



*Supplement of*

## **Development of an ecophysiology module in the GEOS-Chem chemical transport model version 12.2.0 to represent biosphere–atmosphere fluxes relevant for ozone air quality**

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## S1.1 Leaf biochemistry

Formulations of photosynthesis rates for C<sub>3</sub> and C<sub>4</sub> plants were derived from leaf biochemistry and formulated as in Collatz et al. (1991) and Collatz et al. (1992), respectively. It is calculated from the three potentially limiting rates:

### 1. Rubisco-limited rate:

CO<sub>2</sub> assimilation is limited by the availability of CO<sub>2</sub> in intercellular space, the kinetic properties of active sites of Rubisco, and/or the available amount of Rubisco. It is modeled as:

$$W_c = \begin{cases} V_{\text{cmax}} \left( \frac{c_i - \Gamma}{c_i + K_c (1 + o_i / K_o)} \right) & \text{for C}_3 \text{ plants} \\ V_{\text{cmax}} & \text{for C}_4 \text{ plants} \end{cases} \quad (\text{S1})$$

where  $V_{\text{cmax}}$  is the maximum carboxylation rate ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ),  $c_i$  and  $o_i$  are the partial pressures (Pa) of CO<sub>2</sub> and O<sub>2</sub> in intercellular space, respectively,  $\Gamma$  is the CO<sub>2</sub> photorespiration compensation point (Pa), and  $K_c$  and  $K_o$  are the Michaelis–Menten coefficients (Pa) for carboxylation and oxygenation, respectively.  $c_i$  is calculated in Sect. 2.1.4.  $o_i$  is assumed to be equal to the partial pressure of O<sub>2</sub> in the lowest model level. Detailed formulations of temperature-dependent parameters are included in the supplementary materials.

### 2. RuBP-limited rate (light-limited rate):

It describes the regeneration rate of RuBP, which depends on the amount of ATP and NADPH. This ultimately depends on the availability of absorbed photons, and is modeled as:

$$W_l = \begin{cases} \alpha c_\phi \phi \left( \frac{c_i - \Gamma}{c_i + 2\Gamma} \right) & \text{for C}_3 \text{ plants} \\ \alpha c_\phi \phi & \text{for C}_4 \text{ plants} \end{cases} \quad (\text{S2})$$

where  $\alpha$  is the quantum efficiency of photosynthesis ( $\text{mol CO}_2 \text{ mol}^{-1} \text{ PAR}$ ),  $c_\phi = 4.6 \mu\text{mol PAR J}^{-1}$  is a conversion constant, and  $\phi$  is the absorbed photosynthetically active radiation (PAR,  $\text{W m}^{-2}$ ).

### 3. Product-limited rate:

It refers to the rate of transport of photosynthetic products for C<sub>3</sub> plants and PEP carboxylase limitation for C<sub>4</sub> plants. It is modeled as:

$$W_e = \begin{cases} 0.5 V_{\text{cmax}} & \text{for C}_3 \text{ plants} \\ 2 \times 10^4 V_{\text{cmax}} (c_i / P_s) & \text{for C}_4 \text{ plants} \end{cases} \quad (\text{S3})$$

where  $P_s$  is the surface air pressure (Pa).

The leaf-level net photosynthesis ( $A_n$ ,  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ) is calculated as a smoothed minimum (see supplementary materials) of the three potentially limiting rates minus dark respiration ( $R_d$ ,  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ):

$$A_n = \min(W_c, W_l, W_e) - R_d \quad (\text{S4})$$

where  $R_d$  is linearly proportional to  $V_{\text{cmax}}$  by the dark respiration coefficient  $f_{\text{dr}}$ :

$$R_d = f_{\text{dr}} V_{\text{cmax}} \quad (\text{S5})$$

## S1.2 Photosynthesis as a diffusive flux

30 The leaf-level net photosynthesis  $A_n$  can also be represented as a diffusive flux of  $\text{CO}_2$  modulated by the leaf-level stomatal conductance  $g_{s0}$  ( $\text{m s}^{-1}$ ). Therefore, we can find  $g_{s0}$  using:

$$g_{s0} = \frac{1.6 \times 10^{-6} A_n}{c_c - c_i} R_* T \quad (\text{S6})$$

where  $c_c$  is the canopy  $\text{CO}_2$  partial pressure (Pa), 1.6 accounts for different diffusivities of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  through leave stomata,  $R_* = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$  is the universal molar gas constant, and  $T$  is the canopy air temperature (K). We assume  $c_c$  and  $T$  to be  
35 equal to the ambient  $\text{CO}_2$  concentration and the 2 m temperature respectively.

