



OPINION PAPER

# Constraints to the potential efficiency of converting solar radiation into phytoenergy in annual crops: from leaf biochemistry to canopy physiology and crop ecology

Xinyou Yin\* and Paul C. Struik

Centre for Crop Systems Analysis, Department of Plant Sciences, Wageningen University, PO Box 430, 6700 AK Wageningen, The Netherlands

\* To whom correspondence should be addressed. E-mail: [xinyou.yin@wur.nl](mailto:xinyou.yin@wur.nl)

Received 31 May 2015; Revised 4 July 2015; Accepted 8 July 2015

Editor: Christine Raines

## Abstract

A new simple framework was proposed to quantify the efficiency of converting incoming solar radiation into phytoenergy in annual crops. It emphasizes the need to account for (i) efficiency gain when scaling up from the leaf level to the canopy level, and (ii) efficiency loss due to incomplete canopy closure during early and late phases of the crop cycle. Equations are given to estimate losses due to the constraints in various biochemical or physiological steps. For a given amount of daily radiation, a longer daytime was shown to increase energy use efficiency, because of the convex shape of the photosynthetic light response. Due to the higher cyclic electron transport,  $C_4$  leaves were found to have a lower energy loss via non-photochemical quenching, compared with  $C_3$  leaves. This contributes to the more linear light response in  $C_4$  than in  $C_3$  photosynthesis. Because of this difference in the curvature of the light response, canopy-to-leaf photosynthesis ratio, benefit from the optimum acclimation of the leaf nitrogen profile in the canopy, and productivity gain from future improvements in leaf photosynthetic parameters and canopy architecture were all shown to be higher in  $C_3$  than in  $C_4$  species. The indicative efficiency of converting incoming solar radiation into phytoenergy is ~2.2 and 3.0% in present  $C_3$  and  $C_4$  crops, respectively, when grown under well-managed conditions. An achievable efficiency via future genetic improvement was estimated to be as high as 3.6 and 4.1% for  $C_3$  and  $C_4$  crops, respectively.

**Key words:** Annual crops, biomass energy, canopy-leaf photosynthesis ratio, radiation use efficiency.

## Introduction

Use of fossil fuels in energy services causes the emission of greenhouse gases into the atmosphere and leads to global climate change. Furthermore, use of fossil fuels is not sustainable. Biomass has the potential to increasingly become one of the global primary renewable energy sources (Berndes *et al.*, 2003; Yuan *et al.*, 2008), given high biomass production potential in some species (Piedade *et al.*, 1991, 1994;

Dohleman *et al.*, 2009). One of the sources for bioenergy production from agriculture-based systems is the cultivation of annual crops (Carpita & McCann, 2008). For example, currently, corn grain and soybeans are the feed stocks used in the USA to produce liquid transportation fuel (bioethanol and biodiesel), although arguably annual crops should remain major sources of food.

Abbreviations: CCM, carbon-concentrating mechanism;  $e^-$ , electron(s); LAI, leaf area index; N, nitrogen; NPQ, non-photochemical quenching; PAR, photosynthetically active radiation; PS, photosystem; Rubisco, ribulose-1,5-bisphosphate carboxylase/oxygenase; RuBP, ribulose-1,5-bisphosphate.

A typical solar energy conversion efficiency by annual crops is very humble,  $\leq 1\%$  on the basis of incoming global solar radiation across a full growing season (de Groot, 2008). It is important to analyse where energy is lost, in order to find ways of improving the energy conversion efficiency of crop production systems.

The questions on energy conversion efficiency have been addressed for decades (e.g. Loomis & Williams, 1963; Monteith, 1972; Goudriaan *et al.*, 1991; Loomis & Amthor, 1999; Long *et al.*, 2006; Zhu *et al.*, 2008; Amthor, 2010; DeLucia *et al.*, 2014). Earlier analyses (e.g. Loomis & Williams, 1963; Monteith, 1972) gave a linear step-wise routine, in which the fate of solar radiation incident on a plant community was traced through a series of processes or steps, each step being evaluated for its output:input ratio using physical or biochemical theories or based on empirical observations, and the overall efficiency was determined by multiplying the efficiencies of individual steps. The crux of these approaches is their simplicity in assessing energy conversion efficiency without using sophisticated numerical simulation based on dynamic modelling. However, not all biophysical, biochemical, or physiological components were specifically considered in these early calculations. More recent analyses, again without engaging numerical simulation, were based on a detailed understanding of the biochemistry of leaf photosynthesis (Zhu *et al.*, 2008), or of both photosynthesis and respiration (Amthor, 2010).

These previous and recent analyses (e.g. DeLucia *et al.*, 2014) were mostly on potential maximum conversion efficiency, making little quantitative allowance for the case of light saturation of photosynthesis. More importantly, they gave little consideration to the scaling up of the evaluation at the leaf level into quantitative information at the canopy level in space, or for the extension from the instantaneous leaf assimilation to daily and seasonal totals. Annual crops germinate, flower, and mature in a single growth season, during which the crop canopy expands initially, reaches its maximum size, and then senesces. An explicit procedure for scaling up from the instantaneous leaf assimilation to daily canopy photosynthesis and subsequently to total biomass production over a crop cycle is crucial for an accurate quantification of the solar energy conversion efficiency. While this can be addressed by running numerical simulations using a full crop growth model, it is valuable to have a mathematically simple, yet physiologically sound, framework that scales up from leaf to canopy to crop.

The objective of this study was to describe a systems framework that quantifies (without engaging numerical simulation), in steps, constraints to realizing efficient conversion of solar radiation into phytoenergy in annual arable crops when grown under well-managed conditions. Equations for calculating the loss at each step were formulated from state-of-the-art models at leaf, canopy, and crop scales, respectively. We wanted to specifically answer the following questions: (i) Can the whole-system efficiency always be calculated as the product of efficiencies of individual steps? (ii) Is the linear, single-series framework as formulated by Monteith (1972) accurate to estimate the efficiency of annual crops? (iii) Is the efficiency

of annual crops indeed humble ( $< 1\%$ )? (iv) Are there differences between crop types ( $C_3$  vs  $C_4$ ) in potential for improvement? Based on the analysis, avenues to enhance the solar energy use efficiency of annual crops are outlined.

## Theoretical maximum efficiency of photosynthesis

We used the theoretical maximum quantum efficiency of  $\text{CO}_2$  assimilation as the baseline for our analysis. This maximum efficiency has long been known as  $0.125 \text{ mol CO}_2 (\text{mol photons})^{-1}$  (Emerson, 1958). This value can be expected theoretically from the facts that: (i) assimilating  $1 \text{ mol CO}_2$  in the Calvin cycle requires  $2 \text{ mol NADPH}$ ; (ii) production of  $1 \text{ mol NADPH}$  requires  $2 \text{ mol electrons } (e^-)$ ; and (iii) moving  $1 \text{ mol } e^-$  along the linear  $e^-$  transport chain requires  $1 \text{ mol absorbed photons}$  for each of the two photosystems. This maximum quantum efficiency of photosynthesis implies that the condition of three ATPs required per  $\text{mol CO}_2$  assimilation is fulfilled as well, which can be exactly achieved by the scenario that the  $\text{H}^+ : e^-$  ratio is 3 and the  $\text{H}^+ : \text{ATP}$  ratio is 4 (von Caemmerer, 2000; Allen, 2003). To estimate conversion efficiency, we assume that: (i) 50% of the total solar short-wave radiation is the photosynthetically active radiation (PAR) (Goudriaan & van Laar, 1994); (ii) absorptance of incoming PAR by photosynthetic pigments in entirely healthy leaves is 90% (Zhu *et al.*, 2008); (iii)  $1 \text{ MJ PAR}$  of natural solar light is equivalent to  $4.56 \text{ mol photons}$  (Goudriaan & van Laar, 1994); and (iv) a unit of  $\text{CH}_2\text{O}$  in glucose contains  $0.48 \text{ MJ energy}$  (Zhu *et al.*, 2008). Therefore, the theoretical maximum energy conversion efficiency by photosynthesis on the basis of incident total solar radiation is  $0.125 \times 0.48 \times 4.56 \times 0.9 \times 0.5 \times 100 = 12.3\%$ . The two largest losses are: (i) the unavailability of  $\sim 50\%$  of short-wave solar radiation to higher plant photosynthesis; and (ii) a low intrinsic energy conversion efficiency [ $0.48 / (8 / 4.56) \times 100 = 27.4\%$ ] in the photosynthetic reactions. The latter low efficiency results from losses predominantly in the generation of ATP and NADPH in the light reactions and to a much less extent in the operation of the dark reactions – the Calvin cycle for  $\text{CH}_2\text{O}$  synthesis (Taiz & Zeiger, 2010).

