FORCAsT-gs: Importance of stomatal conductance parameterisation to estimated ozone deposition velocity

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November 23, 2022

Abstract

The role of stomata in regulating photosynthesis and transpiration, and hence governing global biogeochemical cycles and climate, is well-known. Less well-understood, however, is the importance of stomatal control to the exchange of other trace gases between terrestrial vegetation and the atmosphere. Yet these gases determine atmospheric composition, and hence air quality and climate, on scales ranging from local to global, and seconds to decades. Vegetation is a major sink for ground-level ozone via the process of dry deposition and the primary source of many biogenic volatile organic compounds (BVOCs). The rate of dry deposition is largely controlled by the rate of diffusion of a gas through the stomata, and this also governs the emission rate of some key BVOCs. It is critical therefore that canopy-atmosphere exchange models capture the physiological processes controlling stomatal conductance and the transfer of trace gases other than carbon dioxide and water vapour. We incorporate three of the most widely used coupled stomatal conductance-photosynthesis models into the one-dimensional multi-layer FORest Canopy-Atmosphere Transfer (FORCAsT1.0) model to assess the importance of choice of parameterisation on simulated ozone deposition rates. Modelled GPP and stomatal conductance across a broad range of ecosystems differ by up to a factor of 3 between the best and worst performing model configurations. This leads to divergences in seasonal and diel profiles of ozone deposition velocity of 1-30% and deposition rate of up to 10%, demonstrating that the choice of stomatal conductance parameterisation is critical in understanding ozone deposition.

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Key Points:

- Medlyn coupled stomatal conductance-photosynthesis model best reproduces observed plant productivity (GPP) across various ecosystems
- Modelled GPP and stomatal conductance across forest ecosystems differ by up to a factor of 3 between different model configurations
- Ozone deposition rates could vary by ~10% depending on stomatal conductance model used with implications for estimated tropospheric ozone

Abstract

The role of stomata in regulating photosynthesis and transpiration, and hence governing global biogeochemical cycles and climate, is well-known. Less well-understood, however, is the importance of stomatal control to the exchange of other trace gases between terrestrial vegetation and the atmosphere. Yet these gases determine atmospheric composition, and hence air quality and climate, on scales ranging from local to global, and seconds to decades. Vegetation is a major sink for ground-level ozone via the process of dry deposition and the primary source of many biogenic volatile organic compounds (BVOCs). The rate of dry deposition is largely controlled by the rate of diffusion of a gas through the stomata, and this also governs the emission rate of some key BVOCs. It is critical therefore that canopy-atmosphere exchange models capture the physiological processes controlling stomatal conductance and the transfer of trace gases other than carbon dioxide and water vapour. We incorporate three of the most widely used coupled stomatal conductance-photosynthesis models into the one-dimensional multi-layer FORest Canopy-Atmosphere Transfer (FORCAsT1.0) model to assess the importance of choice of parameterisation on simulated ozone deposition rates. Modelled GPP and stomatal conductance across a broad range of ecosystems differ by up to a factor of 3 between the best and worst performing model configurations. This leads to divergences in seasonal and diel profiles of ozone deposition velocity of 1-30% and deposition rate of up to 10%, demonstrating that the choice of stomatal conductance parameterisation is critical in understanding ozone deposition.

Plain language summary

Plants open and close their stomata to regulate the uptake of carbon dioxide (photosynthesis) and the release of water vapour into the atmosphere. Trace gases like ozone can also enter the stomata causing damage to leaves, reducing plant growth and productivity in the process. Stomatal conductance, the measure of stomatal opening, is therefore important for assessing the concentration of ozone in the atmosphere and the impacts of pollutants on plants. It is critical that canopy-atmosphere exchange models capture the processes controlling stomatal conductance and the transfer of trace gases other than carbon dioxide and water vapour. We incorporate three widely used coupled stomatal conductance-photosynthesis models into a 1-Dimensional multi-layer model to assess how the choice of model parameters affect the rate at which ozone is deposited onto plant surfaces. We first validate the model using observation from various forests sites and then compare ozone deposition rates between the best and worst performing model at each site. We found that ozone deposition rates could vary by up 10% in response to changes in model parameters, demonstrating that the choice of stomatal conductance parameterisation is crucial in understanding ozone deposition, a major process through which ozone is removed from the troposphere.

1 Introduction

Photosynthesis and transpiration of the world's forests drive the carbon, hydrological and nutrient cycles, governing climate, ecosystem health and productivity, and biodiversity. Forests also serve as a sink for trace gases which are deposited onto plant surfaces and taken up through the stomata. Dry deposition of ozone is of particular importance as it represents a major sink of this tropospheric pollutant. It is also of particular concern because ozone can damage photosynthetic apparatus limiting growth and productivity. The rates of photosynthesis and uptake of ozone are both dependent on the degree of stomatal opening, referred to as stomatal conductance. Plants open and close the stomata to maintain a balance between photosynthesis (CO_2 uptake) and leaf transpiration (water loss), thereby regulating the exchange of CO_2 and water vapour between vegetation and the atmosphere (Hetherington & Woodward, 2003).

Gases and particles deposited on leaf surfaces may be taken up through the stomata or cuticle into the leaf tissue. Stomatal uptake is the dominant of these routes for most reactive trace gases like ozone (Royal Society, 2008). As gases diffuse through the stomata, their concentrations are reduced at the leaf surface, increasing the concentration gradient between the leaf and the atmosphere above it. This concentration gradient drives deposition and has the net effect of increasing the speed at which the gas reaches the plant surface, known as the deposition velocity. The rate of stomatal diffusion and uptake is dependent on both the diffusivity of the gas and the size of the stomata. Deposition velocities are therefore dependent on stomatal conductance: the wider the stomatal aperture the lower the resistance to diffusion through the stomata.

It is critical that models that couple the land surface and the atmosphere are able to accurately reproduce stomatal conductance in order to account fully for the processes driving photosynthesis and trace gas deposition rates. Many empirical and semi-empirical approaches have been developed to simulate stomatal conductance. One of the earliest and most widely used is a multiplicative model

(Jarvis, 1976) which reduces stomatal conductance from its potential maximum according to observed responses to changing environmental conditions. Each environmental influence is assumed independent of the others (Damour et al., 2010) and does not consider physiological interactions or feedbacks that could alter stomatal movement (Yu et al., 2004).

Subsequent research demonstrated that stomatal aperture was also directly regulated by current photosynthesis rate (Wong et al., 1979) leading to the development of semi-empirical coupled models that assume a linear relationship between photosynthesis (*An*) and *gs*, and iterate to simultaneously solve for both (e.g. Ball et al., 1987). More recently, optimisation theory has been applied to these coupled photosynthesis-stomatal conductance models to replicate the 'regulatory' role of stomata, i.e. that plants control stomatal aperture to maximize carbon gain while minimizing water loss (Medlyn et al., 2011; Cowan and Farquhar, 1977).

The multi-layer canopy-atmosphere model FORCAsT1.0 (FORest Canopy-Atmosphere Transfer) was initially developed as an atmospheric chemistry tool for upscaling leaf-level biogenic emissions to the canopy scale and interpreting measurement data from intensive field campaigns at forest sites (CACHE; Forkel et al., 2006). It has since been modified to better capture observed dynamics and turbulent transport (CACHE; Bryan et al., 2012) and to reflect our improved understanding of the atmospheric chemistry of biogenic volatiles, particularly in low-NOx environments (FORCAsT1.0; Ashworth et al., 2015). Parameterisations of the response of isoprene emissions to water stress and re-wetting have also been incorporated into the model and demonstrated to improve model reproduction of changes in isoprene concentrations at a temperate deciduous woodland during an extended heatwave-drought (Otu-Larbi et al., 2020a).

FORCAsT1.0 contains explicit representations of canopy structure and leaf distribution to directly calculate photosynthetically active radiation (PAR) extinction through the canopy layers, and hence perform a full canopy energy balance, at every timestep. The resulting vertical temperature gradient drives turbulence and mixing within the canopy, and transport of energy, momentum, and

mass across the canopy sub-layer into the atmospheric boundary layer above, but physiology is limited to a simple parameterisation of stomatal conductance (Ashworth et al., 2015). The model has demonstrated considerable skill in reproducing observed concentrations and fluxes of short-lived biogenic reactive trace gases and their products over short time periods at a number of Northern Hemisphere forest sites (Forkel et al., 2006; Bryan et al., 2012; 2015; Ashworth et al., 2015). However, production outweighs loss processes for some gaseous species, suggesting that either deposition rates or vertical transport out of the canopy are too slow, or foliage emissions overestimated. These processes are dependent on the rate of gas exchange through the stomata, and hence the skill of the model in capturing stomatal conductance over time periods from minutes, to hours, to seasons.

Explicit inclusion of physiological processes in FORCAsT1.0 has the additional benefit of enabling model performance to be evaluated against canopy-scale photosynthesis and transpiration (canopy-top fluxes of CO_2 and water vapour) which are routinely measured and readily available over long time periods across a wide range of ecosystems. This allows a more thorough exploration and constraint of the physical and dynamical processes occurring within the canopy than is possible from concentration and flux measurements of short-lived reactive species made during short intensive field campaigns. Constraining these processes would allow us to focus more closely on the mechanisms of the production and loss of short-lived atmospherically relevant biogenic trace gases.

We incorporate three parameterisations of stomatal conductance and photosynthesis into FORCAsT1.0 to assess:

1) the ability of different coupled stomatal conductance-photosynthesis models to reproduce observed CO_2 fluxes across a range of different forest ecosystems and climate regions

2) the divergence of simulated ozone deposition velocities and deposition rates due to differences in stomatal conductance modelling approach and parameterisation

We use data from five forest sites within the FLUXNET2015 dataset (Pastorello et al., 2020), the most comprehensive high-quality data available from worldwide flux networks, to evaluate the performance of each of the three stomatal conductance-photosynthesis models. The sites cover three different forest ecosystems classified by IGBP as Evergreen Broadleaf Forests (EBF), Evergreen Needleleaf Forests (ENF) and Deciduous Broadleaf Forests (DBF); and three climate regions: boreal, temperate and tropical, with two of the temperate sites further sub-classified as Mediterranean. Our ultimate goal is to understand and quantify the uncertainties in modelled gross primary productivity and ozone deposition rates due to choice of stomatal conductance model, and model parameters.