## S1.3 Canopy scaling

A simple big-leaf approach is applied to scale up leaf-level variables to the canopy-level variables. It is assumed that incident light is attenuated by the canopy according to Beer's law:

$$I(L) = I_0 e^{-kL} \quad (\text{S7})$$

40 where  $I(L)$  and  $I_0$  are the irradiance at the height of the canopy with cumulative leaf area index  $L$  and at the top of the canopy, respectively, and  $k$  is the PAR extinction coefficient of the canopy. It is also assumed that the in-canopy leaf photosynthetic capacity  $V_{\text{cmax}}$  at different heights vary proportionally to the in-canopy light profile. Therefore, from Eq. (S4), (S5) and (S6), leaf-level net photosynthesis rate  $A_n$ , dark respiration rate  $R_d$ , and stomatal conductance  $g_{s0}$  also follow the same profile. Integrating over the entire canopy, the canopy-level net photosynthesis  $A_c$ , respiration  $R_{dc}$  and stomatal conductance  $g_s$  are  
45 given by:

$$A_c = A_n \frac{1 - e^{-kL_c}}{k} \quad (\text{S8})$$

$$R_{dc} = R_d \frac{1 - e^{-kL_c}}{k} \quad (\text{S9})$$

$$g_s = g_{s0} \frac{1 - e^{-kL_c}}{k} \quad (\text{S10})$$

where  $L_c$  is the canopy total leaf area index ( $\text{m}^2 \text{ m}^{-2}$ ).

## 50 S1.4 Stomatal closure parameterization

A third equation by Jacobs (1994) relating  $c_i$  and  $g_s$  via canopy humidity deficit  $D$  ( $\text{kg}_w \text{ kg}_a^{-1}$ ) is included to obtain a closed set of equations for  $A_n$ ,  $g_{s0}$  and  $c_i$ . This formulation was discussed in detail by Cox et al. (1998).

$$\frac{c_i - \Gamma}{c_c - \Gamma} = f_0 \left( 1 - \frac{D}{D_*} \right) \quad (\text{S11})$$

where  $f_0$  and  $D_*$  are PFT-specific parameters.  $D$  is evaluated as the difference between the saturation specific humidity ( $\text{kg}_w \text{ kg}_a^{-1}$ ) evaluated at leaf temperature  $T_l$  and the 2 m specific humidity. We assume a thin leaf boundary layer,  $T_l$  would be equal  
55 to the 2 m air temperature.

### S1.5 Soil moisture stress

Under dry soil conditions,  $A_n$ ,  $R_d$  and  $g_{s0}$  are reduced due to limited availability of water. An extra factor  $\beta_t$ , which ranges from 0 to 1, is multiplied to all three quantities. It is modeled as:

$$\beta_t = \begin{cases} 1 & \text{for } \theta > \theta_c \\ \frac{\theta - \theta_w}{\theta_c - \theta_w} & \text{for } \theta_w < \theta \leq \theta_c \\ 0 & \text{for } \theta \leq \theta_w \end{cases} \quad (\text{S12})$$

where  $\theta = S \times \theta_s$  is the root zone soil moisture,  $S$  is the root zone soil wetness (in terms of fraction of soil pore space), and  $\theta_s$ ,  $\theta_c$  and  $\theta_w$  are the saturation, critical and wilting soil moisture, respectively. We use the soil ancillary maps that contain  $\theta_s$ ,  $\theta_c$  and  $\theta_w$  at  $0.5^\circ \times 0.5^\circ$  resolution from HadGEM2-ES.

### S1.6 O<sub>3</sub> damage

The O<sub>3</sub> damage scheme in JULES is based on Sitch et al. (2007). When the ambient O<sub>3</sub> concentration is high enough,  $A_n$ ,  $R_d$  and  $g_{s0}$  is further reduced due to O<sub>3</sub> damage on plant cells. An O<sub>3</sub> damage factor  $\beta_{O_3}$ , which ranges from 0 to 1, is multiplied to the three quantities. The damage factor is given by:

$$\beta_{O_3} = 1 - a \times \max[F_{O_3} - F_{O_3 \text{ crit}}, 0] \quad (\text{S13})$$

where  $F_{O_3}$  is the O<sub>3</sub> deposition flux through stomata ( $\text{nmol m}^{-2} \text{ s}^{-1}$ ),  $F_{O_3 \text{ crit}}$  is the threshold for stomatal O<sub>3</sub> uptake ( $\text{nmol m}^{-2} \text{ s}^{-1}$ ), and  $a$  is the gradient of the O<sub>3</sub> dose response function ( $\text{nmol}^{-1} \text{ m}^2 \text{ s}$ );  $a$  and  $F_{O_3 \text{ crit}}$  are PFT-specific parameters. There are two sets of values of  $a$  corresponding to “high” and “low” sensitivities. The stomatal O<sub>3</sub> deposition flux is modeled using a flux gradient approach:

$$F_{O_3} = \frac{[O_3]}{r_a + r_b + \kappa_{O_3} r_s} \quad (\text{S14})$$

where  $[O_3]$  is the molar concentration of O<sub>3</sub> at the lowest model level,  $r_a$  is the aerodynamic resistance ( $\text{s m}^{-1}$ ),  $r_b$  is the quasi-laminar sublayer resistance,  $r_s = 1 / g_s$  is the stomatal resistance, and  $\kappa_{O_3} = 1.61$  accounts for the relative difference in diffusivities of O<sub>3</sub> and H<sub>2</sub>O through leaf stomata. Since  $r_s$  in equation (14) depends on  $\beta_{O_3}$ , equations (S13) and (S14) can be combined into a quadratic equation and solved analytically to give  $\beta_{O_3}$ .

### S1.7 Open vs. closed stomata

It is important to note that open and closed stomata are treated differently in the module. Open stomata follow the processes described above. Closed stomata are assigned a minimum value of stomatal conductance  $g_{\min} = 10^{-6} \text{ m s}^{-1}$ . Photosynthesis and O<sub>3</sub> deposition cannot occur, and thus  $A_n$  is only affected by  $R_d$  and  $\beta_t$ :

$$A_n = -R_d \beta_t \quad (\text{S15})$$

Closed stomata are determined by

1.  $g_{s0} \leq g_{\min}$ , which indicates that  $g_{s0}$  is close to zero and the associated fluxes can be neglected,
2.  $A_n \leq 0$ , which indicates that photosynthesis is not effective, and thus plants close the stomata,
3.  $D \geq D_*$ , which implies  $c_i \leq \Gamma$  from Eq. (S11), hence there is no net uptake of  $\text{CO}_2$  across stomata,
4.  $\beta_t = 0$ , which implies a dry soil condition inhibiting photosynthesis, or
5.  $\phi = 0$ , which implies that PAR is not available for photosynthesis.

### S1.8 Photosynthesis-dependent isoprene emission

In priorGEOS-Chem, canopy isoprene emission is computed by MEGAN v2.1, which calculates biogenic VOC emissions of various species as functions of canopy-scale PFT-specific emission factors modulated by environmental activity factors to account for changing temperature, light, leaf age and LAI, weighted by the PFT fraction in each grid cell to give the grid cell-level emission fluxes. The activity factors are essentially semi-empirical functions constrained by experimental data, not explicitly linked to mechanistic ecophysiological processes. Here in the ecophysiology module, canopy isoprene emission ( $E_{\text{isoprene}}$ ,  $\text{kg C m}^{-2} \text{ s}^{-1}$ ) is linked explicitly to photosynthesis, based on Pacifico et al. (2011):

$$E_{\text{isoprene}} = \text{IEF } \rho_{\text{leaf}} \frac{A_c + R_{\text{dc}}}{(A_n)_{\text{st}} + (R_d)_{\text{st}}} f_T f_{\text{CO}_2} \quad (\text{S16})$$

where IEF is the PFT-specific isoprene emission factor ( $\mu\text{g C g dw}^{-1} \text{ h}^{-1}$ , “dw” means dry weight), i.e., base emission rate of isoprene at the leaf level under standard conditions (i.e., temperature of  $30^\circ\text{C}$ , photosynthetically active radiation of  $1000 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ,  $\text{CO}_2$  concentration of 370 ppm and without any  $\text{O}_3$  damage or soil moisture stress),  $\rho_{\text{leaf}}$  is the dry leaf area density ( $\text{g dw}^{-1} \text{ m}^{-2}$ ),  $f_T$  and  $f_{\text{CO}_2}$  are temperature- and  $\text{CO}_2$ -dependent empirical factors to account for variation with changing temperature and  $\text{CO}_2$  level. Variables with subscript “st” are calculated under standard conditions.  $f_T$  and  $f_{\text{CO}_2}$  are calculated as:

$$f_T = \min[e^{a_T(T - T_{\text{st}})}; 2.3] \quad (\text{S17})$$

$$f_{\text{CO}_2} = (c_i)_{\text{st}} / c_i \quad (\text{S18})$$

where  $a_T = 0.1 \text{ K}^{-1}$ ,  $T_{\text{st}} = 300 \text{ K}$ ,  $c_i$  is the partial pressure of  $\text{CO}_2$  in the intercellular space. We note that, as opposed to Pacifico et al. (2011), our model does not capture a reduction in  $c_i$  following soil moisture limitation because we use prescribed 2 m specific humidity data in the meteorological input to calculate  $c_i$ . The effect of soil moisture stress on isoprene emission is only captured in the calculation of  $A_c$  and  $R_{\text{dc}}$ . This may lead to a lower isoprene emission rate compared to the original scheme, but direct comparison is not possible due to different input meteorology used in our study.