## Constraints at the leaf level

The actual photon use efficiency by photosynthesis in healthy leaves will be analysed first for limiting-light conditions, and then for non-limiting-light conditions.

### *Actual efficiency under limiting light*

The actual photon use efficiency by photosynthesis for the limiting-light condition is much lower than  $0.125$ . For example, in the crop model SUCROS (Goudriaan & van Laar, 1994), the value used for this parameter is  $12.5 \text{ mg CO}_2 (\text{J PAR})^{-1}$ , which can be converted to  $0.063 \text{ mol CO}_2 (\text{mol photons})^{-1}$ , i.e. about half of the theoretical maximum photon efficiency.

The theoretical maximum quantum efficiency can be obtained only if: (i) there is no loss due to photorespiration; (ii) there is no alternative  $e^-$  transport; and (iii) both photosystems operate at the absolute maximum photochemical efficiency of  $1 \text{ mol } e^- (\text{mol photons})^{-1}$ . None of these conditions can be met in leaves. Under normal atmospheric conditions, photorespiration accounts for a significant loss of  $\text{CO}_2$  assimilation in  $\text{C}_3$  species as a result of oxygenation of ribulose-1,5-bisphosphate (RuBP). Even for the circumstances where photorespiration is suppressed, e.g. in  $\text{C}_4$  species, or in  $\text{C}_3$  species using a gas mixture of low  $\text{O}_2$  combined with high  $\text{CO}_2$  levels, alternative  $e^-$  transport (either in the cyclic form, or the pseudocyclic form for supporting processes like nitrate reduction) can occur in chloroplasts. Furthermore, neither photosystem [especially not photosystem II (PSII)] can run at absolute maximum photochemical efficiency (Rutherford *et al.*, 2012). Actually, the photochemical efficiency of PSII as revealed by chlorophyll fluorescence for the dark-adapted leaves ( $\Phi_{2\text{DK}}$ ) is generally not higher than 0.83–0.85 (Björkman & Demmig, 1987; Schreiber *et al.*, 1995), although the exact value of  $\Phi_{2\text{DK}}$  is still under debate (Schansker *et al.*, 2014). Also, the photochemical efficiency of PSII under strictly limiting light ( $\Phi_{2\text{LL}}$ ) appears smaller than this (Bernacchi *et al.*, 2003), and is only about  $0.92\Phi_{2\text{DK}}$  (Yin *et al.*, 2014).

Based on the biochemical model of Farquhar *et al.* (1980), Yin *et al.* (2004) described an extended model that analytically integrates the current understandings and uncertainties of  $e^-$  transport-limited photosynthesis (see Supplementary Appendix A available at *JXB* online). The loss of photosynthetic photon efficiency under limiting light can now be quantified well from this model, for both  $\text{C}_3$  and  $\text{C}_4$  photosynthesis. The photon efficiency of photosynthetic  $\text{CO}_2$  assimilation under limiting light ( $\Phi_{\text{CO}_2\text{LL}}$ ) can be derived, from Eqns (A8)–(A10) in Supplementary Appendix A, as:

$$\Phi_{\text{CO}_2\text{LL}} = \frac{\Phi_{2\text{LL}}(C_c - \Gamma^*)(1 - f_{\text{cyc}} - f_{\text{pseudo}})}{4(C_c + 2\Gamma^*)(1 - f_{\text{cyc}} + \Phi_{2\text{LL}}/\Phi_{1\text{LL}})} \quad (1)$$

where  $\Phi_{1\text{LL}}$  and  $\Phi_{2\text{LL}}$  are the photochemical efficiencies of PSI and PSII, respectively, under strictly limiting light;  $f_{\text{cyc}}$  and  $f_{\text{pseudo}}$  are the fraction of total PSI  $e^-$  fluxes that follow the cyclic and pseudocyclic pathways, respectively;  $C_c$  is the  $\text{CO}_2$  level at the carboxylation sites of ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco – the primary  $\text{CO}_2$ -fixing enzyme in the Calvin cycle); and  $\Gamma^*$  is the  $\text{CO}_2$  compensation point, at which the  $\text{CO}_2$  fixation rate is equal to the rate of  $\text{CO}_2$  release by photorespiration. Eqn (1) well quantifies the three physiological reasons as mentioned earlier (i.e. photorespiration, alternative  $e^-$  transport, and the loss of PSII photochemical efficiency) that lead to the quantum yield of  $\text{CO}_2$  assimilation being lower than 0.125. The equation predicts that the maximum  $\Phi_{\text{CO}_2\text{LL}}=0.125$  is achieved if there are: (i) absolute efficiencies (i.e.  $\Phi_{1\text{LL}}=\Phi_{2\text{LL}}=1$ ); (ii) no alternative  $e^-$  transport (i.e.  $f_{\text{cyc}}=f_{\text{pseudo}}=0$ ); and (iii) no photorespiration (i.e.  $\Gamma^*=0$  or  $C_c \rightarrow \text{infinity}$ ).

#### Loss due to primary photochemical inefficiency of photosystems

Eqn (1) can be applied to calculate  $\Phi_{\text{CO}_2\text{LL}}$  of both  $\text{C}_3$  (Yin *et al.*, 2006) and  $\text{C}_4$  (Yin & Struik, 2012) leaves.  $\text{C}_3$  and  $\text{C}_4$

species do not differ much in either  $\Phi_{1\text{LL}}$  or  $\Phi_{2\text{LL}}$ . Although values of  $\Phi_{1\text{LL}}$  and  $\Phi_{2\text{LL}}$  are hard to measure with certainty (Baker *et al.*, 2007), it is generally believed that these values are lower than the absolute efficiency of 1.0. Therefore, the fraction of energy that is lost due to primary photosystems photochemical inefficiency ( $F_{\text{ppi}}$ ) can be derived, based on Eqn (1), as:

$$F_{\text{ppi}} = 1 - \frac{\Phi_{2\text{LL}}(2 - f_{\text{cyc}})}{1 - f_{\text{cyc}} + \Phi_{2\text{LL}}/\Phi_{1\text{LL}}} \quad (2)$$

An interesting emergent property from Eqn (2) is that the loss due to photosystem inefficiencies depends not only on  $\Phi_{1\text{LL}}$  and  $\Phi_{2\text{LL}}$  but also on the other parameter  $f_{\text{cyc}}$ , and  $F_{\text{ppi}}$  becomes totally independent of  $f_{\text{cyc}}$  only if  $\Phi_{2\text{LL}}$  equals  $\Phi_{1\text{LL}}$ , i.e. then  $F_{\text{ppi}}=1-\Phi_{2\text{LL}}$ . However, most likely, the  $\Phi_{2\text{LL}}:\Phi_{1\text{LL}}$  ratio can be assigned as 0.85, to account for the more irretrievable primary loss of PSII, relative to PSI.  $\Phi_{2\text{LL}}$  can be assigned the value of 0.78 ( $=0.85 \times 0.92$ , where 0.85 is the PSII efficiency of dark-adapted leaves  $\Phi_{2\text{DK}}$  and 0.92 is an approximate value for the ratio of  $\Phi_{2\text{LL}}$  to  $\Phi_{2\text{DK}}$ ). Note that these coefficients are only indicative and their exact values are debatable (Rutherford *et al.*, 2012; Schansker *et al.*, 2014). To estimate the loss due to the photosystem inefficiency, we assume that  $f_{\text{cyc}}$  is negligible for  $\text{C}_3$  species (Johnson, 2011). Eqn (2) then predicts that  $F_{\text{ppi}}=0.16$ . The photon efficiency of  $\text{CO}_2$  assimilation  $\Phi_{\text{CO}_2\text{LL}}$  becomes 0.105 because of this loss. As a result, the energy conversion efficiency drops from the maximum 12.3% to 10.3%. In the case of  $\text{C}_4$  species where  $f_{\text{cyc}}$  is much higher,  $\sim 0.45$  (see below), Eqn (2) predicts a lower loss due to photosystem inefficiency, i.e.  $F_{\text{ppi}}=0.14$ . As a result, the energy conversion efficiency drops from the maximum 12.3% to 10.6%. Such a slightly lower loss in  $\text{C}_4$  is expected because the cyclic  $e^-$  transport operates around PSI only, and PSI is more efficient than PSII for  $e^-$  transport. Such a small difference in  $F_{\text{ppi}}$  between  $\text{C}_3$  and  $\text{C}_4$  species can only be identified by the model used here and was not included in previous analyses (e.g. Zhu *et al.*, 2008).

