Modelling assimilation and intercellular CO₂ from measured conductance: a synthesis of approaches

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ABSTRACT

A spectrum of models that estimate assimilation rate A from intercellular carbon dioxide concentration (Cᵢ) and measured stomatal conductance to CO₂ (gₛ) were investigated using leaf-level gas exchange measurements. The gas exchange measurements were performed in a uniform loblolly pine stand (Pinus taeda L.) using the Free Air CO₂ Enrichment (FACE) facility under ambient and elevated atmospheric CO₂ for 3 years. These measurements were also used to test a newly proposed framework that combines basic properties of the A–Cᵢ curve with a Fickian diffusion transport model to predict the relationship between Cᵢ/Cₐ and gₛ, where Cₐ is atmospheric carbon dioxide concentration. The widely used Ball–Berry model and five other models as well as the biochemical model proposed by Farquhar et al. (1980) were also reformulated to express variations in Cᵢ/Cₐ as a function of their corresponding driving mechanisms. To assess the predictive capabilities of these approaches, their respective parameters were estimated from independent measurements of long-term stable carbon isotope determinations (δ¹³C), meteorological variables, and ensemble A–Cᵢ curves. All eight approaches reproduced the measured A reasonably well, in an ensemble sense, from measured water vapour conductance and modeled Cᵢ/Cₐ. However, the scatter in the instantaneous A estimates was sufficiently large for both ambient and elevated Cₐ to suggest that other transient processes were not explicitly resolved by all eight parameterizations. An important finding from our analysis is that added physiological complexity in modeling Cᵢ/Cₐ (when gₛ is known) need not always translate to increased accuracy in predicting A. Finally, the broader utility of these approaches to estimate assimilation and net ecosystem exchange is discussed in relation to elevated atmospheric CO₂.

Key-words: carbon isotope; conductance; CO₂ assimilation; elevated CO₂; Free Air CO₂ Enrichment; intercellular CO₂; pine forest.

INTRODUCTION

Considerable research effort is devoted to measuring annual carbon balance of vegetation either by enumeration of carbon storage in biomass components and soils, or by monitoring ecosystem–atmosphere carbon dioxide (CO₂) exchange. Knowledge of long-term ecosystem CO₂ fluxes or net ecosystem exchange (NEE), may be attained using the eddy-covariance (EC) technique, which is now being applied at a number of sites world-wide (Hollinger et al. 1994; Amthor et al. 1994; Fan et al. 1995; Waring et al. 1995; Greco & Baldocchi 1996; Baldocchi & Vogel 1996; Baldocchi et al. 1996; Baldocchi, Vogel & Hall 1997a,b; Frohling et al. 1996; Goulden et al. 1996a,b, 1998; Katul et al. 1997a,b; Baldocchi & Meyers 1998; Kaiser 1998; Lai et al. 2000a). Despite the wide usage of EC methods, quantifying NEE from estimates of gross primary productivity (GPP) and ecosystem respiration (Rₑ) remains a critical research thrust in quantifying annual carbon balance because such a separation (i.e. NEE = GPP – Rₑ) resolves the effects of environmental perturbations and transient ecosystem properties on carbon sources from the effects on sinks. This study focuses on practical methods to estimate net assimilation rate A, the primary variable needed to compute GPP.

One approach to estimating net assimilation is to relate CO₂ uptake to conductance derived from water vapour. Establishing such a relationship is practical for two reasons:

1 Water vapour flux measurements are readily available for estimating conductance. Water vapour fluxes can be measured by a wide range of techniques other than EC such as sapflux (Granier 1987; Phillips & Oren 1998; Pataki, Oren & Tissue 1998; Oren et al. 1998a), heat balance (Cermak et al. 1995; Katul et al. 1997c), energy balance-Bowen ratio methods (Andre et al. 1988) which were used in FIFE and HAPEX-MOBILHY, aerodynamic methods (Brutsaert, Parlange & Gash 1989), and long-term hydrologic budget approaches (Jarvis & McNaughton 1986; Gourtorbe et al. 1989; Oren et al. 1998b). Much of the historical long-term water vapour fluxes have been monitored by such techniques.

2 Recent developments in Free Air CO₂ Enrichment (FACE) experiments presently in Arizona (Pinter et al. 1996), Switzerland, North Carolina (Ellsworth et al. 1995; Hendrey et al. 1999), Nevada (Jordan et al. 1999) and elsewhere do not allow for routine monitoring of CO₂ fluxes.
by EC because of the large CO2 source produced by the FACE system (Hendrey et al. 1999). In such experiments, estimating ecosystem CO2 flux is achieved by a hybrid combination of model development and carbon storage measurements in all the ecosystem carbon pools. Such budget calculations require carbon measurements collected at a wide range of spatial and temporal scales to represent the mean for plots > 20 m in diameter, many of which are not invariant to aggregation and scaling uncertainties.

A practical solution to these problems is estimating or measuring water vapour fluxes and subsequent conductance at the desired spatial scale and inferring CO2 fluxes from such conductance measurements. This approach exploits the well-known coupling of photosynthesis and stomatal conductance as CO2 and water vapour exchange between leaves and the atmosphere occur through the stomatal aperture (Cowan & Farquhar 1977; Wong, Cowan & Farquhar 1979; Nikolov, Massman & Schoettle 1995; Jarvis, Mansfield & Davies 1999). However, the approach is complicated by the need to estimate intercellular CO2 concentration (Ci), which itself depends on ambient CO2 concentration (Ca), the leaf conductance to CO2 (gc) and its CO2 exchange rate. Hence, the objective of this study is to explore practical formulations for Ci with the aim of predicting A from available gc. Extensive gas exchange measurements, collected in the Free Air CO2 Enrichment (FACE) facility at Duke Forest over a 3 year period, are used in our investigation.

We consider a class of methods spanning from a simple constant Ci/Ca hypothesis proposed by Wong et al. (1979) and Norman (1982) to a detailed biochemical model of photosynthesis of Farquhar (Farquhar, von Caemmerer & Berry 1980; Farquhar & von Caemmerer 1982) which is widely employed in both leaf and canopy-scale gas exchange studies (Collatz et al. 1991; Harley et al. 1992; Lloyd et al. 1995; Sellers et al. 1996; Baldocchi & Meyers 1998; Arneth et al. 1999). To successfully predict A at multiple scales, we sought models that would be independently parameterized from available physiological measurements and would well-reproduce leaf gas exchange measurements. Hence, this study differs from previously reported comparisons (e.g. Leuning 1995; Baldocchi & Meyers 1998; Jarvis et al. 1999) in that (1) gc is directly measured and used in the A estimation; (2) independent experiments are conducted to estimate all model parameters to avoid the circularity of using a subset of the gas exchange measurements in both the model calibration and its evaluation; and (3) the comparison among models is performed using the same gas exchange measurement technique with data collected for ambient and elevated atmospheric CO2. Thus rather than assessing how well the models describe the measurements, our aim is to investigate the predictive capacity of these models for estimating A from independent measurements and in situations where CO2 fluxes are difficult to measure at the canopy scale. The broader implications of these findings to estimating carbon fluxes in elevated CO2 experiments such as those employing the FACE technique are also discussed.

**THEORY**

The relationship between CO2 assimilation (A) and conductance (gc) is given by a system of equations based on Fick’s law

\[
A = -g_c(C_i - C_a);
\]

\[
g_c = \frac{D_{CO2}}{D_q} \frac{E}{q^s - q}
\]

where \(D_{CO2}\) and \(D_q\) are the molecular diffusivities of CO2 and water vapour, respectively, \(E\) is the evaporation rate (in molar units), \(q^s\) and \(q\) are the saturation and actual water vapour mole fractions within the leaf corresponding to surface \(T_s\) and bulk air \(T_a\) temperatures, respectively. The variables \(g_c\) and \(g_w\) (conductance to water vapour) can be equated by the ratio of the diffusivities of CO2 and water vapour in air (= 1.6) if the diffusion pathways are assumed identical. With estimates of \(g_c\) from transpiration measurements, and with measured \(C_a\), Fick’s law equations in (1) can not predict A because \(C_i\) is unknown. Additional equations relating \(C_i\) to other known quantities is required to mathematically ‘close’ this system in (1). Next, we consider eight ‘closure’ formulations representing a wide spectrum of biochemical approaches used as principal models or hypotheses employed in canopy–atmosphere carbon exchange (Sellers et al. 1996; Wang & Leuning 1998; Arneth et al. 1999).

