Title: A derivation error that affects carbon balance models exists in the current implementation of the Johnson et al. (1942) modified Arrhenius function

Running Title: Derivation error in modified Arrhenius model

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Summary

- Understanding biological temperature responses is crucial to predicting global carbon fluxes. The current approach to modelling temperature responses of photosynthetic capacity in large scale modelling efforts uses a modified Arrhenius equation.
- We rederived the modified Arrhenius equation from the source publication from 1942 and uncovered a missing term that was completely dropped by 2002. We compare fitted temperature response parameters between the new and old derivation of the modified Arrhenius equation.
- We find that most parameters are minimally affected, though activation energy is impacted quite substantially. We then scaled the impact of these small errors to whole plant carbon balance and found that the impact of the rederivation of the Arrhenius on modelled daily carbon gain causes a meaningful deviation of ~18% day^{-1}.
- This suggests that the error in the derivation of the modified Arrhenius equation has impacted the accuracy of predictions of carbon fluxes at larger scales. We recommend that the derivation error be corrected in modelling efforts moving forward.

Keywords: Arrhenius, temperature, photosynthesis, gas exchange, modelling, carbon balance

Introduction

Globally, photosynthesis and autotrophic respiration are the largest biological carbon fluxes, with photosynthesis removing ~120 Gt C $year^{-1}$ from the atmosphere and autotrophic respiration releasing ~60 Gt C $year^{-1}$ back to the atmosphere (Amthor, 2000; Ciais *et al.*, 2013). Given the temperature sensitivity of these large carbon fluxes (Lombardozzi *et al.*, 2015), understanding how photosynthesis and respiration respond on acute, acclimatory, and adaptive timescales is crucial for predicting vegetative and carbon cycle responses to future global climates (Rogers *et al.*, 2017; Stinziano *et al.,* 2018). Biological temperature responses including photosynthesis and respiration are typically assumed to be exponential or peaked (Way & Yamori, 2014; Smith & Dukes, 2017; Kumarathunge *et al.*, 2019). Exponential responses are usually modelled based on an Arrhenius-type curve (Arrhenius, 1915):

$$f(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad \text{Equation 1,}$$

or equivalently,

$$f(T) = k_{25} \exp\left[\frac{E_a(T-298.15)}{RT298.15}\right] \quad \text{Equation 2}$$

where f(T) is the rate of the process at temperature T, A is a pre-exponential factor, T in K, k_{25} is the rate of the process at 298.15 K, E_a is the activation energy in J mol^{-1}, R is the universal gas constant of 8.314 J mol^{-1} K^{-1}, and 298.15 is the reference temperature in K. As for peaked responses, while a few options are available (Kruse *et al.,* 2008; Hobbs *et al.*, 2013; Heskel *et al.*, 2016), the most commonly implemented version is the modified Arrhenius model of Johnson *et al.* (1942) as presented in Medlyn *et al.* (2002):

$$f(T) = k_{25} \exp\left[\frac{E_a(T-298.15)}{RT298.15}\right]\left[\frac{1+\exp\left(\frac{298.15\Delta S - H_d}{298.15R}\right)}{1+\exp\left(\frac{T\Delta S - H_d}{TR}\right)}\right] \quad \text{Equation 3}$$

where H_d is the deactivation energy in J mol^{-1}, and ΔS is the entropy of the process in J mol^{-1} K^{-1}.

Equation 3 is used for modelling the temperature responses of photosynthetic capacity (i.e. maximum carboxylation capacity of rubisco, V_{cmax}, maximum electron transport capacity, J_{max}, and triose phosphate utilization capacity (TPU); see Rogers *et al.*, 2017 for a review of models using Equation 3). These parameters are then used in ecophysiological studies to understand thermal acclimation of photosynthesis (see Kattge & Knorr, 2007; Smith & Dukes, 2017; and Kumarathunge *et al.,* 2019 for examples). Furthermore, this equation is also used in terrestrial biosphere models to predict the future carbon cycling (e.g. Rogers *et al.*, 2017).

Due to the ubiquity of Equation 3 in modelling temperature responses and the thermal acclimation of photosynthetic capacity (e.g. Kattge & Knorr, 2007; Rogers *et al.*, 2017; Smith & Dukes, 2017; Kumarathunge *et al.*, 2019), we revisited the original Johnson *et al.* (1942) modified Arrhenius function to rederive Equation 3. In the process of this rederivation, we uncovered a term that was completely dropped sometime between Johnson *et al.* (1942) and Medlyn *et al.* (2002) which causes a systematic error in the application of Equation 3 for modelling photosynthetic capacity in individual species (e.g. Medlyn *et al.*, 2002) to modelling global scale carbon uptake (e.g. Rogers *et al.*, 2017). We then refit a freely available dataset (Kumarathunge *et al.*, 2019), with both versions of the modified Arrhenius model, and fed the temperature response fits through a carbon balance model to estimate the impact of the derivation error on modelled plant carbon balance. We predicted that the derivation error would cause substantial variation in fitted temperature response parameters, and that these differences would propagate through to modelled daily carbon balance.

Description

Rederivation of the modified Arrhenius equation

Johnson *et al.* (1942, equation 24) describe the temperature response of the light intensity of a luciferase reaction as:

$$I = \frac{c'' T \exp\left(\frac{-\Delta H‡}{RT}\right)}{1+\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right)} \qquad \text{Equation 4}$$

where I is the intensity of the luciferase reaction, c'' is not explicitly defined in Johnson *et al.* (1942), but appears to represent a constant based on the derivation of Equation 4, T is the temperature in K, R is the universal gas constant of 8.314 J mol^{-1} K^{-1}, ΔH‡ is the activation energy in J mol^{-1}, ΔH is the deactivation energy in J mol^{-1}, and ΔS is the entropy in J mol^{-1} K^{-1}. We can relativize the equation to a reference temperature by dividing Equation 4 at a hypothetical temperature by Equation 4 at a standard temperature (i.e. 25 °C):

$$\frac{I}{I_{25}} = \frac{\left[\frac{c'' T \exp\left(\frac{-\Delta H‡}{RT}\right)}{1+\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right)}\right]}{\left[\frac{c''298.15 \exp\left(\frac{-\Delta H‡}{298.15R}\right)}{1+\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{298.15R}\right)}\right]} \quad \text{Equation 5}$$

