063–2101.
- Baghi R, Helmig D, Guenther A, Duhl T, Daly R. Contribution of flowering trees to urban atmospheric biogenic volatile organic compound emissions. *Biogeosciences*. 2012; 9:3777–3785.
- Ball, JT.; Woodrow, IE.; Berry, JA. A model predicting stomatal conductance and its contribution to the control of photosynthesis under different environmental conditions. In: Biggins, J., editor. *In Progress in photosynthesis research*. Martinus-Nijhoff Publishers; Dordrecht, The Netherlands: 1987. p. 221–224.
- Calfapietra C, Fares S, Manes F, Morani A, Sgrigna G, Loreto F. Role of Biogenic Volatile Organic Compounds (BVOC) emitted by urban trees on ozone concentration in cities: A review. *Environmental Pollution*. 2013; 183:71–80. [PubMed: 23597803]
- Clark DB, Mercado LM, Sitch S, Jones CD, Gedney N, Best MJ, Pryor M, Rooney GG, Essery RLH, Blyth E, Boucher O, Harding RJ, Huntingford C, Cox PM. The Joint UK Land Environment Simulator (JULES), model description – Part 2: Carbon fluxes and vegetation dynamics. *Geosci.Model Dev*. 2011; 4:701–722.
- Collatz GJ, Ball JT, Grivet C, Berry JA. Physiological and environmental regulation of stomatal conductance, photosynthesis and transpiration: a model that includes a laminar boundary layer. *Agricultural and Forest Meteorology*. 1991; 54(2-4):107–136.
- Collatz GJ, Ribas-Carbo M, Berry JA. Coupled photosynthesis-stomatal conductance model for leaves of C4 plants. *Australian Journal of Plant Physiology*. 1992; 19:519–538.

- Dai Y, Dickinson RE, Wang YP. A Two-Big-Leaf Model for Canopy Temperature, Photosynthesis, and Stomatal Conductance. *Journal of Climate*. 2004; 17(12):2281–2299.
- DeLucia EH, Thomas RB. Photosynthetic responses to CO₂ enrichment of four hardwood species in a forest understory. *Oecologia*. 2000; 122:11–19.
- Eichelmann H, Oja V, Rasulov B, Padu E, Bichele I, Pettai H, Mölst T, Kasparova I, Vapaavuori E, Laisk A. Photosynthetic parameters of birch (*Betula pendula* Roth) leaves growing in normal and in CO₂- and O₃-enriched atmospheres. *Plant, Cell & Environment*. 2004; 27(4):479–495.
- Evans JR. Photosynthesis and nitrogen relationships in leaves of C3 plants. *Oecologia*. 1989; 78(1):9–19.
- Farquhar GD, Von Caemmerer S, Berry JA. A biochemical model of photosynthetic CO₂ assimilation in leaves of C₃ species. *Planta*. 1980; 149:78–90. [PubMed: 24306196]
- Flexas J, Medrano H. Drought-inhibition of photosynthesis in C3 plants: stomatal and non-stomatal limitations revisited. *Annals of Botany*. 2002; 89:183–189. [PubMed: 12099349]
- Fowler D, Pilegaard K, Sutton MA, Ambus P, Raivonen M, Duyzer J, Simpson D, Fagerli H, Fuzzi S, Schjoerring JK, Granier C, Neftel A, Isaksen ISA, Laj P, Maione M, Monks PS, Burkhardt J, Daemmgen U, Neirynek J, Personne E, Wichink-Kruit R, Butterbach-Bahl K, Flechard C, Tuovinen JP, Coyle M, Gerosa G, Loubet B, Altimir N, Gruenhage L, Ammann C, Cieslik S, Paoletti E, Mikkelsen TN, Ro-Poulsen H, Cellier P, Cape JN, Horvath L, Loreto F, Niinemets Ü, Palmer PI, Rinne J, Misztal P, Nemitz E, Nilsson D, Pryor S, Gallagher MW, Vesala T, Skiba U, Brüggemann N, Zechmeister-Boltenstern S, Williams J, O'Dowd C, Facchini MC, De Leeuw G, Flossman A, Chamerliac N, Erismann JW. Atmospheric composition change: Ecosystems-Atmosphere interactions. *Atmospheric Environment*. 2009; 43(33):5193–5267.
- Funk JL, Giardina CP, Knohl A, Lerdau MT. Influence of nutrient availability, stand age, and canopy structure on isoprene flux in a *Eucalyptus saligna* experimental forest. *Journal of Geophysical Research*. 2006; 111(G02012) doi:10.1029/2005JG000085.
- Garcia-Quijano J, Deckmyn G, Ceulemans R, van Orshoven J, Muys B. Scaling from stand to landscape scale of climate change mitigation by afforestation and forest management: a modeling approach. *Climatic Change*. 2008; 86(3):397–424.
- Grassi G, Bagnaresi U. Foliar morphological and physiological plasticity in *Picea abies* and *Abies alba* saplings along a natural light gradient. *Tree Physiology*. 2001; 21(12-13):959–967. [PubMed: 11498343]
- Grote R, Lavoie AV, Rambal S, Staudt M, Zimmer I, Schnitzler J-P. Modelling the drought impact on monoterpene fluxes from an evergreen Mediterranean forest canopy. *Oecologia*. 2009; 160(2): 213–223. [PubMed: 19219456]
- Grote R, Mayrhofer S, Fischbach RJ, Steinbrecher R, Staudt M, Schnitzler J-P. Process-based modelling of isoprenoid emissions from evergreen leaves of *Quercus ilex* (L.). *Atmospheric Environment*. 2006; 40:152–165.
- Grote R, Monson R, Niinemets Ü. Leaf-level models of constitutive and stress-driven volatile organic compound emissions. In: Niinemets Ü, Monson RK, editors. *Biology, Controls and Models of Tree Volatile Organic Compound Emission*. Springer; Netherlands: 2013. p. 315–355.
- Grote R, Niinemets Ü. Modeling volatile isoprenoid emissions - A story with split ends. *Plant Biology*. 2008; 10:8–28. [PubMed: 18211545]
- Guenther A. Upscaling Biogenic Volatile Compound Emissions from Leaves to Landscapes. In: Niinemets Ü, Monson RK, editors. *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*. Springer; Netherlands: 2013. p. 391–414.
- Guenther AB, Jiang X, Heald CL, Sakulyanontvittaya T, Duhl T, Emmons LK, Wang X. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev*. 2012; 5:1471–1492.
- Hardacre CJ, Palmer PI, Baumanns K, Rounsevell M, Murray-Rust D. Probabilistic estimation of future emissions of isoprene and surface oxidant chemistry associated with land-use change in response to growing food needs. *Atmospheric Chemistry and Physics*. 2013; 13:5451–5472.
- Harley PC, Baldocchi DD. Scaling carbon dioxide and water vapour exchange from leaf to canopy in a deciduous forest. I. Leaf model parameterization. *Plant, Cell & Environment*. 1995; 18(10):1146–1156.

