

SUPPLEMENTARY DATA

A1. MEGAN - G93 (Guenther et al., 1993, 2006)

MEGAN is the most widely used model for prediction of isoprene emission from vegetation. This model was built on the Guenther et al. (1993) algorithm (G93) where the emission rate of isoprene (Iso) is calculated by multiplying a species-specific standard emission rate (I_s) by a set of empirical equations taking in account changes in environmental factors. The standard conditions for estimation of I_s are a leaf temperature of 30°C and a PAR of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$. For this study, we used the Guenther et al. (1993) algorithm (G93), where solely changes in PAR and temperature are taken in account:

$$\text{Iso} = I_s C_L C_T, \quad (\text{A1})$$

with

$$C_L = \alpha C_{L1} \text{PAR} / \sqrt{(1 + \alpha^2 \text{PAR}^2)} \quad (\text{A1a})$$

$$C_T = \exp (C_{T1} (T - T_s) / (R T_s T)) / (C_{T3} + \exp (C_{T2} (T - T_m) / (R T_s T))) \quad (\text{A1b})$$

T (K) is the leaf temperature, T_s is the temperature at standard conditions (= 303 K), R is the gas constant (= 8.314 $\text{J K}^{-1} \text{mol}^{-1}$), PAR is the photosynthetically active radiation. C_{L1} , α , C_{T1} , C_{T2} , C_{T3} and T_m are empirical coefficients:

$C_{L1} = 1.066$, $\alpha = 0.027$, $C_{T1} = 95\,000 \text{ J mol}^{-1}$, $C_{T2} = 230\,000 \text{ J mol}^{-1}$, $C_{T3} = 0.961 \text{ J mol}^{-1}$ and $T_m = 314 \text{ K}$.

A2. Niinemets model (Niinemets et al., 1999)

The Niinemets model is based on quantifying the NADPH cost for isoprene synthesis.

It builds on the Farquhar model of photosynthesis.

The general concept is that a temperature-dependent fraction of the electron flux (ε) is used for isoprene production.

$$\varepsilon = J_{\text{iso}} / J_{\text{tot}}, \quad (\text{A2})$$

Where J_{iso} is the electrons flux required for a certain isoprene production (Iso) and J_{tot} is the total photosynthetic electron flux.

The total electron flux is approximated from the Farquhar model as follows:

$$J_{\text{tot}} \approx J_{\text{CO}_2+\text{O}_2} = (A_{j_{\text{net}}} + R_d) (4 c_i + 8 \Gamma^*) / (c_i - \Gamma^*), \quad (\text{A2a})$$

where $A_{j_{\text{net}}}$ is the net light-limited carbon assimilation, R_d the dark respiration, c_i internal CO_2 concentration and Γ^* the CO_2 compensation point in the absence of dark respiration.

Given that one molecule of isoprene requires six carbon atoms and that the NADPH cost per molecule of carbon is 1.17 higher for isoprene production than for carbon assimilation, the electron flux needed for a given isoprene production Iso is calculated by:

$$J_{\text{iso}} = 6 \text{ Iso } 1.17 (4 c_i + 8 \Gamma^*) / (c_i - \Gamma^*), \quad (\text{A2b})$$

Rearranging, we obtain:

$$\text{Iso} = \varepsilon J_{\text{tot}} (c_i - \Gamma^*) / (7.02 (4 c_i + 8 \Gamma^*))$$

$$= \varepsilon / 7.02 A_j, \quad (\text{A2c})$$

where A_j is the gross assimilation under light-limited conditions.

The fraction of electrons allocated to isoprene production is calculated as from Arneeth et al. (2007) and Pacifico et al. (2011):

$$\varepsilon = \varepsilon_s \tau, \quad (\text{A2d})$$

where ε_s is the fraction of electrons for isoprene production under the standard conditions of leaf temperature of $T_s = 30^\circ\text{C}$ and PAR of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and $\tau = \min\{\exp[0.1 (T - T_s)] ; 2.3\}$, is a function which mimics the enzymatic response reported by Niinemets et al. (1999).

A1. Model of photosynthetic carbon assimilation (Farquhar et al., 1980)

The model for photosynthetic carbon assimilation is based on the Farquhar model (Farquhar et al., 1980). Temperature responses of the different parameters are described in Medlyn et al. (2002), and based on previous work from (Harley et al., 1986; Long, 1991; Harley et al., 1992; Harley and Baldocchi, 1995; Lloyd et al., 1995; Bernacchi et al., 2001).

Calculation of the light limited electron flux (J):

$$J = ((\alpha\text{PAR} + J_{\max}) - \sqrt{((\alpha\text{PAR} + J_{\max})^2 - 4\alpha\theta J_{\max}\text{PAR})}) / (2\theta) \quad (\text{A3a})$$

$$J_{\max} = J_{\max 25} \cdot \exp(E_{aJ} (1/298.15 - 1/T) / R). J_1/J_2 \quad (\text{A3b})$$

$$J_1 = 1 + \exp((298.15 \Delta S - E_{dJ}) / R / 298.15) \quad (\text{A3c})$$

$$J_2 = 1 + \exp((T \Delta S - E_{dJ}) / R / T) \quad (\text{A3d})$$

$J_{\max 25}$ is the value of J_{\max} at 25°C, $\alpha = 0.385$ mol electron mol⁻¹ photon, θ is a curvature parameter of the light curve response and T is the temperature in K. Other symbols are summarized in Table A1.1