Next, rearrange fractions for clarity:

$$\frac{I}{I_{25}} = \left[\frac{c'' T \exp\left(\frac{-\Delta H‡}{RT}\right) c'' T e^{\frac{-\Delta H‡}{RT}}}{c''298.15 \exp\left(\frac{-\Delta H‡}{298.15R}\right) c''298.15 e^{\frac{-\Delta H‡}{R298.15}}}\right]\left[\frac{1+\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{298.15R}\right)1+e^{\frac{\Delta S}{R}}e^{\frac{-\Delta H}{R298.15}}}{1+\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right)1+e^{\frac{\Delta S}{R}}e^{\frac{-\Delta H}{RT}}}\right] \quad \text{Equation 6}$$

Cancel out c'', use exponent rules to simplify:

$$\frac{I}{I_{25}} = \frac{T}{298.15}\exp\left(\frac{-\Delta H‡}{RT} - \frac{-\Delta H‡}{R298.15}\right)\left[\frac{1+e^{\frac{\Delta S}{R}+\frac{-\Delta H}{R298.15}}\exp\left(\frac{\Delta S}{R}+\frac{-\Delta H}{R298.15}\right)}{1+e^{\frac{\Delta S}{R}+\frac{-\Delta H}{RT}}\exp\left(\frac{\Delta S}{R}+\frac{-\Delta H}{RT}\right)}\right] \quad \text{Equation 7}$$

Simplify further by setting a common denominator within exponential terms:

$$I = I_{25}\frac{T}{298.15}\exp\left(\frac{-\Delta H‡298.15 \mp \Delta H‡T}{RT298.15}\right)\left[\frac{1+\exp\left(\frac{298.15\Delta S-\Delta H}{298.15R}\right)}{1+\exp\left(\frac{T\Delta S-\Delta H}{TR}\right)}\right] \quad \text{Equation 8}$$

Simplify exponential terms further:

$$I = I_{25}\frac{T}{298.15}\exp\left(\frac{\Delta H‡(T-298.15)}{RT298.15}\right)\left[\frac{1+\exp\left(\frac{298.15\Delta S-\Delta H}{298.15R}\right)}{1+\exp\left(\frac{T\Delta S-\Delta H}{TR}\right)}\right] \quad \text{Equation 9}$$

Harmonizing the notation scheme to that typically used in plant ecophysiology:

$$f(T) = k_{25}\frac{T}{298.15}\exp\left(\frac{E_a(T-298.15)}{RT298.15}\right)\left[\frac{1+\exp\left(\frac{298.15\Delta S-H_d}{298.15R}\right)}{1+\exp\left(\frac{T\Delta S-H_d}{TR}\right)}\right] \quad \text{Equation 10}$$

Note the difference between Equations 3 and 10: the term T / 298.15 is missing from Equation 3. There are several alternative expressions of Equation 4 (e.g. Farquhar *et al*., 1980; Harley *et al.*, 1986; Harley *et al.*, 1992; Harley & Baldocchi, 1995; Lloyd, 1995), however when relativized to a common temperature, the equations presented in Farquhar *et al.* (1980), Harley *et al.* (1992), Harley & Baldocchi (1995), and Lloyd (1995) are all identical to Eq. 3 when relativized by temperature, while the Harley *et al.* (1986) equation is identical to our derivation when relativized to a common temperature (see Appendix A for the relativizations of Farquhar *et al.* (1980), Harley *et al.* (1986), and Harley *et al.* (1992); Harley & Baldocchi (1995) uses an identical equation to Eq. 18 from Medlyn *et al.* (2002), while Lloyd (1995) uses an identical equation to Eq. 17 from Medlyn *et al.* (2002)). This derivation error introduces multiple systematic errors. First, errors are introduced into the fitted parameters E_a, H_d, and ΔS. Second, k_{25} is scaled using the wrong equation, introducing an error in f(T). And third, acclimation equations describing E_a, H_d, and ΔS will then be in error due to errors in the fitted parameters at each temperature. Here we focus on the impact of the dropped term on fitted temperature response parameters and modelling whole-plant carbon balance.

Data analysis

Using A-C_i curve data compiled in Kumarathunge *et al.* (2019), available from the Kumarathunge *et al.* (2018) repository, we used the {fitacis} function from the R package {plantecophys} (Duursma, 2015), setting fitmethod = "bilinear", Tcorrect = FALSE, and fitTPU = TRUE, to obtain V_{cmax} and J_{max}. We then fit Equations 3 and 10 to the data, allowing H_d to be fit. To ensure that the curves could be fit (i.e. that there were enough data to fit 4 parameters), we only used data where A-C_i curves were measured at 5 or more temperatures. This reduced the number of candidate temperature responses from 729 to 403. We used the R package {minpack.lm} (Elzhov *et al.,* 2016), using Equation 2 to obtain starting values for E_a and k_{25}, while the other initial parameters were ΔS = 0.650 kJ mol^{-1} K^{-1}, and H_d varying

from 1 to 1000 kJ mol^{-1}, followed by the {BIC} function to select the best model based on Bayesian Information Criteria. We obtained 341 and 337 successful V_{cmax} temperature response curve fits for Equations 3 and 10, respectively, and 241 and 242 successful J_{max} temperature response curve fits for Equations 3 and 10, respectively. This resulted in a total of 547 fitted temperature response curves which we filtered further, requiring that E_a, ΔS, and H_d were all positive values and that the V_{cmax} and J_{max} data were paired, resulting in 196 complete pairs of V_{cmax} and J_{max} temperature responses for analysis. The data covered a temperature range from 1 °C to 50 °C across all curves, with a median range of 14 °C to 42.6 °C.