- Harley PC, Thomas RB, Reynolds JF, Strain BR. Modelling photosynthesis of cotton grown in elevated CO₂. *Plant, Cell & Environment*. 1992; 15:271–282.
- Harley PC, Weber JA, Gates DM. Interactive effects of light, leaf temperature, CO₂ and O₂ on photosynthesis in soybean. *Planta*. 1985; 165(2):249–263. [PubMed: 24241050]
- Harrison SP, Morfopoulos C, Srikanta Dani KG, Prentice IC, Arneth A, Atwell BJ, Barkley MP, Leishman MR, Loreto F, Medlyn B, Niinemets Ü, Possell M, Peñuelas J, Wright IJ. Volatile isoprenoid emissions from plastid to planet. *New Phytologist*. 2013; 197(1):49–57. [PubMed: 23145556]
- Hirose T, Ackerly DD, Traw MB, Ramseier D, Bazzaz FA. CO₂ elevation, canopy photosynthesis, and optimal leaf area index. *Ecology*. 1997; 78(8):2339–2350.
- Hogrefe C, Isukapalli SS, Tang X, Georgopoulos PG, He S, Zalewsky EE, Hao W, Ku J-Y, Key T, Sista G. Impact of biogenic emission uncertainties on the simulated response of ozone and fine particulate matter to anthropogenic emission reductions. *J. Air Waste Manag. Assoc.* 2011; 61(1): 92–108. [PubMed: 21305893]
- Hüve K, Bichele I, Rasulov B, Niinemets Ü. When it is too hot for photosynthesis: heat-induced instability of photosynthesis in relation to respiratory burst, cell permeability changes and H₂O₂ formation. *Plant, Cell & Environment*. 2011; 34(1):113–126.
- Kattge J, Knorr W. Temperature acclimation in a biochemical model of photosynthesis: a reanalysis of data from 36 species. *Plant, Cell & Environment*. 2007; 30(9):1176–1190.
- Keenan T, Garcia R, Friend AD, Zaehle S, Gracia C, Sabaté S. Improved understanding of drought controls on seasonal variation in Mediterranean forest canopy CO₂ and water fluxes through combined in situ measurements and ecosystem modelling. *Biogeosciences*. 2009a; 6:1423–1444.
- Keenan T, Niinemets Ü, Sabaté S, Gracia C, Peñuelas J. Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties. *Atmospheric Chemistry and Physics*. 2009b; 9(12):4053–4076.
- Keenan T, Niinemets Ü, Sabaté S, Gracia C, Peñuelas J. Seasonality of monoterpene emission potentials in *Quercus ilex* and *Pinus pinea*: Implications for regional VOC emissions modeling. *J. Geophys. Res.* 2009c; 114 doi:10.1029/2009JD011904.
- Keenan T, Sabaté S, Gracia C. Soil water stress and coupled photosynthesis-conductance models: Bridging the gap between conflicting reports on the relative roles of stomatal, mesophyll conductance and biochemical limitations to photosynthesis. *Agricultural and Forest Meteorology*. 2010; 150(3):443–453.
- Knorr W, Heimann M. Uncertainties in global terrestrial biosphere modeling: 1. A comprehensive sensitivity analysis with a new photosynthesis and energy balance scheme. *Global Biogeochem. Cycles*. 2001; 15(1):207–225.
- Kulmala, M.; Nieminen, T.; Chellapermal, R.; Makkonen, R.; Bäck, J.; Kerminen, V-M. Climate Feedbacks Linking the Increasing Atmospheric CO₂ Concentration, BVOC Emissions, Aerosols and Clouds in Forest Ecosystems. In: Niinemets, Ü.; Monson, RK., editors. *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*. Springer; Netherlands: 2013. p. 489–508.
- Laohawornkitkul J, Taylor JE, Paul ND, Hewitt CN. Biogenic volatile organic compounds in the Earth system. *New Phytologist*. 2009; 183(1):27–51. [PubMed: 19422541]
- Lerdau M, Litvak M, Palmer P, Monson R. Controls over monoterpene emissions from boreal forest conifers. *Tree Physiology*. 1997; 17:563–569. [PubMed: 14759829]
- Li Z, Sharkey TD. Metabolic profiling of the methylerythritol phosphate pathway reveals the source of post-illumination isoprene burst from leaves. *Plant, Cell & Environment*. 2013a; 36(2):429–437.
- Li, Z.; Sharkey, TD. Molecular and Pathway Controls on Biogenic Volatile Organic Compound Emissions. In: Niinemets, Ü.; Monson, RK., editors. *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*. Springer; Netherlands: 2013b. p. 119–151.
- Limousin JM, Misson L, Lavoie AV, Martin NK, Rambal S. Do photosynthetic limitations of evergreen *Quercus ilex* leaves change with long-term increased drought severity? *Plant, Cell & Environment*. 2010; 33(5):863–875.
- Litvak ME, Loreto F, Harley PC, Sharkey TD, Monson RK. The response of isoprene emission rate and photosynthetic rate to photon flux and nitrogen supply in aspen and white oak trees. *Plant, Cell & Environment*. 1996; 19(5):549–559.