**The Norman model**

Wong et al. (1979) and Norman (1982) were among the first to conjecture that \(C_i/C_a\) in plant leaves may be nearly constant for a wide range of environmental conditions, but that this constant varies from species to species. In a series of experiments Wong et al. (1979) found that perturbations in A resulted in parallel changes in \(g_c\), such that a nearly constant \(C_i/C_a\) (= \(R_c\)) was maintained for a wide range of environmental conditions. A constant \(R_c\) was also reported from a wide range of field experiments (Ehleringer 1993; Ellsworth 1999) as well as from detailed eco-physiological model simulations (Baldocchi 1994). Sage (1994) and Drake, Gonzalez-Meler & Long (1997) summarized results from many elevated CO2 studies and also found that despite a large increase in \(C_a\), the \(C_i/C_a\) of leaves grown in elevated CO2 was generally not significantly different from that of ambient leaves. This lends support to the use of a single \(R_c\) for a given species as a first order approximation.

With a constant \(R_c\) and measured \(g_c\) Eqn 1 reduces to:

\[
A = -g_cC_a(R_c - 1)
\]

Hence, with a known \(R_c\), which may be measured from stable carbon isotope \(\delta^{13}C\) (Farquhar, Ehleringer & Hubick 1989), A can be readily computed.
**The Cowan–Farquhar (1977) model**

In Cowan and Farquhar (1977), optimal stomatal behaviour was defined as the state that maintains ∂E/∂A constant (= kC) provided ∂²E/∂A² > 0. Upon defining water use efficiency (WUE) as (∂E/∂A)^-1, and approximating (∂E/∂A)^-1 by A/E leads to

\[
\frac{C_i}{C_s} = 1 - \frac{D}{C_s} WUE
\]

(3a)

where D is the vapour pressure deficit, and WUE is a constant. Hence, the WUE approximation leads to a linear dependence of C_i/C_s on D. In Farquhar et al. (1993) and Lloyd & Farquhar (1994), it was suggested that coupling the Cowan–Farquhar approximation of constant ∂E/∂A with a linearized relationship between carboxylation efficiency and C_i leads to

\[
\frac{C_i}{C_s} = 1 - \frac{16(DC_s - \Gamma)}{\lambda_c C_s}
\]

(3b)

which leads to C_i/C_s ∝ √D rather than linear, and Γ is the leaf CO₂ compensation point.

A third variant on this model is that proposed by Wong and Dunin (1987) in which C_i/C_s was fitted by a quadratic function to D and is given by:

\[
\frac{C_i}{C_s} = 0.96 - 0.0194D + 3.282 \times 10^{-4} D^2
\]

(4)

where D is in units of mbars (see their Fig. 8). The above relationship was derived for Eucalyptus maculata and is assumed to be similar for Pinus here.

**The Ball–Berry model**

One widely used g_c model is the Ball–Berry model (see Collatz et al. 1991), given by:

\[
g_c = m \frac{ARH}{C_s} + b'
\]

(5)

where m and b' are empirical parameters, C_s and RH are the CO₂ concentration and relative humidity at the leaf surface, respectively. Using Eqn 1 to quantify A while neglecting the leaf boundary layer resistance relative to g_c⁻¹ (i.e. C_s ≈ C_s), a closure model for C_i/C_s given by

\[
\frac{C_i}{C_s} = 1 - \frac{1}{m RH}
\]

(6)

can be derived if b' is neglected (Baldocchi & Harley 1995). The combination of Eqn 1 and Eqn 6 permit direct estimation of A if g_c and RH are measured. The above relation constrains m RH > 1 or m > RH⁻¹. With a maximum RH = 1, m must exceed unity for all plants. In fact, m ranges from 3 to 10 for a wide range of species (Leuning 1995; Baldocchi et al. 1997a).

A variant on this approach is the Leuning (1990, 1995) approach in which RH in Eqn 5 is replaced by a vapour pressure deficit correction function f_i(D) to reflect a more appropriate driving mechanism for stomatal response (Aphalo & Jarvis 1991; Monteith 1995; Oren et al. 1999). Using similar approximation, the Leuning (1995) model reduces to:

\[
\frac{C_i}{C_s} = 1 - \frac{1}{m_i f_i(D)} \frac{1 - \Gamma}{1 - \frac{D}{D_s}}
\]

(7)

where m_i is a constant analogous (but not identical) to m in the Ball–Berry formulation and D_s is an empirical constant describing the species sensitivity to D. We note that f_i(D) shown above is not unique and may vary in formulation. The f_i(D) above was suggested by Leuning (1995) after detailed analysis on 20 species.

**The Farquhar model**

For C₃ plants, the well-defined relationship between A and C_i (hereafter referred to as the A–C_i curve), can be used to provide the additional equations to close (1). The A–C_i curves are used to parameterize the biochemical model of C₃ photosynthesis as described by Farquhar et al. (1980) and Farquhar & von Caemmerer (1982) with recent modifications (see Harley et al. 1992; Medlyn et al. 1999). According to the model which we refer to hereafter as the Farquhar model, light-saturated leaf CO₂ assimilation rate (A) is limited either by regeneration of ribulose 1,5-bisphosphate (RuBP) in the photosynthetic carbon reduction cycle or by the catalytic activity of Rubisco when the chloroplast RuBP concentration is saturating. Thus the initial slope of the relationship between A and C_i (here for C_i < 250 μmol mol⁻¹) is considered to be the region of limitation by Rubisco activity under light saturation. Under these conditions, A is given by

\[
A = \frac{V_{cmax} (C_i - \Gamma^*)}{C_i + k_c \left( \frac{O_i}{k_o} \right)} - R_d
\]

(8)

where \( V_{cmax} \) is the maximum catalytic activity of Rubisco with saturating RuBP, \( \Gamma^* \) is the compensation point, but in the absence of photosynthesis, \( R_d \) is the dark respiration rate, \( O_i \) is the intercellular O₂ concentrations, and \( k_c \) and \( k_o \) are the Michaelis coefficients of Rubisco for CO₂ and O₂, respectively. The temperature dependencies of the kinetic parameters \( k_c, k_o \), and \( R_d \) are calculated as described in De Pury & Farquhar (1997) and Medlyn et al. (1999). When \( C_i \) is close to saturation for photosynthesis such that RuBP regeneration limits photosynthesis, A is given by

\[
A = J \frac{C_i - \Gamma^*}{45C_i + 105\Gamma^*} - R_d
\]

(9)

where J is the rate of electron transport. Both Eqn 8 and Eqn 9 provide the necessary closure equations to link A to C_i thus permitting the estimation of A if the above Farquhar model parameters are known. The above application of the
Farquhar model differs from other comparisons because\(g_c\) is directly measured and not modelled. Previous approaches commonly combine Eqns 8 and 9 from the Farquhar model with Eqns 1 and 5 from the Ball–Berry model to solve for \(g_c, A,\) and \(C_i\) (Sellers et al. 1996; Baldocchi & Meyers 1998; Arneth et al. 1999; Lai et al. 2000a).

