# Defra report for ESX-$DO_3SE$ modelling work


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### 1. Background

This project was part funded by Defra (£10k), Chalmers University (£25k) and SEI York (£7k). The project provided resources for programming of the new ESX deposition scheme into the EMEP chemistry transport model. Specifically this programming allowed new $DO_3SE$ algorithms (capable of modelling photosynthesis and soil water status) to be incorporated into the ESX-$DO_3SE$ model and consequently into future versions of the European EMEP model. This ensures that the flux-based ozone deposition and damage estimates that have been developed in recent years supported by Defra funding, are incorporated into the new EMEP European modelling tool that is used for policy negotiations within the UNECE LRTAP Convention.

The ESX model provides a new method of estimating atmospheric and in canopy exchange of pollutants. This model was developed by colleagues at EMEP (Dr. David Simpson) and the Finnish Meteorological Institute (FMI, Dr. Juha-Pekka Tuovinen). The ESX scheme is not based on resistances but relies on numerically solving diffusion equations for different pollutants with a parameterised exchange coefficient; essentially these equations replace the atmospheric and boundary layer resistances currently in the EMEP and $DO_3SE$ models. The benefit of this unique approach is that these models are able to estimate both downward and upward flux of pollutants (i.e. can cope with pollutants that are both deposited to- as well as emitted from- vegetation such as ammonia ($NH_3$)). Prior to this project ESX existed as a first-version matlab code and 'in development' Fortran code. This project had three main aims:

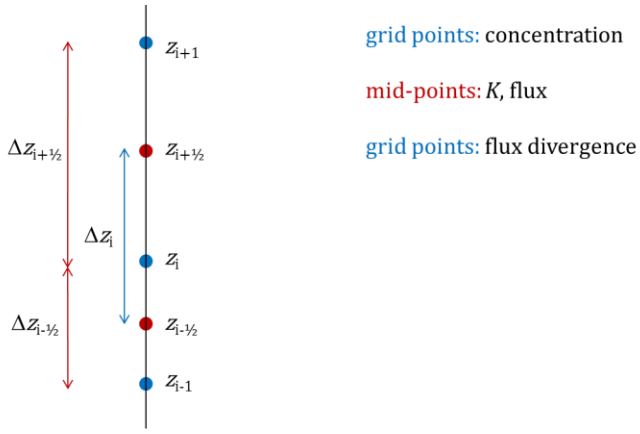
i. develop the Fortran coding of the ESX-$DO_3SE$ model so that the model embeds within the EMEP CTM scheme;
ii. incorporate the $DO_3SE$ models photosynthesis and coupled photosynthesis-stomatal conductance module and;
iii. incorporate the $DO_3SE$ soil moisture module.

### 2. Brief overview of the ESX scheme

The ESX model includes a layer-based canopy framework, numerical solutions to pollutant dispersal and the EMEPs model atmospheric chemistry algorithms. Each layer contains pollutant sources and sinks (e.g. due to presence of vegetation), has chemical interactions calculated within it, and is affected by dispersal between layers (see Figure 1; where $z_i$ relates to pollutant

mass transfer either as a source ($z_i$+1) or a sink ($z_i$-1) from a pollutant concentration defined at $z_i$). The model is designed to run over a short time step to work within EMEP's larger scale chemical transport model.

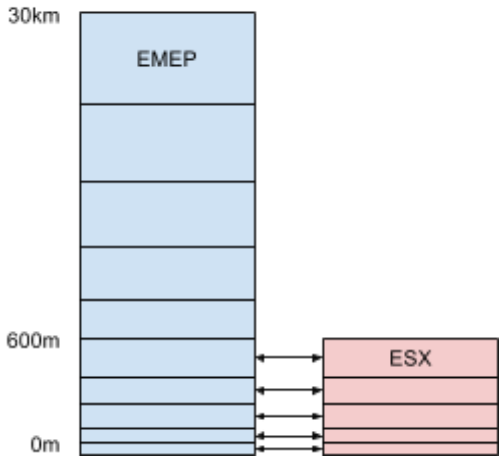
**Figure 1.** A conceptualisation of the quantification of pollutant fluxes between layers within the ESX model.