- Llusia J, Peñuelas J, Ogaya R, Alessio G. Annual and seasonal changes in foliar terpene content and emission rates in *Cistus albidus* L. submitted to soil drought in Prades forest (Catalonia, NE Spain). *Acta Physiologiae Plantarum*. 2010; 32(2):387–394.
- Magel E, Mayrhofer S, Müller A, Zimmer I, Hampp R, Schnitzler J-P. Photosynthesis and substrate supply for isoprene biosynthesis in poplar leaves. *Atmospheric Environment*. 2006; 40:138–151.
- Martin MJ, Stirling CM, Humphries SW, Long SP. A process-based model to predict the effects of climatic change on leaf isoprene emission rates. *Ecological Modelling*. 2000; 131:161–174.
- Medlyn BE, Robinson AP, Clement R, McMurtrie RE. On the validation of models of forest CO₂ exchange using eddy covariance data: some perils and pitfalls. *Tree Physiology*. 2005; 25:839–857. [PubMed: 15870053]
- Monson RK, Grote R, Niinemets Ü, Schnitzler J-P. Modeling the isoprene emission rate from leaves. *New Phytologist*. 2012; 195(3):541–559. [PubMed: 22738087]
- Monson RK, Trahan N, Rosenstiel TN, Veres P, Moore D, Wilkinson M, Norby RJ, Volder A, Tjoelker MG, Briske DD, Karnosky DF, Fall R. Isoprene emission from terrestrial ecosystems in response to global change: minding the gap between models and observations. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2007; 365(1856):1677–1695.
- Morfopoulos C, Prentice IC, Keenan TF, Friedlingstein P, Medlyn BE, Peñuelas J, Possell M. A unifying conceptual model for the environmental responses of isoprene emissions from plants. *Annals of Botany*. 2013 DOI: 10.1093/aob/mct206.
- Morfopoulos C, Sperlich D, Penuelas J, Filella Cubells I, Llusia J, Medlyn BE, Niinemets Ü, Possell M, Sun Z, Prentice IC. Experimental support for a model of plant isoprene emission based on available reducing power. *New Phytologist*. submitted.
- Niinemets Ü, Copolovici L, Hüve K. High within-canopy variation in isoprene emission potentials in temperate trees: Implications for predicting canopy-scale isoprene fluxes. *J.Geophys.Res.* 2010a; 115(G4):G04029.
- Niinemets Ü, Hauff K, Bertin N, Tenhunen JD, Steinbrecher R, Seufert G. Monoterpene emissions in relation to foliar photosynthetic and structural variables in Mediterranean evergreen *Quercus* species. *New Phytologist*. 2002a; 153(2):243–256.
- Niinemets Ü, Kännaste A, Copolovici L. Quantitative patterns between plant volatile emissions induced by biotic stresses and the degree of damage. *Frontiers in Plant Science*. 2013; 4:1–15. [PubMed: 23346092]
- Niinemets Ü, Keenan TF. Photosynthetic responses to stress in Mediterranean evergreens: mechanisms and models. *Environmental and Experimental Botany*. 2013 in press.
- Niinemets, Ü.; Monson, RK. State-of-the-art of BVOC research: what do we have and what have we missed? A synthesis. In: Niinemets, Ü.; Monson, RK., editors. In *Biology, controls and models of tree volatile organic compound emissions*. Springer; Berlin: 2013. p. 509-528.
- Niinemets Ü, Monson RK, Arneth A, Ciccioli P, Kesselmeier J, Kuhn M, Noe S, Peñuelas J, Staudt M. The leaf-level emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling. *Biogeosciences*. 2010b; 7:1809–18032.
- Niinemets Ü, Seufert G, Steinbrecher R, Tenhunen JD. A model coupling foliar monoterpene emissions to leaf photosynthetic characteristics in Mediterranean evergreen *Quercus* species. *New Phytologist*. 2002b; 153(2):257–273.
- Niinemets Ü, Tenhunen JD, Harley PC, Steinbrecher R. A model of isoprene emission based on energetic requirements for isoprene synthesis and leaf photosynthetic properties for *Liquidambar* and *Quercus*. *Plant, Cell & Environment*. 1999; 22(11):1319–1335.
- Oleson, KW.; Lawrence, DM.; Bonan, GB.; Flanner, MG.; Kluzek, E.; Lawrence, PJ.; Levis, S.; Swenson, SC.; Thornton, PE. In NCAR Technical Note. Boulder; Colorado: 2010. Technical Description of version 4.0 of the Community Land Model (CLM); p. 1-266.
- Ormeno E, Fernandez C, Bousquet-Melou A, Greff S, Morin E, Robles C, Vila B, Bonin G. Monoterpene and sesquiterpene emissions of three Mediterranean species through calcareous and siliceous soils in natural conditions. *Atmospheric Environment*. 2007; 41(3):629–639.

- Owen, S.; Hewitt, CN.; Rowland, C. Scaling Emissions from Agroforestry Plantations and Urban Habitats. In: Niinemets, Ü.; Monson, RK., editors. In *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*. Springer; Netherlands: 2013. p. 415–450.
- Owen SM, Peñuelas J. Opportunistic emissions of volatile isoprenoids. *Trends in Plant Science*. 2005; 10:420–426. [PubMed: 16098785]
- Pacifico F, Folberth GA, Jones CD, Harrison SP, Collins WJ. Sensitivity of biogenic isoprene emissions to past, present, and future environmental conditions and implications for atmospheric chemistry. *J.Geophys.Res.* 2012; 117(D22):D22302.
- Pacifico F, Harrison SP, Jones CD, Sitch S. Isoprene emission and climate. *Atmospheric Environment*. 2009; 43(39):6121–6135.
- Park J-H, Goldstein AH, Timkovsky J, Fares S, Weber R, Karlik J, Holzinger R. Active Atmosphere-Ecosystem Exchange of the Vast Majority of Detected Volatile Organic Compounds. *Science*. 2013; 341(6146):643–647. [PubMed: 23929979]
- Piccot SD, Watson JJ, Jones JW. A global inventory of volatile organic compound emissions from anthropogenic sources. *Journal of Geophysical Research*. 1992; 97(D9):9897–9912.
- Pike RC, Young PJ. How plants can influence tropospheric chemistry: the role of isoprene emissions from the biosphere. *Weather*. 2009; 64(12):332–336.
- Porter WC, Barsanti KC, Baughman EC, Rosenstiel TN. Considering the air quality impacts of bioenergy crop production: A case study involving *Arundo donax*. *Environmental Science & Technology*. 2012; 46(17):9777–9784. [PubMed: 22852528]
- Possell M, Hewitt CN. Isoprene emissions from plants are mediated by atmospheric CO₂ concentrations. *Global Change Biology*. 2011; 17(4):1595–1610.
- Possell M, Hewitt NC. Gas exchange and photosynthetic performance of the tropical tree *Acacia nigrescens* when grown in different CO₂ concentrations. *Planta*. 2009; 229(4):837–846. [PubMed: 19123062]
- Possell, M.; Loreto, F. The Role of Volatile Organic Compounds in Plant Resistance to Abiotic Stresses: Responses and Mechanisms. In: Niinemets, Ü.; Monson, RK., editors. *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*. Springer; Netherlands: 2013. p. 209–235.
- Poupkou A, Giannaros T, Markakis K, Kioutsoukios I, Curci G, Melas D, Zerefos C. A model for European Biogenic Volatile Organic Compound emissions: Software development and first validation. *Environmental Modelling & Software*. 2010; 25:1845–1856.
- Rambal S. The differential role of mechanisms for drought resistances in a Mediterranean evergreen shrub: a simulation approach. *Plant, Cell & Environment*. 1993; 16:35–44.
- Rasulov B, Hüve K, Bichele I, Laisk A, Niinemets Ü. Temperature response of isoprene emission in vivo reflects a combined effect of substrate limitations and isoprene synthase activity: A kinetic analysis. *Plant Physiology*. 2010; 154(3):1558–1570. [PubMed: 20837700]
- Rasulov B, Hüve K, Laisk A, Niinemets Ü. Induction of a longer term component of isoprene release in darkened aspen leaves: Origin and regulation under different environmental conditions. *Plant Physiology*. 2011; 156(2):816–831. [PubMed: 21502186]
- Rasulov B, Hüve K, Valbe M, Laisk A, Niinemets Ü. Evidence that light, carbon dioxide, and oxygen dependencies of leaf isoprene emission are driven by energy status in hybrid aspen. *Plant Physiology*. 2009; 151(1):448–460. [PubMed: 19587097]
- Silim S, Ryan N, Kubien D. Temperature responses of photosynthesis and respiration in *Populus balsamifera* L.: acclimation versus adaptation. *Photosynthesis Research*. 2010; 104(1):19–30. [PubMed: 20112068]
- Šimpraga M, Verbeeck H, Demarcke M, Joo E, Pokorska O, Amelynck C, Schoon N, Dewulf J, Van Langenhove H, Heinesch B, Aubinet M, Laffineur Q, Müller JF, Steppe K. Clear link between drought stress, photosynthesis and biogenic volatile organic compounds in *Fagus sylvatica* L. *Atmospheric Environment*. 2011; 45(30):5254–5259.
- Simpson D, Benedictow A, Berge H, Bergström R, Emberson LD, Fagerli H, Flechard CR, Hayman GD, Gauss M, Jonson JE, Jenkin ME, Nyiri A, Richter C, Semeena VS, Tsyro S, Tuovinen J-P, Valdebenito A, Wind P. The EMEP MSC-W chemical transport model – technical description. *Atmos. Chem. Phys.* 2012; 12(16):7825–7865.

