**Title: A systematic error exists in the current use of the Johnson et al. (1942) modified Arrhenius function due to a missing term**

**Running Title: Derivation error in modified Arrhenius model**

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**Abstract**

Understanding biological temperature responses is crucial to predicting global carbon fluxes. The current approach to modeling photosynthetic temperature responses in large scale modeling efforts uses a modified Arrhenius equation. We rederived the modified Arrhenius equation from the source and uncovered a missing term that was dropped between 1942 and 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 small errors still exist. 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 carbon gain causes a substantial deviation. This suggests that the error in the derivation of the modified Arrhenius equation has impacted predictions of carbon fluxes at larger scales. We argue that it is time to move beyond the modified Arrhenius paradigm since the current implementation is categorically incorrect and to use more thermodynamically-grounded temperature response equations going forward.

*Keywords: Arrhenius, temperature, photosynthesis, gas exchange, modeling, carbon balance*

**Introduction**

Globally, photosynthesis and autotrophic respiration are the largest biological carbon fluxes, with photosynthesis removing ~120 Gt C year-1 and autotrophic respiration releasing ~60 Gt C year-1 (Amthor, 2000; Ciais et al., 2013). Given the temperature sensitivity of these large carbon fluxes, 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 and Yamori, 2014; Smith & Dukes, 2017; Kumarathunge et al., 2019). Exponential responses are usually modelled based on an Arrhenius-type curve (Arrhenius, 1915):

Equation 1

Equation 2

where f(T) is the rate of the process at temperature, A is a pre-exponential factor, T in K, k25 is the rate of the process at 298.15 K, Ea 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):

Equation 3

where Hd is the deactivation energy in J mol-1, and ΔS is the entropy of the process in J mol-1.

Equation 3 is used for modeling the temperature responses of photosynthetic capacity (based on Farquhar et al., 1980): maximum carboxylation capacity of rubisco, Vcmax, maximum electron transport capacity, Jmax, and related kinetics as well as Sharkey (1985) and Harley & Sharkey (1991) in their calculation of triose phosphate utilization capacity (TPU) 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 state of the Earth system (e.g. Rogers et al., 2017).

Due to its ubiquity, 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 dropped sometime between Johnson et al. (1942) and Medlyn et al. (2002) that causes a systematic error in the application of Equation 3 in calculations covering individual species (e.g. Medlyn et al., 2002) to global scale processes (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.

**Materials & methods**

**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:

Equation 4

where I is the intensity of the luciferase reaction, c’’ is not explicitly defined in Johnson et al. (1942), but presumably represents a second derivative of the rate, 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. We can relativize the equation to a reference temperature:

Equation 5

Equation 6

Equation 7

Equation 8

Equation 9

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

Equation 10

Note the difference between Equations 3 and 10: the term T / 298.15 is missing from Equation 3. This introduces multiple systematic errors:

1. fitted parameters Ea, Hd, and ΔS;
2. scaling the rate variable using the wrong equation;
3. acclimation of Ea, Hd, and/or ΔS as errors due to 1) at each acclimation temperature.

**Data analysis**

Using data from Kumarathunge et al. (2019), available from Kumarathunge et al. (2018), we fit Equations 3 and 10 to the data, both setting Hd to 200,000 J mol-1 and allowing Hd to be fit. We obtained 92 successful curve fits for the fixed Hd case, and 84 successful curve fits for the fitted Hd case. This allows us to explore the impact of the missing term on the output data under a typical fitting scenario (Hd is fixed) and under the full fitting scenario.

**Modeling**

We modelled the impact of the equations 3 and 10 on daily net plant carbon balance under conditions of Hd = 200,000 J mol-1 and fitted Hd. 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). 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. Root respiration for white spruce was taken from Weger and Guy (1991) and we assumed that stem respiration was equal to root respiration (Table 1).

**Table 1. Parameters used in modeling daily carbon gain.**

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Group | Value | Reference |
| Respiration | Rdark | 2.78 μmol m-2 s-1 | Stinziano & Way, 2017 |
|  | Rday | 0.7 \* Rdark | Ayub et al., 2011 |
|  | Rroot | 0.0095 μmol g-1 s-1 | Weger & Guy, 1991 |
|  | Rstem | 0.0095 μmol g-1 s-1 | Assumed |
|  | Q10 | 2.015 | Atkin & Tjoelker, 2003 |
| Γ\* | 25 °C | 42.75 μmol mol-1 | Bernacchi et al., 2001 |
|  | Ea | 37.83 kJ mol-1 | Bernacchi et al., 2001 |
| Km | 25 °C | 718.4 μmol mol-1 | Bernacchi et al., 2001 |
|  | Ea | 65.51 kJ mol-1 | Bernacchi et al., 2001 |
| α |  | 0.8 | Campbell & Norman, 1998 |
| ϕ |  | 0.08 | Campbell & Norman, 1998 |
| Leaf Area | Low R | 0.015 m2 | Stinziano & Way, 2017 |
|  | High R | 0.025 m2 | 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 |

**Q10: thermal sensitivity coefficient; Γ\*: photorespiratory CO2 compensation point; Km: Michaelis-Menten constant for rubisco; α: absorbance of photosynthetically activation radiation; ϕ: maximum quantum efficiency of photosynthetic electron transport; Ea: activation energy; Rdark: leaf respiration in the dark; Rday: leaf respiration in the light; Rroot: root respiration; Rstem: stem respiration; Low R: low respiration scenario; High R: high respiration scenario.**