### S1.9 Photosynthesis model parameterization

Parametrizations of  $V_{\text{cmax}}$ ,  $\Gamma$ ,  $K_c$  and  $K_o$  in the photosynthesis model follows from Clark et al. (2011).

Maximum carboxylation rate  $V_{\text{cmax}}$  is parametrized using PFT-specific values of  $n_e$  (mol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> kg C (kg N)<sup>-1</sup>), top leaf nitrogen concentration  $n_0$  (kg N (kg C)<sup>-1</sup>), and an optimal temperature range represented by  $T_{\text{upp}}$  (°C) and  $T_{\text{low}}$  (°C).  $V_{\text{cmax}}$  is formulated as:

$$115 \quad V_{\text{cmax}} = \frac{n_e n_0 f_T(T_c)}{[1 + e^{0.3(T_c - T_{\text{upp}})}][1 + e^{0.3(T_{\text{low}} - T_c)}]} \quad (\text{S19})$$

where  $T_c$  is the canopy air temperature (°C) and  $f_T$  is the  $Q_{10}$  temperature dependence with default value of  $Q_{10\_leaf} = 2$ :

$$f_T(T_c) = Q_{10\_leaf}^{0.1(T_c - 25)} \quad (\text{S20})$$

CO<sub>2</sub> photorespiration compensation point  $\Gamma$  is modelled as

$$\Gamma = \begin{cases} \frac{o_a}{\tau} & \text{for } C_3 \text{ plants} \\ 0 & \text{for } C_4 \text{ plants} \end{cases} \quad (\text{S21})$$

120 where  $o_a$  is the partial pressure (Pa) of O<sub>2</sub> and  $\tau$  is the Rubisco specificity for CO<sub>2</sub> relative to O<sub>2</sub> with default value of  $Q_{10\_rs} = 0.57$ :

$$\tau = 2600 Q_{10\_rs}^{0.1(T_c - 25)} \quad (\text{S22})$$

The Michaelis-Menten coefficients  $K_c$  and  $K_o$  are also calculated using the  $Q_{10}$  temperature dependence with default values of  $Q_{10\_Kc} = 2.1$  and  $Q_{10\_Ko} = 1.2$ :

$$125 \quad K_c = 30 Q_{10\_Kc}^{0.1(T_c - 25)} \quad (\text{S23})$$

$$K_o = 30000 Q_{10\_Ko}^{0.1(T_c - 25)} \quad (\text{S24})$$

### S1.10 Smooth minimum of co-limiting photosynthesis rates

To smoothen the transition from one limiting rate to another, double quadratic equations with convexity factors  $\beta_1 = 0.83$  and  $\beta_2 = 0.93$  are used:

$$130 \quad \beta_1 W_p^2 - (W_c + W_l)W_p + W_c W_l = 0 \quad (\text{S25})$$

$$\beta_2 W^2 - (W_p + W_e)W + W_p W_e = 0 \quad (\text{S26})$$

The smaller quadratic root of each equation is used.

135 **Table S1: PFT-specific parameters used in the ecophysiology module. #, ^ and + indicates the parameters are taken from Clark et al. (2011), Raoult et al. (2016) and Sitch et al. (2007) respectively.**

Symbol	Unit	Name	Broadleaf	Needleleaf	C <sub>3</sub>	C <sub>4</sub>	Shrub
			tree	tree	grass	grass	
$k$	/	PAR extinction coefficient <sup>#</sup>	0.5	0.5	0.5	0.5	0.5
$\alpha$	mol CO <sub>2</sub> mol <sup>-1</sup> PAR	Quantum efficiency <sup>#</sup>	0.131	0.096	0.179	0.118	0.102
$n_0$	kg N (kg C) <sup>-1</sup>	Top leaf nitrogen concentration <sup>^</sup>	0.061	0.065	0.07	0.051	0.041
$n_e$	$\frac{\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}}{\text{kg N (kg C)}^{-1}}$	Ratio of $V_{\text{cmax}}$ to $n_0$ <sup>#</sup>	800	800	800	400	800
$T_{\text{upp}}$	°C	Upper temperature parameter <sup>^</sup>	38.578	34.721	36.242	44.897	35.385
$T_{\text{low}}$	°C	Lower temperature parameter <sup>^</sup>	1.203	-8.698	-1.985	11.37	-5.208
$f_{\text{dr}}$	/	Dark respiration coefficient <sup>#</sup>	0.015	0.015	0.015	0.025	0.015
$D^*$	kg <sub>w</sub> kg <sub>a</sub> <sup>-1</sup>	Closure parameter <sup>^</sup>	0.048	0.036	0.086	0.046	0.077
$f_0$	/	Closure parameter <sup>^</sup>	0.765	0.737	0.817	0.765	0.782
$a$	nmol <sup>-1</sup> m <sup>2</sup> s	Slope of O <sub>3</sub> dose response <sup>+</sup> (Low sensitivity)	0.04	0.02	0.25	0.13	0.03
-	-	Slope of O <sub>3</sub> dose response <sup>+</sup> (High sensitivity)	0.15	0.075	1.40	0.735	0.10
$F_{\text{O3 crit}}$	nmol m <sup>-2</sup> s <sup>-1</sup>	O <sub>3</sub> uptake threshold <sup>#</sup>	1.6	1.6	5.0	5.0	1.6