**Hybrid approach**

Hybrid modelling approaches have the parsimonious advantages of requiring few parameters, yet retaining the mechanistic form of the \(A–C_i\) curve. Approaches such as the Ball–Berry, Leuning, and Norman have such parsimony yet ignore well-established characteristics of the \(A–C_i\) relationship. In contrast, Farquhar’s model considers the full \(A–C_i\) curve at the expense of requiring a larger number of physiological parameters that are not trivial to determine for a wide variety of species and sites. Hence, there is a need for intermediate approaches that are simple enough to be parameterized robustly, but retain mechanistic attributes. One such approach was described by Jarvis et al. (1999), and we propose a similar formulation below. A principal distinction between the proposed approach and the Jarvis et al. (1999) approach is in the definition of the relationship between \(g_c\) and \(A\), and how the model is parameterized.

Typical \(A–C_i\) curves exhibit three well-defined regimes: a flat regime in which \(A\) becomes nearly independent of \(C_i\) so that \(\partial A/\partial C_i = 0\) and which is often referred to as RuBP regeneration-limited \(A\) (Farquhar & von Caemmerer 1982); a curvilinear regime in which \(\partial A/\partial C_i\) is nonlinearly related to \(C_i\); and a linear regime in which \(\partial A/\partial C_i\) is a constant independent of \(C_i\) and which is often referred to as the carboxylation-limited portion of the curve as specified by the Farquhar & von Caemmerer (1982) model. The ‘flat-regime’ is associated with large \(C_i\) values rarely encountered in field conditions (including many FACE experiments). The linear portion of the \(A–C_i\) curve represents the common state under field conditions for many \(C_i\) canopies in sun. Hence, the proposed hybrid model explicitly considers the linear portion of the \(A–C_i\) curve, parameterizes the nonlinear portion following a simplistic assumption, and neglects the CO\(_2\)-saturated portion. We first consider the hybrid model with reference to the curvilinear portion of the \(A–C_i\) curve.

**The curvilinear regime of the \(A–C_i\) curve**

In such a regime, the \(A–C_i\) curve is influenced by a wide range of environmental conditions. However, if plants are operating at a high \(g_c\) such that \(C_i\) is sufficiently high as to approach CO\(_2\) saturation, then any changes in \(g_c\) will have minimal effects on \(A\). Thus to simplify, we assume that plants operating in this region of the \(A–C_i\) curve tend to buffer the effects of environmental perturbations on \(A\) such that \(\partial A/\partial g_c = 0\). In combination with (1), this assumption naturally leads to a constant \(C_i/C_a\). In essence, our proposed hybrid approach adopts Norman’s (1982) hypothesis for the curvilinear portion of the \(A–C_i\) curve only (vis-à-vis the full \(A–C_i\)). Model simulations by Baldocchi (1994) demonstrate that for large \(g_c\), \(C_i/C_a\) approaches a constant (hereafter referred to as \(R_g\) for consistency with Norman’s model). For clarity, we refer to the conductance associated with such a large \(C_i\) as \(g_{opt}\).

**The approximately linear portion of the \(A–C_i\) curve**

When \(g_c < g_{opt}\), the \(A–C_i\) curve is no longer in the curvilinear portion but can be described by its linear component, given by

\[ A = (aC_i - b) \]  

(10)

where the slope \(a\) and the intercept \(b > 0\). Following the Farquhar photosynthesis model formalism (Farquhar & von Caemmerer 1982; Harley, Tenhunen & Lange 1986), \(a\) can be equated to carboxylation efficiency which is a function of \(V_{\text{cmax}}\) for the Rubisco enzyme, and \(b\) can be derived from the CO\(_2\) compensation point \(\Gamma^* = b/a\). Hence, upon eliminating \(A\) by equating Eqn 1 to Eqn 10, we obtain an explicit relationship for \(C_i\) as a function of \(a\) and \(b\) given by

\[ C_i = \frac{g_c + b}{C_a} \frac{C_a}{g_c + a} \]  

(11)

The above relationship constitutes the hybrid model closure approximation for a linear \(A–C_i\). Equation 11 predicts the correct limits of \(C_i/C_a\) for a wide range of environmental conditions and reduced \(g_c\) (i.e. \(g_c < g_{opt}\)) if the following arguments are considered.

**Case 1:** \(g_c < b/C_a\). This condition typically occurs when quantum flux density \(Q\) limits \(g_c\). For such a condition, the slope of the \(A–C_i\) curve rapidly decays so that \(a >> 0\). With \(a = 0\) and \(g_c > 0\) Eqn 11 correctly predicts a \(C_i/C_a > 1\) consistent with model simulation results in Baldocchi (1994) and Farquhar & Wong (1984). Based on this limit, it is expected that \(C_i/C_a\) exceed unity as evening conditions are approached. This condition will not be considered in great detail since the magnitude of \(A\) is likely to be small at these times, but with \(a = f(Q)\), the hybrid model can predict light-limited \(A\). As an illustration, we compare the relationship between \(C_i/C_a\) and \(Q\) computed by the hybrid model with the idealized relationship reported in Farquhar & Wong (1984; their Fig. 1). Both models showed a constant \(C_i/C_a\) for most of the range in \(Q\) (e.g. \(Q > 100\) mmol m\(^{-2}\) s\(^{-1}\), Fig. 1) and also show increasing \(C_i/C_a\) with very low \(Q\) (\(Q < 30\) mmol m\(^{-2}\) s\(^{-1}\)). However, the hybrid model further accounts for the reduction in \(C_i/C_a\) with decreasing \(g_c\) when \(Q\) is sufficiently large (\(Q ~ 150\) mmol m\(^{-2}\) s\(^{-1}\)) and so resolves well changes in \(C_i/C_a\) for a wide range of light levels.

**Case 2:** When \(g_c >> b/C_a\). This condition typically occurs if sufficient \(Q\) is available to maintain partially open stomates but still \(g_c < g_{opt}\). For this condition Eqn 11 reduces to:
\[ f(g_c) = \frac{C_i}{C_a} = \frac{1}{1 + \frac{a}{g_c}} \]  

(12)

such that:

\[ \frac{\partial f(g_c)}{\partial g_c} = \frac{1}{a + g_c} - \frac{g_c}{(a + g_c)^2} = \frac{a}{(a + g_c)^2} \]  

(13)

which is positive \((a, g_c > 0)\) suggesting that \(C_i/C_a\) decreases with decreasing \(g_c\). Such conditions are common when soil moisture (\(\theta\)) or water vapour pressure deficit (\(D\)) limits stomatal opening.

The critical (and usually variable) conductance \((g_{\text{critical}})\) responsible for the transition from constant to variable \(C_i/C_a\) can be estimated by equating Eqn 11 to \(R_c\), which after some algebraic manipulation, results in:

\[ g_{\text{critical}} = \frac{aR_c - b}{C_a} \]  

(14)

The result in Eqn 14 sets a lower conductance limit to the onset of Norman’s (1982) constant \(C_i/C_a\) approximation for the hybrid scheme. In summary, \(C_i/C_a\) for the two regimes of the \(A-C_i\) curve, when \(Q\) is not limiting, are given by:

\[ \frac{C_i}{C_a} = \begin{cases} R_c & \text{if } g_c > g_{\text{critical}} \\ \frac{b}{g_c + \frac{C_o}{a + g_c}} & \text{if } 0 < g_c < g_{\text{critical}} \end{cases} \]  

(15)

The predictions in Eqn 15 are well supported by a wide range of \(C_3\) vegetation experiments shown in Fig. 2. Particularly, leaf-level measurements by Brodribb (1996) demonstrated the strong coupling between \(C_i/C_a\) and \(g_c\) in a soil drying experiment. Their measurements (Fig. 2, triangle angle) showed a decrease in \(C_i/C_a\) with decreasing \(g_c\) resulting from a decrease in \(\theta\). The predictions using Eqn 15 (Fig. 2, thick solid line) is in good agreement with their measured \(C_i/C_a\). The result in Eqn 15 and the measurements in Fig. 2 may appear to contradict model simulation findings in Baldocchi (1994 – his Fig. 6) for which \(C_i/C_a\) increased with decreasing \(g_c\). However, the model calculations in Baldocchi (1994) are based on \(Q\)-limited \(g_c\) with \(a \sim 0\) and \(g_c > 0\). Table 1 summarizes all models discussed above along with a list of required parameters to estimate \(A\) from measured \(g_c\) and \(C_a\).