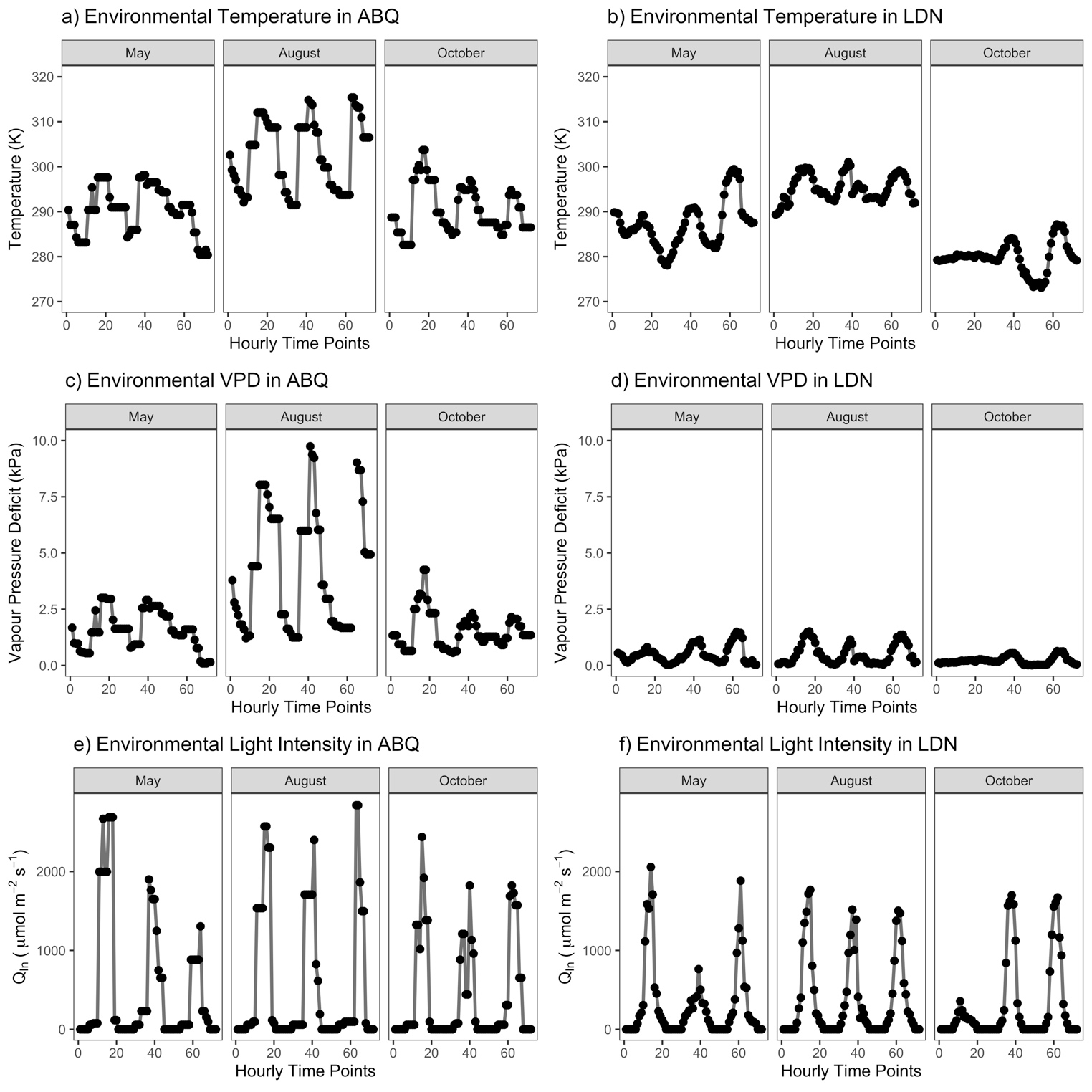
For the full model structure and equations, please see the accompanying R package {arrhenius.comparison} (Stinziano & Murphy, 2020) (see Table 2 for equations). Briefly, we linked the Medlyn et al. (2011) stomatal conductance model with the Farquhar et al. (1980) C3 photosynthesis model, assuming infinite mesophyll conductance to CO2 as these assumptions were used in fitting the data from Kumarathunge et al. (2018). Photosynthetic capacity, both maximum rubisco carboxylation capacity, Vcmax, and maximum electron transport rate, Jmax 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.

**Table 2. Equations used in modeling daily carbon uptake.**

|  |  |
| --- | --- |
| Equation | Reference |
|  | Atkin & Tjoelker, 2003 |
|  | Arrhenius, 1915 |
|  | Johnson et al., 1942; Medlyn et al., 2002 |
|  | Johnson et al., 1942; this study |
|  | Farquhar et al., 1980 |
|  | Farquhar et al., 1980; Way et al., 2011 |
|  |  |
|  |  |
|  | Medlyn et al., 2011 |
|  |  |
|  |  |
|  |  |