2 Methods

2.1 FORCAsT-gs

The 1-D (vertical column) model, FORest Canopy-Atmosphere Transfer (FORCAsT1.0), was developed to simulate exchanges of reactive biogenic volatiles between a forest site and the atmospheric boundary layer. Previous versions (CACHE: Forkel et al., 2006; Bryan et al, 2012; 2015; and FORCAsT1.0: Ashworth et al., 2015; Otu-Larbi et al., 2020a) have focused on the atmospheric processes governing the concentration and distribution of these volatiles and their oxidation products within and above the canopy. FORCAsT uses 40 vertical levels as a default, 20 of which are in the vegetation canopy space, with the remainder of the levels representing the planetary boundary layer above. The thickness of the layers increases with height, permitting greater resolution in the canopy levels, which are further sub-divided into a trunk space (10 levels) and crown space (10 levels). More details about how vegetation is treated in the model can be found in Ashworth et al. (2015).

Heat and mass fluxes are calculated at each model level by solving the continuity equations, shown here for (gas-phase) mass:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(K\frac{\partial c}{\partial z}\right) + S_c, \qquad (1)$$

where c is the concentration or mixing ratio of a chemical species, z is the height of the layer, K is the turbulent exchange coefficient and S_c represents all sources and sinks (i.e. emissions, deposition, chemical production and loss, and advection) of water vapour or chemical compounds. All are explicitly parameterised within the model and have been fully described by Bryan et al. (2012) and Ashworth et al. (2015). We briefly re-cap those that remain unchanged from FORCAsT1.0

(Ashworth et al., 2015) before fully describing the coupled stomatal conductance-photosynthesis models we have now incorporated into FORCAsT-gs.

Leaf-level volatile emissions are calculated for each foliated canopy layer in FORCAsT-gs following the light- and temperature-dependent emission algorithms developed by Guenther et al. (1995):

$$F = LAI \cdot \varepsilon \cdot \gamma_{TS} \cdot \gamma_{LS}, \qquad (2)$$

where LAI is the leaf area index in each leaf-angle class and layer, ε is the emission factor or base emission rate (i.e. at standard conditions of 30 ºC and 1000 μmol m^{-2} s^{-1} photosynthetically active radiation, PAR) and γ_{TS} and γ_{LS} are activity factors that scale the base emission rate according to actual temperature and PAR. For temperature-dependent-only emissions from specialised storage pools, γ_{TS} and γ_{LS} in Eqn. 2 is replaced by γ_{TP} based on Steinbrecher et al. (1999). Further details of the activity factors and parameters are presented in Ashworth et al. (2015).

The chemistry in FORCAsT-gs is unchanged from that described by Ashworth et al. (2015). Users can use either the Regional Atmospheric Chemistry Mechanism (RACM; Stockwell et al., 1997; Geiger et al., 2003) or the Caltech Atmospheric Chemistry Mechanism (CACM; Griffin et al., 2003, 2005; Chen et al., 2006). The former includes 84 species and 249 reactions, and the latter 300 species and 630 gas-phase reactions with partitioning to aerosol via the Model to Predict the Multiphase Partitioning of Organics (MPMPO; Chen et al., 2006; Ashworth et al., 2015).

Vertical mixing in and above the canopy are based on Baldocchi (1988) and Gao et al. (1993) respectively, following first-order K-theory (Blackadar, 1963). Eddy diffusivity is constrained by friction velocity measurements made close to but just above the top of the canopy as K-theory breaks down in the highly turbulent canopy sub-layer (Bryan et al., 2012).

Deposition onto vegetated surfaces and stomatal uptake is a major sink for tropospheric ozone (Royal Society, 2008). Ozone taken up through stomata is known to diminish plant growth

and health leading to a decrease in productivity rates and causing billions of dollars in crop losses annually (Ainsworth et al., 2012, Avnery et al., 2011). Stomatal conductance is a key factor controlling ozone deposition velocity and deposition rates, and therefore the extent and severity of damage. However, estimates of stomatal conductance are sensitive to model formulation and the choice of model parameters used in vegetation models leading to uncertainty in estimated impacts of O_3 on vegetation (Damour et al., 2010). Here, we describe how FORCAsT1.0 estimates deposition velocity and subsequently investigate how the choice of model formulation and parameters affect these estimates.

The rate of dry deposition to the soil and foliage is calculated for all gas-phase compounds for each model layer in the canopy following the parameterisations of Wesely (1989) and Gao et al. (1993), and is described in full in Bryan et al. (2012). Deposition is assumed to occur at a rate dependent on a species-specific Henry's law coefficient, diffusivity relative to water vapour and a nominal reactivity factor accounting for enhanced uptake of some species due to reactions occurring within plant cells following uptake. Of importance here is the method of calculating the deposition velocity within the foliar layers, based on four resistances: the quasi-laminar boundary layer at the leaf surface (R_b), stomatal (R_s), mesophyll (R_m), and cuticular (R_c) resistances, such that for each trace gas (i), the deposition velocity (v_d) at each level is:

$$v_{d,i}(z) = \frac{1}{R_{b,i}(z) + R_s(z)\frac{D_{H2O}}{D_i} + R_{m,i}(z)} + \frac{2}{R_{b,i}(z) + R_{c,i}(z)} \tag{3}$$

where z is the height of the midpoint of the model level, and D_{H2O}/D_i (=1.6) is the ratio of the molecular diffusivities of water to ozone (Gao et al.,1993). Resistances depend on factors such as LAI, leaf length and the reactivity factor of the trace gas and are calculated on-line in the model. Stomatal resistance, R_s, is deduced as the inverse of stomatal conductance (Ashworth et al., 2015).

Ozone deposition rate, D_r, is then calculated as:

$$D_r = v_d \times [O_3] \quad (4)$$

where $[O_3]$ is the average concentration of ozone in the canopy layers.

In FORCAsT1.0, stomatal conductance was calculated using the Jarvis multiplicative model. Here we extend the Jarvis approach to include photosynthesis and incorporate two coupled stomatal conductance-photosynthesis models into FORCAsT-gs, allowing the user to select between three different approaches to calculating photosynthesis and stomatal conductance (see Section 2.2). In all other respects, dry deposition remains unchanged (Bryan et al., 2012; Ashworth et al., 2015).

2.2 Physiology: coupled stomatal conductance-photosynthesis models

There are currently three distinct approaches to modelling stomatal conductance and net photosynthesis: empirical multiplicative models that estimate stomatal conductance and thence photosynthesis rate (e.g. Jarvis, 1976); coupled stomatal conductance-photosynthesis models that simultaneously solve for both (e.g. Ball et al., 1987); and optimisation models that simultaneously maximise carbon assimilation while minimising water loss (e.g. Medlyn et al., 2011). We describe below the key aspects of the three that we incorporated into FORCAsT-gs. A more detailed description of the mathematical formulations for each model is presented in the supplementary information.

The Jarvis model (Jarvis, 1976) assumes stomatal aperture is downregulated from a theoretical maximum by the effects of environmental conditions such as temperature, PAR, and leaf age. The scale of each down-regulation is based on experimental observations and g_s is then calculated as:

$$g_s = g_{max} \times f_{phen} \times f_{light} \times max\left\{f_{min}, \left(f_{temp} \times f_{VPD} \times f_{SWC}\right)\right\} \quad (5)$$

where g_s (mol m^{-2} s^{-1}) is stomatal conductance at each model level and g_{max} (mol m^{-2} s^{-1}) is the plant species-specific maximum value of canopy stomatal conductance for H_2O. The scaling functions,

f_{phen}, f_{light}, f_{temp}, f_{VPD}, and f_{SWC} have values between 0 and 1 and account for the reduction in stomatal conductance due to leaf age (phenology), photosynthetic photon flux density (PPFD, μmol m^{-2} s^{-1}; defined as the intensity of PAR reaching each square meter of the canopy per second), temperature (T, °C), vapour pressure deficit (VPD, kPa), and volumetric soil water content (SWC, m^3 m^{-3}), respectively. f_{min} is the minimum stomatal conductance during daylight. Details of the calculations of each of the functions are given in S1.1.

Net photosynthesis rate, A_n, is then assumed to be directly proportional to the conductance, g_s, such that:

$$A_n = g_s \times C_i \tag{6}$$

where C_i is the ratio of ambient to internal concentrations of CO_2 and is normally taken as 0.7. Parameter values for each site were determined from field measurements, lab-based experiments or taken from literature for the nearest equivalent and are shown in Table S2.

The Ball-Berry coupled stomatal conductance-photosynthesis model assumes that stomatal conductance is regulated directly by the instantaneous rate of photosynthesis to balance CO_2 concentrations inside the leaf with ambient levels. Photosynthesis rate (A; μmol m^{-2} s^{-1}) at each level in the canopy is calculated following the formulations of Farquhar et al. (1980), Harley et al. (1992) and Baldocchi (1994):

$$A = V_c - 0.5 V_o - R_d \tag{7}$$

where V_c is the carboxylation rate, V_o the oxygenation rate, R_d the dark respiration rate and

$$V_C - 0.5 V_O = \min\left[A_C, A_j\right] \times \left(1 - \Gamma / C_i\right) \tag{8}$$

i.e. assuming that photosynthesis rate is limited by either Ribulose bisphosphate saturation during carboxylation (A_c) or by the rate of electron transport for Ribulose bisphosphate regeneration during oxygenation (A_j). Γ is the CO_2 compensation point (the CO_2 concentration at which net CO_2 fixation

is zero at a given O_2 level and temperature (Moss et al., 1969)) in the absence of dark respiration, and C_i is the intercellular CO_2 concentration (Farquhar and von Caemmerer, 1982).

The internal CO_2 concentration of the leaf, C_i is:

$$C_i = C_s - \frac{A}{g_s} \tag{9}$$

where g_s is stomatal conductance and C_s is the CO_2 concentration at the leaf surface. Here, g_s was calculated following Ball et al. (1987) as:

$$g_s = g_o + m\frac{A * RH}{C_s} \tag{10}$$

where g_o is the residual stomatal conductance as A tends to zero, m is a species-specific coefficient expressing the sensitivity of g_s to changes in A, and RH is the relative humidity at the leaf surface.

Medlyn et al. (2011) also assume that photosynthesis rate at each level in the canopy is the minimum of carboxylation and electron transport rate. The version incorporated into FORCAsT-gs is based on the parameterisations of Farquhar et al. (1980) for photosynthesis rate (A; μmol m^{-2} s^{-1}) in C3 plants such that:

$$A = min\left(A_j, A_c\right) - R_d \tag{11}$$

where R_d (mol m^{-2} s^{-1}) is the leaf dark respiration.