Modelling

We modelled the impact of the Equations 3 and 10 on daily net plant carbon balance. Data for leaf area, root and shoot masses, as well as leaf dark respiration at 25 °C were taken for white spruce (*Picea glauca*) from Stinziano & Way (2017), while stomatal conductance model parameters were calculated with the gas exchange data reported in Stinziano & Way (2017). Briefly, Stinziano and Way (2017) grew white spruce in growth chambers under a simulated autumn treatment based on temperatures and photoperiods from Trenton, ON, with weekly harvesting of biomass and gas exchange measurements across 17 weeks as a control treatment, along with a warming treatment where temperatures were +5 °C of the control, a constant summer day/night temperature with declining photoperiod, and a constant summer photoperiod with ambient changes in temperature. Here we only used data from Stinziano & Way (2017) that were from the control treatment. Mean data were taken from the control treatment at weeks 0 and 12 to provide contrasting biomass allocation patterns such that week 0 is a low respiration scenario and week 12 is a high respiration scenario. These different respiration scenarios were used to reduce bias in any conclusions regarding the impact of Equations 3 and 10 on carbon balance, as the ratio of photosynthesis to respiration may alter the sensitivity of net carbon balance to the Arrhenius equation used. Root respiration for white spruce was taken from Weger & Guy (1991) and we assumed that stem respiration was equal to root respiration (Table 1).

For the full model structure and equations, please see the accompanying R package {arrhenius.comparison} (“arrhenius.comparison_1.0.1.tar.gz”; Stinziano & Murphy, 2020) (see Table 2

for equations). Briefly, we linked the Medlyn *et al.* (2011) stomatal conductance model with the Farquhar *et al.* (1980) C_3 photosynthesis model, assuming infinite mesophyll conductance to CO_2 as these assumptions were used in fitting the data from Kumarathunge *et al.* (2018). Photosynthetic capacity, both maximum rubisco carboxylation capacity, V_{cmax}, and maximum electron transport rate, J_{max} were scaled to temperature using either Equation 3 or 10, while respiration was scaled according to (Atkin & Tjoelker, 2003). Photosynthesis and respiration were summed across each modelled day to calculate daily plant carbon assimilation.

Modelling was performed on 18 total days of environmental data, with three days of data from three months (17^{th} – 19^{th} of May, August, and October, 2019) obtained from external irradiance sensors at the Biotron Experimental Climate Change Research Centre at the University of Western Ontario and the remaining environmental data from Environment Canada historical climate data for South London (43.01°N, 81.27°W, altitude: 251 m; temperature range: -0.1 – 27.9 °C) and the rooftop greenhouse at the University of New Mexico (35.08°N, 106.62°W, altitude: 1587 m; temperature range: 7.2 – 42.2 °C) to capture different levels of environmental variability (Fig. **1**).

Overall, the modelling approach allows us to assess the relative differences between Equations 3 and 10 under a low- and high- respiration scenario across different ranges of seasonal variability.

Statistical analysis

Data were analyzed using the {lm} function in R v.3.6.2 (R Core Team, 2019), regressing the data obtained from Equation 3 against the data obtained from Equation 10 for each of $V_{cmax,25}$, $J_{max,25}$, $E_{a,Vcmax}$, $E_{a,Jmax}$, ΔS_{Vcmax}, ΔS_{Jmax}, $H_{d,Vcmax}$, $H_{d,Jmax}$, BIC values for the fits of Equations 3 and 10, daily photosynthesis, daily net carbon balance, and daily photosynthesis : daily respiration ratios. Intercepts in the regression, when significant, were interpreted as a bias in the parameter, while deviations in slope from a 1:1 relationship where interpreted as percentage over- or under-estimation of the parameter (i.e. [parameter slope – 1] · 100 = % estimation error). All p-values were corrected for multiple testing using the p.adjust() function in R with Holm's method. All code and data will be made freely available on GitHub upon publication in the {arrhenius.comparison} R package (Stinziano & Murphy, 2020).

Results

Equations 3 and 10 exhibited similar performance

The performance between Equations 3 and 10 for fitting V_{cmax} temperature responses were essentially identical when assessed based on BIC, with a slope of 1.001 ± 0.001 ($F_{1,195} = 5.52 \cdot 10^5$, R^2 = 0.9996, $P < 2.2 \cdot 10^{-16}$; Fig. **2a**), as was the case for J_{max} with a slope of 1.001 ± 0.001 ($F_{1,195} = 2.43 \cdot 10^6$, R^2 = 0.9999, $P < 2.2 \cdot 10^{-16}$; Fig. **2b**). However, while some fitted temperature responses appeared identical, there were some cases where the fitted shape differed (Figs. **2c-f**).

Estimates of $V_{cmax,25}$ were essentially identical between the Equation 3 fitting (y-axis) and the Equation 10 fitting (x-axis) with a slope of 1.002 ± 0.004 ($F_{1,195} = 5.84 \cdot 10^4$, R^2 = 0.9967, $P < 2.2 \cdot 10^{-16}$; Fig. **3e**), as was the case for $J_{max,25}$ with a slope of 1.001 ± 0.001 ($F_{1,195} = 6.56 \cdot 10^5$, R^2 = 0.9997, $P < 2.2 \cdot 10^{-16}$; Fig. **3f**). $E_{a,Vcmax}$ was generally underestimated with a slope of 0.847 ± 0.024 and a positive bias of 9.73 ± 2.59 kJ mol^{-1} when using Equation 3 ($F_{1,194}$ = 1202, R^2 = 0.8610, $P < 2.2 \cdot 10^{-16}$; Fig. **3a**), while $E_{a,Jmax}$ was underestimated with a slope of 0.832 ± 0.013 and a positive bias of 5.98 ± 1.06 kJ mol^{-1} ($F_{1,194}$ = 3834, R^2 = 0.9518, $P < 2.2 \cdot 10^{-16}$; Fig. **3b**). ΔS_{Vcmax} was essentially identical between Equation 3 and 10 with a slope of 1.000 ± 0.0233 ($F_{1,195}$ = 1849, R^2 = 0.9046, $P < 2.2 \cdot 10^{-16}$; Fig. **3c**), as was the case with ΔS_{Jmax} with a slope of 0.988 ± 0.033 ($F_{1,195}$ = 904, R^2 = 0.8226, $P < 2.2 \cdot 10^{-16}$; Fig. **3d**), and $H_{d,Vcmax}$ with a slope of 1.002 ± 0.005 ($F_{1,195} = 4.12 \cdot 10^4$, R^2 = 0.9953, $P < 2.2 \cdot 10^{-16}$; Fig. **3g**). However, $H_{d,Jmax}$ was underestimated with a slope of 0.952 ± 0.024 and a positive bias of 31.48 ± 8.93 kJ mol^{-1} ($F_{1,194}$ = 1592, R^2 = 0.8914, $P < 2.2 \cdot 10^{-16}$; Fig. **3h**).