**f(T): rate of a process at a given temperature; T: temperature in K; k25: rate of a process at 25 °C; Q10: thermal sensitivity coefficient; Ea: activation energy in kJ mol-1; ΔS: entropy parameter in kJ mol-1; Hd: deactivation energy in kJ mol-1; R: universal gas constant in 0.008314 kJ mol-1 K-1; Wc: rate of CO2-limited carboxylation; Wj: rate of RuBP regeneration-limited carboxylation; Vcmax: maximum rate of rubisco carboxylation capacity; Jmax: maximum rate of electron transport; Ci: intercellular CO2 concentration; Γ\*: photorespiratory CO2 compensation point; Km: Michaelis-Menten constant for rubisco; α: absorbance of photosynthetically active radiation; ϕ: maximum quantum efficiency of electron transport; Qin: incident photosynthetically active radiation; Agross: gross CO2 assimilation; Anet: net CO2 assimilation; Rday: leaf day respiration; gs: stomatal conductance to water; go: intercept for the Medlyn et al. 2011 model; g1: slope for the Medlyn et al. 2011 model; VPD: vapor pressure deficit; Ca: CO2 concentration at the leaf surface; Aplant: whole plant net CO2 assimilation; LA: leaf area; Rdark: leaf dark respiration; Rstem: stem respiration; Rroot; root respiration; SM: stem mass; RM: root mass; Cbalance: whole plant daily carbon balance.**

Modeling was performed on 18 total days of environmental data, with three days of data from three months (17th – 19th 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 Environmental Canada historical climate data for South London (43.01°N, 81.27°W, altitude: 251 m) and the rooftop greenhouse at the University of New Mexico (35.08°N, 106.62°W, altitude: 1587 m) to capture different levels of environmental variability (Fig. 1).



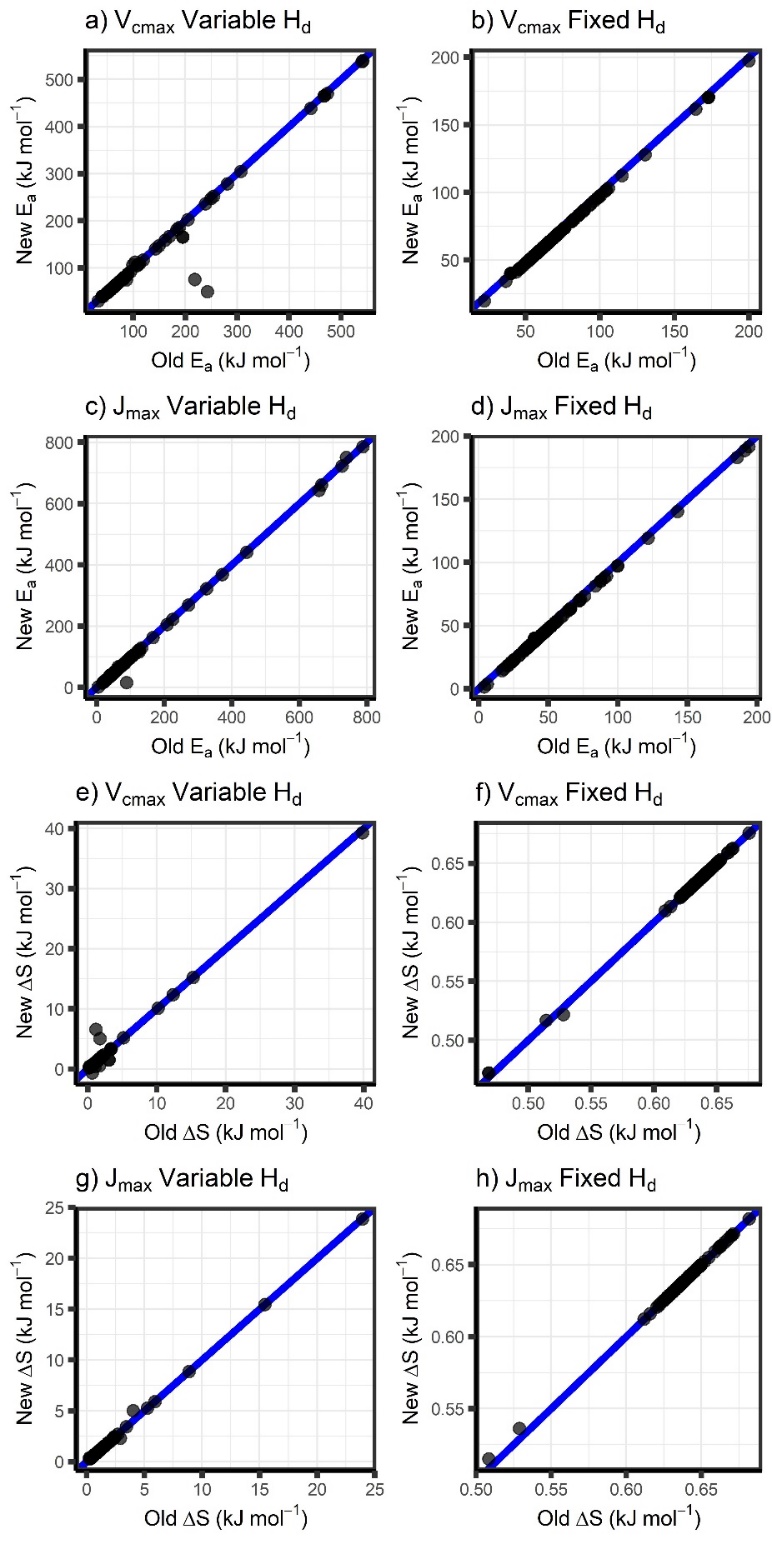
**Figure 1. Environmental data used to drive the model in Table 1. (a,c,e) Albuquerque, NM, USA; (b,d,e) London, ON, Canada.**