Stomatal conductance (g_s) is then modelled following optimisation theory (Medlyn et al., 2011) in which stomatal aperture is regulated to maximise carbon gain while simultaneously minimising water loss:

$$g_s \approx g_o + \left(1 + \frac{g_1}{\sqrt{D}}\right)\frac{A}{C_s} \tag{12}$$

where g_o (mol m^{-2} s^{-1}) is the residual stomatal conductance as A approaches zero and g_1 is the slope of the sensitivity of g_s to changes in A. D (kPa) is the vapour pressure deficit and C_s (µmol mol^{-1}) the CO_2 concentration at the leaf surface as before. The values of g_o and g_1 are determined at the species- or PFT-level from experimental data, and in this study were obtained from Lin et al. (2015) and De Kauwe et al. (2015). Values for each site are listed in Tables S2.

The Jarvis model includes soil moisture stress as one of the factors limiting stomatal conductance. The relationship between SWC and g_s is modelled following Büker et al. (2015):

$$f_{SWC} = ¿ \tag{13}$$

where PAW is plant available water and is given by:

$$PAW = \frac{\theta - \theta_w}{\theta_f - \theta_w} \tag{14}$$

where θ is the volumetric soil water content (SWC, m^3 m^{-3}), θ_f and θ_w are the SWC at field capacity and wilting point respectively, and PAW_t is a site-specific threshold of the fraction of water in the soil that is available to the plant estimated from site soil characteristics.

For both the Ball-Berry and Medlyn models, we assumed the effect of water stress on photosynthesis to be the result of biochemical limitations as demonstrated in previous studies (e.g see Egea et al., 2011). A soil moisture stress function (β) was therefore applied to the maximum rate of RuBP carboxylation (V_{cmax}) and the maximum rate of electron transport (J_{max}) to reflect the impact of soil moisture deficit on plant gas exchange.

β ranges between 1 (in the absence of water stress) to 0 (at wilting point) and is calculated based on soil water content following Porporato et al. (2001); Keenan et al. (2009); Keenan et al. (2010):

$$\beta = \begin{cases} 1 \; for \; \theta \geq \theta_C \\ \left[\dfrac{(\theta - \theta w)}{(\theta_C - \theta w)} \right]^q \; for \; \theta_w < \theta < \theta_C \\ 0 \; for \theta < \theta_w \end{cases} \tag{15}$$

where θ ($m^3\ m^{-3}$) is the volumetric soil moisture, θ_w is the wilting point ($m^3\ m^{-3}$), and θ_c is a critical soil moisture content above which water stress is found not to affect plant-atmosphere CO_2 and water vapour exchange (Egea et al., 2011). q is a site-specific empirical factor describing the non-linearity of the effects of soil water stress on tree physiological processes, and here, was derived from observations at each site.

Photosynthesis and stomatal conductance are then estimated using the water-stressed values V_{cmax*} and J_{max*}:

$$V_{cmax^{¿}} = V_{cmax} \times \beta \tag{16a}$$

$$J_{max^{¿}} = J_{max} \times \beta \tag{16b}$$

The Medlyn model further assumes direct limitation to stomatal conductance due to water stress following De Kauwe et al. (2015), such that, stomatal conductance becomes:

$$g_s \approx g_o + \left(1 + \frac{g_{1\beta}}{\sqrt{D}} \right) \frac{A}{C_s} \tag{17}$$

These soil moisture stress functions are applied in all of the simulations conducted here.

2.3 FLUXNET sites

An overview of the five sites is given below with further information provided in Table S1 and Figure S1. The sites are included in the FLUXNET2015 dataset which categorises each location

by IGBP ecosystem type (Loveland et al., 2000). “Forests” indicates >60% of landcover is woody vegetation at least 2 m in height. “Evergreen Forests” retain green foliage throughout the year, while “Deciduous Forests” exhibit a seasonal cycle in which there are periods with foliage on the tress and other periods when there is no foliage.

2.3.1 Santarém-Km67-Primary Forest (BR_Sa1)

BR_Sa1 is in Amazonian Brazil and consists of primary forest comprising a wide range of tree species of varied ages, epiphytes, and high numbers of decaying logs. A flux tower, which was established in 2000 for the Large-scale Biosphere-Atmosphere (LBA) experiment (Rice et al., 2004) is sited on a large level plateau with forest cover stretching 5-40 km in all directions (Goulden et al., 2004). There is closed-canopy forest to an average height of 40 m within the footprint of the flux tower, with numerous emergent trees up to 55m in height (Rice et al., 2004).

Figure 1 shows volumetric soil moisture and meteorological data from BR_Sa1 (yellow line) for an average annual profile. The site is categorised as Tropical Evergreen Forest and has a hot humid tropical environment with average rainfall of 1920 mm y^{-1} and relative humidity of 85% (Parotta et al., 1995). Although a number of intense precipitation events occur during the dry season (Aug-Dec each year), the majority of the rainfall occurs during the wet season (Dec-Jul) with maximum intensity between 13h00-16h00 local time (da Rocha et al., 2004). Annual average temperature is ~25ºC, with little diurnal or seasonal variability (Rice et al., 2004). Daily maximum temperatures range between 24-32ºC and minimum 20-25ºC. The wet season is ~1-3ºC cooler than the dry, with incoming solar radiation substantially lower due to cloud cover (da Rocha et al., 2004).

The clay soil has little organic content and retains water well. Soil moisture is not routinely measured at BR_Sa1 and we use data from a nearby site (BR_Sa3 at the 83 km marker) located in the same area of forest. A selective logging experiment commenced at BR_Sa3 shortly after the main LBA campaign and has continued to this day. Less than 5% of aboveground biomass is removed

each time, leaving only small gaps between areas of closed-canopy forest (Goulden et al., 2004). Soil moisture at 5 cm depth at BR_Sa3 responds quickly to precipitation, ranging between ~0.30-0.47 m^3 m^{-3}. At a depth of 250 cm, there is little variation with soil moisture relatively constant at ~0.46 m^3 m^{-3} during the wet season, declining gradually to ~0.42 m^3 m^{-3} by the end of the dry season (Rice et al., 2004).

2.3.2 Hyytiälä (FI_Hyy)

FI_Hyy is located in the sub-boreal climate zone at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relation) boreal forest research station at Hyytiälä, ~220km NW of Helsinki (Hari and Kulmala, 2005; Rinne et al., 2007). The 73-m flux tower is situated on relatively level ground, surrounded by predominantly uniform age (~60-year-old) Scots pine (*Pinus sylvestris*) with an average canopy height of 14 m (Hari and Kulmala, 2005; Suni et al., 2003).

Figure 1 shows volumetric soil moisture and meteorological data from FI_Hyy (blue line) for an average year. The site is categorised as Boreal Evergreen Forest with climatological (1959-2014) average annual temperature of 3.5ºC and precipitation of 693 mm y^{-1} falling predominantly as snow during the winter months (Suni et al, 2003; SMEARII, 2021). Average monthly temperatures range between -7.7 ºC in February, and 16 ºC in July (SMEARII, 2021). Prevailing winds are SSW and are generally moderate, with average annual windspeed of ~2.8 m s^{-1} and maximum of 14 m s^{-1} (SMEARII, 2021). The soil comprises sandy and coarse silty glacial till (Suni et al., 2003). Soil moisture peaks at >0.45 m^3 m^{-3} after snow melt and drops to ~0.30 m^3 m^{-3} or lower during occasional summer droughts.

2.3.3 Castelporziano (IT_Cp2)

IT_Cp2 is located at “Grotta di Piastra” within the Presidential Estate at Castelporziano, on the Thyrrenian coast ~25 km SW of Rome. The 6000 ha Estate has been used for environmental research since 1951 with a flux tower first installed in 1996. The current tower is ~20 m tall and

surrounded almost exclusively by even-aged Holm oak (*Quercus ilex*) of average ~14 m height (Fares et al., 2019). This is a typical macchia species, well-adapted to an environment characterised by hot dry summers and nutrient-poor sandy soils (Fares et al., 2009).

Figure 1 shows volumetric soil moisture and meteorological data from IT_Cp2 (red line) for an average year. The site is categorised as Temperate Evergreen Forest and has a Mediterranean environment with an average rainfall of 745 mm y^{-1} of which <100 mm y^{-1} falls in the summer months (May-early September). Between 1996-2011, mean monthly temperatures ranged between 8.4-24.7ºC, with a maximum temperature of 30.3 ºC and minimum of 5.0 ºC recorded in August and February respectively (Fusaro et al., 2015).

The soil is sandy and freely draining. Soil moisture is thus highly variable and tightly coupled to precipitation events. Soil moisture averaged over a depth of 10-50 cm ranges from ~5% at the end of the summer drought period to ~32% during the winter (Fares et al., 2019).

2.3.4 Blodgett Forest (US_Blo)

US_Blo is located in a uniform-age Ponderosa pine plantation in the Sierra Nevada mountain range on the western coast of the continental USA. The plantation was established in 1990 and a 15-m flux tower, which has been the site of long-term monitoring and numerous intensive field campaigns, erected in 1997 (Goldstein, 2000). The average height of the canopy is ~9 m (Park et al., 2014).

Figure 1 shows volumetric soil moisture and meteorological data from US_Blo (black line) for an average year. The site is categorised as Temperate Evergreen Forest with a Mediterranean climate. Annual average precipitation is ~1630 mm y^{-1} with little rain during the summer months (May-early September). Average daily temperatures range between 17-24 ºC in the summer, and 0-9 ºC in the winter (Goldstein, 2000).

The soil is predominantly free draining loam, and soil moisture tracks precipitation (Goldstein, 2000). Average soil moisture at a depth of 10-20 cm ranges from ~0.10 m^3 m^{-3} during summer droughts to just below 0.35 m^3 m^{-3} in the winter.

2.3.5 Harvard Forest (US_Ha1)

US_Ha1 is located within a ~1600 ha area of old-growth (75+ years) mixed forest in NE USA that has been the site of long-term ecological and environmental monitoring since 1907. A 30-m flux tower was erected in 1990 and has been used for continuous measurements and summer field campaigns since (Goldstein et al., 1998; McKinney et al., 2011). The average height of the canopy is ~24 m (Clifton et al., 2019)

Figure 1 shows volumetric soil moisture and meteorological data from US_Ha1 (grey line) for an average year. The site is categorised as Temperate Deciduous Forest with the footprint of the tower dominated by red oak (*Quercus rubra*) and red maple (*Acer rubrum*), although there are a number of red and white pines (*Pinus resinosa* and *P. strobus*) to the NW of the tower (Clifton et al., 2019).