**EXPERIMENT**

**General site description**

The gas exchange measurements were collected at the Blackwood Division of the Duke Forest near Durham, North Carolina (35°98'N, 79°8'W, elevation = 163 m). The site is a uniformly aged managed loblolly pine (\(Pinus taeda\) L.) forest that extends at least 1000 m in the north–south direction and 300 m to 600 m in the east–west direction (Katul et al 1999). The stand was originally grown from \(P. taeda\) seedlings planted at 2·0 m ¥ 2·4 m spacing in 1983 following clear cutting and burning. The mean canopy height was 13·0 m (± 0·5 m) in 1998.

**Leaf level gas exchange measurements**

The leaf-level measurements of \(A\) and \(g_c\) described in Ellsworth (1999) and Ellsworth (2000) were performed using a portable infra-red gas analyser system for CO\(_2\) and water vapour (CIRAS-1, PP-Systems, Hitchin, Herts, UK). The system was operated in open flow mode with a 5·5 cm
long leaf chamber and an integrated gas CO$_2$ supply system. The chamber was modified with an attached Peltier cooling system to maintain chamber temperature near ambient atmospheric temperature. The data were collected for upper canopy foliage at 11–12 m height, accessed with a system of towers and mobile vertically telescoping lifts. All measured gas exchange rates are reported on a unit projected area basis in this article so as to be more consistent with planar fluxes, although they were originally calculated using a geometric approximation to calculate all-sided fluxes for the needle surface (Ellsworth 1999). For the modelling here, we use measurements collected over a broad range of environmental conditions spanning 70 sampling days over a 3 year period (May 1996 to October 1999), excluding severe winter periods. Year-to-year and seasonal variation in leaf CO$_2$ and water vapour exchange have been analysed elsewhere (Ellsworth 2000).

The Free Air CO$_2$ Enrichment (FACE) setup

Measurements on elevated CO$_2$-grown foliage are from the FACE facility at the Duke Forest site and were made in parallel with the measurements in ambient atmospheric CO$_2$ (Ellsworth 1999). In 30 m diameter circular plots, an array of vertical pipes was used to emit air with enhanced CO$_2$ concentration into the stand in a controlled manner (Hendrey et al. 1999). The data used here are from measurements collected over a broad range of environmental conditions spanning 70 sampling days over a 3 year period (May 1996 to October 1999), excluding severe winter periods. Year-to-year and seasonal variation in leaf CO$_2$ and water vapour exchange have been analysed elsewhere (Ellsworth 2000).

Model parameter estimation

Because our objective is to contrast the eight models (Table 1) in terms of their ability to predict $A$ (vis-à-vis describe $A$), it is desirable to estimate the model parameters independently from the gas exchange measurements described in the experimental set-up. Separate experiments were conducted to estimate these model parameters, which are derived for ambient and elevated CO$_2$ measurements pooled together. For predictive purposes, we assume that elevated CO$_2$ itself has no direct effect on any of the parameters, which is generally consistent with Ellsworth (1999) and Myers, Thomas & DeLucia (1999). The model parameters were determined as follows:

Norman’s (1982) model

The parameter $R_c$ (see Table 1) was estimated from long-term stable carbon isotope determinations ($\delta^{13}C$). Farquhar et al. (1989) describe the approach for calculating $C_i/C_a$ on the basis of leaf $\delta^{13}C$. Upper crown foliage samples (2 mg) were collected in September of 1997 in parallel with the leaf-level gas exchange measurements, and analyzed for $\delta^{13}C$ content relative to a peee-dee belemnite standard at the Duke University Phytotron Stable Carbon Ratio facility. The $C_i/C_a$ was estimated for the foliage samples according to calculations in Farquhar et al. (1989), assuming a source air $\delta^{13}C$ as given in Ellsworth (1999) and ignoring internal conductances to CO$_2$ transfer from the cell surfaces to the sites of carboxylation. The estimated assimilation-weighted
Table 1. Summary of model formulation and closure approximations for predicting $A$ from $g_c$ and $C_a$ for different models. The $g_c$ from water vapour flux measurements is an assumed input for all the models

<table>
<thead>
<tr>
<th>Model</th>
<th>Closure</th>
<th>$A$ calculation</th>
<th>Needed parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norman (1982)</td>
<td>$\frac{C_l}{C_a} = R_c = \text{constant}$</td>
<td>$A = -g_c C_l (R_c - 1)$</td>
<td>$R_c$</td>
</tr>
<tr>
<td>Cowan–Farquhar (1977) with constant WUE</td>
<td>$\frac{C_l}{C_a} = 1 - \frac{WUE}{C_a}$</td>
<td>$A = g_c (WUE D)$</td>
<td>WUE and measured $D$</td>
</tr>
<tr>
<td>Farquhar et al. (1993)</td>
<td>$\frac{C_l}{C_a} = 1 - \sqrt{\frac{16D(C_e - \Gamma)}{\lambda_c C_a^2}}$</td>
<td>$A = -g_c (C_l - C_a)$</td>
<td>$\lambda_c, \Gamma$ and measured $D$</td>
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<td>Wong–Dunin (1987)</td>
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<td>$\frac{C_l}{C_a} = 1 - \frac{1}{m \text{RH}}$</td>
<td>$A = \frac{g_c C_l}{m \text{RH}}$</td>
<td>$m$ and measured $\text{RH}$</td>
</tr>
<tr>
<td>Leuning (1995)</td>
<td>$\frac{C_l}{C_a} = 1 - \frac{C_c}{C_a} \left(1 + \frac{D}{D_o}\right)$</td>
<td>$A = \frac{g_c C_l}{m_l \left(1 - \frac{1}{C_a} \left(1 + \frac{D}{D_o}\right)\right)}$</td>
<td>$m_l, D_o, \Gamma$ and measured $D$</td>
</tr>
<tr>
<td>Farquhar et al. (1980)</td>
<td>$A = f(C_l)$, where $f(.)$ is computed from Eqsns 8 and 9</td>
<td>$A = -g_c (C_l - C_a)$</td>
<td>$V_{\text{max}}, J, \Gamma^*,$ and measured $\text{PAR}$ and $T_i$</td>
</tr>
<tr>
<td>Hybrid model</td>
<td>$\frac{C_l}{C_a} = \begin{cases} R_c &amp; \text{if } g_c &gt; g_{\text{critical}} \ \frac{g_c + b C_l}{a + g_c} &amp; \text{if } 0 &lt; g_c &lt; g_{\text{critical}} \end{cases}$</td>
<td>$A = -g_c (C_l - C_a)$</td>
<td>$a, b$ and $R_c$</td>
</tr>
</tbody>
</table>

$C_l/C_a$ (hereafter referred to as $\bar{C_l}/C_a$) from the $\delta^{13}C$ measurements of upper crown $\text{Pinus taeda}$ foliage was 0.66 ± 0.02 for eight trees in the stand (Ellsworth 1999). Accounting for source air $\delta^{13}C$ from the constant-label used in the Duke Forest FACE study, Ellsworth (1999) found no significant difference in $\bar{C_l}/C_a$ between foliage grown in ambient and elevated CO2 during the first full summer of CO2 exposure. Leaf $\delta^{13}C$ content was assayed on foliage at different points during the growing season to confirm the constant $\bar{C_l}/C_a$ in the elevated CO2 experiment (data not shown). We repeated analyses for samples from 1998 and 1999 and found that $\bar{C_l}/C_a$ is within ± 0.03 of the 1997 value for both ambient and elevated CO2 foliage. Hence, we used $\bar{C_l}/C_a = 0.66$ as our best estimate of $R_c$.