- Singsaas EL, Laporte MM, Shi J-Z, Monson RK, Bowling DR, Johnson K, Lerdau M, Jasentuliytana A, Sharkey TD. Kinetics of leaf temperature fluctuation affect isoprene emission from red oak (*Quercus rubra*) leaves. *Tree Physiology*. 1999; 19(14):917–924. [PubMed: 12651303]
- Singsaas EL, Sharkey TD. The regulation of isoprene emission responses to rapid leaf temperature fluctuations. *Plant, Cell & Environment*. 1998; 21(11):1181–1188.
- Staudt M, Joffre R, Rambal S. How growth conditions affect the capacity of *Quercus ilex* leaves to emit monoterpenes. *New Phytologist*. 2003; 158(1):61–73.
- StPaul NKM, Limousin J-M, Rodríguez-Calcerrada J, Ruffault J, Rambal S, Letts MG, Misson L. Photosynthetic sensitivity to drought varies among populations of *Quercus ilex* along a rainfall gradient. *Functional Plant Biology*. 2012; 39:25–37.
- Sun Z, Hüve K, Vislap V, Niinemets Ü. Elevated growth [CO₂] magnifies isoprene emissions under heat, alters environmental responses and improves thermal resistance in hybrid aspen. *Journal of Experimental Botany*. 2013 in press.
- Sun Z, Niinemets Ü, Hüve K, Noe SM, Rasulov B, Copolovici L, Vislap V. Enhanced isoprene emission capacity and altered light responsiveness in aspen grown under elevated atmospheric CO₂ concentration. *Global Change Biology*. 2012; 18(11):3423–3440.
- Turnbull M, Whitehead D, Tissue D, Schuster W, Brown K, Engel V, Griffin K. Photosynthetic characteristics in canopies of *Quercus rubra*, *Quercus prinus* and *Acer rubrum* differ in response to soil water availability. *Oecologia*. 2002; 130(4):515–524.
- Unger N, Harper K, Zheng Y, Kiang NY, Aleinov I, Arneth A, Schurgers G, Amelynck C, Goldstein A, Guenther A, Heinesch B, Hewitt CN, Karl T, Laffineur Q, Langford B, McKinney KA, Misztal P, Potosnak M, Rinne J, Pressley S, Schoon N, Serça D. Photosynthesis-dependent isoprene emission from leaf to planet in a global carbon–chemistry–climate model. *Atmos. Chem. Phys.* 2013; 13:10243–10269.
- Urban O, Ac A, Kalina J, Priwitzer T, Sprtova M, Spunda V, Marek MV. Temperature dependences of carbon assimilation processes in four dominant species from mountain grassland ecosystem. *Photosynthetica*. 2007; 45(3):392–399.
- Van Wassenhove FA, Dirinck PJ, Schamp NM, Vulsteke GA. Effect of nitrogen fertilizers on celery volatiles. *Journal of Agricultural and Food Chemistry*. 1990; 38(1):220–226.
- Vaz M, Pereira JS, Gazarini LC, David TS, David JS, Rodrigues A, Maroco J, Chaves MM. Drought-induced photosynthetic inhibition and autumn recovery in two Mediterranean oak species (*Quercus ilex* and *Quercus suber*). *Tree Physiology*. 2010; 30(8):946–956. [PubMed: 20571151]
- Velikova V, Tsonev T, Loreto F, Centritto M. Changes in photosynthesis, mesophyll conductance to CO₂, and isoprenoid emissions in *Populus nigra* plants exposed to excess nickel. *Environmental Pollution*. 2011; 159(5):1058–1066. [PubMed: 21126813]
- Vitale M, Salvatori E, Loreto F, Fares S, Manes F. Physiological responses of *Quercus ilex* leaves to water stress and acute ozone exposure under controlled conditions. *Water, Air, & Soil Pollution*. 2008; 189(1):113–125.
- Von Caemmerer, S.; Farquhar, G.; Berry, J. Biochemical Model of C3 Photosynthesis. In: Laisk, A.; Nedbal, L.; Govindjee, L., editors. *In Photosynthesis in silico: Understanding Complexity from Molecules to Ecosystems*. Springer Science+Business Media B.V.; 2009. p. 209-230.
- Wang Q, Tenhunen J, Falge E, Bernhofer C, Granier A, Vesala T. Simulation and scaling of temporal variation in gross primary production for coniferous and deciduous temperate forests. *Global Change Biology*. 2003; 10(1):37–51.
- Warren CR. The photosynthetic limitation posed by internal conductance to CO₂ movement is increased by nutrient supply. *Journal of Experimental Botany*. 2004; 55(406):2313–2321. [PubMed: 15310814]
- Werner C, Ryel RJ, Correia O, Beyschlag W. Effects of photoinhibition on whole-plant carbon gain assessed with a photosynthesis model. *Plant, Cell & Environment*. 2001; 24(1):27–40.
- Zimmer W, Brüggemann N, Emeis S, Giersch C, Lehning A, Steinbrecher R, Schnitzler J-P. Process-based modelling of isoprene emission by oak leaves. *Plant, Cell & Environment*. 2000; 23:585–595.