The site has been shown to be relatively homogeneous in all directions from the tower with energy budget closure achieved to within 20% (Goldstein et al., 1998). Annual average precipitation is ~1000 mm y^{-1} and is relatively evenly distributed through the year. Average daily temperatures range between ~20 ºC in the summer, and ~1 ºC in the winter.

The soil around the flux tower is a sandy loam (Allen, 1995). Soil moisture typically ranges from ~0.25-0.55 m^3 g^{-3}, but can drop below 0.20 m^3 m^{-3} during (infrequent) drought years (Clifton et al., 2019).

2.4 Simulations

Stomatal conductance, photosynthesis rate (instantaneous fluxes of CO_2) and deposition velocity are calculated for each leaf angle class (9 sunlit and 1 shaded) for each foliage-containing

level within the canopy in FORCAsT-gs using each of the three physiological approaches outlined in Section 2.2. These are then weighted by leaf angle fraction and leaf area distribution at each level and summed over all model layers to obtain canopy-scale conductance, photosynthesis rates (canopy-top fluxes of CO_2) and deposition velocity. FLUXNET2015 sites report the total rate of photosynthesis throughout the canopy as Gross Primary Productivity (GPP), deduced from the Penrose-Monteith physiology model. We therefore evaluate model performance via comparison of modelled canopy CO_2 fluxes to measured GPP.

During preliminary model configuration at each site, site-specific phenological and canopy structure were set to best fit modelled to observed GPP. However, the physiological parameters used in each of the three coupled stomatal conductance-photosynthesis algorithms were set to average values reported from previous studies in-situ at similar ecosystems or in controlled environments. These semi-optimised configurations provided our baseline simulations at each site (hereafter referred to as BASE).

To determine the sensitivity of the model to perturbations in the physiological parameters, which are mostly derived from controlled environment experiments, and to provide uncertainty bounds for our estimates of GPP and ozone deposition rates, we conducted a series of sensitivity tests. Only parameters with a direct relationship to stomatal conductance were used in these sensitivity tests to ensure consistency in approach.

In the Jarvis multiplicative model, stomatal conductance is estimated by scaling the maximum conductance observed in saturating light conditions (g_{max}; Eqn. 5) according to environmental and phenological limitations. Average values of g_{max} for specific plant functional types are generally used, but Hoshika et al. (2018) found variations of up to 70 % between the upper and lower bounds of g_{max} and the mean for different PFTs. Here, we use the mean values for different

forest ecosystems for baseline simulations (JV) and the upper and lower bounds as JV+ and JV- respectively (Table S1).

For the Ball-Berry coupled stomatal conductance-photosynthesis model, the coefficient *m* (Eqn. 10) describing the relationship between stomatal conductance and photosynthesis typically ranges between 9 and 12. We use these as our lower (BB-) and upper (BB+) bounds, with the baseline (BB) set to a value of 10. See Table S3 for further details of parameter settings.

The equivalent coefficient, g_1 (Eqn. 12), is tested in the Medlyn optimisation model. We take the upper (MD+) and lower (MD-) bounds of g_1 as reported by De Kauwe et al. (2015) and Lin et al (2015) for different forest ecosystems with error margins of 2-10%. Our baseline simulations (MD) use the average value for each site. Further details of parameter settings are given in Table S3.

Simulations for each site were driven with observed half-hourly meteorological and environmental conditions for as many years as the site has been active (see Table 1). At the end of the simulation period, average annual and diel profiles of total canopy photosynthesis were calculated and compared with observed GPP. To assess the relative performance of each model at each of the five sites, we define a single summary statistic, that reduces the three individual Taylor model performance indicators to a single value. This summary statistic is the product of the difference between modelled and observed Taylor statistics calculated as:

$$Summary = cRMSE \times \left(1.0 - r^2\right) \times \left|normSD - 1.0\right| \qquad (18)$$

where r^2 is Pearson's correlation coefficient, normSD the normalised standard deviation and cRMSE the centred root mean square error. The closer this value is to zero, the closer the model fit to observations.

3 Results

3.1 BASE

We first evaluate the skill of each of the three stomatal conductance-photosynthesis models to reproduce the average diel and annual profiles of GPP at each site for the time periods shown in Table S1. The BASE simulations presented here use the parameter values given in Table S2.

3.1.1 Jarvis (JV)

As shown by the orange lines on Figure 2, the multiplicative stomatal conductance model (JV) reproduces the seasonal variation in GPP at all sites except for BR_Sa1, although it substantially overestimates seasonal GPP at the three broadleaf forests (BR_Sa1, IT_Cp2 and US_Ha1) and underestimates at the Boreal needleleaf forest (FI_Hyy). At BR_Sa1, JV overestimates GPP by a factor of 1.5-2. At IT_Cp2 and US_Ha1,however, while JV overestimates GPP by 50-100% in spring and summer it performs well in the rest of the year. For FI_Hyy, JV consistently underestimates productivity from summer through to early autumn, by a factor of 2. However, the model reproduces GPP at US_Blo, which is also a needleleaf forest, to within 20% of the observations at all times of the year. This suggests that the phenology of Boreal ecosystems is not well-captured.

The diel profiles of modelled GPP using JV follows a similar inter-site pattern to that of the seasonal profile with overestimation of diurnal GPP at BR_SA1, IT_Cp2 and US_Ha1 by 5-200%, and underestimation of ~75% at FI_Hyy.

Of the three, JV is the poorest performer across all the sites. The summary statistics shown in Table S4 ranges from 0.02 at US_Blo where JV performed well at reproducing observed GPP to 28.86 at BR_Sa1 where it overestimates both seasonal and diurnal profile of GPP. Seasonal cRMSE

ranging between 1.24-10.64, normSD between 0.40-3.72 and r^2 as low as 0.01 at BR_Sa1, further confirms the relatively poor performance of this model.

3.1.2 Ball Berry (BB)

The coupled stomatal conductance-photosynthesis model (BB) reproduces the observed seasonality and magnitude of GPP within 10-50% at all but the tropical BR_Sa1 ecosystem as shown by the brown lines on the first column of Figure 2. BB underestimates summer GPP at FI_Hyy by 30% but overestimates GPP at IT_Cp2 by a similar margin in the summer when seasonal drought occurs. It closely matches observed GPP throughout the season at US_Blo and US_Ha1 with <10% variation between model estimates and observations. Although BB overestimates GPP by as much as 50% at BR_Sa1 throughout the year, it outperforms both JV and MD at this site.

The diurnal profile of GPP estimated by BB confirms its superior performance at the tropical site BR_Sa1, with modelled GPP closely matching the observations during the day. The diurnal profile at the other sites shows that BB underestimates GPP by ~5% in the early hours of the day at FI_Hyy and IT_Cp2 but tends to overestimate GPP by ~20% in the later afternoons.

As shown by the Summary statistic in Table S4, which ranges between 0.01 and 0.99, BB outperforms JV at all sites. As summarised by the Taylor diagram in Figure 3, BB's performance is better than that of JV, with cRMSE of 1.07 - 2.47, r^2 of 0.85-0.97 (excluding BR_Sa1) and normSD of 0.80-1.82.

3.1.3 Medlyn (MD)

Output from the Medlyn model (MD) is shown in blue in Figure 2. While MD follows the seasonal fluctuation of GPP at BR_Sa1, estimated fluxes are a factor of ~1.5 higher than observations throughout the year. This overestimation of GPP at the tropical site is also apparent in the profile over the course of an average day. By contrast, at the two Mediterranean sites, MD

reproduces both the observed seasonal and diurnal profile of GPP and is within 20% of the observed values at any time during the year or day. MD also shows excellent agreement with both the magnitude and timing of observed GPP throughout the year at FI_Hyy but overestimates the average diurnal profile of GPP by ~20%. MD performs best at the temperate deciduous forest site, US_Ha1, where there is <5% between model estimates and observations across both the year and day.

The superior performance of MD across sites is confirmed by the Taylor diagrams in Figure 3 and the summary statistics in Table S4. MD exhibits high correlation (0.56-0.98), and low deviations (1.01-1.92) and error (0.90-3.03). Summary statistics ranging between 0.0003 and 1.25 confirm it as the best performing model overall.

These results show that MD provides the best estimates of GPP at four of the five forest sites used in this study (FI_Hyy, IT_Cp2, US_Blo and US_Ha1) while BB was the overall best performer at BR_Sa1. JV was the least skilful of the three models, substantially overestimating GPP at BR_Sa1, IT_Cp2, US_Ha1 and underestimating at FI_Hyy. All three BASE models were most successful in reproducing observed GPP at the temperate deciduous forest, US_Ha1, and poorest at the tropical forest, BR_Sa1.

3.2 Sensitivity of stomatal conductance to model parameters

The BASE simulations used mid-range values for species-specific parameters g_{max} (JV; Eqn. 5), m (BB; Eqn. 10), and g_l (MD; Eqn. 12). As described in Section 2.4, we carried out sensitivity tests using lower and upper bound estimates for these parameters. Here we analyse the effect that those parameter changes have on estimated photosynthesis rates for each of the three models, identifying similarities and differences in responses between sites and providing an estimate of uncertainty bounds for GPP and stomatal conductance in each case.

3.2.1 JV

The plant species-specific theoretical maximum value of canopy stomatal conductance for H_2O (g_{max}; Eqn 5) is central to the performance of the JV model in reproducing observed plant gas exchange. Changes in g_{max} lead to proportional changes in both stomatal conductance (Figure S4) and GPP (Figure 4) at all sites. In general, decreasing g_{max} to its lower limit decreases GPP by between ~75-120% depending on the site, while an increase to the upper bound increases GPP by similar magnitudes.

At the tropical and temperate forests (BR_Sa1, IT_Cp2, US_Blo and US_Ha1) where JV over-estimated GPP, using instead the lower limit of g_{max} (JV-) provided the best model-observation fit in both seasonal and diel cycles at BR_Sa1, but substantially underestimated GPP at IT_Cp2, US_Blo and US_Ha1.

By contrast, at FI_Hyy, where JV underestimated GPP, the use of the upper bound of g_{max} (JV+) reduced, but did not completely overcome, model underestimation through the seasons or over the course of an average day. JV+ modelled GPP was around half to two-thirds of observed fluxes, a substantial improvement on the factor of 2 underestimations in JV.