### Cowan–Farquhar model

The Cowan–Farquhar model (with constant WUE) requires an estimate of the species-specific WUE in the calculation of $A$ as in Table 1. Upon averaging the model formulation for $C_l/C_a$, we obtain:

$$\bar{C_l} = 1 - \frac{\bar{D}}{C_a} \text{WUE}$$

A consequence of the constant WUE is that the interaction between $D$ and WUE is no longer relevant in the averaging. Using the $\delta^{13}C$ measured $\bar{C_l}/C_a = 0.66$ and the long-term daytime $\bar{D} = 2.1 \text{ kPa}$, the WUE $= 6.0 \times 10^{-3} \text{mol CO}_2 \text{[mol H}_2\text{O]}^{-1}$. This estimate of WUE is very consistent with values for $\text{Pinus taeda}$ in Ellsworth et al. (1995), Fites & Teskey (1998), and Ellsworth (1999). For elevated atmospheric CO2, $\bar{C_l} = 560 \text{ ppm}$ leading to WUE $= 9.0 \times 10^{-3} \text{mol CO}_2 \text{[mol H}_2\text{O]}^{-1}$.

For the Farquhar et al. (1993) version of the model, $\lambda_{cf}$ can also be estimated from $\delta^{13}C$ measured $\bar{C_l}/C_a$ and $\bar{D}$ using

$$\lambda_{cf} = \frac{16\bar{D}(C_a - \Gamma)}{C_a^2 \left(1 - \frac{\bar{C_l}}{C_a}\right)}$$

Using $\bar{D} = 2.1 \text{ kPa}$ and $\bar{C_l}/C_a = 0.66$ we obtain $\lambda_{cf} = 708 \text{ mol mol}^{-1}$ for $C_a = 360 \text{ mmol mol}^{-1}$.

This estimate is similar to the generic $\lambda_{cf}$ for warm mixed evergreen forests in Lloyd & Farquhar (1994).

### Wong–Dunin model

If their proposed empirical quadratic function is used without alteration, then the Wong–Dunin model does not require any parameter estimation. Fortuitously, with $\bar{D} = 2.1 \text{ kPa}$ from the leaf-level measurements used here, the estimated $\bar{C_l}/C_a = 0.7$, sufficiently close to our $\delta^{13}C$ measured $\bar{C_l}/C_a$.

### Ball–Berry model

We estimated $m$ from $\bar{C_l}/C_a$ derived from the $\delta^{13}C$ measurements using

$$m = \frac{1}{\bar{\text{RH}}} \left(1 - \frac{\bar{C_l}}{C_a}\right)$$

where $\bar{RH}$ is the assimilation-weighted relative humidity. The latter quantity was calculated for 1996–99 using 30 min $RH$ measurements conditionally averaged for $Q$ exceeding 200 $\mu$mol m$^{-2}$ s$^{-1}$. The instruments and setup used for the $RH$ and $Q$ measurements is reported in Oren et al. (1999b). This weighted averaging scheme yielded an $\bar{RH} = 0.49$, which, when combined with $C_i/C_a = 0.66$ resulted in $m = 6.0$ (unitless).

**Leuning’s model**

In a first-order analysis of parameter estimation and assuming $\Gamma/C_a$ is known, the parameters $m_L$ and $D_o$ of the Leuning (1995) model are related to $C_i/C_a$ and $D$ via:

$$C_i/C_a = \left(1 - \frac{1 - \frac{\Gamma}{C_a}}{m_L} \right) \left(1 - \frac{1 - \frac{\Gamma}{C_a}}{m_L D_o} \right) D$$

If measurements of $C_i/C_a$ and $D$ are available, then regressing $C_i/C_a$ on $D$ directly permits estimating $m_L$ from the regression intercept, and subsequently $D_o$ from the regression slope. We used this method on the $C_i/C_a$ versus $D$ in measurements reported for *P. taeda* in Fites & Teskey (1988) and found $D_o = 17.84$ and $m_L = 6.84$. The resulting model runs for these parameters showed very poor fits to measured $A$ for the dataset from Ellsworth (1999; 2000). Given that the Leuning model does not permit independent estimates of $m_L$ and $D_o$ as in all other approaches, we determined $m_L$ and $D_o$ using a subset of the gas exchange measurements (specifically, measurements collected in 1996, less than 20% of the entire data set). With this subset, the estimated $D_o = 30$ and $m_L = 4.0$. These parameters were used in subsequent model inter-comparisons.

**The Farquhar model**

Steady-state $A–C_i$ curve measurements were conducted during the growing season using a temperature-controlled photosynthesis system (PP-Systems CIRAS-1, Hitchin, Herts, UK or Li-Cor 6400, Lincoln, NE, USA). Measurements were performed at saturating quantum flux density $Q$ and leaf temperatures of 28 or 30 °C and at leaf-air vapour pressure differences < 1.7 kPa. A projector bulb emitting white light (PP-Systems) or light-emitting diodes (Li-Cor) was used to achieve $Q > 1500$ $\mu$mol m$^{-2}$ s$^{-1}$. These $A–C_i$ gas exchange measurements began at the ambient CO$_2$ concentration and stepped through eight to ten different CO$_2$ concentrations from the CO$_2$ compensation point to CO$_2$ saturation ($C_i > 1000$ $\mu$mol mol$^{-1}$). The $V_{c max}$ and $R_d$ were determined by least-squares regression fits to the data for $C_i < 250$ $\mu$mol mol$^{-1}$ for curves measured on four to six separate trees at three different points in the growing season. The above equations were then solved for the values of $J_{max}$, the potential rate of electron transport in photosystem II, that provided the best fit for the entire $A–C_i$ curve for each tree. In the calculations, $\Gamma^*$ is determined from the polynomial function in Jordan & Ogren (1984). $V_{c max}$ and $J_{max}$ parameters were adjusted for temperature using the Arrhenius function and activation energy parameters $E_{Vc max} = 68 000$ J mol$^{-1}$ and $E_{Jmax} = 199 000$ J mol$^{-1}$ (see De Pury & Farquhar 1997; Medlyn et al. 1999). Other parameters in the model were used as described in De Pury & Farquhar (1997).

**The hybrid model**

The hybrid model parameter $a$ was estimated from the $A–C_i$ curve data shown in Fig. 3. The current analysis assumes that the concentration of CO$_2$ at the chloroplast surface ($C_{chl}$) is near that in the intercellular air space. The parameter $b$ was estimated from $\Gamma^*$, described above, and $R_c$ is identical to Norman’s model (see Table 2).

**RESULTS**

We compared measured and modelled $A$ for ambient and elevated atmospheric CO$_2$. The sensitivity of $A$ in a subset of the models to their respective primary variables for ambient and enriched atmospheric CO$_2$ conditions is discussed in the Appendix. The sample models are chosen to reflect different classes of closure approximations (see Appendix), and the sensitivity analysis indicates that the models were all well-parameterized from the independent measurements or formulations.
The eight models recovered measured fundamental differences in the closure schemes, six out of and are derived from independent measurements. Despite assumed to be identical, except for the Wong–Dunin model, CO2 model predictions. For the Farquhar and Hybrid schemes, the unit area of the parameter is based on the projected leaf area ambient and elevated atmospheric CO2 calculations are considered here is that the model parameters used for the short-term C4 dynamics are well resolved by all these models. An important consideration here is that the model parameters used for the ambient and elevated atmospheric CO2 calculations are assumed to be identical, except for the Wong–Dunin model, and are derived from independent measurements. Despite fundamental differences in the closure schemes, six out of the eight models recovered measured A with comparable root-mean squared error (RMSE). Table 3 reports the statistical details of the comparisons between modelled and measured A. All the models underestimated the measured A when A was larger than 15 μmol m⁻² s⁻¹ for ambient atmospheric CO2 conditions as evidenced by the significant departure from unity for the regression slopes. All models, except the Ball–Berry and the Cowan–Farquhar (constant WUE), explained more than 60% of the measured A variability in ambient CO2 conditions. Interestingly, Norman’s constant C4/Ca model, the hybrid approach, and the Leuning models all yielded the lowest RMSE in this case despite differences in the closure assumptions (Table 1). Additionally, the Farquhar et al. (1993) version leads to C4/Ca α √D thereby reducing the sensitivity of modelled A on D, analogous to Norman’s model.