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

**Results**

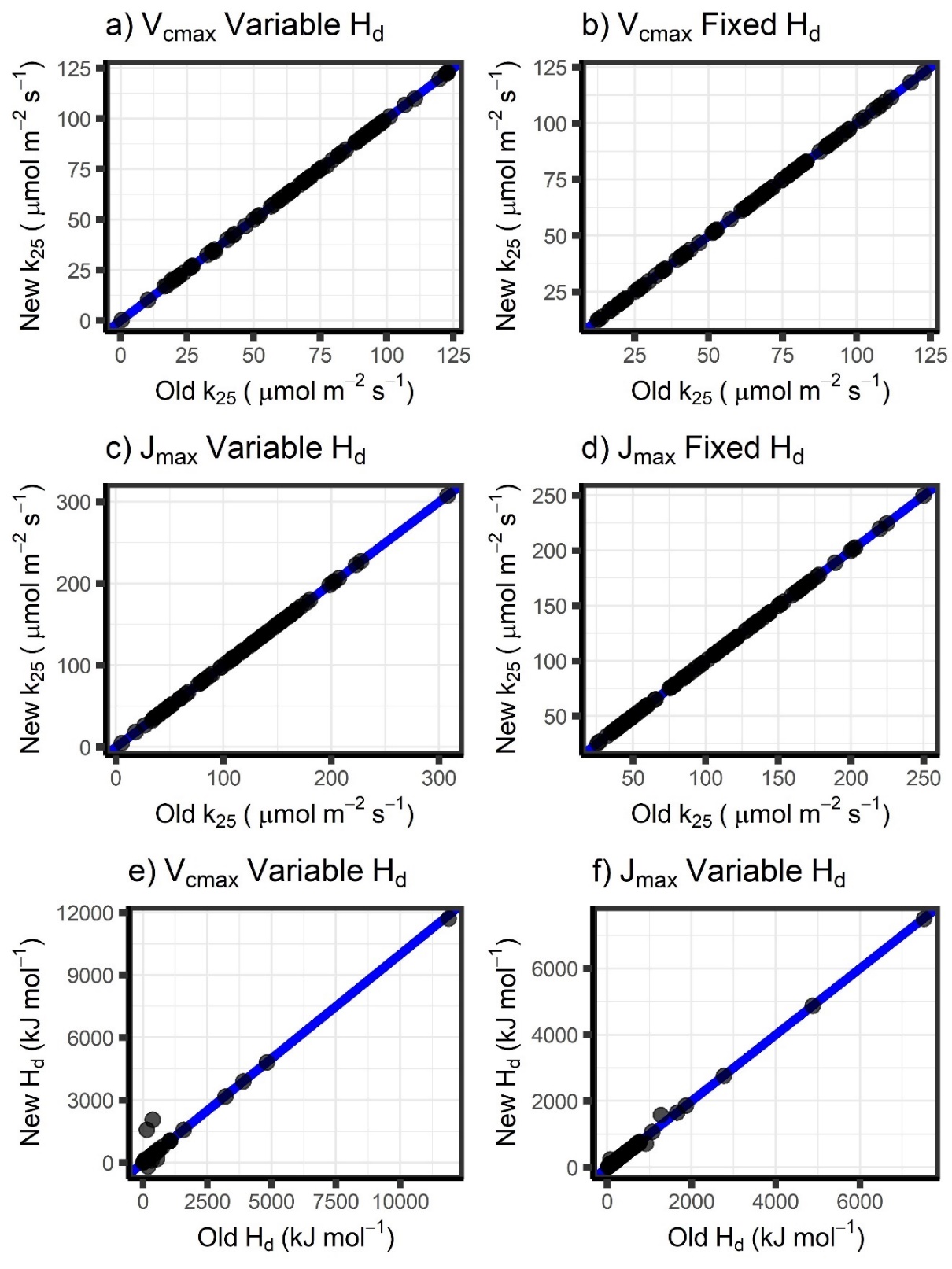
*Fixed Hd of 200,000 J mol-1*

Incorporating the missing term into Equation 3 to produce Equation 10 caused small differences in the fitting of Ea for Vcmax, with a slope of 0.997 ± 0.001 and intercept of -2.162 ± 0.119 kJ mol-1 (*F*1,90 = 4.56 ∙ 105, *R2* = 0.9998, *P* < 2.2 ∙ 10-16) (Fig. 2b). For ΔS, the slope was 0.991 ± 0.003 and an intercept of 0.005 ± 0.002 kJ mol-1 (approximately 1% of fitted ΔS) (*F*1,90 = 1.23 ∙ 105, *R2* = 0.9993, *P* < 2.2 ∙ 10-16) (Fig. 2f). Meanwhile Vcmax25 was identical between both approaches with a slope of 1.000 ± 1.1 ∙ 10-5 (intercept not significant; *F*1,91 = 8.2 ∙ 109, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 3b). For Jmax, there were small differences in the fitting of Ea for Jmax, with a slope of 0.998 ± 0.002 and intercept of -2.230 ± 0.108 kJ mol-1 (*F*1,91 = 3.3 ∙ 105, *R2* = 0.9997, *P* < 2.2 ∙ 10-16) (Fig. 2d). For ΔS, the slope was 0.962 ± 0.003 and an intercept of 0.025 ± 0.002 kJ mol-1 (approximately 5% of fitted ΔS) (*F*1,90 = 1.1 ∙ 105, *R2* = 0.9992, *P* < 2.2 ∙ 10-16) (Fig. 2h). Meanwhile Vcmax25 was identical between both approaches with a slope of 1.000 ± 1.2 ∙ 10-5 (intercept not significant; *F*1,92 = 6.7 ∙ 109, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 3d).