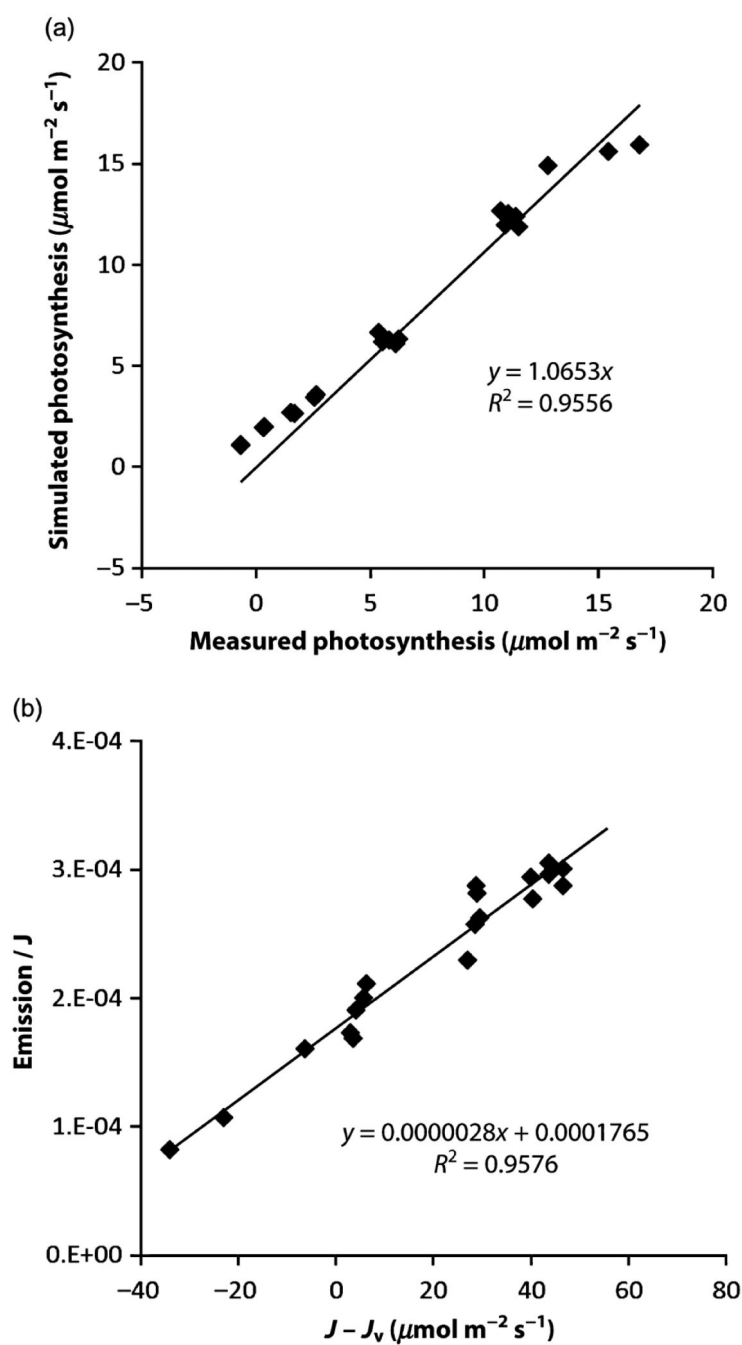


Figure 1.

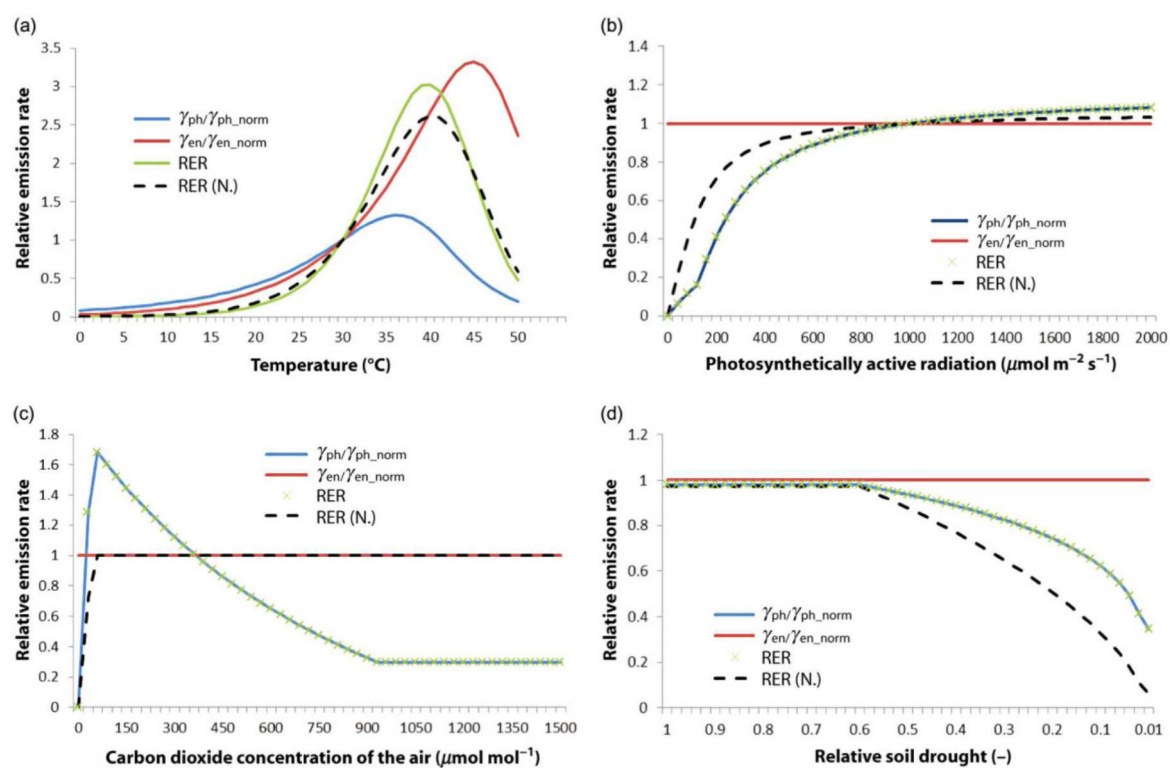


Figure 2.