For elevated atmospheric CO2 conditions, the Farquhar, Wong–Dunin, Cowan–Farquhar (both constant WUE and the Farquhar et al. 1993 version), and Leuning model predictions were statistically similar to the measurements. All the models, except the Ball–Berry explained more than 50% of the variations in measured A. The hybrid, Leuning, and Farquhar models as well as the Farquhar et al. (1993) version of the Cowan–Farquhar model had the lowest RMSE when contrasted with the other models.

It is important to note that the Farquhar model requires the largest number of independent parameters (Table 1); hence, errors in any of these parameter measurements or estimates tend to amplify errors in modelled C4 and A. A basic difference between the ambient and elevated data is the increase in C4 leading to an increased likelihood of J regulating A. This may explain why the hybrid model did not have a 1 : 1 regression slope when compared to the Farquhar model performance. The uncertainty in estimating A when Eqn 8 limits the assimilation rate is typically larger than Eqn 9. We found that 18% of our data points at elevated atmospheric CO2 were limited by J for C4 of 560 p.p.m. For these time points, the RMSE was four times higher than the RMSE for elevated CO2 modeling A with C4 limited for elevated atmospheric CO2, since additional parameters for the light response of leaves are used to characterize the J-limited part of the A–C4 curve.

To further investigate the closure approximations, a comparison between measured and modelled C4/Ca is shown in Fig. 5. Seasonal droughts resulted in declines in measured C4/Ca with g4, consistent with Brodribb’s (1996) measurement.

### Model assessment with independent parameters

The modelled A for all closure schemes generally compared well with leaf-level measured A for ambient and elevated atmospheric CO2 conditions (Fig. 4) in an ensemble sense. The scatter in the instantaneous runs is large suggesting that not all the processes affecting short-term C4 dynamics are well resolved by all these models. An important consideration here is that the model parameters used for the ambient and elevated atmospheric CO2 calculations are assumed to be identical, except for the Wong–Dunin model, and are derived from independent measurements. Despite fundamental differences in the closure schemes, six out of the eight models recovered measured A with comparable root-mean squared error (RMSE). Table 3 reports the statistical details of the comparisons between modelled and measured A. All the models underestimated the measured A when A was larger than 15 μmol m⁻² s⁻¹ for ambient atmospheric CO2 conditions as evidenced by the significant departure from unity for the regression slopes. All models, except the Ball–Berry and the Cowan–Farquhar (constant WUE), explained more than 60% of the measured A variability in ambient CO2 conditions. Interestingly, Norman’s constant C4/Ca model, the hybrid approach, and the Leuning models all yielded the lowest RMSE in this case despite differences in the closure assumptions (Table 1). Additionally, the Farquhar et al. (1993) version leads to C4/Ca α √D thereby reducing the sensitivity of modelled A on D, analogous to Norman’s model.

For elevated atmospheric CO2 conditions, the Farquhar, Wong–Dunin, Cowan–Farquhar (both constant WUE and the Farquhar et al. 1993 version), and Leuning model predictions were statistically similar to the measurements. All the models, except the Ball–Berry explained more than 50% of the variations in measured A. The hybrid, Leuning, and Farquhar models as well as the Farquhar et al. (1993) version of the Cowan–Farquhar model had the lowest RMSE when contrasted with the other models.

It is important to note that the Farquhar model requires the largest number of independent parameters (Table 1); hence, errors in any of these parameter measurements or estimates tend to amplify errors in modelled C4 and A. A basic difference between the ambient and elevated data is the increase in C4 leading to an increased likelihood of J regulating A. This may explain why the hybrid model did not have a 1 : 1 regression slope when compared to the Farquhar model performance. The uncertainty in estimating A when Eqn 8 limits the assimilation rate is typically larger than Eqn 9. We found that 18% of our data points at elevated atmospheric CO2 were limited by J for C4 of 560 p.p.m. For these time points, the RMSE was four times higher when compared with the Vc max-limited A for elevated atmospheric CO2, since additional parameters for the light response of leaves are used to characterize the J-limited part of the A–C4 curve.

To further investigate the closure approximations, a comparison between measured and modelled C4/Ca is shown in Fig. 5. Seasonal droughts resulted in declines in measured C4/Ca with g4, consistent with Brodribb’s (1996) measurement.

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**Table 2.** Estimated or measured model parameter for each closure scheme. These parameters are unaltered for enriched atmospheric CO2 model predictions. For the Farquhar and Hybrid schemes, the unit area of the parameter is based on the projected leaf area.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Method of estimation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norman</td>
<td>R4 = 0.66</td>
<td>Long-term leaf δ13C</td>
</tr>
<tr>
<td>Cowan–Farquhar with constant WUE</td>
<td>WUE = 6 × 10⁻³ C4/360 C4 in ppm.</td>
<td>Long-term leaf δ13C and measured D</td>
</tr>
<tr>
<td>Farquhar et al. (1993)</td>
<td>λdf = 708(360/C4) mol mol⁻¹</td>
<td>Long-term leaf δ13C and measured D</td>
</tr>
<tr>
<td>Wong–Dunin</td>
<td>No parameters are required</td>
<td>Regression analysis on A = C4/mRHg4 for leaf gas exchange data, and independently for R4 = 0.66 along with measured RH = 0.49.</td>
</tr>
<tr>
<td>Ball–Berry</td>
<td>m = 5.9</td>
<td>Estimated from 1996 subset of gas exchange measurements</td>
</tr>
<tr>
<td>Leuning</td>
<td>D4 = 30 and m3 = 4.</td>
<td>Ensemble-averaging A–C4 curves for upper crown foliage</td>
</tr>
<tr>
<td>Farquhar et al. (1980)</td>
<td>Vc max = 98.98 (μmol m⁻² s⁻¹)</td>
<td>Ensemble-averaging A–C4 curves for upper crown foliage (Fig. 3), and leaf δ13C</td>
</tr>
<tr>
<td></td>
<td>J max = 2.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Γ* = 3.69 + 0.188(Ta – 25) + 0.0036(Ta – 25)²</td>
<td></td>
</tr>
<tr>
<td>Hybrid model</td>
<td>a = 0.076 μmol m⁻² s⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b = 6.70 μmol m⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R4 = 0.66</td>
<td></td>
</tr>
</tbody>
</table>

ments shown in Fig. 2 and were partially reproduced by a variety of models, including the hybrid model in both ambient and elevated CO₂ (Fig. 5). Such summer droughts are common in the region (Oren et al. 1998a, Ellsworth 1999). Again, the instantaneous scatter in modelled \( \frac{C_i}{C_a} \) was sufficiently large and indicated that processes affecting the dynamics of \( \frac{C_i}{C_a} \) were not resolved by all closure models, at least with their static parameters. We restate again that these measurements were all conducted for \( Q > 1200 \) mmol m\(^{-2}\) s\(^{-1}\); hence, the reduction in \( g_c \) shown in Fig. 5 is due to environmental and hydrologic conditions, but not \( Q \).