**Figure 2 – The modified Arrhenius equation with the missing term (Equation 10) gives**

**similar temperature response parameters as Equation 3 for Ea (a-d) and ΔS (e-h) for both Vcmax (a, b, e, f) and Jmax (c, d, g, h) under scenarios where Hd is allowed to vary (a, c, e, g) and is fixed to 200 kJ mol-1 (b, d, f, h). “New” indicates Equation 10, “Old” indicates Equation 3. Ea: activation energy, ΔS: entropy parameter, Hd: deactivation energy, Vcmax: maximum capacity of rubisco carboxylation, Jmax: maximum rate of electron transport. Blue line indicates 1:1 line.**



**Figure 3 – The modified Arrhenius equation with the missing term (Equation 10) gives**

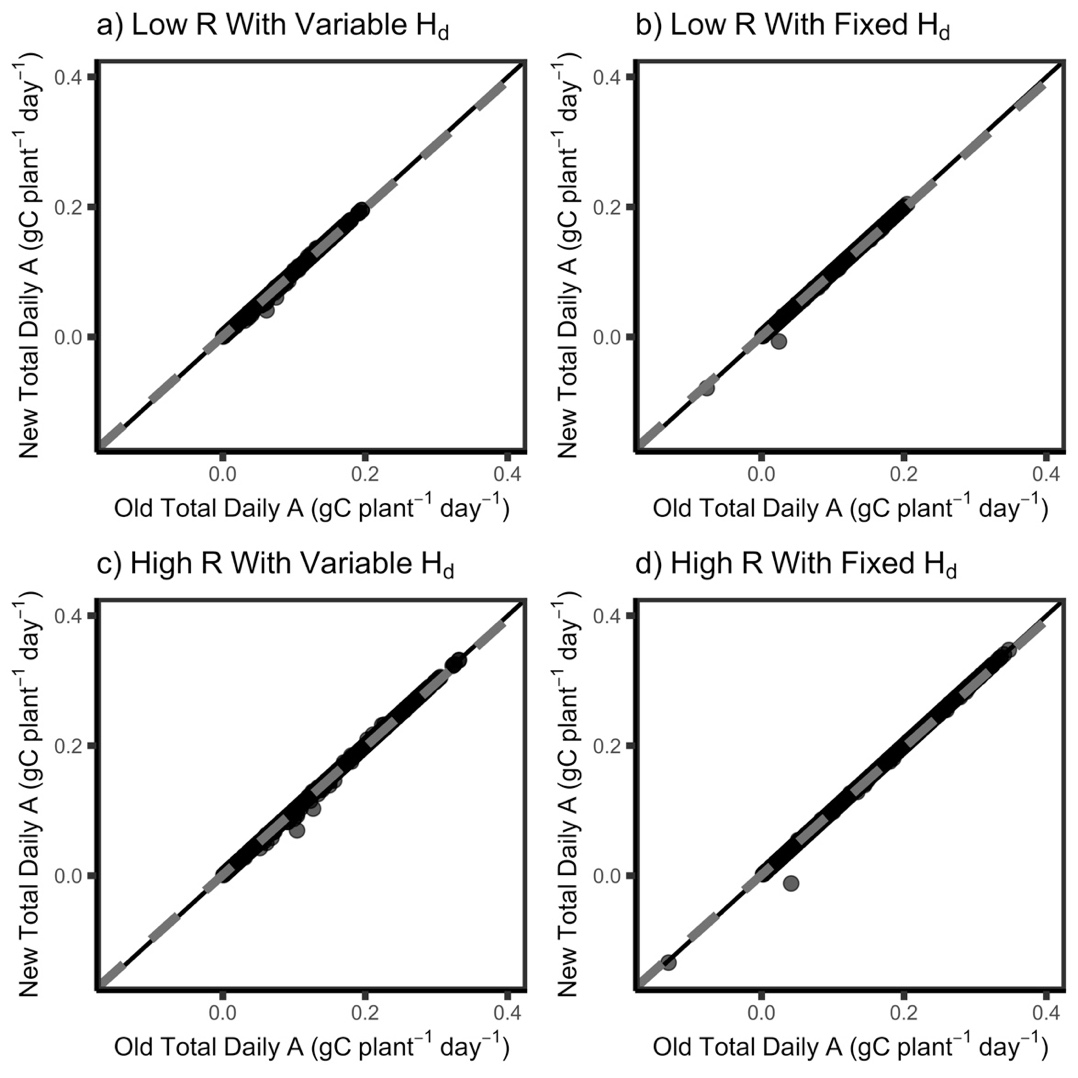
**similar temperature response parameters as Equation 3 for k25 (a-d) and Hd (e, f) for both Vcmax (a, b, e) and Jmax (c, d, f) under scenarios where Hd is allowed to vary (a, c, e, f) and is fixed to 200 kJ mol-1 (b, d). “New” indicates Equation10, “Old” indicates Equation 3. k25: rate of the process at 25 °C, Hd: deactivation energy, Vcmax: maximum capacity of rubisco carboxylation, Jmax: maximum rate of electron transport. Blue line indicates 1:1 line.**