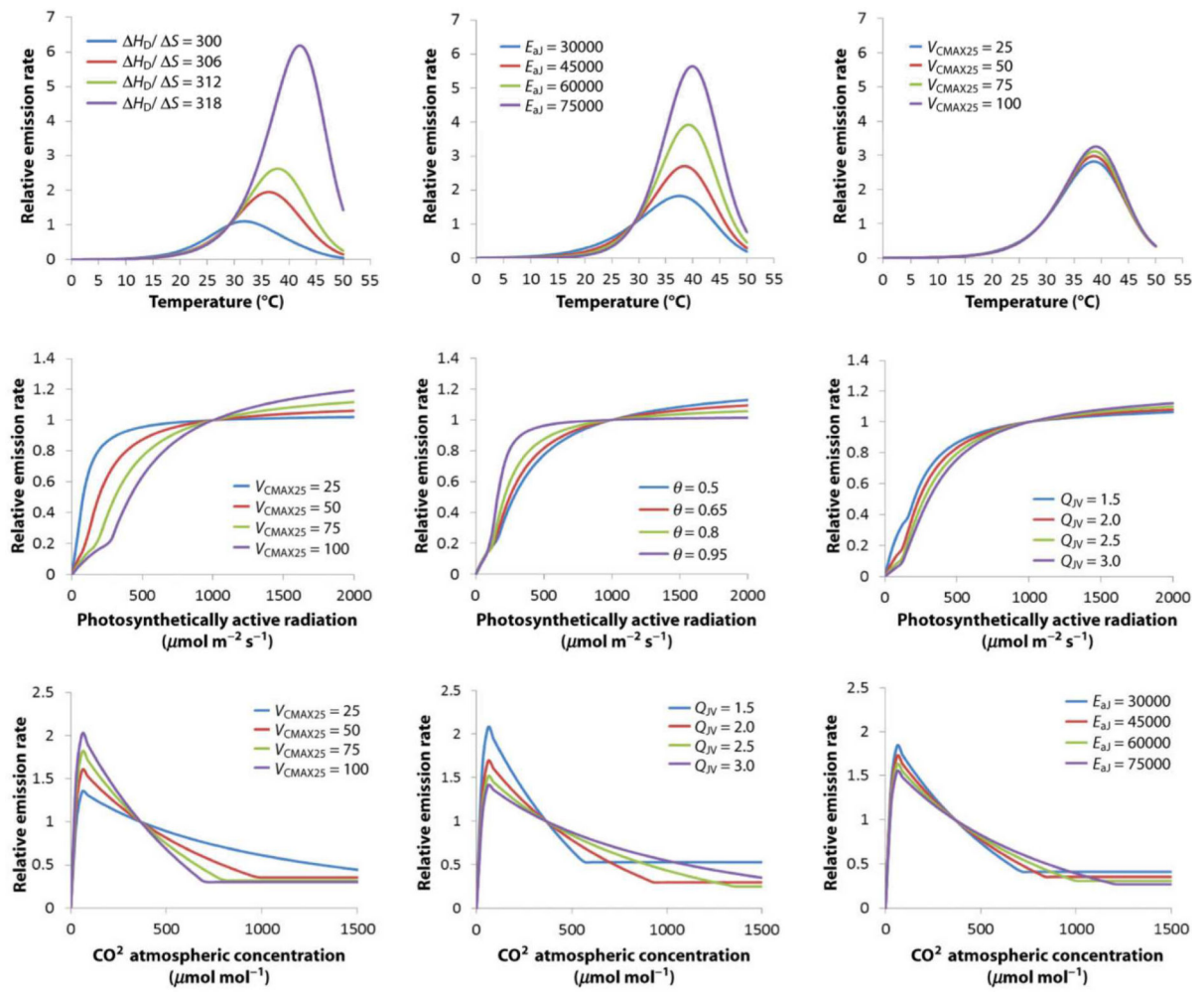


Figure 3.

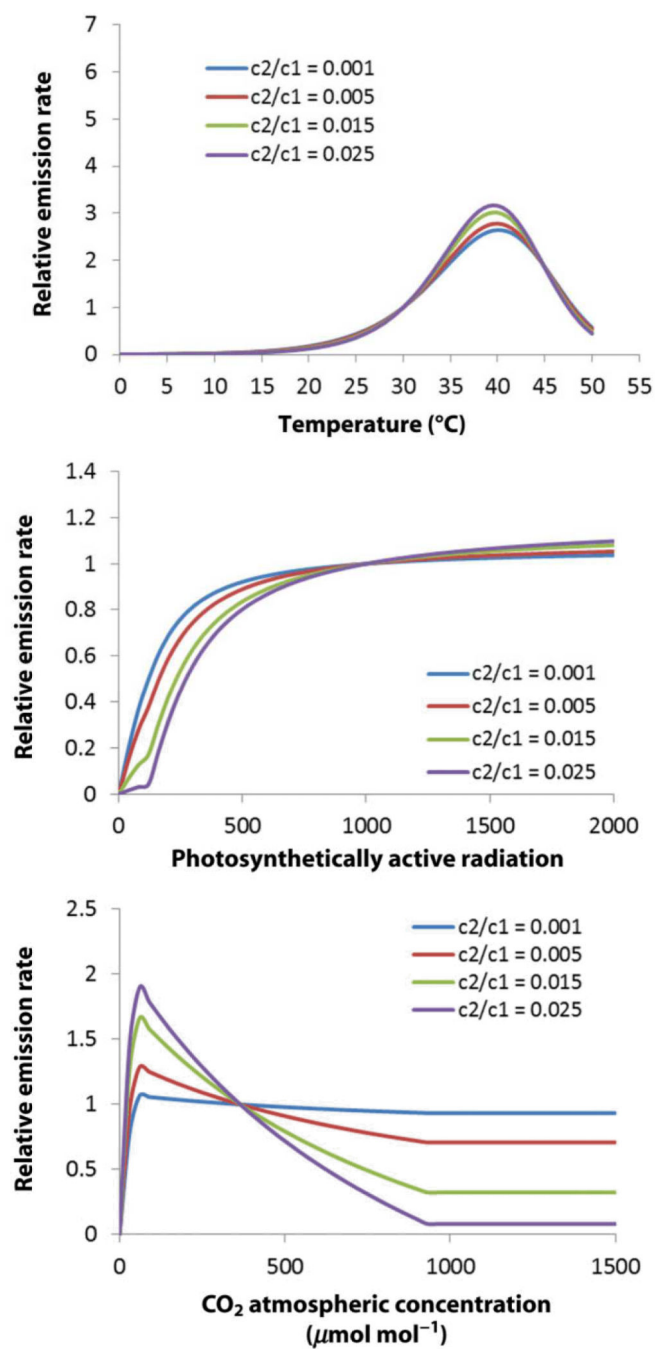


Figure 4.

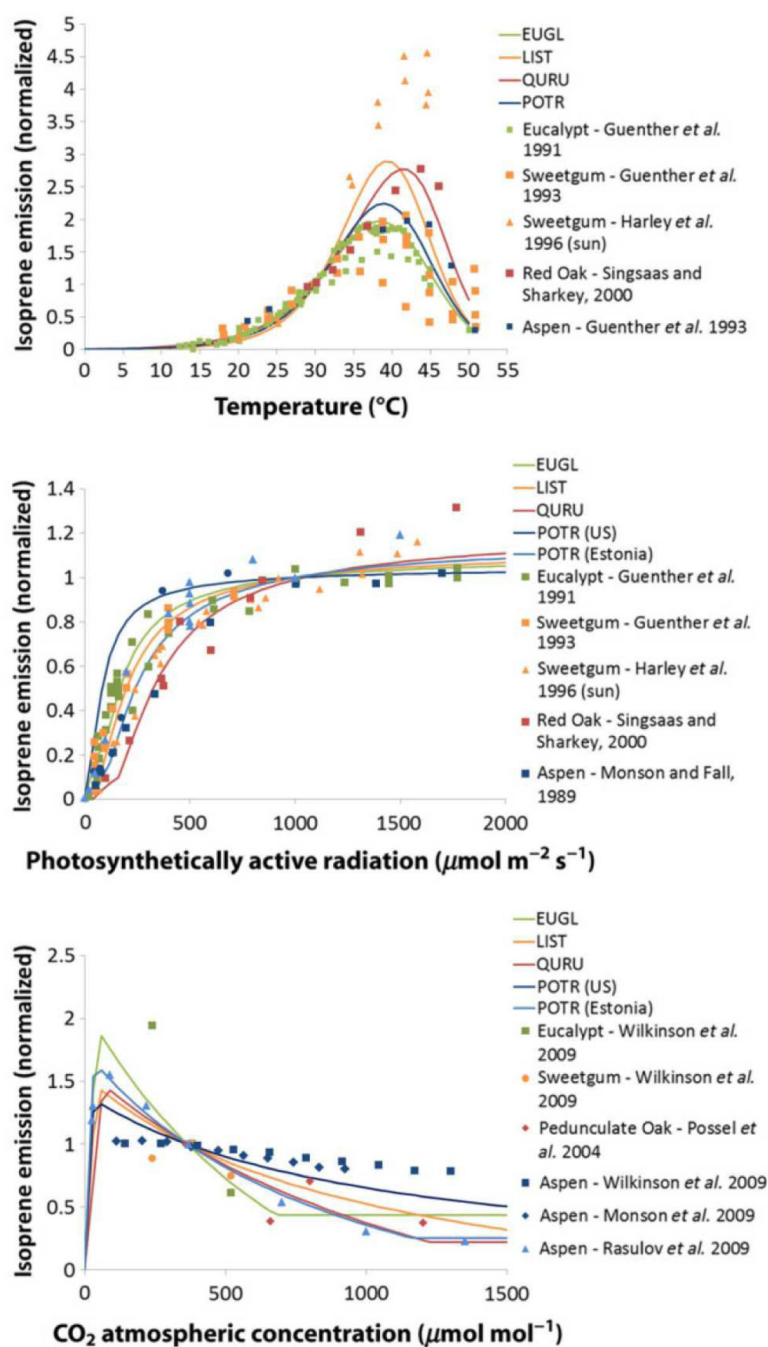


Figure 5.