Impacts on modelled net carbon balance

In general, the differences in thermal response parameters were amplified when integrated at the whole-plant level. For modelled daily photosynthesis (A), the slope for the low respiration model was 0.819 ± 0.013 and the intercept was 0.018 ± 0.002 g plant^{-1} day^{-1} (Eq. 3 versus Eq. 10; approximately 18% of modelled A) ($F_{1,3523} = 4.168 \cdot 10^3$, R^2 = 0.5418; $P < 2.2 \cdot 10^{-16}$) (Fig. **4a**). For the high respiration model of daily A, the slope was 0.819 ± 0.013 and the intercept was 0.031 ± 0.003 g plant^{-1} day^{-1} (approximately 18% of modelled A) ($F_{1,3523} = 4.168 \cdot 10^3$, R^2 = 0.5418; $P < 2.2 \cdot 10^{-16}$) (Fig. **4b**). The low respiration model of total daily carbon (C) gain had a slope of 0.836 ± 0.012 and an intercept of 0.012

± 0.001 g plant^{-1} day^{-1} (approximately 16% of modelled C gain) (Eq. 3 versus Eq. 10; $F_{1,3523} = 4.539 \cdot 10^3$, $R^2 = 0.5629$; $P < 2.2 \cdot 10^{-16}$) (Fig. **4c**). The high respiration of total C gain similarly had a slope of 0.859 ± 0.012 and an intercept of 0.011 ± 0.002 g plant^{-1} day^{-1} (approximately 14% of modelled C gain) (Eq. 3 versus Eq. 10; $F_{1,3523} = 5.364 \cdot 10^3$, $R^2 = 0.6035$; $P < 2.2 \cdot 10^{-16}$) (Fig. **4d**). The ratio of the total daily photosynthesis: respiration (A/R) was also considered when comparing models. The low respiration model of A/R had a slope of 0.982 ± 0.007 and the intercept was 0.146 ± 0.031 (approximately 2% of modelled A/R) (Eq. 3 versus Eq. 10; $F_{1,3523} = 2.096 \cdot 10^4$, $R^2 = 0.8561$; $P < 2.2 \cdot 10^{-16}$) (Fig. **4e**). The high respiration model had a similar slope of 0.982 ± 0.007 and the intercept was 0.082 ± 0.017 (approximately 2% of modelled A/R) (Eq. 3 versus Eq. 10; $F_{1,3523} = 2.097 \cdot 10^4$, $R^2 = 0.8562$; $P < 2.2 \cdot 10^{-16}$) (Fig. **4f**).

Discussion

We sought to determine whether the missing term in Equation 3 had a meaningful impact on fitted temperature response parameters due to its prevalence in photosynthetic temperature response data and vegetation modelling (Kattge & Knorr, 2007; Duursma & Medlyn, 2012; Rogers *et al.,* 2017; Smith & Dukes, 2017; Stinziano *et al.,* 2018; Stinziano *et al.,* 2019; Kumarathunge *et al.,* 2019). Our present analysis suggests that there is a large impact on E_a for both V_{cmax} and J_{max}, however there were minimal impacts on k_{25}, H_d, and ΔS (though note that H_d for Jmax was underestimated) (Fig. **3**). In general, fitting Equation 3 instead of Equation 10 results in E_a reductions of around 15% with positive bias. These findings are promising in that one of the parameters to which modelled carbon gain is particularly sensitive, H_d (Stinziano *et al.,* 2018), is minimally affected by the missing term. However, since temperature responses are non-linear, small changes in the shape of an accelerating curve can have a strong impact on the integral of the response (Jensen, 1906; i.e. changes in the shape of the temperature response of carbon assimilation can have strong impacts on total carbon fixation). Despite fit performance being nearly identical, the differences due to E_a values between the equations led to an 18% reduction in modelled daily photosynthesis for Equation 3 compared to Equation 10, leading ~14-16% reduction in modelled net daily carbon gain. Overall, comparisons of low-respiration to high-respiration scenarios resulted in similar percent changes in daily C balance with similar variation.

Not only did we compare the impact of the missing term in Equation 3 on different respiration scenarios, but we also modelled data across a range of environmental conditions to understand the impact on C balances of plants under different temperature regimes and how these impacts could scale up in global models. A ~15% reduction in net daily carbon gain is substantial by itself, but this difference would also be amplified over time for a single plant. Plant growth follows the compound interest law (Blackman, 1919). As leaf area increases with growth so does the rate of photosynthesis and thus the amount of carbon available to further increase growth and metabolism, hence why relative growth rates are commonly utilized in the literature (e.g. Shipley, 1989; Causton, 1991; Tjoelker *et al.*, 1999; Loveys *et al.,* 2003; Poorter *et al.,* 2012; Pommereng & Anders, 2015). A reduction of 18% in modelled daily photosynthesis caused by using the modified equation with the missing term (Eq. 3) would become compounded long-term with plant growth and may result in underestimations of future carbon uptake. It is thus likely that the differences we observed would accumulate to even larger carbon flux errors across large spatial and temporal scales with fluctuating temperatures.