Calculation of the maximum Rubisco capacity V_{\max} , Γ^ , K_c , K_o :*

$$V_{\max} = V_{\max 25} \exp(E_a (1/298.15 - 1/T) / R) \quad (\text{A3e})$$

$$K_c = 404.9 \exp(79430 (T - 298.15)/(298.15 RT)) \quad (\text{A3f})$$

$$K_o = 278.4 \exp(36380 (T - 298.15)/(298.15 RT)) \quad (\text{A3g})$$

$$\Gamma^* = 42.75 \exp(37830 (T - 298.15)/(298.15 RT)) \quad (\text{A3h})$$

$V_{\max 25}$ is the value of V_{\max} at 25°C, K_c and K_o are the Michaelis coefficients of Rubisco for CO₂ and O₂ respectively and Γ^* is the CO₂ compensation point in the absence of dark respiration. Other symbols are summarized in Table A1.1

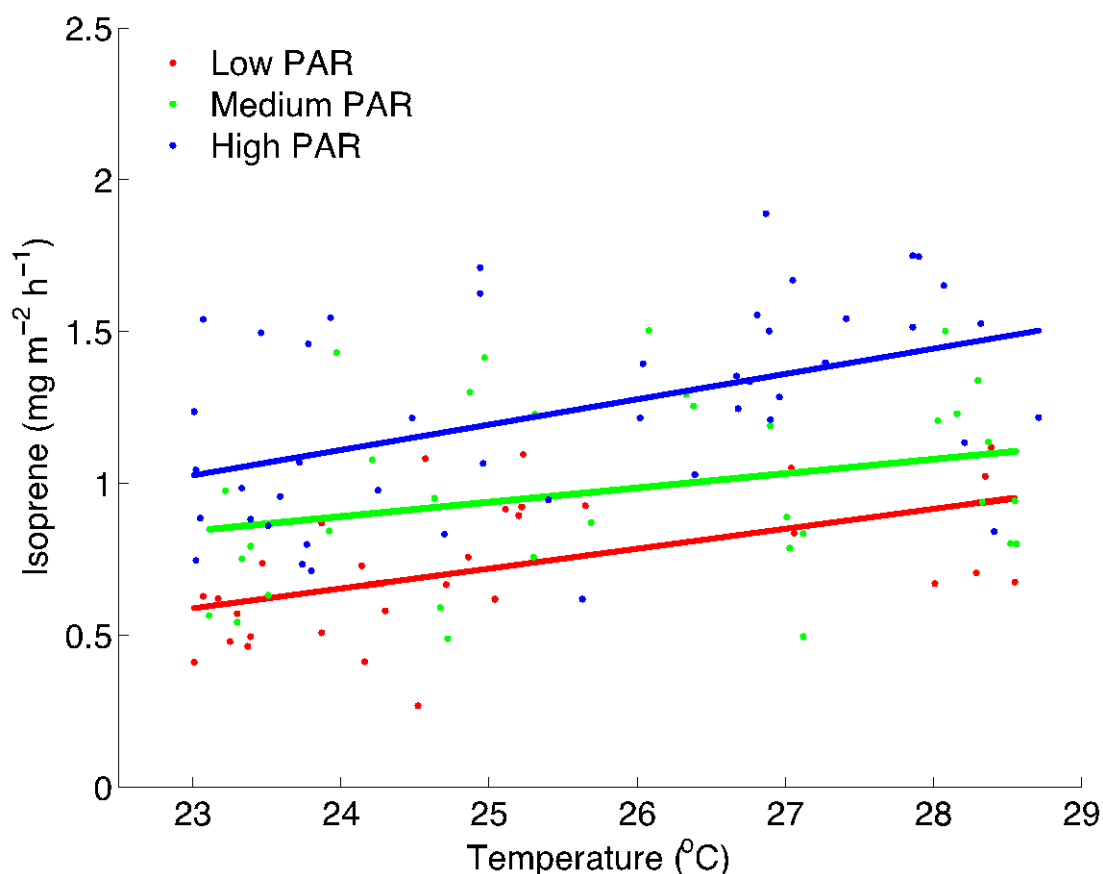
Table A1.1 Description and values of the parameters of Farquhar model used in standard simulations (Medlyn et al., 2005)

| Symbol | Definition | Unit | Value |
|------------|--|------------------------------------|--------|
| E_{aJ} | Activation energy for J | kJ mol^{-1} | 38.670 |
| E_{dJ} | Desactivation energy for J | kJ mol^{-1} | 200 |
| E_a | Activation energy for V_{cmax} | kJ mol^{-1} | 58.520 |
| E_d | Desactivation energy for V_{cmax} | kJ mol^{-1} | 200 |
| ΔS | Entropy term | $\text{kJ mol}^{-1} \text{K}^{-1}$ | 0.6381 |

Table A1.2 Values of the parameters of Farquhar and isoprene models for Fig. 3 and Fig.6

| Symbol | Unit | Value (Fig.3) | Value (Fig.6) |
|---------------------|--------------------------------------|---------------------|----------------------|
| $J_{\text{max}25}$ | $\mu\text{mol m}^{-2} \text{s}^{-1}$ | 99.53 | 54.32 |
| $V_{\text{cmax}25}$ | $\mu\text{mol m}^{-2} \text{s}^{-1}$ | 62.8 | 56.9 |
| a | unitless | $2.2 \cdot 10^{-4}$ | $4.86 \cdot 10^{-5}$ |
| b | unitless | $7 \cdot 10^{-5}$ | $5 \cdot 10^{-6}$ |

Figure A1: Above canopy isoprene emissions in relation to air temperature for three ranges of PAR - Low (1000-1250 $\mu\text{mol m}^{-2} \text{s}^{-1}$), Medium (1250-1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$) and High (1500-1750 $\mu\text{mol m}^{-2} \text{s}^{-1}$). Data from flux measurements at Harvard Forest.



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