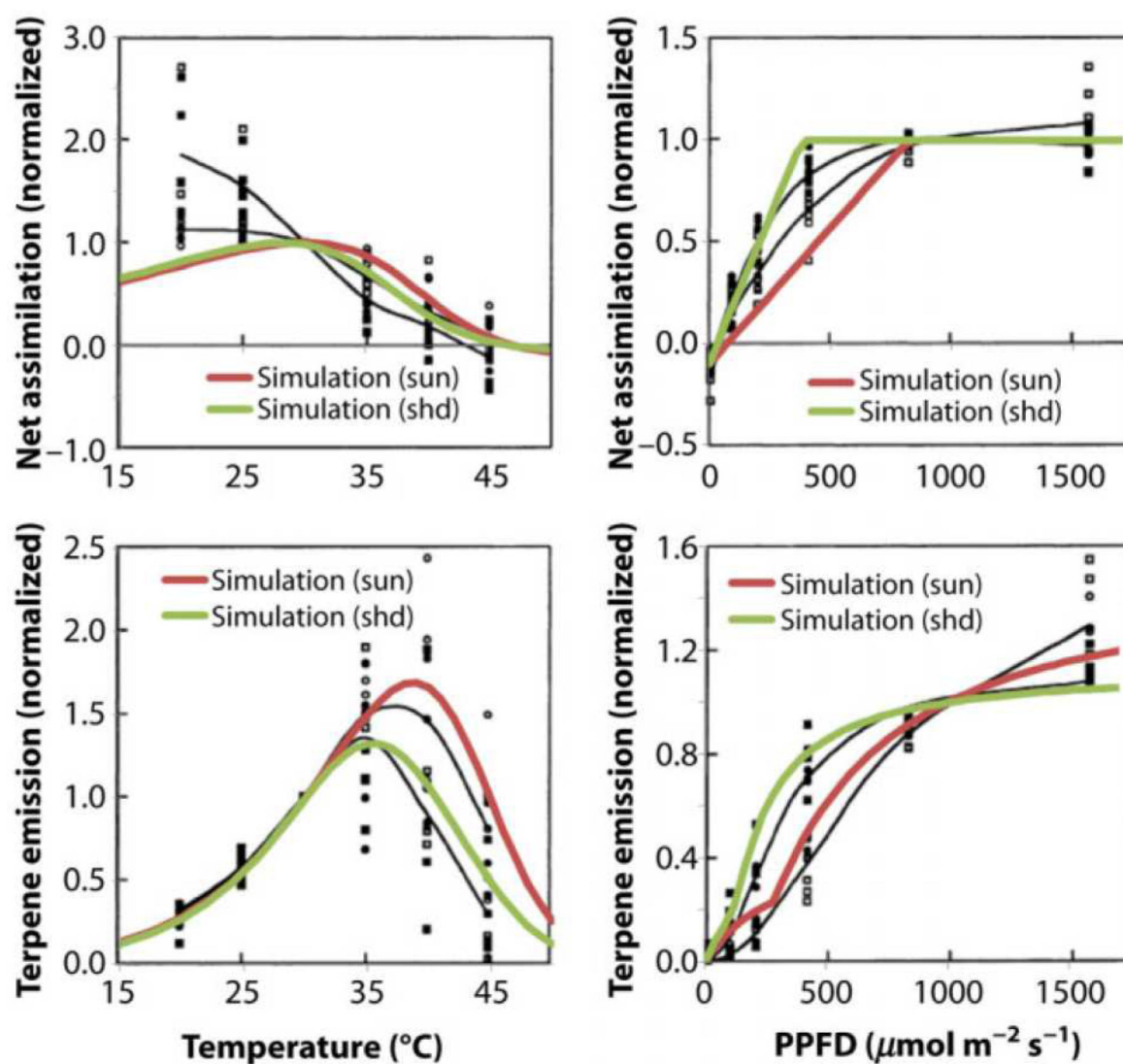


Figure 6.

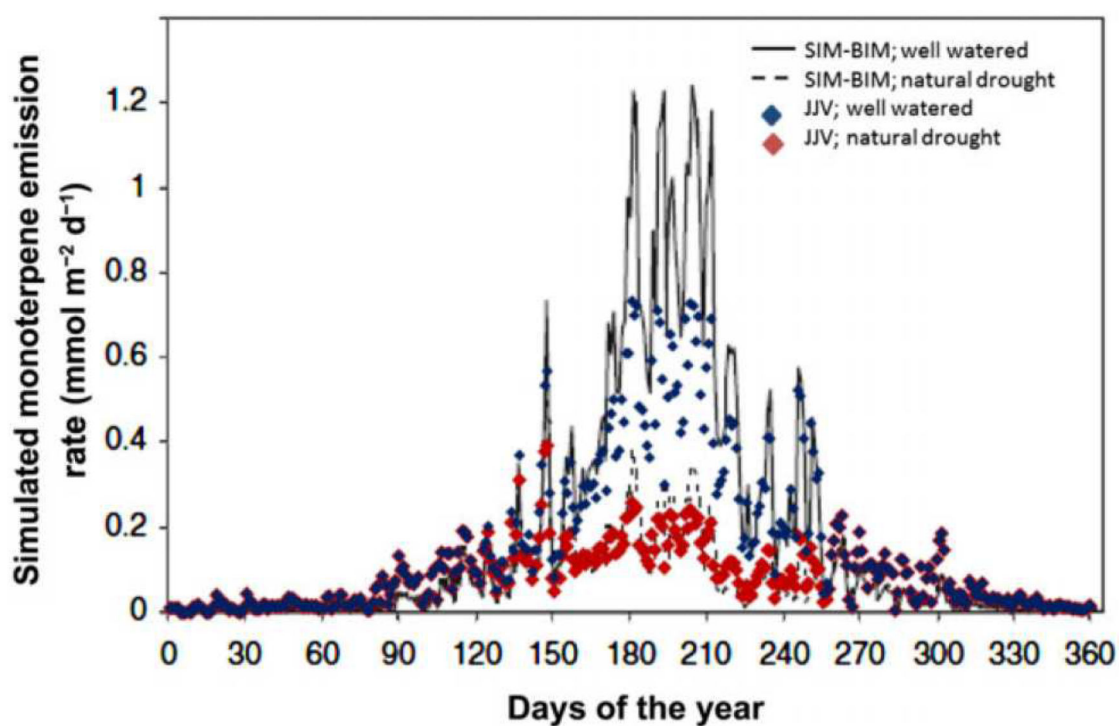


Figure 7.