#### Loss due to basal alternative electron transport

In either  $\text{C}_3$  or  $\text{C}_4$  photosynthesis, a basal alternative (including cyclic and pseudocyclic)  $e^-$  pathway occurs, partly as a means for a balanced ATP:NADPH ratio to meet metabolic requirements. The fraction of energy that is lost due to the basal alternative  $e^-$  pathway ( $F_{\text{bep}}$ ) can be derived, also based on Eqn (1), as:

$$F_{\text{bep}} = 1 - \frac{(1 + \Phi_{2\text{LL}}/\Phi_{1\text{LL}})(1 - f_{\text{cyc}} - f_{\text{pseudo}})}{1 - f_{\text{cyc}} + \Phi_{2\text{LL}}/\Phi_{1\text{LL}}} \quad (3)$$

In the absence of cyclic  $e^-$  transport, the equation is simplified as  $F_{\text{bep}}=f_{\text{pseudo}}$ .

For  $\text{C}_3$  plants grown under favourable conditions, there is little cyclic  $e^-$  transport (Johnson, 2011), especially under limiting light ( $f_{\text{cyc}} \rightarrow 0$ ). However, in  $\text{C}_4$  species, a high  $f_{\text{cyc}}$  is essential. Five ATPs and two NADPHs are required to assimilate one  $\text{CO}_2$ , since, in addition to three ATPs required for assimilating 1 mol  $\text{CO}_2$  by the Calvin cycle, two ATPs are required



for the phosphorylation of pyruvate to phosphoenol pyruvate. These two extra ATPs represent a light-energy-driven pump, which transports CO<sub>2</sub> from the outer mesophyll cells and concentrates it at the site of Rubisco in the inner bundle sheath cells (see below). Such extra ATP requirement can be met by high cyclic e<sup>-</sup> transport, and it was estimated that the required  $f_{cyc}$  for the NADP-ME subtype of C<sub>4</sub> photosynthesis (which includes major C<sub>4</sub> annual crops like maize and sorghum) is ~0.45 (Yin & Struik, 2012). There is appreciable non-cyclic e<sup>-</sup> transport in support of processes like nitrate reduction, named here as the *basal pseudocyclic e<sup>-</sup> transport*, in both C<sub>3</sub> and C<sub>4</sub> leaves, which can be estimated by comparing the O<sub>2</sub> evolution rate with the CO<sub>2</sub> fixation rate. Based on such information,  $f_{pseudo}$  for the limiting-light condition was estimated as ~0.10 for C<sub>3</sub> species (Yin *et al.*, 2006) and ~0.07 for C<sub>4</sub> species (Yin & Struik, 2012). This, together with the above-mentioned photosystem inefficiencies, would predict that the photon efficiency of CO<sub>2</sub> assimilation is 0.095 for C<sub>3</sub> species and 0.067 for C<sub>4</sub> species under non-photorespiratory conditions [calculations using Eqn (1)], agreeable with  $\Phi_{CO2LL}$  measured for the same conditions (Björkman & Demmig, 1987; Long *et al.*, 1993). The equivalent energy conversion efficiency drops to 9.4% for C<sub>3</sub> species and to 6.6% for C<sub>4</sub> species, due to the operation of cyclic and basal pseudocyclic e<sup>-</sup> transport. Such a higher energy conversion efficiency in C<sub>3</sub> compared with C<sub>4</sub> type thus far is because  $f_{cyc}$  is much higher in C<sub>4</sub> than in C<sub>3</sub> species.

#### Loss due to photorespiration

There is a substantial loss due to photorespiration in C<sub>3</sub> leaves as a result of the fixation of O<sub>2</sub> by RuBP. Each oxygenation results in 1 mol glycolate, and 2 mol glycolates are metabolized through the photorespiratory cycle, releasing 1 mol CO<sub>2</sub>. This process therefore consumes the recently assimilated CO<sub>2</sub>, and also requires both ATP and NADPH, thereby lowering the efficiency of photosynthesis. Oxygenation competes with carboxylation for Rubisco, so depends on the relative level of CO<sub>2</sub> and O<sub>2</sub> at Rubisco and on the relative CO<sub>2</sub>/O<sub>2</sub> specificity factor of Rubisco ( $S_{c/o}$ ). A high level of O<sub>2</sub> and a low value of  $S_{c/o}$  will favour photorespiration; as such, the CO<sub>2</sub> compensation point ( $\Gamma^*$ ) as defined earlier can be quantified as  $0.5O_2/S_{c/o}$ , where 0.5 refers to 0.5 mol CO<sub>2</sub> released per mol O<sub>2</sub> fixed in photorespiration (Farquhar *et al.*, 1980; Supplementary Appendix A). The fraction for the loss due to photorespiration ( $F_{pr}$ ) can be derived, also based on Eqn (1), as:

$$F_{pr} = 1 - \frac{C_c - \Gamma^*}{C_c + 2\Gamma^*} \quad (4)$$

A typical value of the specificity at 25 °C,  $S_{c/o,25}$ , is ~2.8 mmol O<sub>2</sub> (μmol CO<sub>2</sub>)<sup>-1</sup> (von Caemmerer *et al.*, 1994). However, the specificity decreases, and thus photorespiration increases, with increasing temperature ( $T$ , °C), and this is commonly quantified using the Arrhenius equation (see Supplementary Appendix A). The energy of activation for  $\Gamma^*$  in the Arrhenius equation is ~35 000 J mol<sup>-1</sup> – the average value from several studies (Yin *et al.*, 2014).

For C<sub>3</sub> leaves, there is a gradient between  $C_c$  and the ambient CO<sub>2</sub> level ( $C_a$ ), given the barrier set by stomatal and mesophyll resistances to CO<sub>2</sub> diffusion inside leaves. At the current atmospheric CO<sub>2</sub> level (almost 400 μmol mol<sup>-1</sup>),  $C_c$  in Eqn (1) may be set to ~250 μmol mol<sup>-1</sup> or μbar for the limiting-light conditions. Also, at the standard O<sub>2</sub> level (21% or 210 mmol mol<sup>-1</sup>),  $\Gamma^*$  is 38 (i.e.  $0.5 \cdot 210 / 2.8$ ) μmol mol<sup>-1</sup>. Then the factor  $(C_c - \Gamma^*) / (C_c + 2\Gamma^*)$  in Eqn (4) is 0.65, meaning that photorespiration decreases the C<sub>3</sub> efficiency by ~35%. This would decrease  $\Phi_{CO2LL}$  from 0.095 to 0.061 for C<sub>3</sub> species, and decrease the energy conversion efficiency from 9.4 to 6.0%, if  $T=25$  °C. At a higher temperature, 30 °C,  $\Phi_{CO2LL}$  and the energy conversion efficiency will become 0.054 and 5.4%, respectively.

In a C<sub>4</sub> plant, Rubisco locates in bundle sheath cells where CO<sub>2</sub> is concentrated to a very high value as a result of their coordinated functioning with mesophyll cells. The high  $C_c$  around Rubisco virtually suppresses photorespiration [i.e. the factor  $(C_c - \Gamma^*) / (C_c + 2\Gamma^*)$  approaches 1]; and therefore  $\Phi_{CO2LL}$  in C<sub>4</sub> plants hardly responds to a change in temperature (Ehleringer & Pearcy, 1983). However, this carbon-concentrating mechanism (CCM) operates at the cost of 2 mol extra ATP per CO<sub>2</sub> fixed (see earlier). Under limiting-light conditions, the supply of ATP can be limiting to CCM (Kromdijk *et al.*, 2010; Ubierna *et al.*, 2011; Yin *et al.*, 2011; Bellasio & Griffiths, 2014), which implies that some photorespiration occurs under limiting light. Following Amthor (2010), 0.015 is assumed here as the  $\Gamma^*:C_c$  ratio; then  $\Phi_{CO2LL}$  will drop slightly, from 0.067 to 0.064, and the energy conversion efficiency will be reduced from 6.6 to 6.3%. These values are very similar to those for C<sub>3</sub> plants at 25 °C for the current atmospheric CO<sub>2</sub> level.