Based on the above analysis, the impact of the missing term in the modified Arrhenius equation substantially alters E_a and net daily carbon balance at a whole-plant level. Given that carbon balance is the time integral of net CO_2 assimilation, this may lead to substantial impacts over a long time period. Despite the robust use of Equation 3 (e.g. Kattge & Knorr, 2007; Oikawa *et al.,* 2016; Rogers *et al.,* 2017; Smith & Dukes, 2017; Mercado *et al.,* 2018; Kumarathunge *et al.,* 2019), Equation 3 is still incorrect. We therefore recommend the switch from Equation 3 to Equation 10 because: 1) Equation 3 is the result of a derivation error, and 2) Equations 3 and 10 lead to different net daily carbon estimates due to the derivation error, which may currently be compensated by other factors in large-scale models.

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Author Contributions

Both authors contributed to all aspects of the study.

Tables

Table 1. Parameters used in modelling daily carbon gain.

Parameter	Group	Value	Reference
Respiration	R_{dark}	2.78 µmol m^{-2} s^{-1}	Stinziano & Way, 2017
	R_{day}	0.7 * R_{dark}	Ayub *et al.*, 2011
	R_{root}	0.0095 µmol g^{-1} s^{-1}	Weger & Guy, 1991
	R_{stem}	0.0095 µmol g^{-1} s^{-1}	Assumed
	Q_{10}	2.015	Atkin & Tjoelker, 2003
Γ*	25 °C	42.75 µmol mol^{-1}	Bernacchi *et al.*, 2001
	E_a	37.83 kJ mol^{-1}	Bernacchi *et al*., 2001
K_m	25 °C	718.4 µmol mol^{-1}	Bernacchi *et al.,* 2001
	E_a	65.51 kJ mol^{-1}	Bernacchi *et al.,* 2001
α		0.8	Norman & Campbell, 1998
ϕ		0.08	Norman & Campbell, 1998
Leaf Area	Low R	0.015 m^2	Stinziano & Way, 2017
	High R	0.025 m^2	Stinziano & Way, 2017
Stem Mass	Low R	0.496 g	Stinziano & Way, 2017
	High R	2.523 g	Stinziano & Way, 2017
Root Mass	Low R	0.498 g	Stinziano & Way, 2017
	High R	5.072 g	Stinziano & Way, 2017

Q_{10}: thermal sensitivity coefficient; Γ*: photorespiratory CO_2 compensation point; K_m: apparent Michaelis-Menten constant for rubisco carboxylation in 21% O_2/air (i.e. $K_{c,air}$); α: absorbance of photosynthetically activation radiation; ϕ: maximum quantum efficiency of photosynthetic electron transport; E_a: activation energy; R_{dark}: leaf respiration in the dark; R_{day}: leaf respiration in the light; R_{root}: root respiration; R_{stem}: stem respiration; Low R: low respiration scenario; High R: high respiration scenario.

Table 2. Equations used in modelling daily carbon uptake.

Equation	Reference
$f(T) = k_{25} Q_{10}^{\frac{T-298.15}{10}}$	Atkin & Tjoelker, 2003
$f(T) = k_{25} e^{\left[\frac{E_a(T-298.15)}{RT298.15}\right]}$	Arrhenius, 1915
$f(T) = k_{25} e^{\left[\frac{E_a(T-298.15)}{RT298.15}\right]} \left[\frac{1+e^{\frac{298.15\Delta S - H_d}{298.15R}}}{1+e^{\frac{T\Delta S - H_d}{TR}}}\right]$	Medlyn *et al.,* 2002

$$f(T) = k_{25}\frac{T}{298.15}e^{\left[\frac{E_a(T-298.15)}{RT298.15}\right]}\left[\frac{1+e^{\frac{298.15\Delta S-H_d}{298.15R}}}{1+e^{\frac{T\Delta S-H_d}{TR}}}\right]$$ Johnson *et al.,* 1942; this study

$$W_c = V_{cmax}\frac{C_i-\Gamma*}{C_i+K_m}$$ Farquhar *et al.,* 1980

$$W_j = J\left(\frac{C_i-\Gamma*}{C_i+2\Gamma*}\right)$$ Farquhar *et al.,* 1980; Way et al., 2011

Where J is calculated as the minimum root of: $\theta J^2-(0.5\alpha\phi Q_{in}+J_{max})J+0.5\alpha\phi Q_{in}J_{max}=0$

$$A_{gross} = min(W_c, W_j)$$

$$A_{net} = A_{gross} - R_{day}$$

$$g_s = g_0 + 1.6\left(1+\frac{g_1}{\sqrt{VPD}}\right)\left(\frac{A_{net}}{C_a}\right)$$ Medlyn *et al.,* 2011

$$C_i = C_a - 1.6\frac{A_{net}}{g_s}$$

$$A_{plant} = A_{net}\times LA - R_{dark}\times LA - R_{stem}\times SM - R_{root}\times RM$$

$$C_{balance} = \sum A_{plant}\times 3600\times\frac{12.01}{1{,}000{,}000}$$

f(T): rate of a process at a given temperature; T: temperature in K; k_{25}: rate of a process at 25 °C; Q_{10}: thermal sensitivity coefficient; E_a: activation energy in kJ mol^{-1}; ΔS: entropy parameter in kJ mol^{-1}; H_d: deactivation energy in kJ mol^{-1}; R: universal gas constant in 0.008314 kJ mol^{-1} K^{-1}; W_c: rate of CO_2-limited carboxylation in µmol m^{-2} s^{-1}; W_j: rate of RuBP regeneration-limited carboxylation in µmol m^{-2} s^{-1}; V_{cmax}: maximum rate of rubisco carboxylation capacity in µmol m^{-2} s^{-1}; J_{max}: maximum rate of electron transport in µmol m^{-2} s^{-1}; C_i: intercellular CO_2 concentration in µmol mol^{-1}; Γ*: photorespiratory CO_2 compensation point in µmol mol^{-1}; K_m: Michaelis-Menten constant for rubisco in µmol mol^{-1}; α: absorbance of photosynthetically active radiation; ϕ: maximum quantum efficiency of electron transport; Q_{in}: incident photosynthetically active radiation; A_{gross}: gross CO_2 assimilation in µmol m^{-2} s^{-1}; A_{net}: net CO_2 assimilation in µmol m^{-2} s^{-1}; R_{day}: leaf day respiration in µmol m^{-2} s^{-1}; g_s: stomatal conductance to water in mol m^{-2} s^{-1}; g_o: intercept for the Medlyn et al. 2011 model; g_1: slope for the Medlyn et al. 2011 model; VPD: vapor pressure deficit in kPa; C_a: CO_2 concentration at the leaf surface in µmol mol^{-1}; A_{plant}: whole plant net CO_2 assimilation; LA: leaf area in m^{-2}; R_{dark}: leaf dark respiration in µmol m^{-2} s^{-1}; R_{stem}: stem respiration in µmol m^{-2} s^{-1}; R_{root};

root respiration in μmol m^{-2} s^{-1}; SM: stem mass in g; RM: root mass in g; $C_{balance}$: whole plant daily carbon balance in g $plant^{-1}$ day^{-1}.