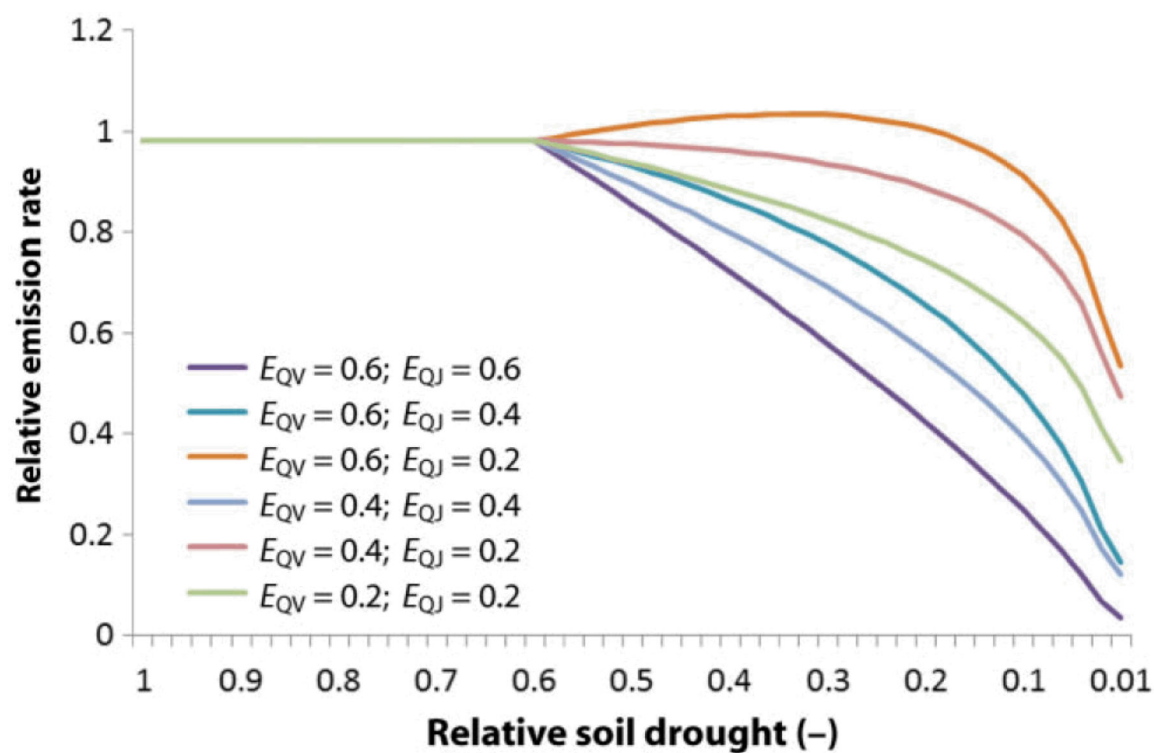


Figure 8.

Tab. 1

Parameters of photosynthesis model and uncertainty range that has been explored regarding its impact on the proposed emission model ('Ref' indicates the reference number for the values in the preceding columns as listed below the table)

Parameter	Abbreviation	Units	Standard value	Ref	Range in literature	Ref
Rubisco capacity at 25 °C	V_{cmax25}	$\mu\text{mol m}^{-2} \text{s}^{-1}$	60	1)	~25 - 100	5), 6)
Michaelis-Menten constant for carboxylation at 25°C	K_{C25}	$\mu\text{mol mol}^{-1} \text{pbar}^{-1}$	300	2)	180 – 590	7), 8)
Michaelis-Menten constant for oxygenation at 25°C	K_{O25}	$\text{mmol mol}^{-1} \text{pbar}^{-1}$	300000	2)	160 – 420	9), 10)
Radiation absorbance efficiency	a_L	-	0.86	2)	0.86 - 0.895	2), 11)
Quantum efficiency of photosystems	α	mol mol^{-1}	0.08	2)	0.06 - 0.525	1), 12)
Deactivation energy of electron transport chain	ΔH_D	J mol^{-1}	220000	2)	200000 - 220000	3), 2)
Enthropy parameter	ΔS	$\text{J K}^{-1} \text{mol}^{-1}$	703	2)	645 - 710	3), 13)
Relation between maximum electron transport rate and Rubisco saturated rate of carboxylation at 25°C	Q_{IV}	-	2	2)	~1.5 – 3.0	14), 15)
Activation energy for electron transport	E_{aI}	J mol^{-1}	49884	3)	28000 - 79500	16), 13)
Curvature parameter	θ	-	0.7	4)	0.5 – 0.95	17), 2)

1) (Oleson et al., 2010);

2) (Collatz et al., 1991);

3) (Kattge and Knorr, 2007);

4) (Evans, 1989)

5) (Grassi and Bagnaresi, 2001);

6) (Silim et al., 2010);

7) (Eichelmann et al., 2004);

8) {Rey, 1997 #12148};

9) (Wang et al., 2003);

10) (Harley and Baldocchi, 1995);

11) (Medlyn et al., 2005);

12) (Harley et al., 1985);

13) (Farquhar et al., 1980);

14) (Harley et al., 1992);

15) (Urban et al., 2007);

16) (Martin et al., 2000);

17) (Hirose et al., 1997)

Tab. 2

Species specific use of photosynthesis parameter for emission modeling ('Ref' denotes the reference column).

Parameter	Units	Eucalypt	Ref	Sweetgum	Ref	Aspen	Ref	Red oak	Ref	Pedunculate oak	Ref
V_{cmax25}	$\mu\text{mol m}^{-2} \text{s}^{-1}$	56.4	1)	30	4)	24.6	5)	51	1)	62	2)
K_{c25}	$\mu\text{mol mol}^{-1} \text{pbar}^{-1}$	300	ST	300	ST	325	5*)	300	ST	300	ST
K_{O25}	$\text{mmol mol}^{-1} \text{pbar}^{-1}$	300000	ST	300000	ST	416000	5*)	300000	ST	300000	ST
K_{C25}/K_{O25}		1)		1)		0.8		1)		1)	
ΔH_D	J mol^{-1}	200000	2)	220000	ST	203000	6)	200000	2*)	200000	2)
ΔS_D	$\text{J K}^{-1} \text{mol}^{-1}$	647	2)	703	ST	651	6)	641	2*)	641	2)
$\Delta H_D/\Delta S_D$		309		313		312		312		312	
Q_{IV}	-	1.73	3)	2.12	4)	2.22	7)	2.4	1)	1.56	7)
E_{aJ}	J mol^{-1}	43790	2)	49884	ST	49884	ST	35870	2*)	35870	2)
θ	-	0.7	ST	0.7	ST	7)	ST	0.7	ST	0.7	ST

1) (Turnbull et al., 2002),

2) (Kattge and Knorr, 2007),

2*) for *Q. robur*,

3) (Warren, 2004),

4) (DeLucia and Thomas, 2000),

5) (Sun et al., 2012),

5*) derived from Sun et al. (2012) data,

6) (Niinemets et al., 1999) for *P. tremula*,

7) (Garcia-Quijano et al., 2008), ST: standard assumptions (see Table 1)