#### Additional constraints for non-limiting-light conditions

The above analysis applies to limiting-light conditions where photosynthesis increases almost linearly with increasing light. Such a linear relationship breaks under non-limiting-light conditions, where photosynthesis increases with light in a diminishing way. Such a diminishing return is caused by the fact that the photosynthetic rate beyond the moderate light level is increasingly limited by the capacity of photosynthetic enzymes (such as Rubisco) or the capacity of other processes. A full photosynthetic light response curve has a convex saturation shape. Therefore, absorbed light energy has an increasing portion not utilized for CO<sub>2</sub> assimilation. When the absorbed light energy exceeds the capacity of the plant to use the trapped energy, damage to photosystems (especially PSII) may occur. To avoid photodamage, plants develop several photoprotective mechanisms, and two major ones are discussed here: non-photochemical quenching and additional alternative electron-utilizing pathways.

#### Loss due to non-photochemical quenching (NPQ)

NPQ refers to the process of dissipation of the excess excitation energy in the PSII antennae as heat, whereby down-regulation of PSII electron transport efficiency is triggered (e.g. Verhoeven *et al.*, 1997). This is a major photoprotection

mechanism when the exposed light intensity is higher than the capacity of energy utilization as set by photosynthetic metabolisms. The full biophysical and molecular mechanism of energy dissipation within PSII is yet to be resolved. Measurements on PSII photochemical efficiency ( $\Phi_2$ ) should enable us to quantify the changes in magnitude of the loss due largely to NPQ across various light levels. Data of  $\Phi_2$  across a spectrum of light intensities can now be routinely assessed by chlorophyll fluorescence (Baker *et al.*, 2007; Murchie & Lawson, 2013) and be converted to the rate of PSII  $e^-$  transport ( $J_2$ ). It has been shown extensively that  $\Phi_2$  decreases with increasing light (Yin *et al.*, 2014) and that  $\Phi_1$  decreases almost in parallel with  $\Phi_2$  (Baker *et al.*, 2007). When converted to  $J_2$ , a saturation type of curve is obtained for  $J_2$  in response to absorbed light intensity,  $I_{\text{abs}}$ , which can be described by Eqns (A9) and (A10) in Supplementary Appendix A. The deviation of  $J_2$  from the line of  $\alpha_{2LL}I_{\text{abs}}$  (where  $\alpha_{2LL}$  is the photochemical efficiency of PSII under limiting light on the basis of both PSI and PSII absorbed light) should be attributed to the loss primarily due to NPQ. The fraction of the energy that is lost via NPQ ( $F_{\text{npq}}$ ) can be expressed as:

$$F_{\text{npq}} = 1 - \frac{J_2}{\alpha_{2LL}I_{\text{abs}}} \quad (5)$$

#### Loss due to additional alternative electron transport

Although NPQ makes  $\Phi_2$  decline with increasing irradiance, the resulting  $e^-$  flux may still be in excess of the requirement set by the capacity of photosynthetic metabolism. There are  $e^-$  utilizing pathways as protection mechanisms, notably the route where non-cyclic electrons are transferred to  $O_2$  for direct  $O_2$  reduction by PSI, through the Mehler ascorbate peroxidase pathway (Asada, 1999; Driever & Baker, 2011). The underlying  $e^-$  transport of this Mehler-type pathway is termed *additional pseudocyclic  $e^-$  transport* in order to distinguish it from the earlier defined *basal pseudocyclic  $e^-$  transport* in support of processes like nitrate reduction.

Within the framework of the model of Farquhar *et al.* (1980), the actual gross photosynthetic rate is quantified as the minimum of the  $e^-$  transport-limited rate ( $A_{g,j}$ ) and the Rubisco-limited rate ( $A_{g,c}$ ) (Supplementary Appendix A). In the absence of the additional  $e^-$  pathways, one expects that the gross photosynthesis is  $A_{g,j}$ , i.e.  $[(C_c - \Gamma^*) / (C_c + 2\Gamma^*)]J/4$ . If  $A_{g,c}$  is the limiting rate, part of the available electrons must be used for Mehler-type pathways, and the fraction of the energy that is lost via these additional alternative electron-utilizing pathways ( $F_{\text{aep}}$ ) can then be simply expressed as:

$$F_{\text{aep}} = 1 - \frac{\min(A_{g,j}, A_{g,c})}{A_{g,j}} \quad (6)$$

However, the Mehler-type reaction is hardly significant (Ruuska *et al.*, 2000), in either  $C_3$  or  $C_4$  species (Driever & Baker, 2011). Archontoulis *et al.* (2012) suggest that in some cases the entire light response curve can be well described by  $A_{g,j}$ . Except for lower ranges of  $[CO_2]$ , a large part of the  $[CO_2]$  response curve can also be described by  $A_{g,j}$ . These

cases indicate that if extra energy is dissipated via NPQ, there is little need to engage the Mehler-type reaction and  $F_{\text{aep}}$  should generally be negligible. Eqn (6) should be used with care if  $[CO_2]$  is very low because the model of Farquhar *et al.* (1980) takes no account of the decrease of  $J$  with decreasing  $[CO_2]$ , a trend that has frequently been observed (e.g. Cheng *et al.*, 2001). This issue is not relevant for our analysis on the situation at the current atmospheric  $[CO_2]$ .

#### Synthesis for the leaf level

Here, we used a set of parameters to illustrate an integrated response of leaf photosynthesis under an atmospheric  $CO_2$  condition, modelled from Eqns (A1), (A2), and (A8)–(A10) in Supplementary Appendix A. Although Rubisco kinetic parameters (catalytic rate,  $S_{c/o}$ ,  $K_{mC}$ , and  $K_{mO}$ ) may differ between  $C_3$  and  $C_4$  species, they are assumed to be the same (Table 1). Thus, unless specified, the primary  $C_3$  and  $C_4$  difference is modelled in this paper to be in  $C_c$  and  $f_{\text{cyc}}$  (Table 1), to mimic the CCM in  $C_4$  photosynthesis and its associated extra ATP cost that should predominantly come from higher cyclic electron transport (Yin & Struik, 2012). Values of  $\chi_{V_{\text{max}}}$  and  $\chi_{J_{\text{max}}}$  [see Eqn (A7) in Supplementary Appendix A] were adjusted so that the modelled value for light-saturated photosynthesis was  $\sim 27$  and  $40 \mu\text{mol m}^{-2} \text{s}^{-1}$  (Fig. 1), commonly observed for healthy leaves of  $C_3$  and  $C_4$  annual crops, respectively. Fig. 1 also illustrates the full light response curve of PSII  $e^-$  transport rate ( $J_2$ ) and the corresponding values of  $F_{\text{npq}}$  (Fig. 1).

With the convex shape in the non-linear light response, the intrinsic efficiency of  $e^-$  transport in either  $C_3$  or  $C_4$  types declines with increasing light. Because of the higher  $f_{\text{cyc}}$ ,  $\alpha_{2LL}$  is lower in  $C_4$  than in  $C_3$  species [see Eqn (A10) in Supplementary Appendix A]. This predicts a significantly lower  $J_2$  in the subsaturating light range for  $C_4$  species (Fig. 1a), despite using the same curvature factor  $\theta$  and  $J_{\text{max}}$  for Eqn (A9) in Supplementary Appendix A. As a consequence, the predicted  $F_{\text{npq}}$  is significantly lower in  $C_4$  than in  $C_3$  species (Fig. 1b), as more light energy is quenched by the cyclic  $e^-$  transport in  $C_4$  species. There is only a small difference between the modelled  $C_3$  and  $C_4$  photosynthetic rates in the light-limited region (Fig. 1c), because the gain from CCM in suppression of photorespiration is largely cancelled out by the loss due to its extra ATP requirements in  $C_4$  leaves. The difference is larger in the light-saturating region. The modelled curve reaches saturation at lower light levels in  $C_3$  than in  $C_4$  type (Fig. 1c), in line with the shape for the light response of  $J_2$  in the two types of photosynthesis (Fig. 1a). The combination of suppressing photorespiration and the relatively lower  $F_{\text{npq}}$  makes the light response curve more linear in  $C_4$  than in  $C_3$  species (Fig. 1c), suggesting that the advantage of  $C_4$  versus  $C_3$  type in energy conversion becomes increasingly significant with increasing light intensity.