Figure Captions

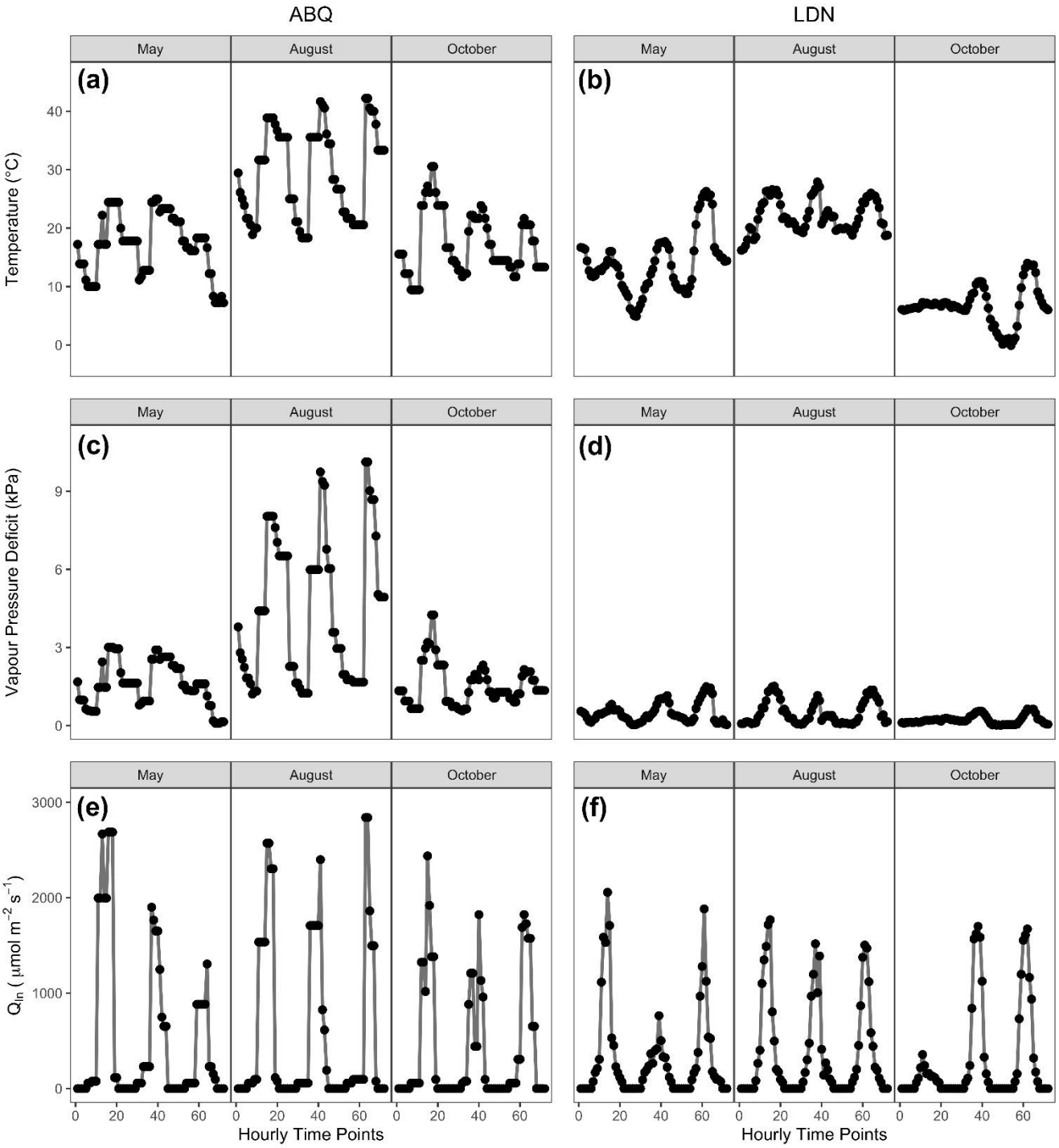
Figure 1. Environmental data used to drive the model in Table 1 covering 3 days (17^{th}, 18^{th}, and 19^{th}) of 3 months. (a,c,e) Albuquerque, NM, USA (ABQ); (b,d,e) London, ON, Canada (LDN). Environmental parameters include: a,b) temperature; c,d) vapour pressure deficit; and e,f) irradiance (Q_{in}).

Figure 2. Relative performance and fit for Equations 3 and 10 for temperature responses of V_{cmax} and J_{max} based on a,b) Bayesian Information Criterion (BIC), and c-f) visual inspection of curve fits.

Figure 3. The modified Arrhenius equation missing the term (Equation 3) compared to Equation 10 fits different values for E_a (a,b), but mostly similar values for ΔS (c,d), k_{25} (e,f) and H_d (f, g) for both V_{cmax} (a, c, e, g) and J_{max} (c, d, f, h). E_a: activation energy, ΔS: entropy parameter, k_{25}: rate of the process at 25 °C, H_d: deactivation energy, V_{cmax}: maximum capacity of rubisco carboxylation, J_{max}: maximum rate of electron transport. Black line indicates 1:1 line and grey dashed line indicates respective modelled slopes and intercepts.