As shown by the Taylor plots presented in Figure 3, and Table S4, both normalised SD and centred RMSE are substantially increased in JV-. While this is a major improvement in overall model performance at BR_Sa1 (with cRMSE reduced from 10.6 in JV to 2.36 in JV-), JV- substantially worsens model fit at all the other sites. JV+ exacerbates the tendency to over-estimation across all sites, with Summary statistics increasing to 0.22-87.40. The correlation coefficient between modelled and measured GPP is unchanged as it essentially summarises the temporal fit.

3.2.2 BB

For both the BB and MD parameterisations, stomatal conductance and net photosynthesis rate are explicitly linked and solved simultaneously. Variations in species-specific response parameters therefore directly affect both g_s and GPP. Similarly to JV, the upper bound increased and lower bound reduced flux estimates compared to the baseline.

In BB, increasing *m*, i.e. the change in photosynthesis rate for a given change in stomatal conductance, results in proportionally larger increases in GPP than the decreases resulting from reducing *m*. GPP was slightly over-estimated by BB at all sites (except during the summer months at FI_Hyy where modelled fluxes were lower than observed). BB- therefore provides a better fit to observed GPP across all sites except FI_Hyy where BB+ performed better. It should be noted however, that changes in GPP (0.5-1.0%) are considerably smaller than those observed for JV between the upper and lower bound simulations.

This is further corroborated by the Taylor diagrams (Figure 3) summarising the average, upper and lower bound simulations. Across all sites, there was little change in correlation between estimated and observed GPP, reflecting the minor changes in temporal profile. NormSD also remained virtually unchanged between simulations for GPP fluxes (~1.0 at US_Blo and US_Ha1, ~0.8 at FI_Hyy and ~2.0 at IT_Cp2). cRMSE is consistently low for all simulations at the extra-tropical sites (~1.0-1.2 for GPP at US_Blo and FI_Hyy, and 1.4-1.8 at IT_Cp2 and US_Ha1), indicating the relatively good match to absolute values. By contrast, cRMSE remained high (>2.5) at the tropical rainforest site, BR_Sa1, where a high normSD and low correlation coefficient also confirm the poor performance of the model at capturing both the magnitude and temporal variations in GPP at this ecosystem. The BASE simulation BB proved the closest fit to observed GPP at BR_Sa1.

3.2.3 MD

Similarly to BB, changes in g_1 in MD result in very small changes in estimated GPP. At the two Mediterranean sites (IT_Cp2 and US_Blo) where GPP was over-estimated by the baseline (MD) simulations, MD- provides a closer fit to observations (Figure 3) although the change is only ~1%. Changes in g_1 have a negligible effect on GPP at BR_Sa1, FI_Hyy or US_Ha1 (Figure 3), where droughts are rare and there is less need for plants to conserve water, i.e. where there is less conflict between maximising photosynthesis and minimising transpiration.

As shown by the Taylor diagrams (Figure 3), increasing the value of g_1 from the average (10.0) to the upper bound (12.0) improves the correlation between estimated and observed GPP at US_Blo, while decreasing the value improves the fit slightly at IT_Cp2. As suggested by the temporal profiles, there is no noticeable change in correlation at BR_Sa1, FI_Hyy or US_Ha1. The normSD for GPP are very close to 1.0 (i.e. a perfect fit to observations) and centred RMSE <0.5 at FI_Hyy, US_Ha1 and US_Blo but near 2.0 and 1.0 respectively at IT_Cp2, again likely a result of the severity of droughts at Castelporziano, where water conservation is a key driver of stomatal conductance. All three statistics remain poor at BR_Sa1, where r^2 remains virtually unchanged at ~0.6, normSD at 2.0, and cRMSE at ~1.8 for all values of g_1. Considering the relatively small changes observed in GPP in response to changes in g_1, we conclude that the mean values of g_1 are sufficient for estimating stomatal conductance and GPP using the Medlyn model at these sites.

3.2.4 Summary of sensitivity tests

As shown by Figures 3 and 4, and Table S4, GPP estimates in JV were more sensitive to variations in g_{max} than BB and MD estimates were to m and g_1, respectively. However, modelled GPP does not vary by the same magnitude as the variation in model parameters. For instance, modelled GPP values in JV- and JV differed from BASE (JV) estimates by as much as 100% in response to up to 60% variation in g_{max} causing substantially differences in model output statistics (Figure 3 and

Table S4). GPP estimates using upper and lower bounds of m (BB) and g_1 (MD) only differed by 1-5% in response to a 10-20% change in the model parameterisation. It must be noted that these sensitivity tests only focused on stomatal conductance parameters in all three models. Tests conducted on photosynthetic parameters such as V_{cmax} and J_{max} have shown a greater difference in estimated GPP compared to what we find here (e.g see Fares et al., 2019) but do not have an equivalent in JV.

3.3 Stomatal conductance

As the three physiology models in FORCAsT-gs explicitly couple photosynthesis and stomatal conductance, we now assume that the parameterisation that best represents GPP (as a proxy for photosynthesis) at each of the sites also best captures fluctuations in stomatal aperture. Figure 5 presents the performance of the models at each site relative to the stomatal conductance or ozone deposition rate simulated by the best-performing model.

The first and second columns of Figure 5 show the average seasonal and diurnal profiles of stomatal conductance at each site with that estimated by the best performing model shown as a black line (i.e. assumed as "truth"). The grey shading indicates the full range of stomatal conductance estimated by the various model configurations.

At the tropical site, BR_Sa1, the BB model, which best captured GPP, is taken to represent observed stomatal conductance. Stomatal conductance estimated with the model that had the lowest GPP estimates (JV-) is ~75% lower while the configuration with the greatest overestimation of GPP (JV+) is ~ 25% higher. The difference between the models remains almost constant throughout the year at this tropical site. The divergences in stomatal conductance at FI_Hyy, IT_Cp2, US_Blo and US_Ha1 are seasonal. For these sites, MD- was used to represent observed g_s due to its lower summary statistics shown in Table S4. The difference between the models that over or

underestimated GPP were <30% in the winter and spring increasing rapidly to >100% at IT_Cp2 and US_Blo in the summer, and >200% at FI_Hyy and US_Ha1.

The diel profile of stomatal conductance between the best and worst performing models is similar to the seasonal profile observed at each site. As shown by the second columns of Figure 5, BR_Sa1, IT_Cp2 and US_Blo show the widest variation in modelled stomatal conductance between the different model configurations during peak periods of the day. There is about 10% overestimation of peak daytime stomatal conductance values at FI_Hyy and US_Ha1 between the best and overestimating model configurations. On the contrary, the models that underestimated GPP at these sites (JV-) also underestimated stomatal conductance by and >50%.

3.4 Ozone deposition

The differences in simulated stomatal conductance between configurations of FORCAsT-gs affects estimated ozone deposition velocity and hence the rate at which ozone is lost to this key sink. Figure S6 shows the seasonal and diel profiles of variations in ozone deposition velocity between the models. The tropical site, BR_Sa1, and the temperate broadleaf forest, US_Ha1, have the highest estimated ozone deposition velocities as expected from their higher g_s compared to the other sites. This higher *gs* and hence ozone deposition velocities are likely due to the fact that plants in these forests also have bigger leaf sizes and higher leaf area index – highlighting the role of forest structure and characteristics in plant physiological processes (Meyers & Baldocchi, 1988; Padro, 1996).

The deposition velocity is however dependent on several resistances as shown in Eqn. 3, including the stomatal resistance (the inverse of g_s). As a result, the models that overestimated GPP and g_s do not necessarily overestimate seasonal deposition velocity when compared to the best performing model across all sites. However, the model configurations that underestimated GPP and g_s do underestimate seasonal ozone deposition velocity, although to a lesser extent. For example, JV- underestimated GPP and g_s by >100% during the peak growing season but only underestimated

deposition velocity by ~15%, with an average value of 0.36 cm s^{-1} compared with 0.42 cm s^{-1} estimated with the best performing model (MD). Similarly, at the tropical site, the average deposition velocity in the optimal model configuration (BB) was 0.88 cm s^{-1}. This value was 13% higher than the average deposition velocity in JV- which underestimated GPP and 6% lower than that of JV+ which overestimated GPP by a factor of 2.

The variation between modelled deposition velocities at FI_Hyy, IT_Cp2 and US_Blo between the model configurations is similar to those described for BR_Sa1 and US_Ha1 although the absolute values are smaller. The only exception here is at IT_Cp2 where JV+ overestimates deposition velocity in the summer just as it did for GPP and g_s. The model divergence in diel profile of ozone deposition velocity exhibits similar variability to that of the seasonal profile.

The seasonal changes in deposition velocity are also very different to that of g_s at their respective sites. Ozone deposition velocities at BR_Sa1, IT_Cp2 and US_Ha1, show the greatest variations, ranging between <5% and ~30% for model configurations that over or underestimated GPP respectively, relative to the model configuration that produces the best summary statistics for each site, as defined by Eqn.32 and summarised in Table S4. The two needleleaf forests, FI_Hyy and US_Blo show the least variation in seasonal deposition velocities of <10%.

As shown in Eqn. 4, ozone deposition rates depend on ozone concentration as well as deposition velocity. Hence, while the differences estimated in deposition velocity would be expected to produce changes in ozone deposition rates at the study sites, they will not be directly proportional.

Figure S7 shows average ozone concentrations for each study site for the relevant simulation time periods. As ozone is produced through photochemical processes concentrations at all sites peak during the spring and summer and decline steadily in the autumn and winter.

Figure 5 shows that the seasonal variation in ozone deposition rate closely follows the seasonal variation in ozone concentration at all sites. On the contrary, the diel profile of ozone deposition differs from that of the concentration. While ozone concentrations at all sites peak in the

late afternoon or early evening, deposition rates are highest just after midday when g_s and deposition velocity are at a maximum. This clearly indicates that deposition velocity, and hence stomatal conductance, is the key determinant of deposition rates on shorter timescales, while atmospheric ozone concentrations drive longer temporal trends. The greatest variations in seasonal and diurnal deposition rates between different model configurations, indicated by the grey shaded areas on Figure 5, were observed at FI_Hyy and US_Ha1, as for the deposition velocities.

The diel profile of ozone deposition rates, and their variations due to changes in stomatal conductance parameterisations, are similar to those of the deposition velocities (Figure S6). Variations in deposition rates estimated by JV+ which overestimated GPP and stomatal conductance, and the best-fit models averaged 0.10% - 10% across sites. A 7-13% difference was also seen in the deposition rates calculated using the best fit and maximal underestimating model configurations.