$DO_3SE$ fits into this scheme by providing a sophisticated approach to calculating stomatal fluxes, and therefore pollutant exchange with the vegetation, in each of the canopy layers. Stomatal conductance is calculated on a per-layer basis using both general meteorological data and per-layer values resulting from the dispersal model (e.g. $CO_2$ concentration) and other canopy-related effects (e.g. attenuation of sunlight).

## 3. Development of the Fortran coding of the ESX-$DO_3SE$ model.

ESX can be described as a one-dimensional chemical transport model, working on a vertical grid, for a single land cover type. EMEP also has vertical transport within its larger 3-dimensional scheme, in addition to the large-scale horizontal grid and for several land covers per grid square. The EMEP model also uses several nested time intervals, most notably daily, 3-hourly, hourly and 20 minutes. As a smaller-scale model, ESX is run for every 20-minute interval, and every appropriate land cover, to solve the localised diffusion and chemical interactions. It is initialised with a starting state from the EMEP model's chemical concentrations data for the vertical range that ESX is being run for, and resulting fluxes are fed back to this data.




The ESX-$DO_3SE$ project started in May with Alan Briolats first 3 week trip to Gothenburg (20th May - 7th June 2013). During this trip meetings were held to transfer knowledge of ESX's design and the Fortran code written so far from the EMEP team to Alan. The already existing code included much of the diffusion and chemical mechanism models (the latter being re-used from EMEP) written by Dave Simpson. From this starting point Alan and Dave worked together to create a framework within which the various parts of the ESX-$DO_3SE$ model could reside, i.e. the data flow between meteorological inputs, chemical concentrations, the diffusion model and $DO_3SE$'s stomatal conductance model. This involved informing Dave of the latest developments in the $DO_3SE$ model, especially regarding the sorts of input data it would need from the rest of the model. A major challenge was to establish how to compromise on the design of both $DO_3SE$ and ESX to allow ESX's version of $DO_3SE$ to easily be updated with the most recent $DO_3SE$ model developments without re-integration being a major undertaking each time changes were made to the $DO_3SE$ model.

Similar considerations were needed to establish how to write ESX code that could be a standalone prototype but also be called from EMEP code. Alan worked on organising data variables within the model, grouping them where appropriate to give a coherent picture of flow within the model and making the code more maintainable. Alan also started re-designing aspects of SEI's version of $DO_3SE$ to allow it to be called from ESX code without hard-to-debug side-effects and without invoking aspects of the $DO_3SE$ model that were in contradiction to the ESX model. This decoupling of $DO_3SE$ methods from each other and the ESX model will allow improvements in this area to be tested within $DO_3SE$, ESX and EMEP with much less effort than before. This first trip resulted in the production of a standalone ESX proof of concept model that could be driven by meteorological data, run a chemical interaction scheme and solve the diffusion model for vertical transport.

Having returned from this first trip, Alan spent time at SEI York implementing the necessary

changes to the $DO_3SE$ model code to allow various components to work independently and be called from the ESX model.

The second 3 week trip to Gothenburg (23rd September - 11th October) started with integrating the newly-adapted $DO_3SE$ code into the ESX code, enabling both multiplicative- and photosynthetic-based stomatal conductance methods to be configured and used by ESX. (N.B. the new photosynthetic-stomatal conductance model is described in Annex 1). Code for the soil moisture part of the $DO_3SE$ model was also integrated (for further details of this module see (Büker et al., 2012). Some additional work was required here to support the modelling of soil water content within ESX. Since ESX was already using some code duplicated from EMEP, ESX was converted to a "sub-project" of EMEP's codebase and a lot of duplication was removed, this allows easier maintainability and integration with EMEP.

Dave Simpson then informed Alan of EMEP's structure and methodology. Some elements of this were relevant for the design of ESX, to keep its eventual position within the EMEP model in mind. This knowledge also provided an understanding of how EMEP actually operates, how data flows between parts of it, and how this would need to be adapted to communicate data to and from the ESX model. The EMEP model runs several nested time loops, and in the innermost loop, deposition is calculated for each land use category. As a starting point, we chose this part of the model to call ESX, driving it with the data available at this stage, and recording the results, without feeding them back into EMEP. This was to allow the behaviour of ESX to be analysed without introducing any feedback-driven anomalies.

On return to SEI York Alan worked to integrate ESX more closely with EMEP. This work is on-going and is funded by the Chalmers portion of funding.