**Long-term stomatal response to changing ambient CO<sub>2</sub> concentration**

According to Franks et al. (2013), the relative change of stomatal conductance can be approximated by:

140 
$$g_{s(\text{rel})} \approx \frac{A_{n(\text{rel})}}{c_{a(\text{rel})}} \tag{S27}$$

where  $g_{s(\text{rel})}$ ,  $A_{n(\text{rel})}$ , and  $c_{a(\text{rel})}$ , are, respectively,  $g_s$ ,  $A_n$  and the ambient CO<sub>2</sub> concentration  $c_a$  relative to their values under a reference ambient CO<sub>2</sub> concentration  $c_{a0}$ .  $A_{n(\text{rel})}$  is further approximated by:

$$A_{n(\text{rel})} = \frac{(c_a - \Gamma^*)(c_{a0} + 2\Gamma^*)}{(c_a + 2\Gamma^*)(c_{a0} - \Gamma^*)} \tag{S28}$$

where  $c_{a0}$  and  $\Gamma^*$  are the reference [CO<sub>2</sub>] (ppm) and CO<sub>2</sub> compensation point (ppm) in absence of dark respiration respectively.

145 Following Franks et al. (2013), we use  $c_{a0} = 360$  ppm and  $\Gamma^* = 40$  ppm. Therefore, for  $c_a = 580$  ppm,  $g_{s(\text{rel})} = 0.698$ .