However, the seasonal variations observed in deposition rates are much lower than the variations in either stomatal conductance or deposition velocity across all sites. There was only ~1% variation between seasonal ozone deposition rates in model configurations which overestimated GPP and the best performing model across sites, apart from IT_Cp2 where deposition rate varied by ~5% in the summer. Similarly, seasonal deposition rates estimated by model configurations with the lowest GPP were 7-13% lower than those estimated with the best performing model configurations (Figure 5). By contrast, modelled stomatal conductance and deposition velocities varied by up to 100% and up to 30% respectively for these same model configurations (Figure 5), confirming the modulating effect of ozone concentrations.

The role of ozone concentrations in determining ozone deposition rates is exemplified at BR_Sa1. Average g_s and deposition velocity were a factor of 2 higher at this site than US_Ha1 which had the next highest values. However, the average ozone deposition rates at BR_Sa1 were approximately the same as those at US_Ha1 (0.18 ppb cms^{-1}). This is due to lower average ozone concentration at BR_Sa1 (20 ppb) compared to US_Ha1 (43 ppb).

4 Discussion and Conclusion

We have found that ozone deposition rates estimated using stomatal conductance simulated by three of the most widely-used stomatal conductance-photosynthesis models can vary by as much as 10% depending on ecosystem, season and time of day. As dry deposition is the primary sink for tropospheric ozone, this has potentially significant implications for estimated ozone budgets across space and time.

By introducing the Jarvis, Ball-Berry and Medlyn parameterisations of stomatal conductance and photosynthesis into FORCAsT1.0, a 1-D column model of trace gas exchange between a forest canopy and the atmosphere (Ashworth et al. 2015; Otu-Larbi et al., 2020a, 2020b), we were able to evaluate the performance of the three physiological models via comparison of simulated photosynthesis with long-term measurements of gross primary productivity (GPP) taken from the FLUXNET2015 dataset (Pastorello et al., 2020). We find that all three models reproduce the seasonal and diel variations in GPP well at a range of forest types, Boreal evergreen (FI_Hyy), Temperate deciduous (US_Ha1), and Mediterranean evergreen (IT_Cp2 and US_Blo), but struggle to capture seasonality at a Tropical broadleaf evergreen site (BR_Sa1).

As shown by Figures 2 and 4, the Medlyn stomatal optimisation model provides the best overall performance at four of the five FLUXNET sites used in this study (FI_Hyy, IT_Cp2, US_Blo and US_Ha1), with estimates of GPP within 20%, but is out-performed by the Ball-Berry coupled stomatal conductance-photosynthesis model at BR_Sa1. The Ball-Berry model also successfully captures GPP across all sites, with divergence from observation mostly <10% except for the drought-prone Mediterranean IT_Cp2 site, at which modelled GPP is 15-20% higher than observed GPP during the middle of the day. The superior performance of MD compared to BB at this site could be expected as MD was specifically developed as an improvement on BB to optimise carbon gain while limiting water loss (Medlyn et al., 2011). Except for US_Blo, where JV reproduced the observed

annual and diel profiles of GPP to within 20%, the Jarvis multiplicative model either substantially overestimated or underestimated GPP, by as much as a factor of 2. The relatively poor performance of JV in reproducing observed GPP is perhaps not surprising since photosynthesis estimates are based on a simple assumption of a linear relationship between stomatal conductance and carbon assimilation (Eqn.6).

The superior performance of the Medlyn optimisation model in the two Mediterranean climates could also be due to the fact that vegetation response to soil moisture stress is better accounted for through a combination of stomatal and biochemical limitations (e.g. see De Kauwe et al., 2015; Lin et al., 2015; Otu-Larbi et al., 2020). BB, by comparison, assumes that drought stress directly downregulates photosynthesis rates or is the result of biochemical limitation only (e.g see Best et al., 2011; Clark et al., 2011; Fares et al., 2019). This finding is supported by previous work which shows that the choice of drought stress parameterisation is an important factor that determines model performance in a water stressed environment (Egea et al.,2011; Keenan et al., 2010).

The poor performance of the models at the tropical evergreen site (BR_Sa1) is likely due to the assumption of a uniform forest structure for this evergreen forest site throughout the year. Subsequently, f_{phen} in JV (Eqn. 5) is set to a value of 1 and constant LAI is used in estimating photosynthetic capacity in BB and MD models. A modelling study by Flack-Prain et al. (2019) indicates that changes in LAI could account for up to 33% of observed variations in Amazonian forest GPP. This suggests the need for an improved understanding of changes in forest structure and phenology in tropical ecosystems to obtain more accurate model estimation of GPP at this and other tropical sites (Rödig et al., 2018). In addition, photosynthetic rates and stomatal conductance are controlled by solar radiation and temperature and limited by stress factors like drought and air pollutants including ozone (Nemani et al., 2003). For BR_Sa1, both temperature and PAR (Figure 1a and b; orange lines) remain fairly constant throughout the year which would lead to higher modelled photosynthetic capacity in BB and MD since modelled V_{cmax} and J_{max} are reliant on temperature.

Seasonal variations in V_{cmax} and J_{max} are reported to be a major source of uncertainty in GPP estimates in Amazonian forests (Flack-Prain et al., 2019). It is worth noting that US_Blo and IT_Cp2 which are also evergreen forest were treated similarly, but as shown in Figures 2 and 4, the models performed better at this site, perhaps due to a compensating error in modelling drought stress.

Results from sensitivity tests conducted on key stomatal conductance parameters in JV, BB and MD models revealed that modelled GPP and stomatal conductance values are highly sensitive to the choice of conductance parameters. Variations of ~5-75% from base model estimates were observed in modelled GPP and stomatal conductance in response to ~10-60% variation in model parameters. Such wide differences could reduce the reliability of estimated reductions in crop or plant productivity due to air pollutants such as ozone.

The findings from this study make it imperative that more measurements of these key conductance parameters are made to improve understanding and model representation of dry deposition. The Jarvis model showed greater sensitivity to choice of parameter value than either Ball-Berry or Medlyn. It must be noted that the Jarvis parameter g_{max} is typically measured in sunlit leaves at the top of the canopy. Leaves below the canopy often differ in their shape and leaf angle classes from those at the top of the canopy (Niinemets, 2010). The JV model as implemented in FORCAsT and elsewhere assumes the same g_{max} for all angle classes and model levels. More work is needed to improve the parameterisation of variations in g_{max} for different levels in the canopy and leaf angle classes.

We conclude that the Medlyn coupled stomatal conductance-photosynthesis model would be the best default selection. However, our model simulations also point to the need for improved stomatal conductance-photosynthesis model parameterisations for tropical ecosystems where seasonality is driven by contrasts in precipitation rather than temperature and solar radiation.

We tested the response of ozone deposition rate at different ecosystems to changes in stomatal conductance parameterisations while keeping model calculations of other resistances

unchanged. The choice of stomatal conductance model parameters was found to be a very important factor in determining ozone deposition rates across all sites. Seasonal and daily deposition rates to the forest canopy changed by as much as 13% with implications for air quality modelling and assessment of ozone damage to crops and plants. Most models used in assessing air quality at global, regional, and local levels consider dry deposition using variants of the same Wesely deposition scheme used in FORCAsT-gs (Hardacre et al., 2015). Many international assessments of ozone damage to crops and forests are based on dose-response parameters developed using the JV model (e.g. see Emberson et al., 2000, Hayes et al., 2007; Mills et al., 2011; Buker et al., 2015). Like air quality models, dose-response relationships rely on ozone deposition rates and their accuracy and reliability could be severely diminished if the appropriate model parameterisations are not used. Large uncertainty in modelled deposition rates due to the choice of model parameters, as found in this study, could therefore affect modelled surface ozone concentrations with negative implications for air quality monitoring as well as assessments of plant productivity losses from ozone damage. This is especially true for models that rely on the Jarvis multiplicative model to estimate stomatal conductance. Our results highlight the need for models to carefully consider the choice of model parameters as this will ultimately determine model performance.

Similar to other studies, we found the highest stomatal conductance and ozone deposition velocities at tropical and broadleaf forest site compared to needleleaf and coniferous forests (e.g. see Emberson et al., 2001; Fowler et al., 2001; 2011; Kumar et al., 2011; Silva & Heald, 2018). The larger LAI at the broadleaf forests (BR_Sa1 and US_Ha1), leads to greater canopy conductance, lower stomatal resistance, and subsequently higher deposition velocity as these are important for estimating total canopy and leaf boundary resistance (Meyers & Baldocchi, 1988; Padro, 1996). Ozone deposition velocities at BR_Sa1 were up to a factor of three higher than those at IT_Cp2, US_Blo and FI_Hyy. However, the difference in ozone deposition rates were much lower (<30%) due to lower ozone concentrations at this remote forest site.

Our findings of the sensitivity of stomatal conductance estimates to parameter and algorithm choice could also have important implications in modelling biogenic volatile organic compound (BVOC) emissions. Current BVOC emission models rely on leaf temperature and solar radiation to drive emission rates and are known to reproduce observations for a range of forest ecosystems and climates within a factor of two (e.g. see Guenther et al., 1993; 1995; 2006). However, such models have been shown to struggle to reproduce diurnal emission patterns of short−chained carboxylic acids and aldehydes, leading to suggestions that the failure to include stomatal conductance in such models could be a limiting factor in model performance (Kesselmeier et al., 1997; Martin et al., 1999; Staudt et al., 2000; Niinemets and Reichstein, 2003). Including stomatal control of emission rates in land-atmosphere models would need to account for the sensitivity of simulated stomatal conductance to the choice of physiological model.

Code availability

FORCAsT-gs is available for download on request to the corresponding author.

Data availability

FLUXNET2015 data for BR_Sa1, FI_Hyy, IT_Cp2, US_Blo, and US_Ha1 can all be accessed and downloaded from https://fluxnet.fluxdata.org/data/fluxnet2015-dataset/; the doi of each dataset is shown in Table 1.

Author contribution

All co-authors were involved in conceptualization of the research and writing of the manuscript. F. Otu-Larbi and K. Ashworth performed model simulations and analysed results.

Competing interests

The authors declare no competing interests.

Acknowledgements

F. Otu-Larbi is grateful to the Faculty of Science and Technology (FST) and Lancaster Environment Centre (LEC) at Lancaster University for funding his PhD Studentship. K. Ashworth is a Royal Society Dorothy Hodgkin Fellow and thanks the Royal Society of London for their support and funding (DH150070). The authors are grateful to the FLUXNET network, and specifically the lead investigators at each of the study sites, for the ready availability of all data collected at these sites.