*Variable Hd*

Incorporating the missing term into Equation 3 to produce Equation 10 caused small differences in the fitting of Ea for Vcmax, with a slope of 0.966 ± 0.026 (intercept not significant; *F*1,74 = 3005, *R2* = 0.976, *P* < 2.2 ∙ 10-16) (Fig. 2a). For ΔS, the slope was 0.989 ± 0.017 (intercept not significant; *F*1,74 = 3339, *R2* = 0.9783, *P* < 2.2 ∙ 10-16) (Fig. 2e), while Hd had a slope of 0.992 ± 0.019 (intercept not significant; *F*1,74 = 2812, *R*2 = 0.9744; *P* < 2.2 ∙ 10-16) (Fig. 3e). Meanwhile Vcmax25 was nearly identical between both approaches with a slope of 0.9996 ± 0.004 (intercept not significant; *F*1,74 = 7.98 ∙ 106, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 3a). For Jmax, there were small differences in the fitting of Ea for Jmax, with a slope of 1.000 ± 0.005 and an intercept of -3.119 ± 1.089 kJ mol-1 (*F*1,80 = 3.6 ∙ 104, *R2* = 0.9978, *P* < 2.2 ∙ 10-16) (Fig. 2c). ΔS was identical, the slope was 1.000 ± 0.004 (intercept not significant; *F*1,81 = 6.4 ∙ 104, *R2* = 0.9987, *P* < 2.2 ∙ 10-16) (Fig. 2g), while Hd was identical with a slope of 1.000 ± 0.004 (intercept not significant; *F*1,81 = 5.2 ∙ 104, *R*2 = 0.9985; *P* < 2.2 ∙ 10-16) (Fig. 3f). Jmax25 was identical between both approaches with a slope of 1.000 ± 0.001 (intercept not significant; *F*1,81 = 5.8 ∙ 107, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 3c).

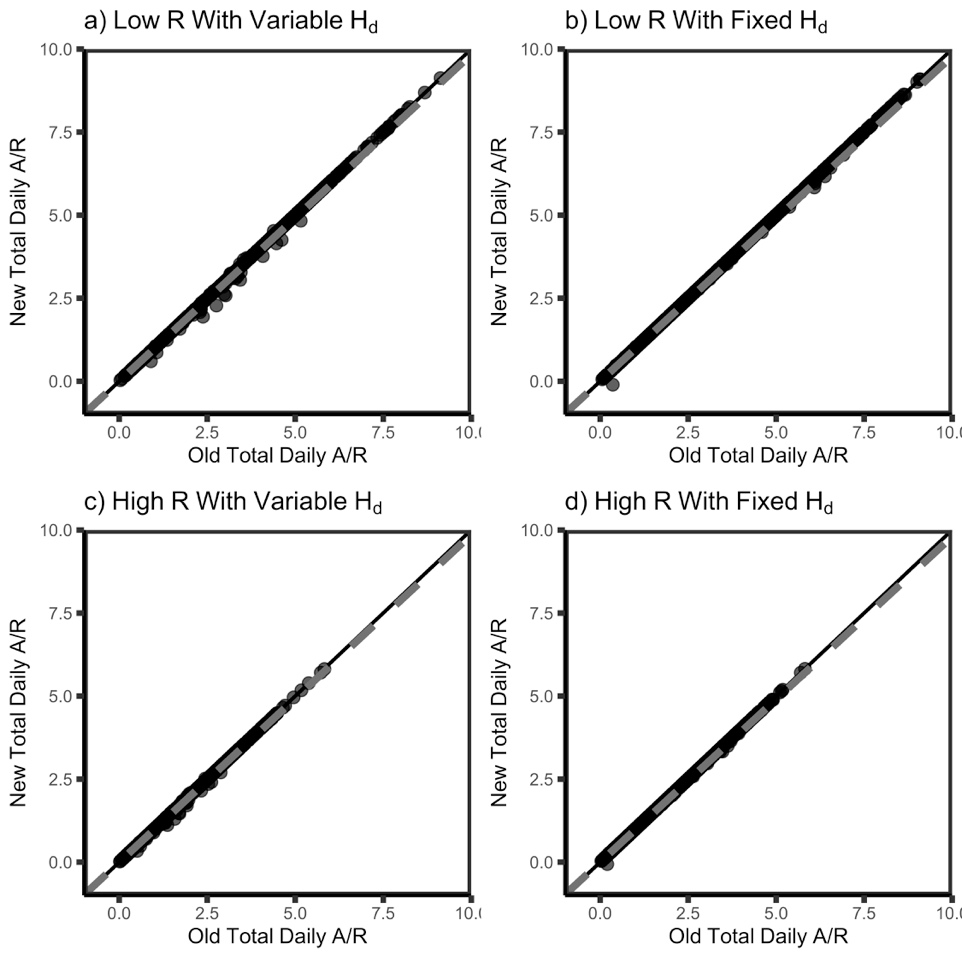
*Impacts on modelled net carbon balance*