#### Scaling up to, and constraints for, daily canopy photosynthesis

Most reports (e.g. Zhu *et al.*, 2008; Amthor, 2010) have been on the potential maximum efficiency of solar energy

**Table 1.** The 'default' and 'achievable' parameter values, the corresponding calculated efficiency of converting solar energy into phytoenergy, and the reduction in the 'achievable' conversion efficiency if a parameter stays at its default value, in C<sub>3</sub> and C<sub>4</sub> crops

| Scale  | Symbol            | Definition (unit)  | Default  | Achievable <sup>a</sup>                                    | Reduction(%) <sup>b</sup> |                |     |
|--|-------------------|--|--|--|---------------------------|----------------|-----|
|  |                   |  |  |  | C <sub>3</sub>            | C <sub>4</sub> |     |
| Leaf   | $\Phi_{1LL}$      | PSI photochemical efficiency under limiting light (mol mol <sup>-1</sup> )                         | 0.92   | 1.00   | 3.1                       | 4.6            |     |
|  | $\Phi_{2LL}$      | PSII photochemical efficiency under limiting light (mol mol <sup>-1</sup> )                        | 0.78   | 0.85   | 3.7                       | 3.1            |     |
|  | $f_{cyc}$         | Fraction of PSI e <sup>-</sup> flux that follows cyclic e <sup>-</sup> transport (-)               | 0.00 (C <sub>3</sub> ), 0.45 (C <sub>4</sub> )                             | -  | -                         | -              |     |
|  | $f_{pseudo}$      | Fraction of PSI e <sup>-</sup> flux that follows pseudocyclic e <sup>-</sup> transport (-)         | 0.10 (C <sub>3</sub> ), 0.07 (C <sub>4</sub> )                             | -  | -                         | -              |     |
|  | $K_{mCO_2}$       | Michaelis-Menten constant of Rubisco for CO <sub>2</sub> at 25°C (μbar)                            | 275  | -  | -                         | -              |     |
|  | $K_{mO_2}$        | Michaelis-Menten constant of Rubisco for O <sub>2</sub> at 25°C (mbar)                             | 180  | -  | -                         | -              |     |
|  | $S_{c/o25}$       | Relative CO <sub>2</sub> /O <sub>2</sub> specificity of Rubisco at 25°C (mbar μbar <sup>-1</sup> ) | 2.8  | - <sup>c</sup>   | -                         | -              |     |
|  | $\theta$          | Convexity of the response for e <sup>-</sup> transport rate to light (-)                           | 0.80   | 0.95   | 10.8                      | 8.5            |     |
|  | $\chi_{V_{cmax}}$ | Slope of the linearity between $V_{cmax25}$ and $n-n_b$ (μmol g <sup>-1</sup> N s <sup>-1</sup> )  | 55   | 70   | 0.0                       | 0.0            |     |
|  | $\chi_{J_{max}}$  | Slope of the linearity between $J_{max25}$ and $n-n_b$ (μmol g <sup>-1</sup> N s <sup>-1</sup> )   | 80   | 100  | 6.0                       | 2.8            |     |
|  | $C_c$             | CO <sub>2</sub> level at the carboxylation sites of Rubisco (μbar)                                 | 210 (C <sub>3</sub> ), 1500 (C <sub>4</sub> )                              | -  | -                         | -              |     |
|  | $n_b$             | Base leaf nitrogen content (g N m <sup>-2</sup> leaf)  | 0.3  | -  | -                         | -              |     |
|  | Canopy            | $N$  | Total leaf nitrogen in canopy (g N m <sup>-2</sup> ground)                 | 12   | -                         | -              | -   |
|  |                   | $L_{max}$  | Maximum LAI in growing season (m <sup>2</sup> leaf m <sup>-2</sup> ground) | 7  | 12                        | 5.5            | 7.9 |
| $k_L$  |                   | Extinction coefficient of PAR in canopy (m <sup>2</sup> ground m <sup>-2</sup> leaf)               | 0.6  | 0.3  | 10.2                      | 4.2            |     |
| $k_n$  |                   | Extinction coefficient of ( $n-n_b$ ) in canopy (m <sup>2</sup> ground m <sup>-2</sup> leaf)       | 0.35 $k_L$   | 0.95 $k_L$   | 9.5                       | 4.7            |     |
| $f_{dir}$  |                   | Fraction of total incoming PAR being direct (-)  | 0.5  | -  | -                         | -              |     |
| $\sigma$   |                   | Leaf scattering coefficient (-)  | 0.05   | -  | -                         | -              |     |
| $\rho_{cb}$  |                   | Canopy reflection coefficients for direct-beam light (-)   | 0.05   | -  | -                         | -              |     |
| $\rho_{cd}$  |                   | Canopy reflection coefficients for diffuse light (-)   | 0.05   | -  | -                         | -              |     |
| $t_e$  |                   | Time at the end of a day (h)   | 15.0   | -  | -                         | -              |     |
| $t_m$  |                   | Time at which incoming PAR is highest in a day (h)   | 7.5  | -  | -                         | -              |     |
| Crop   | $t_e$             | Time at which LAI is at its maximum (d)  | 80   | -  | -                         | -              |     |
|  | $t_m$             | Time at which the increment in LAI is maximal (d)  | 40   | -  | -                         | -              |     |
|  | $F_{cover}$       | Fraction of the energy lost due to incomplete canopy cover (-)                                     | 0.25 (C <sub>3</sub> ), 0.20 (C <sub>4</sub> )                             | 0.15   | 11.8                      | 5.9            |     |
|  | $R:P$             | Season-long crop respiration: photosynthesis ratio (-)   | 0.30   | 0.25   | 6.7                       | 6.7            |     |
| Overall efficiency of converting incident solar radiation into phytoenergy (%) |                   |  | 2.2 (C <sub>3</sub> ), 3.0 (C <sub>4</sub> )                               | <b>3.6</b> (C <sub>3</sub> ), <b>4.1</b> (C <sub>4</sub> ) |                           |                |     |

<sup>a</sup> The achievable parameter value with improvement via future breeding or engineering approaches; the symbol '-' in this column means no change from the default value.

<sup>b</sup> The percentage reduction (%) relative to the overall 'achievable efficiency' (the bold values) if the parameter was set to retain at its default value; the symbol '-' in this column corresponds to those parameters for which no 'achievable' value was proposed.

<sup>c</sup> Although  $S_{c/o}$  can be improved, we assumed it to be the same as the default value because an improvement in  $S_{c/o}$  may be at the cost of decreasing  $V_{cmax}$  (e.g. Kubien *et al.*, 2008).

conversions, thereby focusing the analysis on the leaf level. On the basis of the same amount of incoming solar radiation, the energy conversion efficiency of the canopy could be higher or lower than that of a horizontal leaf. On the one hand, the loss due to light scattering, reflection, and transmission for a canopy can be smaller than that for a horizontal leaf, because the light unabsorbed by upper leaves can be captured by lower leaves in the canopy. On the other hand, the percentage of captured incoming radiation by canopy depends on the leaf area index (LAI) of the canopy (Boote & Loomis, 1991). For a full canopy when LAI is high, parts of leaves are shaded by other leaves that receive directly incoming solar radiation. Shaded leaves are often light limited (so, as discussed earlier,  $F_{ppi}$ ,  $F_{bep}$ , and  $F_{pr}$  may apply therein), whereas sunlit leaves are mostly exposed to non-limiting-light conditions (so, as discussed earlier,  $F_{npq}$  and  $F_{aep}$  as additional losses apply). We first explain canopy physiology to simply, yet accurately, quantify canopy gross photosynthesis ( $A_{canopy}$ ).

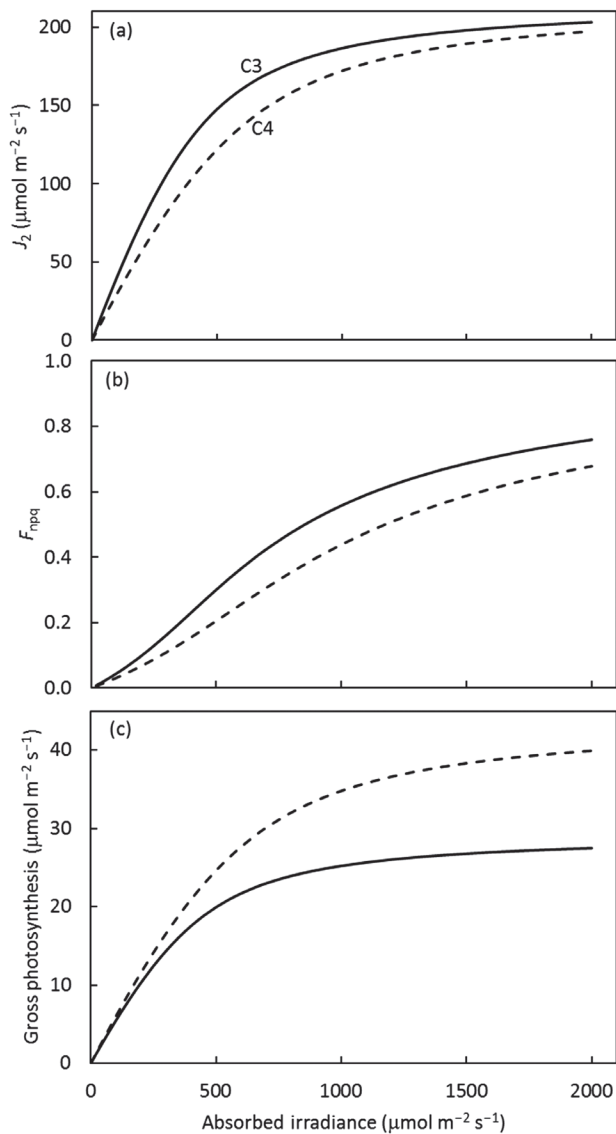
Because of the convex shape in the light response curve of e<sup>-</sup> transport rate and the limit of photosynthetic capacity set