**5. Summary of outputs**

**Complete**

- Knowledge transfer of ESX design to Alan Briolat (SEI York).
- Development of ESX prototype incorporating multi-layer canopy model, diffusion-based transport and chemical mechanisms.
- Knowledge transfer of latest $DO_3SE$ methods to Dave Simpson.
- Incorporation of $DO_3SE$ methods (including the recently developed photosynthesis-stomatal conductance and soil moisture module) into the ESX prototype.
- Knowledge transfer of running/developing EMEP to Alan Briolat (SEI York).

**Annex 1.** Description of the new $DO_3SE$ photosynthesis-stomatal conductance model.

The objective of the coupled photosynthesis-stomatal conductance model ($A_{net}$-$g_{sto}$) model is to quantify leaf or canopy scale $g_{sto}$ with the help of easily accessible environmental parameters such as air temperature ($T_{air}$), ambient $CO_2$ concentration ($c_a$) and irradiance ($PAR$). The $A_{net}$-$g_{sto}$ model consists of a combination of two separate models, whose main components are outlined below and include i. the empirical $A_{net}$-$g_{sto}$ model that estimates $g_{sto}$ (Leuning, 1990) and ii. the mechanistic and biochemical Farquhar model (Farquhar et al., 1980) that estimates net carbon assimilation or net phostosynthesis ($A_{net}$).

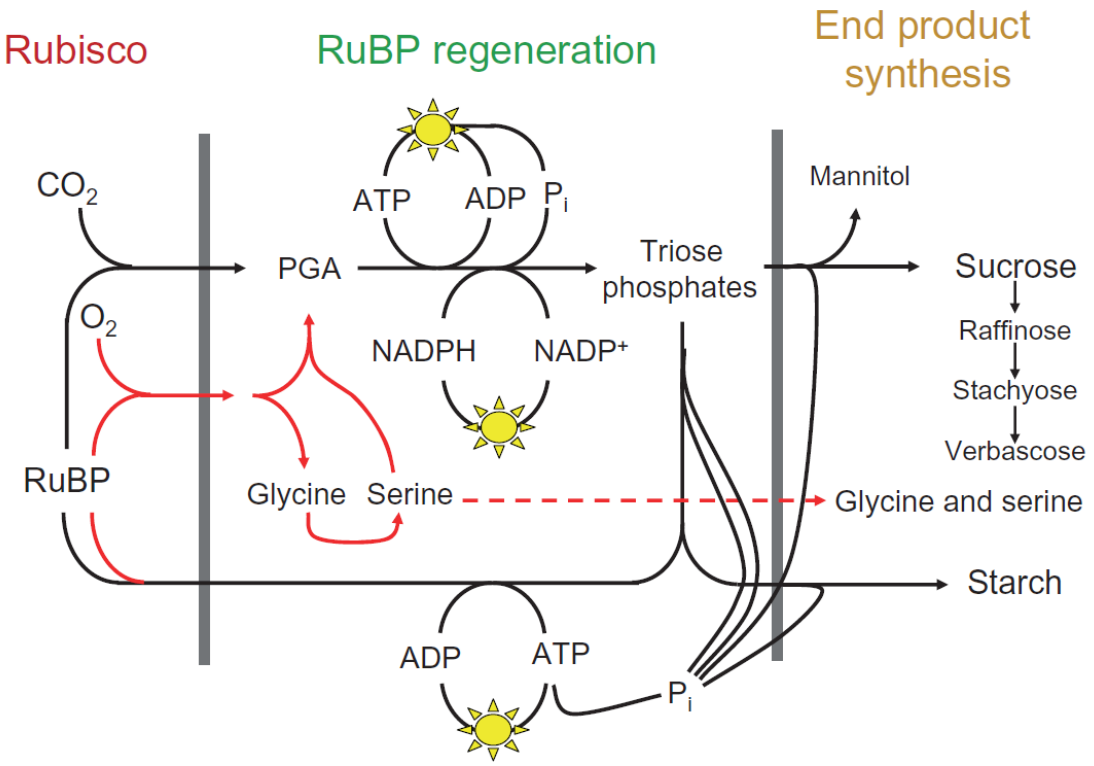
One of the first coupled $A_{net}$-$g_{sto}$ models was that published by (Leuning, 1990) though some other authors are often cited as the originating sources of the model (e.g. Collatz et al., 1991 and Harley et al., 1992). The models they apparently developed independently are essentially equivalent. The order of description of the $A_{net}$-$g_{sto}$ modelling here follows the order in which they have to be computed.