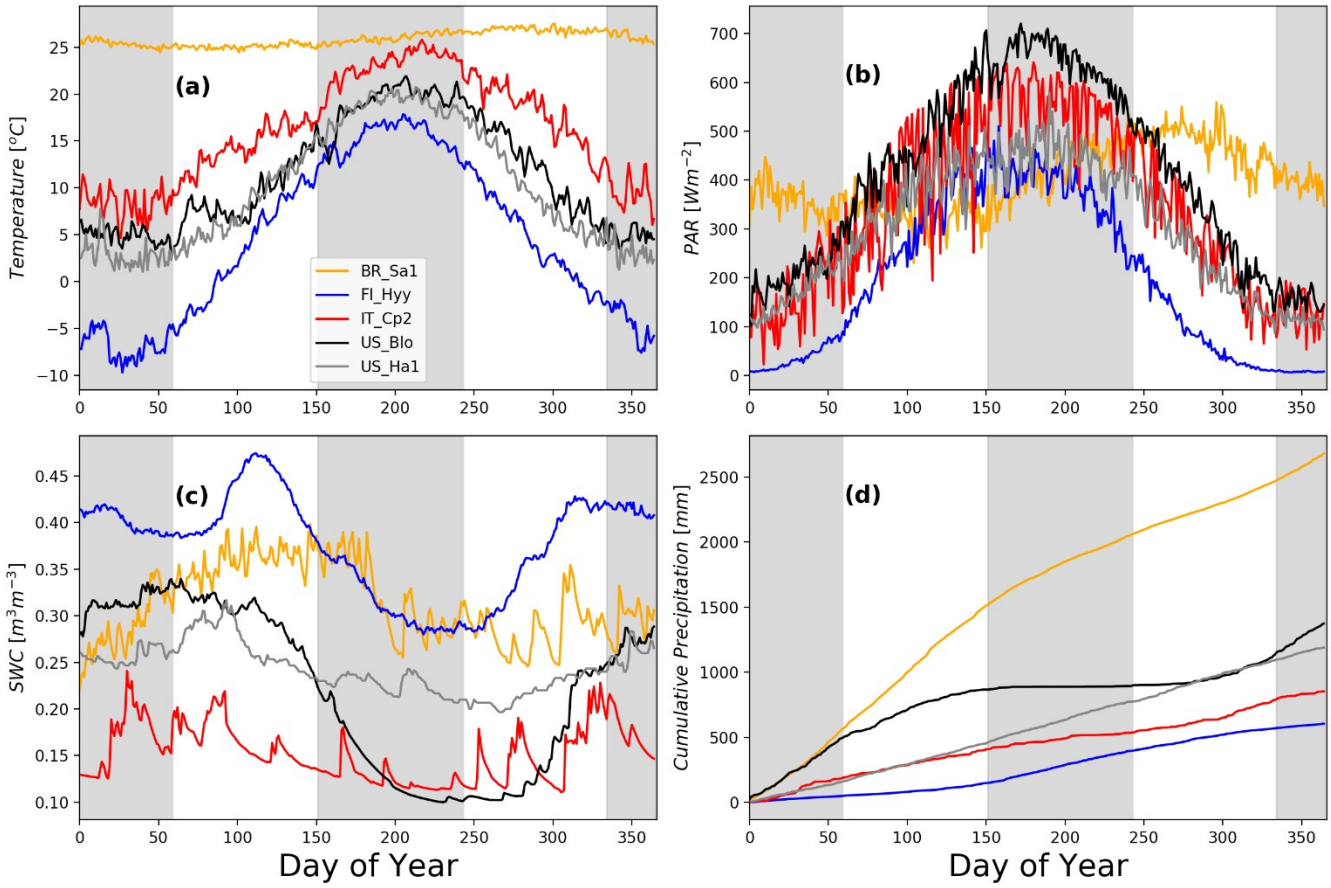

Figure 1: Site conditions and meteorology showing (a) soil moisture (volumetric soil water content, SWC; m^3 m^{-3}); (b) cumulative precipitation (mm); (c) 2-m air temperature (ºC) and (d) photosynthetically active radiation (PAR) at the top of the canopy (W m^{-2}) for an average year at BR_Sa1 (yellow), FI_Hyy (blue), IT_Cp2 (red), US_Blo (black) and US_Ha1 (grey)

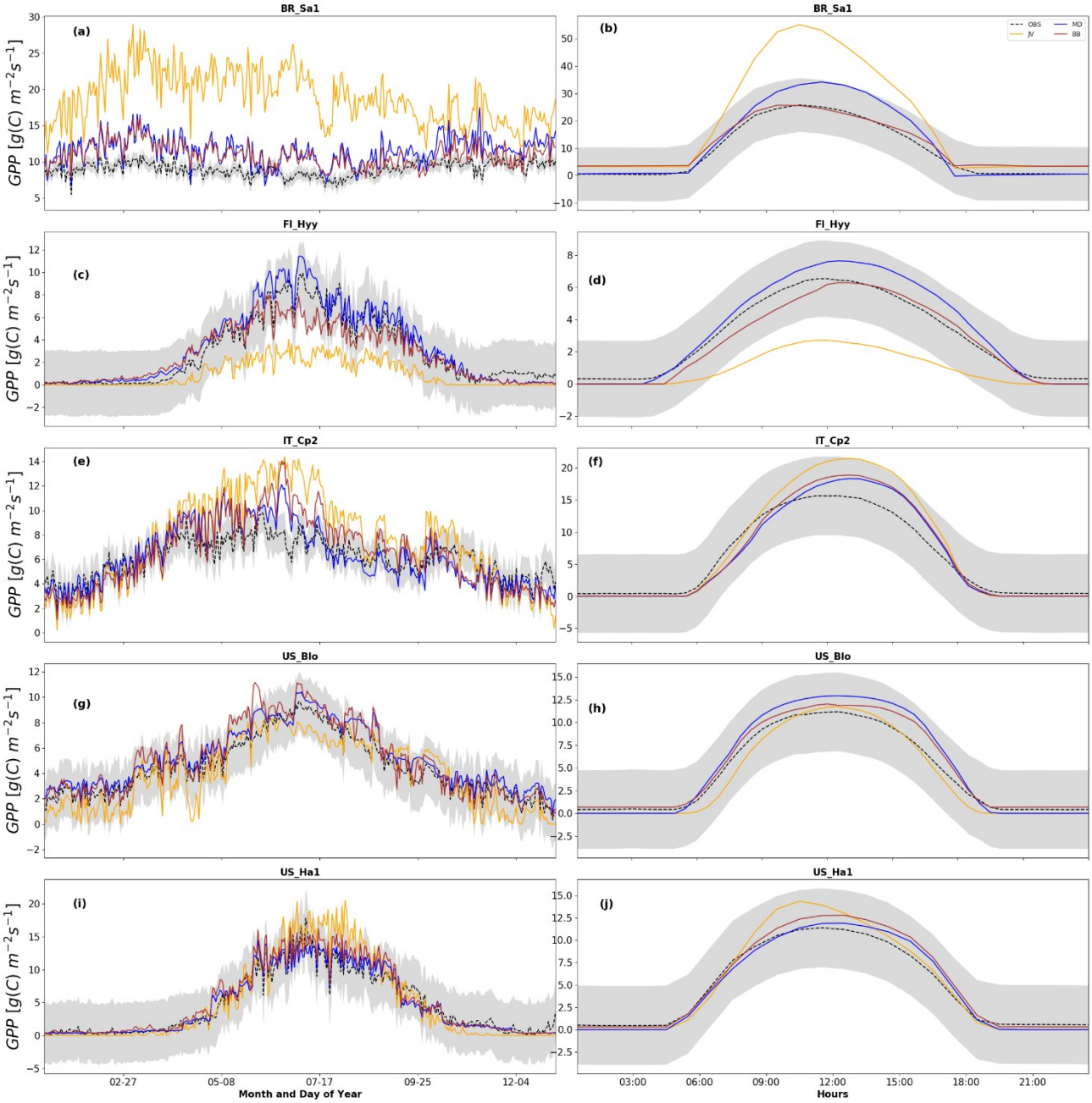

Figure 2: Net photosynthesis for an average year at each of the five FLUXNET sites, from top to bottom: BR_Sa1, FI_Hyy, IT_Cp2, US_Blo, US_Ha1. The first column shows average annual and the second average diel profiles of Gross Primary Productivity (GPP, a measure of photosynthesis rate) estimated from the Jarvis multiplicative (gold), Ball-Berry coupled (red) and Medlyn stomatal optimisation coupled (blue) stomatal conductance-photosynthesis models. The black dashed lines show observed GPP.