Figure 4. The modified Arrhenius equation without the missing term (Equation 3) gives differences in modelled daily carbon fluxes compared to Equation 10 for low R (a,c,e) and high R (b,d,f) under scenarios where H_d is allowed to vary. Modelled carbon fluxes include: a,b) Total daily photosynthesis; c,d) total daily C gain; and e,f) total daily A/R. A: photosynthesis, R respiration, Low R: low respiration, High R: high respiration. Black line indicates 1:1 line and grey dashed line indicates respective modelled slopes and intercepts.

Figures



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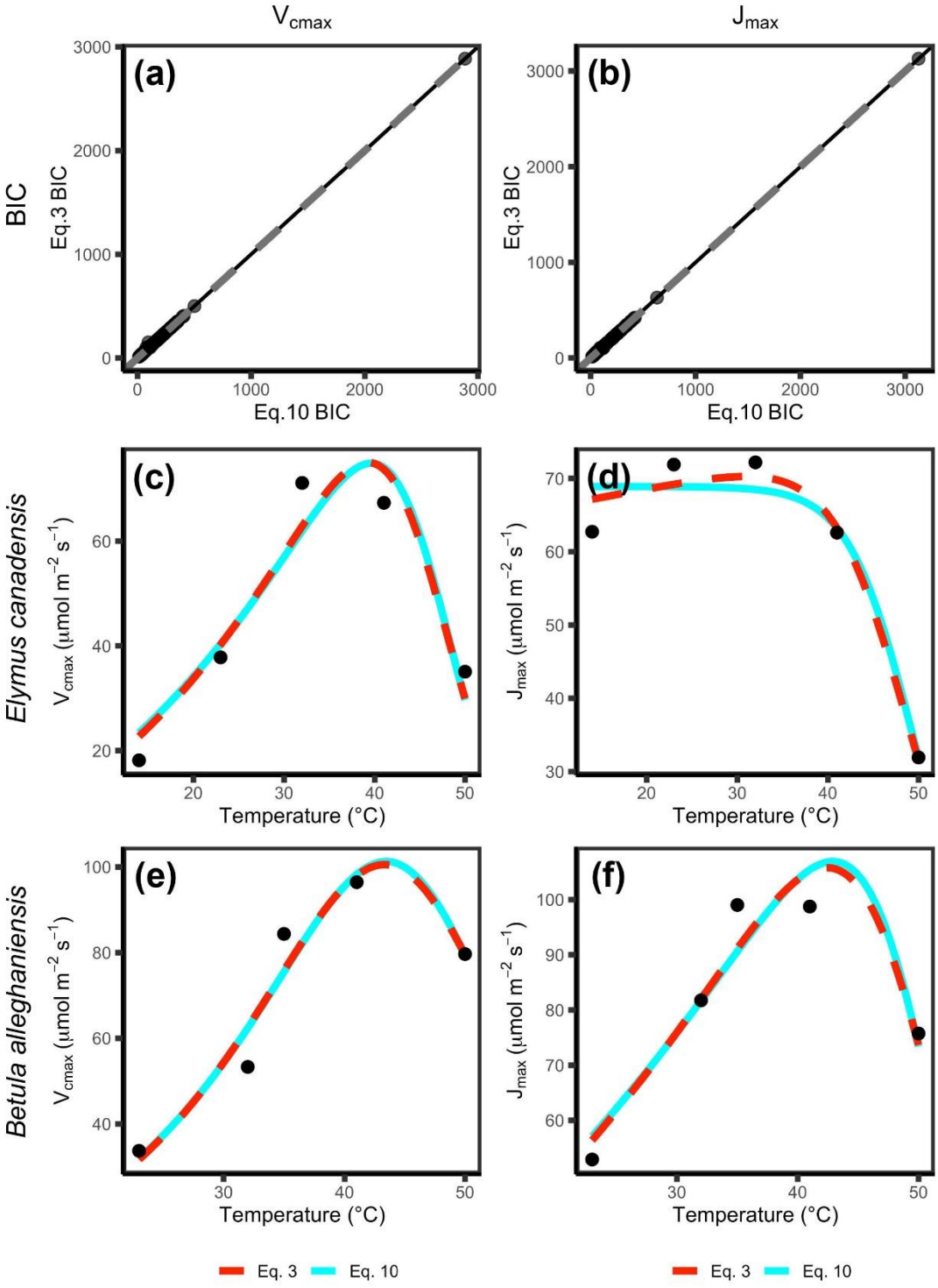