### i. Biochemical Farquhar model for net photosynthesis ($A_{net}$)

The underlying assumption to Farquhars's 1980 model is that, according to prevailing environmental conditions, either rubisco activity ($A_c$) or the regeneration of ribulose-1,5-bisphosphate (RuBP) which is limited by the rate of electron transport ($A_j$) limits photosynthesis. Subsequent to Farquhar's 1980 paper, Harley et al. (1992) identified a third limitation resulting from inadequate rate of transport of photosynthetic products (most commonly this is due to triose phosphate utilization) ($A_p$), this limit has now become standard in many models of $A_{net}$ (e.g. Sellers et al., 1996; Cox et al., 1999) and is included here. Taking these influences on photosynthesis into account $A_{net}$ is calculated by determination of the smaller of these theoretical $CO_2$ assimilation rates less the rate of dark respiration ($R_d$) (Farquhar et al., 1980) as in eq. 1 and as described in Fig 1.

$$\boldsymbol{A_{net} = \min\left(A_c, A_j, A_p\right) - R_d} \qquad 1$$

**Figure 1.** Scheme showing some of the processes that affect photosynthetic rate. For each of the three panels, any process in that panel will cause the photosynthetic rate to vary with $[CO_2]$ in the same way. From Sharkey et al. (2007).




Within the literature there are small variations in the precise methods to estimate Ac, Aj and Ap. One important application of our $A_{net}$-$g_{sto}$ model is that it is to be made with empirical data collected at sites across Europe. This provides the opportunity to use empirical data to parameterise the key components of the model; however methods to perform this parameterisation should be consistent with these methods used to estimate $A_{net}$. Therefore our model will follow the eqs. recently described by Sharkey et al. (2007) since these are expected to represent both the most recent formulations as well as those that are consistent with the derivation of key parameters. The potential rate of assimilation, limited only by Rubisco activity ($A_c$) is calculated according to Sharkey et al. (2007) as in eq 2.

$$A_c = V_{cmax}\left[\frac{C_i - \Gamma*}{C_i + K_c\cdot\left(1+\frac{O_i}{K_o}\right)}\right] \qquad 2$$

Where $V_{Cmax}$ is the maximum rate of Rubisco activity, $c_i$ and $O_i$ are intercellular concentrations of $CO_2$ and $O_2$ respectively, $K_c$ and $K_o$ are the Michaelis-Menten coefficients of Rubisco for $CO_2$ activity (in μmol $mol^{-1}$) and $O_2$ (in mmol $mol^{-1}$) , respectively, and Γ* is the $CO_2$ compensation point in the absence of mitochondrial (dark) respiration.

The potential rate of assimilation when RuBP regeneration is limiting is given in eq. 3.

$$A_j = J.\frac{C_c - \Gamma*}{a.C_c + b.\Gamma*} \qquad 3$$

Where $J$ is the electron transport rate, the parameters $a$ and $b$ denote the electron requirements for the formation of NADPH and ATP respectively. The exact values differ slightly throughout the literature but are all close to $a$=4 and $b$=8 assuming four electrons per carboxylation and oxygenation (Sharkey et al., 2007). $J$ is related to incident photosynthetically active photon flux density ($Q$) where the light response of a plants photosystem first follows a linear rise with an increase in radiation $Q$ until it reaches an area of saturation where the electron transport rate $J$ approaches the maximum value of $J_{max}$. Mathematically this is represented by the quadric relationship shown in eq. 4 after Leuning (1990).

$$J = \frac{(J_{max} + \propto Q) - \sqrt{(J_{max} + \propto Q)^2 - 4 \propto Q \emptyset J_{max}}}{2.\emptyset} \qquad 4$$

Where α is the quantum yield of electron transport, which determines the slope of the linear rise in the low irradiance regime, and Ø is the curvature of the light response curve normally acquired by experimental fitting. The value of α was fixed at 0.3 mol electrons mol-1 photon, based on an average C3 photosynthetic quantum yield of 0.093and a leaf absorptance of 0.8 (cf. Medlyn et al., 2002). The value of Ø was taken to be 0.90 (Medlyn et al., 2002). These parameter values have only a slight effect on the estimated value of $J_{max}$.