either by Rubisco activity or by e<sup>-</sup> transport capacity (Fig. 1), a spatial extension from leaf to canopy photosynthesis cannot be done simply by using irradiance averaged over the whole canopy, as this approach would cause a substantial overestimation of canopy photosynthesis. At a minimum, separating a canopy into sunlit and shaded leaves has long been considered essential for accurate prediction of  $A_{canopy}$  (Sinclair *et al.*, 1976; de Pury & Farquhar, 1997). In addition, the profile of leaf photosynthetic resources should be considered, leaf nitrogen (N) in particular (Hammer & Wright, 1994), as these determine photosynthetic capacity parameters  $V_{cmax}$  and  $J_{max}$  of individual leaf layers [Harley *et al.*, 1992; see Eqn (A7) in Supplementary Appendix A]. The profile of leaf N tends to be similar to that of irradiance in canopies, as a result of leaf acclimation to the light environment (Moreau *et al.*, 2012). However, unlike the optimized leaf N profile that is the basis for the simple 'big-leaf' models (e.g. Sands, 1995) for calculating  $A_{canopy}$ , the leaf N profile is often more uniform than the profile of irradiance in canopies (e.g. Anten *et al.*, 1995; Archontoulis *et al.*, 2011); Buckley *et al.* (2013)



provided theoretical explanations for the difference in leaf N and irradiance profiles. For these reasons, the ‘big-leaf’ model does not suffice for the required accuracy. A more sophisticated yet analytical model that treats sunlit and shaded leaves separately, i.e. the sun/shade model of de Pury & Farquhar (1997; see Supplementary Appendix B available at *JXB* online), is used here, where  $A_{\text{canopy}}$  is the sum of gross photosynthetic rates from sunlit and shaded parts of the canopy.

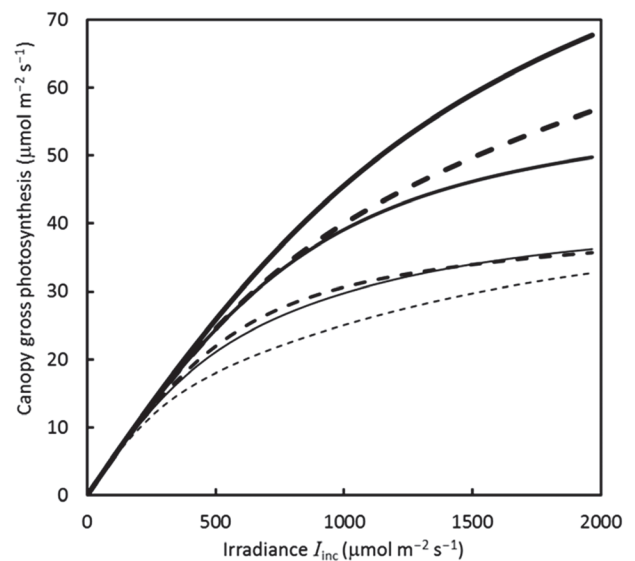
Nevertheless, it is known that  $A_{\text{canopy}}$  can be improved if the leaf N profile follows the light profile (Anten *et al.*, 1995; Sands, 1995), i.e. the photosynthetically active leaf N extinction coefficient  $k_n$  is equal to the light extinction coefficient  $k_L$  – one of the assumptions that the ‘big-leaf’ model takes. This is in analogy to the optimization of the local photosynthetic capacity profile to match the light gradient inside a leaf (Farquhar, 1989). We shall call such a canopy the fully acclimated canopy. Archontoulis *et al.* (2011) observed experimentally that, in actual canopies,  $k_n$  is  $\sim 0.35k_L$ , depending on species, growth stage, and growth



**Fig. 1.** Modelled irradiance response curves of PSII electron transport rate  $J_2$  (a), the fraction of energy lost due to non-photochemical quenching  $F_{\text{npq}}$  (b), and gross rate of leaf photosynthesis (c), in  $C_3$  (solid lines) and  $C_4$  (dashed lines) crop species.

environments. Using a standard set of parameter values (Table 1), simulations with the sun/shade model of de Pury & Farquhar (1997) show that the difference between calculated  $A_{\text{canopyAcclim}}$  (gross photosynthesis of a fully acclimated canopy) and  $A_{\text{canopy}}$  depends of course on the actual difference between  $k_n$  and  $k_L$ , but also on light level, the fraction of direct light in the total light ( $f_{\text{dir}}$ ), and total canopy N ( $N$ ) (Fig. 2). For a given full canopy (say  $\text{LAI}=7 \text{ m}^2 \text{ m}^{-2}$ ), the largest difference between  $A_{\text{canopy}}$  and  $A_{\text{canopyAcclim}}$  is found at saturation light levels and when  $f_{\text{dir}}$  approaches 1 (Fig. 2). For this illustration in Fig. 2, we used the same  $k_L$  value for direct and diffuse lights for practicality (see Hikosaka, 2014), although in reality  $k_L$  differs for the two types of lights (de Pury & Farquhar, 1997) and may change rapidly with sun track and cloudiness in the field.

The impact of light level on the difference between  $A_{\text{canopy}}$  and  $A_{\text{canopyAcclim}}$  is due to the fact that parameters  $V_{\text{max}}$  and  $J_{\text{max}}$  determining light-saturated photosynthesis do, whereas those determining light-limited photosynthesis do not, vary with the leaf N level. Given such an impact of light level, it is more meaningful to investigate the difference between  $A_{\text{canopy}}$  and  $A_{\text{canopyAcclim}}$  on the basis of their daily total. Also, because of the convex nature in photosynthetic irradiance response (Fig. 1c), non-uniform distribution of radiation among various moments of the daytime means that the actual daily total of canopy photosynthesis is lower than that calculated using the daytime average irradiance (Boote & Loomis, 1991). Therefore, it is important to use instantaneous irradiance for calculating instantaneous canopy photosynthesis rates ( $A_{\text{canopy},i}$ ;  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ) and then integrate  $A_{\text{canopy},i}$  into daily total ( $A_{\text{canopy,daily}}$ ;  $\text{mol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ). This can be done on an hourly basis as such:  $A_{\text{canopy,daily}} = (10^{-6}) \sum_{i=0}^D (3600 A_{\text{canopy},i})$ , where  $D$  is daylength (h). For simplicity of illustration, a quadratic equation [Eqn



**Fig. 2.** Modelled instantaneous gross photosynthesis for non-acclimated (dashed lines) and acclimated canopies (solid curves) in  $C_3$  crops in response to incident irradiance  $I_{\text{inc}}$ , under three combinations of direct-light fraction ( $f_{\text{dir}}$ ) and leaf-nitrogen content in canopy ( $N$ ). Thickest lines:  $f_{\text{dir}}=0.50$ ,  $N=12 \text{ g m}^{-2}$ ; thinnest lines:  $f_{\text{dir}}=0.50$ ,  $N=6 \text{ g m}^{-2}$ ; and the medium lines:  $f_{\text{dir}}=0.95$ ,  $N=12 \text{ g m}^{-2}$ . For all cases,  $\text{LAI}=7 \text{ m}^2 \text{ m}^{-2}$  and the light extinction coefficient  $k_L=0.6 \text{ m}^2 \text{ m}^{-2}$ .

(C2) in Supplementary Appendix C available at *JXB* online; based on Yin *et al.*, 2003] is used here to estimate the daytime course of instantaneous PAR for a given amount of daily total PAR. A non-symmetric distribution of PAR may also be dealt with by using the general equations in Supplementary Appendix C. The same procedure can be used to calculate  $A_{\text{canopyAcclim,daily}}$  by setting  $k_n=k_L$ .