In general, the differences in thermal response parameters were amplified when integrated at the whole-plant level. For daily photosynthesis (A) measured at a fixed Hd of 200 kJ mol-1, the slope for the low respiration model was 0.977 ± 7.666 ∙ 10-3 and an intercept of 0.002 ± 9.366 ∙ 10-5 (approximately 2% of modeled A) (*F*1,898 = 1.625 ∙ 106, R2 = 0.9994; *P* <2.2 ∙ 10-16) (Fig 4b). Similarly, the high respiration model for A had a slope of 0.977 ± 7.666 ∙ 10-3 and an intercept of 0.004 ± 1.591 ∙ 10-3 (approximately 2% of modeled A) (*F*1,898 = 1.625 ∙ 106, R2 = 0.9994; *P* <2.2 ∙ 10-16) (Fig4d). For daily A measured at a variable Hd, the slope for the low respiration model was 0.983 ± 9.909 ∙ 10-3 and the intercept was 0.002 ± 1.128 ∙ 10-3 (approximately 2% of modeled A) (*F*1,556 = 9.834 ∙ 105, R2 = 0.9994; *P* <2.2 ∙ 10-16) (fig 4a). For the high respiration model of daily A, the slope was 0.983 ± 9.909 ∙ 10-3 and the intercept was 0.003 ± 9.909 ∙ 10-4 (approximately 2% of modeled A) (*F*1,556 = 9.834 ∙ 105, R2 = 0.9994; *P* <2.2 ∙ 10-16) (Fig 4c).



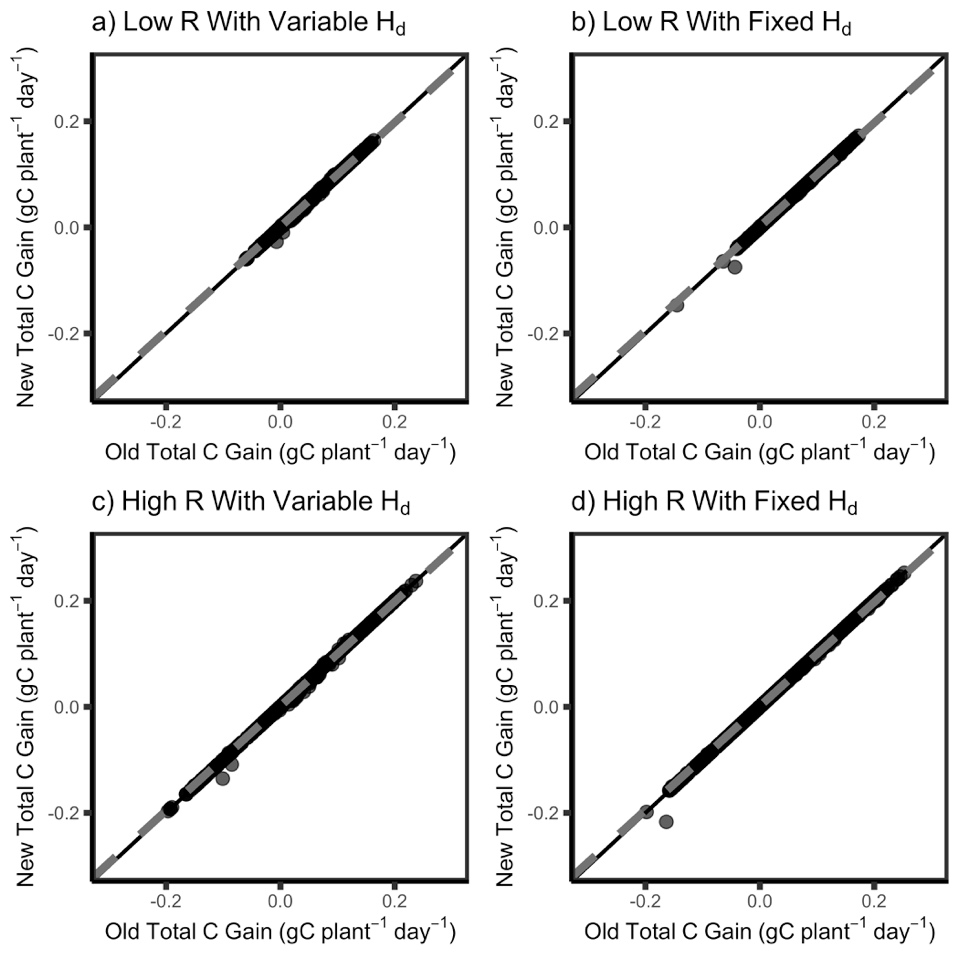
**Figure 4 – The modified Arrhenius equation with the missing term (Equation 10) gives slight differences in modeled total daily photosynthesis compared to Equation 3 for low R (a,b) and high R (c,d) under scenarios where Hd is allowed to vary (a, c) and is fixed to 200 kJ mol-1 (b,d). “New” indicates Equation 10, “Old” indicates Equation 3. A: photosynthesis, Low R: low respiration, High R: high respiration. Black line indicates 1:1 line and grey dashed line indicates respective modeled slopes and intercepts.**