Finally, the potential rate of assimilation when the utilization of triose phosphate is limiting assimilation ($A_p$) (i.e. when the chloroplast reactions have a higher capacity than the capacity of the leaf to use the products of the chloroplasts) is estimated rather simply by eq. 5 after (Collatz et al., 1991).

$$A_p = 0.5\ .V_{cmax} \qquad 5$$

The key parameters of the model $J_{max}$ and $V_{Cmax}$, as well as the parameters $K_c$, $K_o$ and Γ*, all vary with temperature (Medlyn et al., 2002). $J_{max}$ and $V_{Cmax}$ also vary between species, whilst $K_c$, $K_o$ and Γ*are considered intrinsic properties of the Rubisco enzyme and therefore can be assumed

constant between species (Harley et al., 1986). Due to the temperature effects on the Rubisco enzyme which catalyses the corresponding process, Γ* is temperature dependent as well.

The original model of Farquhar et al. (1980) used a purely empirical polynomial from (Brooks & Farquhar, 1985) which approximated the temperature dependence of these different parameters, since then many studies have investigated these temperature dependencies more thoroughly, here we follow the rational of Medlyn et al. (2002) who advised using the temperature relationships provided by Bernacchi et al. (2001) who used an Arrhenius equation to describe the processes and based these functions on measurements made *in vivo* without disturbance of the leaf. The rate of dark respiration $R_d$, Γ* and the Michaelis-Menten constants for $CO_2$ and $O_2$ ($K_c$ and $K_o$) are computed using the standard formulations described in eq 6

and $$P(T) = P_{T,Ref}.exp\left(\frac{\Delta H_a.(T-T_{ref})}{T_{ref}.R.T}\right).\frac{1+exp\left(\frac{T_{ref}\Delta S-\Delta H_d}{T_{ref}.R}\right)}{1+exp\left(\frac{T\Delta S-\Delta H_d}{T.R}\right)}$$ 7.

$$P(T) = P_{T,Ref}.exp\left(\frac{\Delta H.(T-T_{ref})}{T_{ref}.R.T}\right)$$ 6

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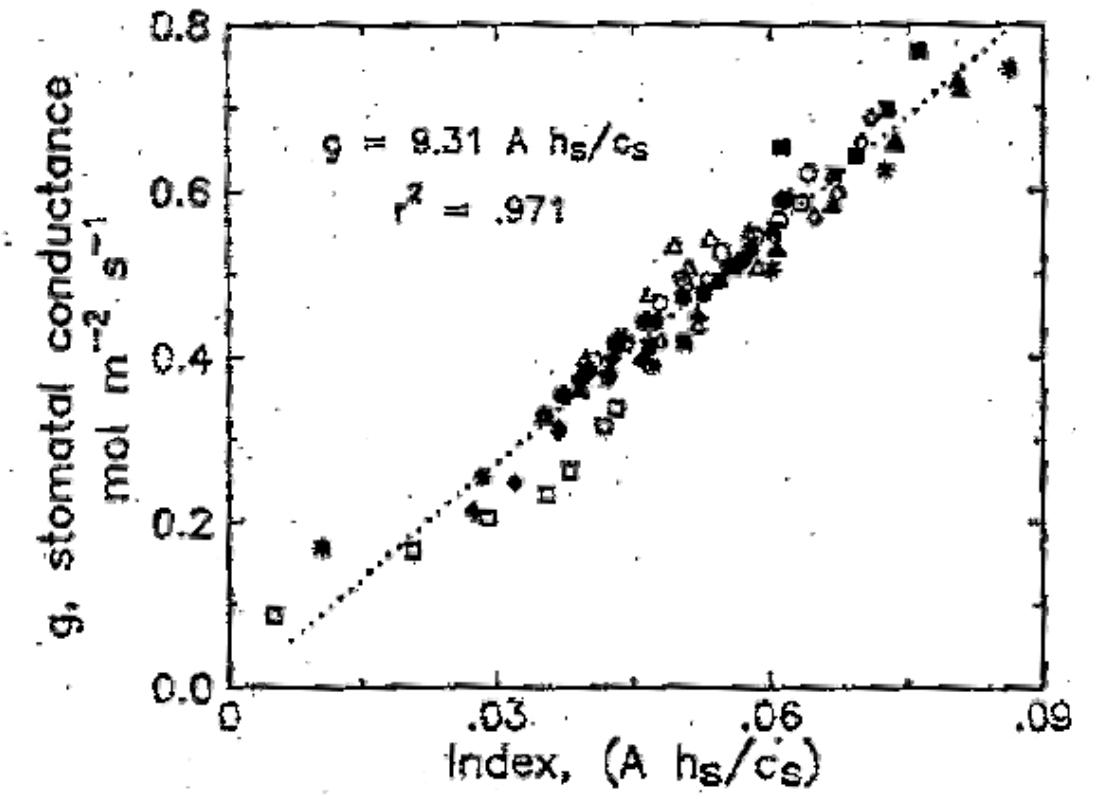
where $P$ denotes the different quantities, $\Delta H$ is the activation energy $\Delta Hd$ is the deactivation energy and $\Delta S$ is entropy for the processes, values for each process follow those given in Bernacchi et al. (2001). In general this formula describes a normal Arrhenius equation modified to incorporate an inhibition term at high temperatures.