We now show the enhancement by canopy photosynthesis, relative to the rate of an uppermost leaf when horizontal ( $A_{\text{upper-leaf}}$ ), for the case of an average  $f_{\text{dir}}=0.5$ , a typical sunny day having a daily PAR of  $10 \text{ MJ m}^{-2}$ , and a typical full green canopy of  $\text{LAI}=7 \text{ m}^2 \text{ m}^{-2}$ ,  $N=12 \text{ g m}^{-2}$ , and  $k_L=0.6 \text{ m}^2 \text{ m}^{-2}$ . Such an enhancement can be clearly seen in non-acclimated canopy during middle-day hours, during which leaf photosynthesis is light saturated whereas canopy photosynthesis, as whole, is not (Fig. 3a). However, the magnitude of enhancement (quantified as the  $A_{\text{canopy}}:A_{\text{upper-leaf}}$  ratio) depends on the closeness of  $k_n$  to  $k_L$ , and also on photosynthesis type and the daylength when integrating for a daily total. As expected,  $A_{\text{canopy,daily}}$  is much higher in the  $C_4$  than in the  $C_3$  type (Fig. 3b). However, canopy photosynthesis has a lower enhancement ratio in  $C_4$  than in  $C_3$  (Fig. 3c), because the light response curve of leaf photosynthesis is more linear in  $C_4$  than in  $C_3$  type (Fig. 1). The potential enhancement ratio can be obtained when comparing  $A_{\text{canopyAcclim,daily}}$  with  $A_{\text{upper-leaf,daily}}$  (Fig. 3c). Both enhancement ratios decline with daylength, and this daylength dependence can be explained by decreasing canopy:leaf photosynthesis ratio with decreasing light

intensity (indirectly shown in Fig. 3a), because a longer day makes lower PAR  $\text{s}^{-1}$  for a given amount of daily PAR. A linear model, such as a light use efficiency model (DeLucia *et al.*, 2014), is unable to account for such an effect of daylength.

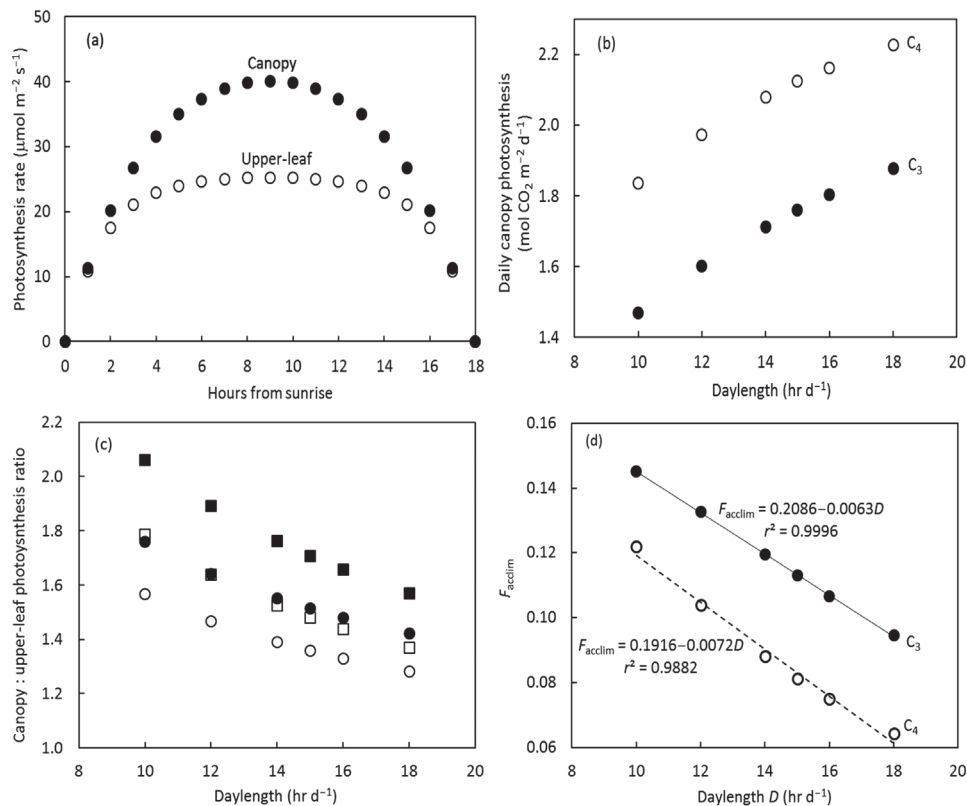
When  $A_{\text{canopy,daily}}$  and  $A_{\text{canopyAcclim,daily}}$  are estimated, one can also calculate the fraction of energy loss due to the absence of the full acclimation,  $F_{\text{acclim}}$ :

$$F_{\text{acclim}} = 1 - \frac{A_{\text{canopy,daily}}}{A_{\text{canopyAcclim,daily}}} \quad (7)$$

The calculated  $F_{\text{acclim}}$  declines almost linearly with daylength  $D$ , ranging from 0.15 to 0.10 for  $C_3$  species, and from 0.12 to 0.06 for  $C_4$  species if daylength varies from 10 to 18 h (Fig. 3d). This dependence on daylength can be explained by decreasing  $A_{\text{canopy}} - A_{\text{canopyAcclim}}$  difference with decreasing light intensity as shown in Fig. 2, and, as just stated, a longer day lowers instantaneous PAR values for a given amount of daily PAR. Our result suggests less benefit from canopy acclimation in  $C_4$  than in  $C_3$  species, which again can be explained by the more linear light response curve of leaf photosynthesis in  $C_4$  than in  $C_3$  species.

### Constraints for season-long canopy photosynthesis

When extended to a growing season, the above discussed effect due to hourly variation in radiation also applies to day-to-day fluctuations of incoming radiation. However, in this section



**Fig. 3.** (a) Diurnal course of  $C_3$  horizontal upper-leaf (open circles) and non-acclimated canopy (filled circles) photosynthesis. (b) Daily (non-acclimated) canopy photosynthesis rate of  $C_3$  and  $C_4$  types. (c) Canopy enhancement, defined as the ratio of daily canopy photosynthesis (squares: acclimated canopy; circles: non-acclimated canopy) to daily upper-leaf photosynthesis in both  $C_3$  (filled symbols) and  $C_4$  (open symbols) types. (d) The estimated values of  $F_{\text{acclim}}$  according to Eqn (7). For the acclimated canopy, nitrogen extinction coefficient  $k_n$ =light extinction coefficient  $k_L$ ; for non-acclimated canopy,  $k_n=0.35k_L$  (see text). Total daily PAR= $10 \text{ MJ m}^{-2} \text{ d}^{-1}$ , direct-light fraction  $f_{\text{dir}}=0.5$ ,  $k_L=0.6$ , LAI= $7 \text{ m}^2 \text{ m}^{-2}$ , and canopy leaf-N= $12 \text{ g m}^{-2}$ .



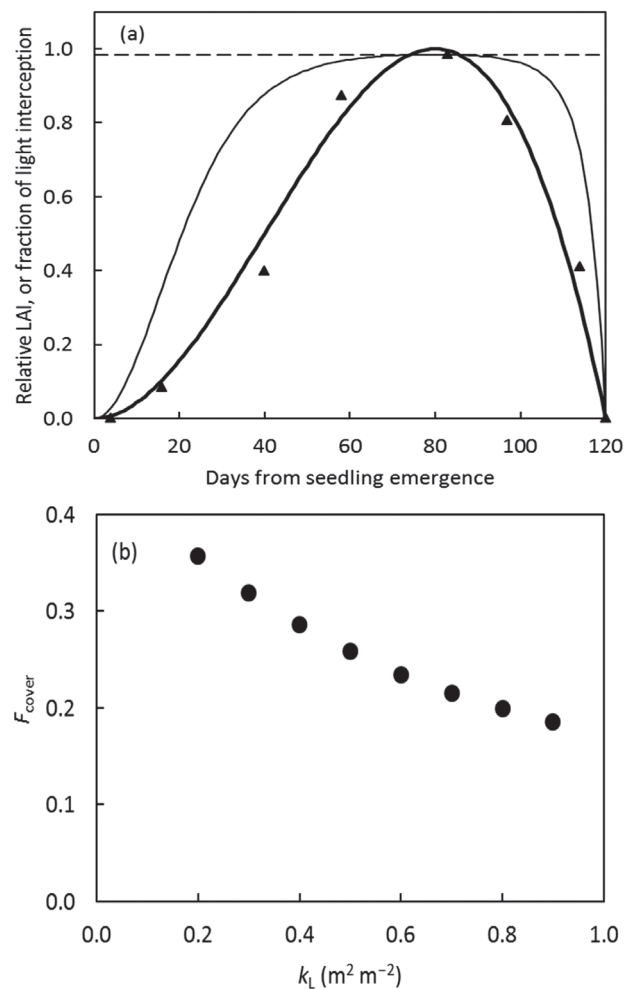
we focus the analysis on the impact of canopy dynamics during the season, which is an important part of crop ecology. The analysis reported by [Zhu \*et al.\* \(2008\)](#) and [Amthor \(2010\)](#) did not consider the energy loss due to incomplete interception of incoming radiation when LAI is low. When we estimate solar energy conversion efficiency of annual arable crops, we cannot ignore this loss, as interception of incoming radiation is incomplete, either during crop establishment or during canopy senescence towards crop maturity. The incomplete canopy cover is also the major reason why biomass yield is lower in the first establishing year than in the succeeding years of perennial crops ([Beale & Long, 1995](#); [Dohleman & Long, 2009](#)).