The ratio of the total daily photosynthesis: respiration (A/R) was also considered when comparing models. Using a fixed Hd of 200 kJ mol-1, the low respiration model of A/R had a slope of 0.993 ± 5.634 ∙ 10-3 and the intercept was 0.025 ± 0.002 (approximately 1% of modeled A/R) (*F*1,898 = 3.109 ∙ 106, R2 = 0.9997; *P* <2.2 ∙ 10-16) (Fig 5b). The high respiration model of A/R was similar; the slope was 0.993 ± 5.628 and the intercept was 0.014 ± 0.001 (approximately 1% of modeled A/R) (*F*1,898 = 3.115 ∙ 106, R2 = 0.9997; *P* <2.2 ∙ 10-16) (Fig 5d). Using a variable Hd, the low respiration model of A/R had a slope of 0.994 ± 0.001 and the intercept was 0.030 ± 0.001 (approximately 1% of modeled A/R) (*F*1,556 = 6.857 ∙ 105, R2 = 0.9992; *P* <2.2 ∙ 10-16) (Fig 5a). The high respiration model had a similar slope of 0.994 ± 0.001 and the intercept was 0.017 ± 0.003 (approximately 1% of modeled A/R) (*F*1,556 = 6.812 ∙ 105, R2 = 0.9992; *P* <2.2 ∙ 10-16) (Fig 5c).



**Figure 5 – The modified Arrhenius equation with the missing term (Equation 10) gives slight differences in modeled total daily A/R compared to Equation 3 for low R (a,b) and high R (c,d) under scenarios where Hd is allowed to vary (a, c) and is fixed to 200 kJ mol-1 (b,d). “New” indicates Equation 10, “Old” indicates Equation 3. A: photosynthesis, R: respiration, Low R: low respiration, High R: high respiration. Black line indicates 1:1 line and grey dashed line indicates respective modeled slopes and intercepts.**

Lastly, total daily carbon (C) gain was also compared between models with different thermal response parameters. Using a fixed Hd of 200 kJ mol-1, the low respiration model of total C gain had a slope of 0.978 ± 7.445 ∙ 10-4 and an intercept of 0.001 ± 7.609 ∙ 10-5 (approximately 2% of modeled C gain) (*F*1,898 = 1.726 ∙ 106, R2 = 0.9995; *P* <2.2 ∙ 10-16) (Fig 6b). Likewise, the high respiration of total C gain had a slope of 0.979 ± 7.261 ∙ 10-4 and an intercept of 0.001 ± 1.116 ∙ 10-4 (approximately 2% of modeled C gain) (*F*1,898 = 1.821 ∙ 106, R2 = 0.9995; *P* <2.2 ∙ 10-16) (Fig 6d). This can be compared to a variable Hd; starting with the low respiration model, total C gain had a slope of 0.985 ± 9.555 ∙ 10-4 and an intercept of 0.001 ± 1.223 ∙ 10-3 (approximately 1.5% of modeled C gain) (*F*1,556 = 1.06 ∙ 106, R2 = 0.9995; *P* <2.2 ∙ 10-16) (Fig 6a). The high respiration of total C gain also had a slope of 0.985 ± 9.110 ∙ 10-4 and an intercept of 0.001 ± 1.290 ∙ 10-4 (approximately 1.5% of modeled C gain) (*F*1,556 = 1.17 ∙ 106, R2 = 0.9995; *P* <2.2 ∙ 10-16) (Fig 6c).



**Figure 6 – The modified Arrhenius equation with the missing term (Equation 10) gives slight differences in modeled total carbon gain compared to Equation 3 for low R (a,b) and high R (c,d) under scenarios where Hd is allowed to vary (a, c) and is fixed to 200 kJ mol-1 (b,d). “New” indicates Equation 10, “Old” indicates Equation 3. C: carbon, Low R: low respiration, High R: high respiration. Black line indicates 1:1 line and grey dashed line indicates respective modeled slopes and intercepts.**

**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 modeling (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 no large impact on the fitted temperature response parameters for Vcmax and Jmax. In general, fitting Equation 10 instead of Equation 3 results in slightly reduced values for Ea and ΔS, with essentially no impact for k25 and Hd when Hd is fit. When Hd is fixed, there are no meaningful differences in the fits except for ΔS for Jmax, where Equation 10 values are ~4% lower than Equation 3 values, and intercepts in the Ea regressions of ~ -2 kJ mol-1, which represents <5% differences between the two equations in most instances. These findings are promising in that one of the parameters to which modelled carbon gain is particularly sensitive, Hd (Stinziano et al., 2018), is minimally affected by the missing term. However, since temperature responses are non-linear, small changes in the shape of the curve can have a strong impact on the integral of the response (Jensen, 1906). This caused the differences in temperature response parameters to cause ~X% changes in daily C balance. If we assumed a growing season length of 180 days, X% difference in daily C balance leads a modelled difference of X% over the entire growing season.

Based on the above analysis, the impact of the missing term in the modified Arrhenius equation may appear negligible based on the parameters, however given that carbon balance is the time integral of net CO2 assimilation, this leads to substantial impacts over a long time period. It is thus possible that the apparently small differences we observed could accumulate to relatively large carbon flux errors across large spatial and temporal scales with fluctuating temperatures. Since Equation 3 is incorrect, there are three arguments for moving beyond the modified Arrhenius paradigm: 1) there are new approaches to modeling biological temperature responses that are better-grounded in thermodynamics (e.g. Macromolecular Rate Theory; Hobbs et al., 2013; Liang et al., 2018); 2) uncertainties in model outputs may accumulate due to the missing term across large spatial and temporal scales, and 3) the modified Arrhenius model as implemented is categorically incorrect due to a missing term. Therefore, we argue that future modeling efforts should move beyond this incorrect paradigm.

**Acknowledgments**

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