Table 3. Comparison between modelled and measured mid-day \( A \) of *Pinus taeda* for all closure schemes. The closure schemes are based on the approaches of Norman (NR), Ball-Berry (BB), the proposed hybrid scheme (HY), Farquhar (FA), Leuning (LEU), Cowan–Farquhar (CF) with constant WUE, Lloyd–Farquhar (LF), and Wong–Dunin (WD) models as parameterized for *Pinus taeda* according to Table 2. The root-mean squared error (RMSE) and the regression statistics (slope, intercept, and correlation coefficient \( R \)) with measured \( A \) as the independent variable are shown. The regression slopes that are statistically different from unity at the 95% level are indicated by *, and the best \( R \), slope and RMSE among the eight models are shown in bold.
Model assessment with optimized parameters

It is conceivable that the scatter in modelled $A$ (Fig. 4a & b, Table 3) is due to our method of parameter estimation. Matching long-term modelled $C_i/C_a$ to the $\delta^{13}C$ measurements may inject biases and degrade the predictive capacity of the closure models, in part because of inconsistencies between the integration period of the $\delta^{13}C$ and the instantaneous gas exchange and meteorological measurements. To minimize such inconsistencies and investigate the model performance for their optimal parameters, we fit the model closure approximations (Table 2) to the instantaneous gas exchange measured $C_i/C_a$ with time-synchronized meteorological drivers ($D$, $RH$, etc.) for the full data record. The outcome summarized in Table 4 revealed that for ambient CO$_2$ conditions, most parameters were comparable to those determined from the independent measurements (see Table 2) though not identical. The Leuning model parameters were most sensitive to the parameterization approach (Table 2, Table 4). The parameters fitted to measured $C_i/C_a$ for ambient CO$_2$ resulted in slopes not statistically different from unity at the 95% confidence level (Table 4). Although the optimized parameters of the Norman, Ball–Berry, hybrid and Cowan–Farquhar models for elevated CO$_2$ were similar to those for ambient CO$_2$, the Farquhar et al. (1993), Leuning and Wong–Dunin parameters were different. The regression slopes in Table 4 for the Leuning, Wong–Dunin and Norman models were also significantly different from unity in elevated CO$_2$. For each CO$_2$ level, the different models were generally comparable in terms of RMSE, suggesting comparable scatter around measured $A$. In short, this analysis suggests that by fitting the closure models to measured $C_i/C_a$, the biases in modelled $A$ were reduced and most of the regression slopes reached unity but this did not generate any significant improvements in RMSE. The consistency in RMSE demonstrates that the refined parameters do not reduce the scatter around measured $A$(Fig. 4) perhaps indicating that assuming static parameters in these physiological models may not be appropriate for such a long time course (3 years). Unavoidable sampling error and spatial inhomogeneity within branches and age classes of needles may also contribute to variability in the data and parameters, along with the knowledge that parameters such as $V_{c max}$, WUE and $m$ have been shown to be dynamic with time (Myers et al. 1999; Ellsworth 2000; Lai et al. 2000b). Thus to highlight the overall model trends with minimal distortion from this intrinsic variability, Figs 4 and 5 also include the ensemble trends for model calculations and measurements.

DISCUSSION AND CONCLUSIONS

This study is the first to compare the performance of eight widely used models employed to estimate net CO$_2$ assimilation from conductance measurements for current and elevated CO$_2$ conditions. The elevated atmospheric CO$_2$ comparison was performed in the Duke Forest free-air CO$_2$ enrichment facility but using parameters derived from independent experiments in ambient CO$_2$ conditions. The models ranged in conceptual approximations and parsimony in number of physiological parameters from a simple

Figure 5. Comparison of modelled $C_i/C_a$ as a function of measured $g_c$ for Pinus taeda measured at mid-day on sunny days for ambient (top panels, a, b) and elevated CO$_2$ (bottom panels, d, e). Scatter plots of the data (left panels, a, d) and their ensemble-averaged runs (right panels, b, e) are shown. The modelled $C_i/C_a$ follows the same symbols as the models shown in Fig. 4, with the measured $C_i/C_a$ (panel c) indicated by $\Delta$ (open symbols for ambient and closed symbols for elevated CO$_2$). The horizontal dashed line is the $C_i/C_a = 0.66$ determined from $\delta^{13}C$ measurements (1997–99).

constant $C_i/C_a$ (Norman 1982) to a detailed biochemical model of photosynthesis (Farquhar et al. 1980). Our use of independent model parameters derived from separate measurements (Table 2) permitted an unbiased comparison of the predictive $A$ performance of these models from measured $g_c$. Many previous studies did not independently measure these parameters but derived them from a subset of the same data set also used to evaluate the model performance, as in Table 4.

The constant $C_i/C_a$ approximation, which is the most parsimonious in number of input parameters, yielded results that are comparable or better than more elaborate models for predicting short-term $A$. This finding is consistent with the framework presented by Jarvis et al. (1999). However, this simple closure approximation clearly does not reflect measured variation in $C_i/C_a$ with environmental conditions underlying reduced $g_c$ such as drought. If seasonal droughts are short in persistence, then this simplification permits robust estimation of long-term $A$ while sacrificing the mechanistically appropriate short-term $A$ estimation during the drought duration. The constant $C_i/C_a$ model does not permit much interpretation of the sources of variability in $A$ other than due to variation in $g_c$. The success of this approach implies that control over leaf gas exchange (particularly $A$) by $g_c$ in *Pinus taeda* is strong (Ellsworth 2000). However, variability in other environmental conditions (e.g. $Q$) over the day can influence $C_i$ and are not explicitly treated in the Norman model. From a practical modelling perspective, the use of classes of models that employ a simple $C_i/C_a$ closure approximation may well be justified for species whose assimilation is much more sensitive to $g_c$ than $C_i/C_a$. As an example for *Pinus taeda*, $g_c$ can decrease by two orders of magnitude for low light whereas $C_i/C_a$ may increase by only 20%. In short, $C_i/C_a$ is a useful parameter to be evaluated in the context of elevated CO$_2$ experiments such as FACE.

The widely used Ball–Berry formulation yielded the poorest $A$ estimates when compared to the other closure schemes. However, the Leuning corrections to the Ball–Berry formulation produced among the best $A$ estimates. Hence, when employing coupled photosynthesis conductance models, revisions to the Ball–Berry model along the several closure model frameworks investigated here will improve the capacity to estimate $A$ as the main determinant of ecosystem GPP without the added complexity of increased number of parameters.

The detailed biochemical photosynthesis model of Farquhar et al. (1980) was also contrasted with simpler models. In terms of minimizing the deviation of predicted and measured $A$ (RMSE), we found no clear statistical advantage to utilizing the Farquhar et al. model for predicting assimilation. It is important to note that the leaf level measurements were made under sunny, mid-day conditions (high $Q$) and hence represent a narrower range of $C_i/C_a$ conditions than may occur diurnally, so the advantages of the $A–C_i$ curve description for longer-term prediction of $A$ is not completely apparent. Nonetheless, for low $Q$ an accurate $C_i/C_a$ description as is given by the Farquhar model is masked by large reductions in $g_c$ from sunlit to shaded conditions.

We also developed and tested a hybrid scheme that adopts the parsimony of Norman’s empirical model but retains the mechanistic advantages of the Farquhar model. Unlike Farquhar’s model, this new approach is computationally simpler to implement and requires only the ensemble-averaged slope of the $A–C_i$ curve. Because of its novelty, we tested the approach for a wide range of species, including the Duke pine forest for ambient and elevated atmospheric CO$_2$, and found that the hybrid approach reproduces well the

### Table 4. A reassessment of modelled versus measured mid-day $A$ of *Pinus taeda* for the parsimonious closure schemes, using model parameters directly calculated from the 3 years of gas exchange measured $C_i/C_a$. The closure schemes are as indicated in Table 3 with the exception of FA, because not all terms in this model could be fully parameterized from the measurements. The parameters shown were optimized for measured $C_i/C_a$ for ambient and elevated atmospheric CO$_2$. The root-mean squared error (RMSE) and the regression statistics (slope, intercept, and correlation coefficient $R$) with measured $A$ as the independent variable are shown. The regression slopes that are statistically different from unity at the 95% level are indicated by $^*$.