In summary, the Farquhar model mathematically quantifies a detailed mechanistic understanding of the biochemical processes in the chloroplasts which govern photosynthesis. It allows for the estimation and calculation of the $CO_2$ assimilation rate as a function of leaf temperature, irradiance and internal $CO_2$ concentration.

### ii. Coupled photosynthesis-stomatal conductance ($A_{net}$-$g_{sto}$) model.

Based on earlier observations of the constant ratio of $g_{sto}$ to net $CO_2$ assimilation rate ($A_{net}$), Ball et al. (1987) discovered an empirical linear relationship, which relates $g_{sto}$ to a combination of $A_{net}$ and environmental parameters, such as leaf surface relative humidity ($D_h$) and $CO_2$ concentration ($C_a$) as shown in Fig 2A).

Figure 2A. The original BWB model. Stomatal conductance plotted against the BWB Index. From Ball et al. (1987).




Leuning (1990 and 1995) modified the original Ball et al. (1987) relationship so that the function used leaf surface $CO_2$ concentration ($C_s$) less the $CO_2$ compensation point (Γ). and. They argued that the use of $C_s$ rather than $C_a$ (the $CO_2$ concentration outside the leaf boundary layer) eliminates complications arising from the transfer of $CO_2$ through the leaf boundary layer. The introduction of the Γ term allows the correct simulation of stomatal behaviour at low $CO_2$ concentrations which will tend towards zero as $A_{net}$ becomes minimal close to the Γ. The use of humidity deficit ($D_s$) rather than relative humidity ($D_h$) accounts for the fact that stomates respond to humidity deficit rather than surface relative humidity; this response is actually mediated through leaf transpiration ($Et_{leaf}$) but the close link between $Et_{leaf}$ and $D_s$ means that the use of $D_s$ is appropriate for simulations. Leuning (1995) found that a hyperbolic function for $D_s$

provided an improved humidity response by accounting for the response of $D_s$ to leaf temperature. The resulting formulation they propose is given in 8.

$$g_{sto} = g_0 + m.\frac{A_{net}}{[(c_s - \Gamma)(1 + D_s/D_0)]} \qquad 8$$

The parameter $g_0$ is interpreted as the minimal $g_{sto}$ (Leuning, 1990) and is equivalent to the intercept of the regression which is sometimes greater, but often close, to zero. The parameter $m$ is the so called composite sensitivity of $g_{sto}$ to assimilation rate and humidity/$CO_2$ concentration, can be obtained *via* a linear regression of $g_{sto}$ against experimental data from steady state gas exchange measurements. The value of $m$ is surprisingly consistent amongst many different species, and ranges between 5 and 15 (Kosugi et al., 2003) (if all quantities are in units consistent with Ball et al. (1987) $m$ is dimensionless).

Despite the empirical and non-mechanistic nature of this model it allows for the mathematical quantification of the key environmental feedbacks on stomatal behaviour: (1) Rising irradiance causes stomata to open (incorporated through the positive influence of radiation on $A_{net}$); (2) Rising $CO_2$ causes stomata to close (incorporated through the negative influence of limited RuBP regeneration); (3) To minimize water loss, stomata close when the transpiration rate rises (incorporated through the response to leaf surface humidity deficit).

However, caution has to be exercised concerning interpretation of the model. It allows for no mechanistic explanation or causal interpretation of the feedbacks between the different parameters (see Aphalo & Jarvis, (1993) for a discussion) and is, strictly speaking, only a statistical correlation.

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