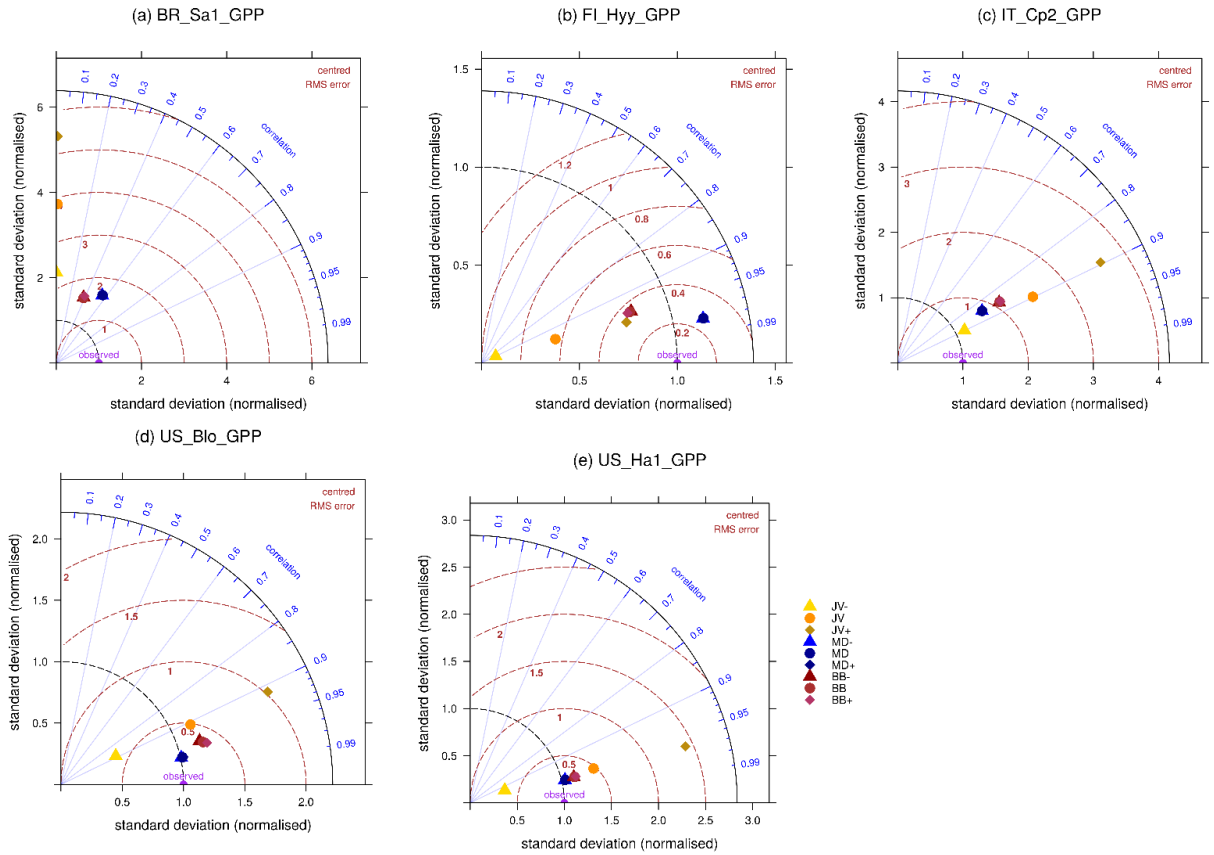

Figure 3: Taylor Diagram summarising model output statistics from FORCAsT sensitivity tests. Observed GPP has SD=1.0, RMSE=0.0 and r=1.0 (purple circle). Black and brown dashed curves and blue lines show normalised standard deviation (SD), centred root mean squared error (RMSE) and correlation coefficients (r) respectively against observations for each model on each diagram. The summary statistics for each JV simulation are shown by gold symbols, BB by red, MD simulation by blue. BASE simulations are denoted by circles, lower bounds (TEST-) by triangles, and upper bounds (TEST+) by diamonds. Note that JV, MD and BB in these plots are the BASE simulations described in sections 2.5.1 and 3.1, and Figure 2.

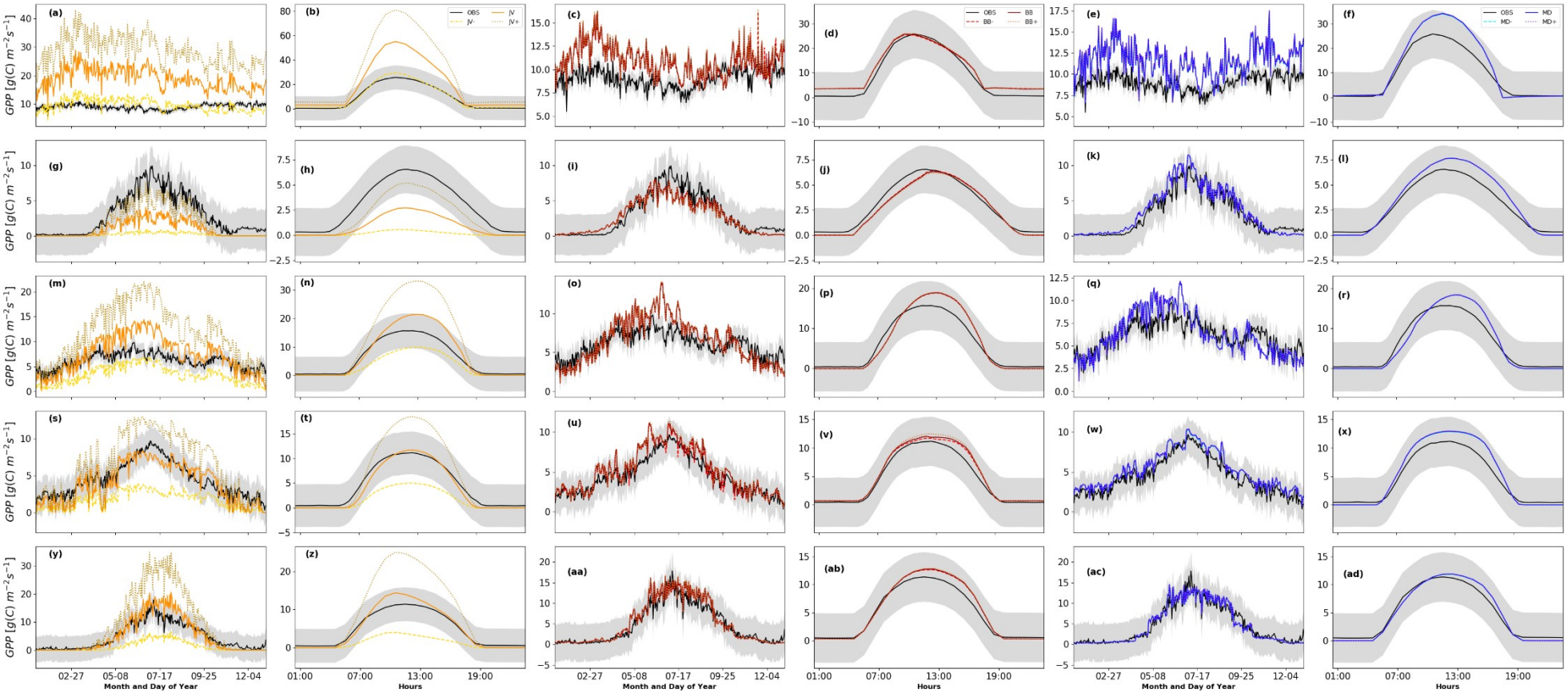

Figure 4: Gas exchange for an average year at each of the five FLUXNET sites, from top to bottom: BR_Sa1, FI_Hyy, IT_Cp2, US_Blo, US_Ha1, for, from left to right, the Jarvis, Ball-Berry and Medlyn stomatal conductance model sensitivity tests. Solid lines denote the unperturbed (BASE) simulation as shown in Figure 2 for each model, with dashed paler line for TEST- and dashed darker line for TEST+ simulations respectively. The black dashed lines show observed GPP at each site.

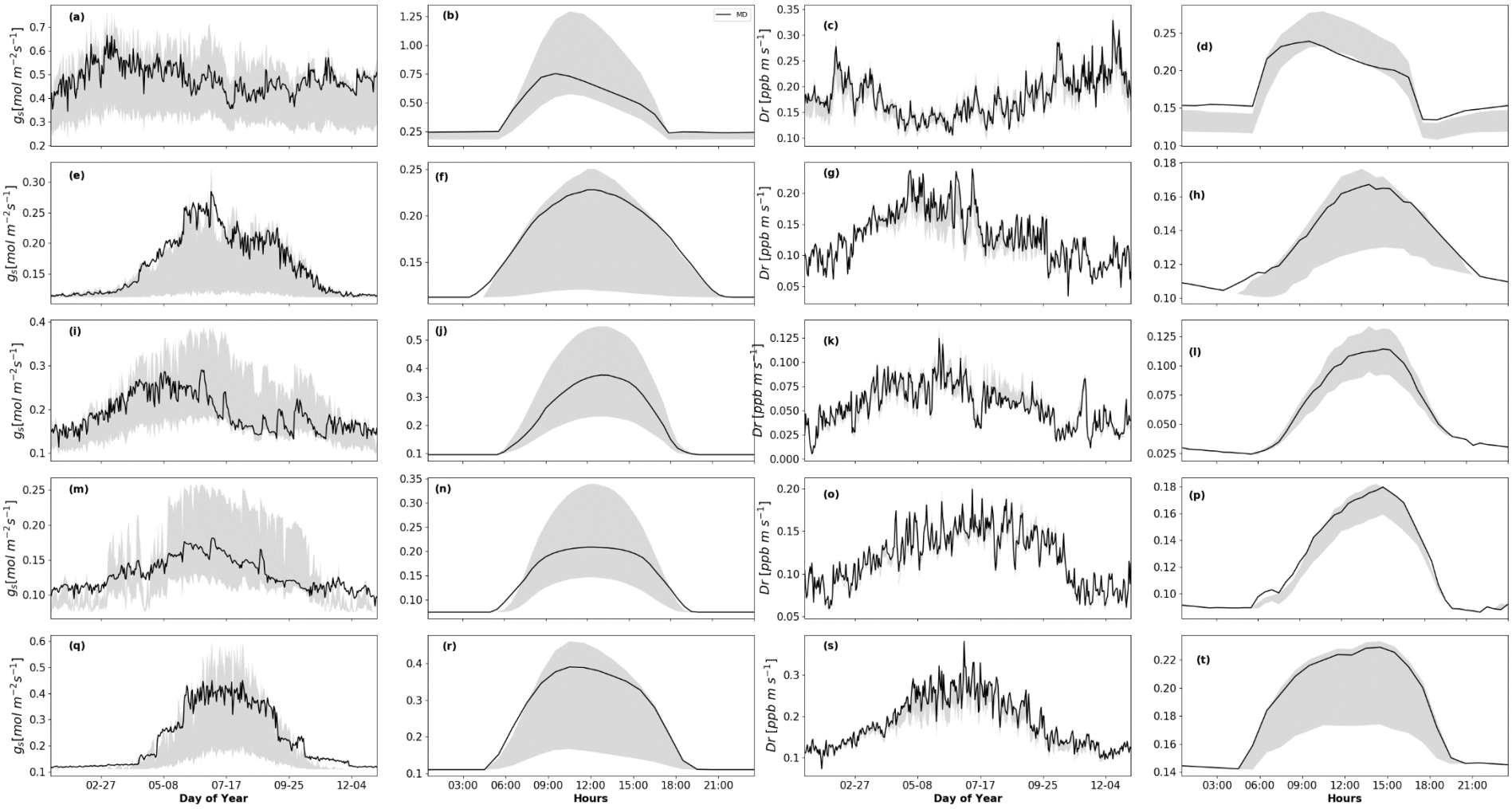

Figure 5: Stomatal conductance and ozone deposition rates for an average year and day at each of the five FLUXNET sites, from top to bottom: BR_Sa1, FI_Hyy, IT_Cp2, US_Blo, and US_Ha1. Solid lines black lines denote the output from the model that best reproduced GPP at each site as shown in Figure 3 and 4. The shaded regions indicate the spread in stomatal conductance and deposition rates across all the model sensitivity tests.

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