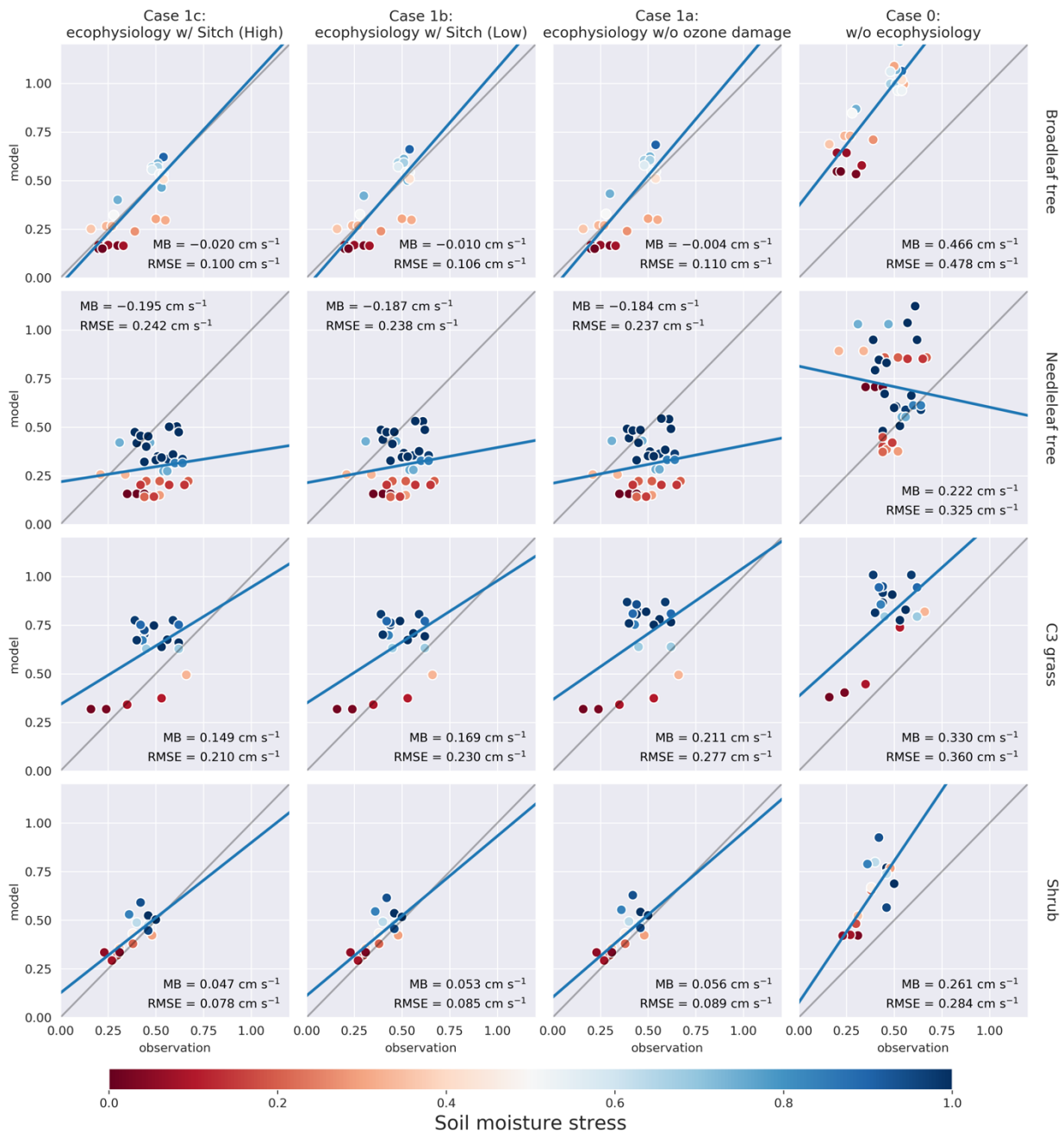
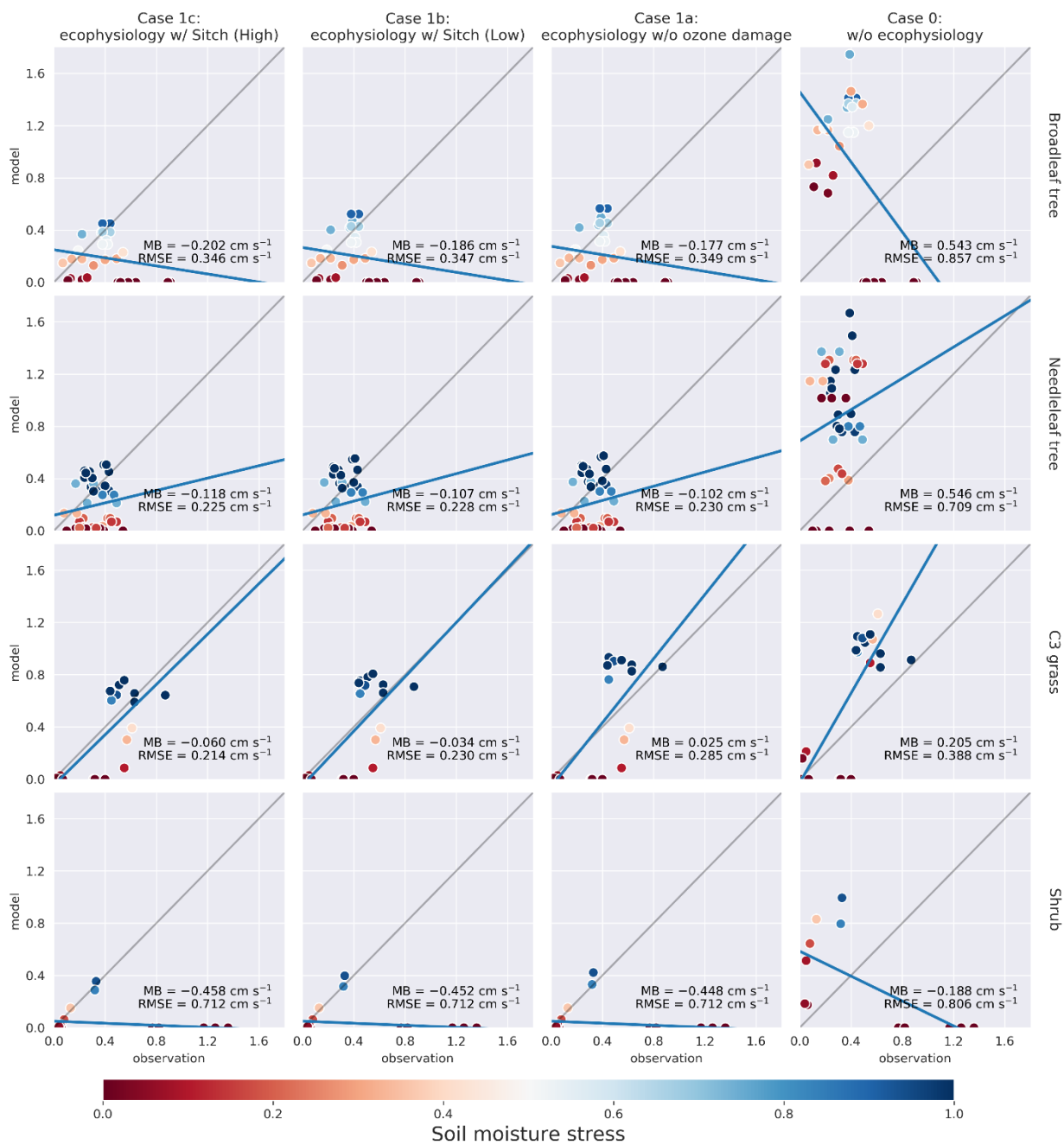