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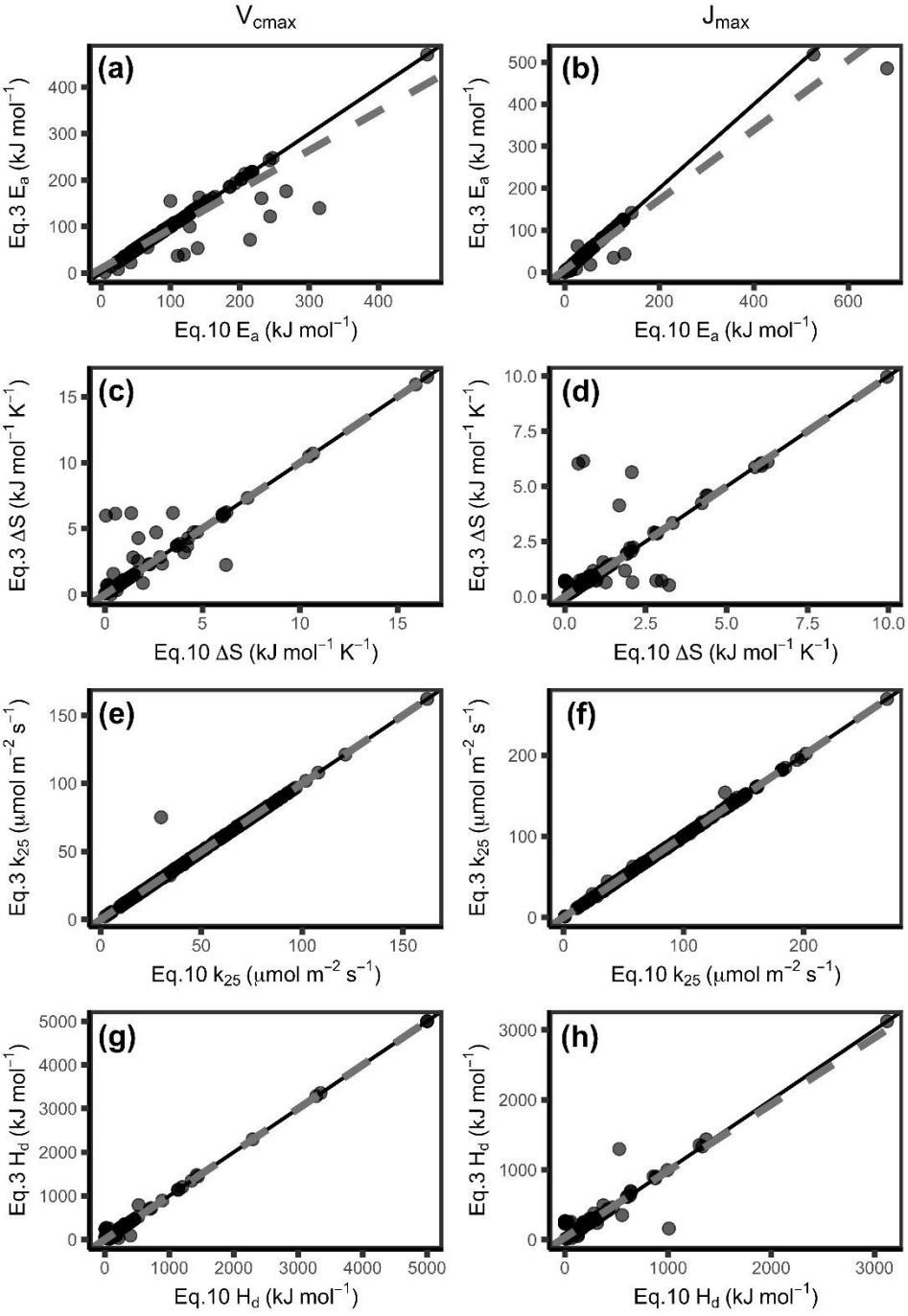

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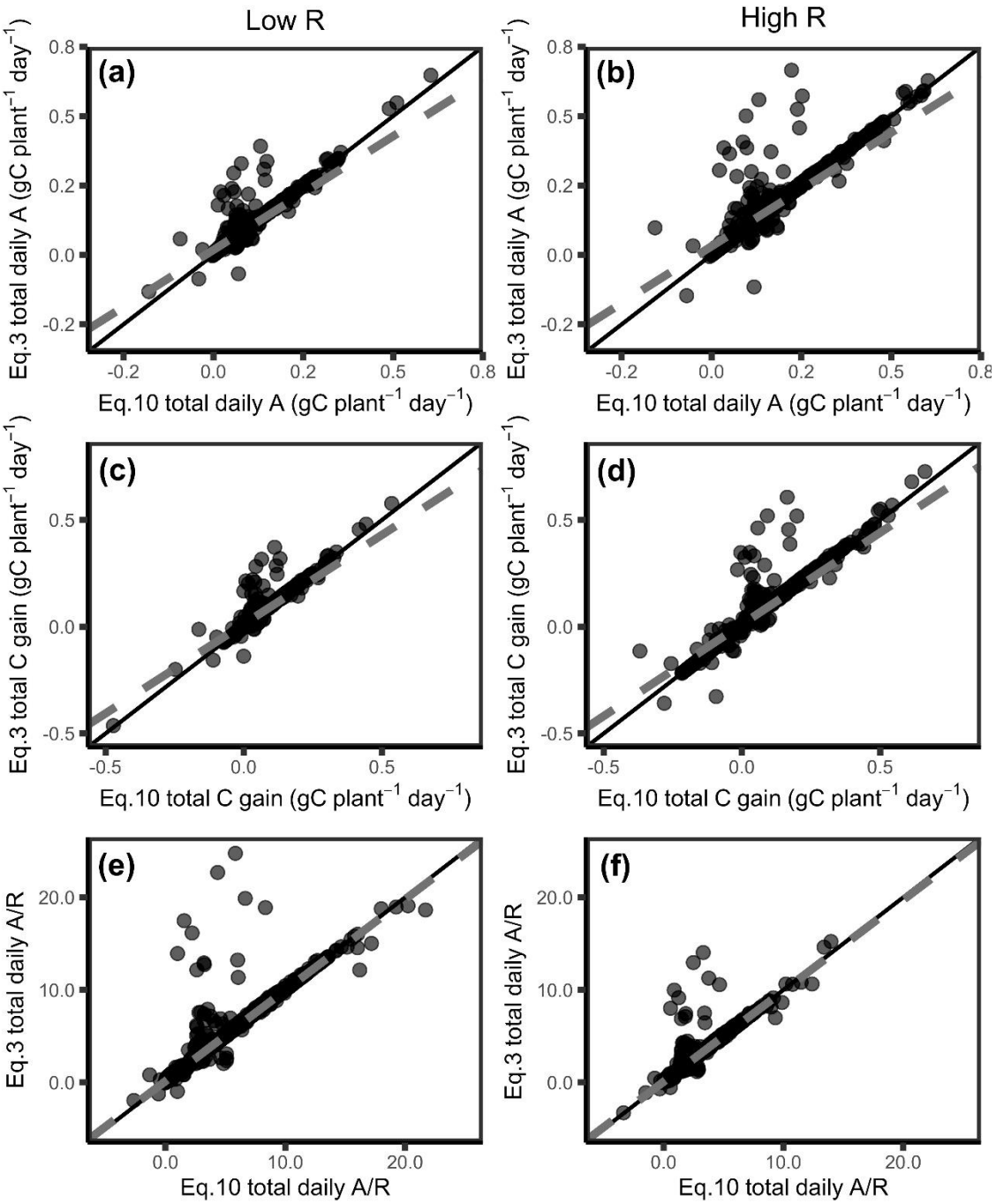

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