<table>
<thead>
<tr>
<th>Assimilation</th>
<th>Model</th>
<th>Parameters</th>
<th>$R$</th>
<th>Slope/Intercept</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>NR</td>
<td>$R_e = 0.58$</td>
<td>0.83</td>
<td>1.04/0.45</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>BB</td>
<td>$m = 5.5$</td>
<td>0.70</td>
<td>0.84/2.9</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>HY</td>
<td>$R_e = 0.58$, Same $a$, $b$</td>
<td>0.83</td>
<td>1.00/0.93</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>CF</td>
<td>$WUE = 7.1$</td>
<td>0.57</td>
<td>0.79/3.0</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>LF</td>
<td>$\lambda_d = 708$ mol mol$^{-1}$</td>
<td>0.60</td>
<td>0.70/3.2</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>LEU</td>
<td>$m_L = 2.24$, $D = 99.5$</td>
<td>0.83</td>
<td>0.99/1.06</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>WD</td>
<td>$C_i/C_a = 0.565 + 0.0052D - 0.0002D^2$</td>
<td>0.83</td>
<td>0.99/1.18</td>
<td>2.1</td>
</tr>
<tr>
<td>Elevated</td>
<td>NR</td>
<td>$R_e = 0.58$</td>
<td>0.81</td>
<td>1.41/5.37</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>BB</td>
<td>$m = 5.5$</td>
<td>0.64</td>
<td>1.05/1.03</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>HY</td>
<td>$R_e = 0.58$, Same $a$, $b$</td>
<td>0.79</td>
<td>1.20/1.3</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>CF</td>
<td>$WUE = 6.9$</td>
<td>0.75</td>
<td>1.26/3.55</td>
<td>4.9</td>
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<tr>
<td></td>
<td>LF</td>
<td>$\lambda_d = 452$ mol mol$^{-1}$</td>
<td>0.76</td>
<td>1.00/1.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>LEU</td>
<td>$m_L = 3.54$, $D = 29.7$</td>
<td>0.86</td>
<td>1.36/4.6</td>
<td>4.4</td>
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<tr>
<td></td>
<td>WD</td>
<td>$C_i/C_a = 0.72 - 0.0047D - 0.00008D^2$</td>
<td>0.85</td>
<td>1.36/4.34</td>
<td>4.5</td>
</tr>
</tbody>
</table>
decrease in $C_i/C_a$ with decreasing $g_c$ (Fig. 2) following drought or high vapour pressure deficit (i.e. not light-limited $g_c$ reduction). The agreement between measured and predicted $A$ by the proposed hybrid scheme is no worse than the Farquhar model (Fig. 4). The hybrid approach (and the closely related version presented in Jarvis et al. 1999) is not proposed as a replacement of the Farquhar model or other closure schemes but a complementary approach that is sensitive to specific mechanisms in the $A$–$C_i$ relationship absent in the simpler closure schemes.

Despite the fact that $RMSE$ of $A$ was larger for elevated atmospheric CO$_2$, all the closure approximations resulted in better goodness of fit (see regression slopes in Tables 3 and 4) when compared to ambient CO$_2$ data with the exception of the Ball–Berry approach. A combination of higher $A$ and reduced sensitivity to absolute errors in $C_i$ (Ellsworth 1999) probably contributed to the better fits in Table 3. Although the Farquhar model best describes the underlying physiological mechanisms affecting $A$, the added number of physiological parameters required to describe these additional interactions also introduces additional uncertainty in parameterization. Caution is needed when applying this approach to understanding variation in $A$ in ambient and elevated atmospheric CO$_2$ in species or environments where few of the kinetic parameters are available or can be inferred. Also, the implication of good ensemble performance (Figs 4 & 5) of the simpler models is that added physiological complexity need not always translate to increased model accuracy.

The comparison here fundamentally differs from the widely used approach of combining the Ball–Berry type conductance or other conductance formulations with Fickian diffusion principles and the $A$–$C_i$ curve description (Collatz et al. 1991; Baldocchi 1994; Leuning 1995; Baldocchi et al. 1997a) in that the degrees of freedom in all model parameterizations have been reduced because $g_c$ is specified from measurements. A direct consequence of such reduced degrees of freedom is that modelled $A$ becomes very sensitive to the physiological parameterizations (e.g. $C_i/C_a$) adopted in all closure schemes thus permitting explicit assessment of such approximations. Each of the modelling approaches that have been summarized (Table 2) can be used with leaf and stand-level $g_c$ measurements made with a variety of techniques (porometry, sapflux by heat-pulse or Granier sensors, micrometeorology, Bowen ratio/energy balance methods, etc.) along with appropriate physiological parameterizations such as the ones considered here.

A continuing area of research focuses on the question of whether the fundamental CO$_2$ response of leaves and the Farquhar parameterization of this response is affected by elevated CO$_2$ (Sage 1994; Drake et al. 1997; Medlyn et al. 1999). Our analysis uses the same parameters for trees grown in ambient and elevated CO$_2$ for 3 years, which reflects the analyses that have been conducted for Pinus taeda (Ellsworth 1999; Myers et al. 1999). However, the analysis may apply for any species and environment so long as the physiological parameters in elevated CO$_2$ are known.

At the canopy scale, effects of elevated CO$_2$ on $A$ of forests cannot be quantified by direct eddy-covariance measurements, but the approaches summarized here can place upper bounds on the enhancement of canopy $A$. For example, using the simplest approach (Norman’s model), the enhancement of $A$ with elevated CO$_2$ ($= \partial A/\partial C_a$) is directly proportional to the enhancement in $C_a$ assuming $\partial g_c/\partial C_a$ is small for the leaf (Ellsworth et al. 1995) and canopy scale (Pataki et al. 1998). However, the approach we have described need not assume that $\partial g_c/\partial C_a$ is zero for all species, but only that $C_i/C_a$ is measured. In the Duke Forest FACE experiment with ambient + 200 p.p.m. CO$_2$, the concentration enhancement is 1.55 and the computed enhancement of $A$ from Norman’s model is also 1.55. This in agreement with direct measurements of $A$ enhancement for upper crown $P. taeda$ foliage during the summer (1.56; Ellsworth 1999), since $C_i$ at elevated atmospheric CO$_2$ largely remains in the linear region of the $A$–$C_i$ curve. In short, when water vapour fluxes are available in conjunction with vapour pressure deficit, $A$ can be estimated with reasonable accuracy if first-order physiological information is available from elevated CO$_2$ experiments.

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APPENDIX

Sensitivity analysis

A sensitivity analysis to assess how uncertainties in model parameters alter the RMSE is shown in Fig. 6. The models assessed include the simplest closure approach of Norman, the widely used Ball–Berry, the multiple parameter Farquhar, and the proposed hybrid approach. Hence, the full spectrum of closure model complexity is resolved in this sensitivity.

It is evident that the main parameters in the Norman, Ball–Berry, and the hybrid models are robust to perturbations around their optimal states. That is, for initial estimates of model parameters close to optimum, a 10% perturbation in the parameter increases the RMSE by less than 10%. These RMSE findings are consistent for ambient and elevated atmospheric CO₂ conditions. It is interesting to note that the independently determined parameters (e.g. $R_c$ from the $\delta^{13}$C measurements) are near their optimum state for minimizing RMSE. Figure 6 suggests that increasing $V_{c\text{ max}}$ in the Farquhar model tend to monotonically improve the RMSE. However, we found that for a $V_{c\text{ max}} > 140$, the number of points for which a positive $C_i$ solution exists to the quadratic equation formed by combining Eqn 8 or Eqn 9 with Eqn 1 diminished by more than 30%. Hence, such large $V_{c\text{ max}}$ are not compatible with the independently measured $g_c$ for at least 30% of the data, and thus much of the reduction in RMSE is attributed to rejecting points for which such convergence is not attained.

Figure 6. Sensitivity of the root-mean square error (RMSE) to primary model parameters (Table 1) for ambient (solid line) and elevated (dotted line) atmospheric CO₂ for four sample closure models (NR, BB, HY and FA models, see Fig. 4) is evaluated. Sensitivity of the Farquhar biochemical model was not evaluated if more than 40% of the data was lost due to lack of convergence with the closure criterion.