Figure S1: Plots of modeled monthly mean dry deposition velocity of  $O_3$  ( $cm\ s^{-1}$ ) in northern summer (JJA) against SynFlux estimates, categorized by site PFT for each simulation case. Columns from right to left represent simulation cases 0, 1a, 1b and 1c. Each row corresponds to a PFT. C4 grass is ignored due to a lack of observational data. The soil moisture stress factor  $\beta_t$  on the corresponding model grid cell is represented by the color of the circle. Mean bias (MB) and root-mean-squared error (RMSE) are shown for each plot.





155 Figure S2: Same as Fig. S1, but for modeled monthly mean stomatal conductance  $g_s$  ( $\text{cm s}^{-1}$ ).

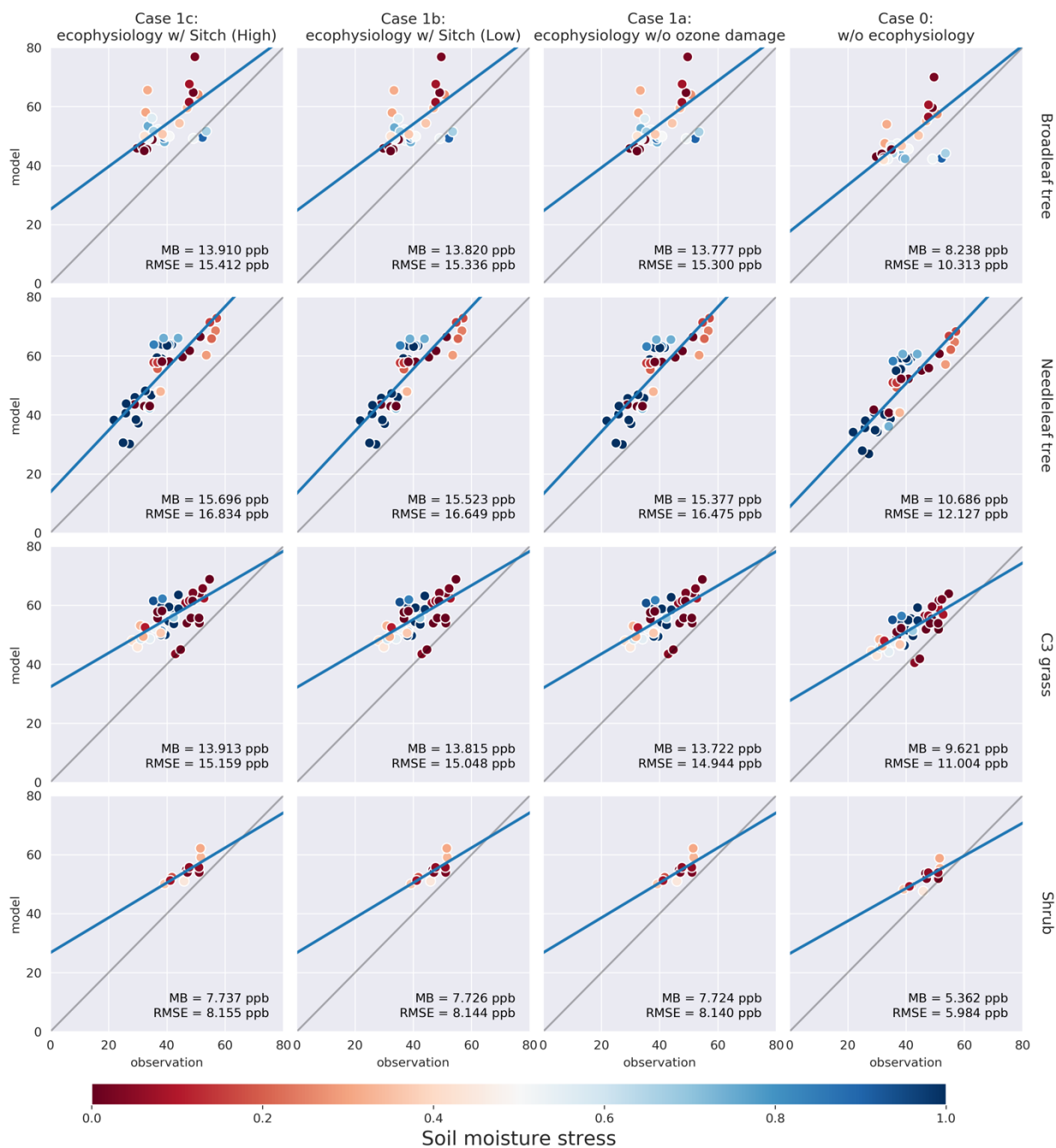
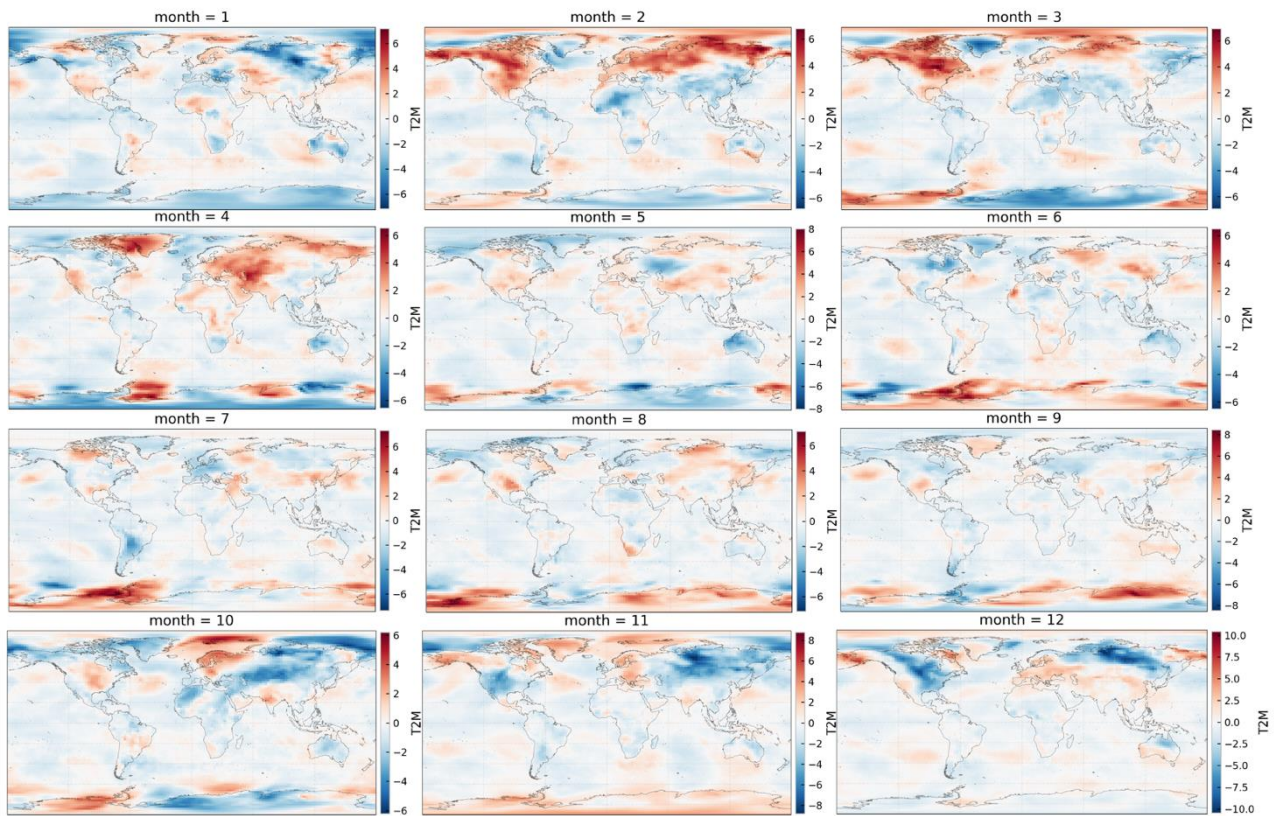


Figure S3: Same as Fig. S2, but for modeled monthly mean  $O_3$  concentration (ppbv).



**Figure S4: Monthly averages of 2 m temperature in year 2000 minus monthly averages from year 2000-2009.**