A good way to estimate the loss due to incomplete canopy closure is to run a crop model and then compare the simulated crop biomass at maturity for an actual field situation with the simulated biomass by setting LAI during the growing season constantly equal to the maximum LAI. Simulations using the GECROS model ([Yin & van Laar, 2005](#)) showed that the loss due to incomplete canopy closure is  $\sim 0.25\text{--}0.30$  (results not shown).

If daily incoming solar radiation fluctuates little among days (e.g. during a dry-season in the tropics), one may use a more practical approach based on a bell-shaped time course of LAI and the Lambert–Beer law to estimate the percentage of light interception. A typical time course of LAI,  $L_{(t)}$ , of a healthy crop can be described by Eqn (C6) in [Supplementary Appendix C](#), in which LAI is modelled to grow fastest at day  $t_m$ , and reaches its maximum  $L_{\max}$  at day  $t_e$  and zero at both seedling emergence and crop maturity at day  $2t_e - t_m$ . A typical time course of  $L_{(t)}$ , relative to  $L_{\max}$ , is given in [Fig. 4a](#). The equivalent time course of an estimated fraction of light interception is shown there as  $(1 - e^{-k_L L_{(t)}})$ , which holds if for a practical reason ([Hikosaka 2014](#)) the same  $k_L$  is used for direct and diffuse light. Obviously large fractions of incoming irradiance are not intercepted in both early and later phases of growing season, thereby significantly decreasing incident solar energy use efficiency. Loss due to incomplete cover,  $F_{\text{cover}}$ , during a growing season (i.e. from day 0 to day  $2t_e - t_m$ ), can be calculated according to:

$$F_{\text{cover}} = 1 - \frac{\sum_{t=0}^{2t_e - t_m} [1 - e^{-k_L L_{(t)}}]}{(2t_e - t_m)(1 - e^{-k_L L_{\max}})} \quad (8)$$

Calculations for a 120-d crop (where  $t_m=40$  d and  $t_e=80$  d) show that, on average, the factor of  $F_{\text{cover}}$  is  $\sim 0.25$ , in line with the above-mentioned result using a full crop simulation model. This consistency means that Eqn (8) is valid although it does not account for the change in leaf photosynthetic capacity during the growing season, largely because the effect of the lower leaf photosynthetic capacity towards maturity than at  $t_e$  roughly cancels out the effect of higher leaf photosynthetic capacity in early growth phase than at  $t_e$ . The calculated value of  $F_{\text{cover}}$  also depends on  $k_L$ : it increases with decreasing  $k_L$  ([Fig. 4b](#)). For  $C_4$  species, one may expect that  $F_{\text{cover}}$  is a little lower, because leaf area growth is probably faster and  $L_{\max}$  can be higher, as a result of higher leaf and canopy photosynthesis, relative to  $C_3$  species.



**Fig. 4.** (a) Typical seasonal time course of relative leaf area index (relative to its maximum value  $L_{\max}$ ) described by Eqn (C4) in [Supplementary Appendix C](#) (thick curve) or experimentally measured values (triangles), of the corresponding fraction of light interception (thin curve), and the expected fraction of light interception if leaf area index remains as  $L_{\max}$  (horizontal dashed line), where  $L_{\max}=7$  and light extinction coefficient  $k_L=0.6$ . (b) The estimated value of  $F_{\text{cover}}$  according to Eqn (8) in relation to the value of  $k_L$ .

### Loss caused by crop respiration

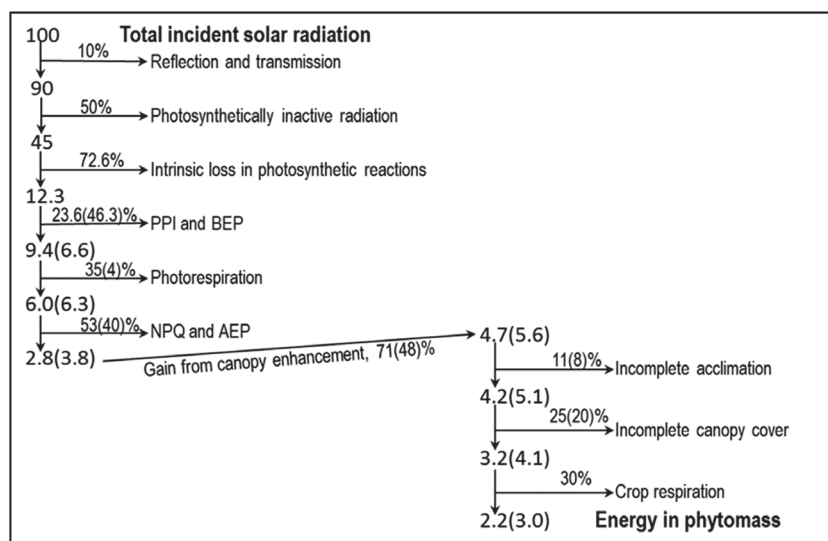
Photosynthesizing leaves respire, and there are various methods to estimate the loss associated with this leaf respiration in the light. While ‘leaf respiration in the light’ is an important parameter in analysing leaf gas exchange measurements ([Farquhar \*et al.\*, 1980](#)), it is usually lumped into total crop respiration for the purpose of crop modelling ([Goudriaan & van Laar, 1994](#)). Conventionally, crop respiration is partitioned into growth respiration and maintenance respiration components ([Penning de Vries \*et al.\*, 1989](#)). Based on theoretical and experimental evidence, [Cannell & Thornley \(2000\)](#) proposed a framework that recognizes individual relationships between respiration and each distinguishable biochemical process that it supports. In this general framework, nine component processes are distinguished: growth, symbiotic di-nitrogen fixation, nitrogen uptake, nitrate reduction, other ion uptake, phloem loading, protein turnover, maintenance of cell ion concentrations and gradients, and any wasteful respiration.

The first six of the nine processes can be quantifiable. For the last three, together equivalent to the old classification of maintenance respiration (Penning de Vries *et al.*, 1989), it is less easy to quantify them, but is empirically related better to total amount of N than to total biomass of the crop (Cannell & Thornley, 2000). Differences in biochemical composition of biomass among species can be accounted for in calculating growth efficiency (Penning de Vries *et al.*, 1989; Amthor, 2010). This framework, when implemented in the GECROS crop model (Yin & van Laar, 2005), predicts that the ratio of daily crop respiration to daily canopy gross photosynthesis depends on the day of the season, but overall the ratio of season-long respiration to season-long gross photosynthesis ( $R:P$ ) is  $\sim 0.30$ – $0.35$ . This is largely in line with the conservative empirical observation for this ratio (e.g. Gifford, 1995). Recent updates by Amthor (2010) from mechanistic analysis of respiration give a similar value for the  $R:P$  ratio. However, the  $R:P$  ratio differs among crops (Gifford, 2003). While a ratio of 0.30 applies for general annual crops (Zhu *et al.*, 2008), a higher value may be used for oil or legume crops because of a higher carbon cost for their biomass synthesis or/and additional cost for di-nitrogen fixation. Furthermore, the value for the ratio may increase if the temperature goes beyond a certain high level.

## Synthesis from leaf to canopy and crop

Traditionally, crop energy conversion is evaluated in a linear step-wise routine, in which the fate of solar radiation incident on a plant community is traced through a single series of processes or steps, each step is evaluated for its output:input ratio, and the overall efficiency is determined by multiplying the efficiencies of individual steps (Monteith, 1972). In this

study, a two-series (first for leaf level, then for canopy and crop) framework is proposed (Fig. 5), which provides a more realistic picture on where energy losses and gains occur during the growth of annual crops, although its steps do not necessarily reflect the time sequence of some biochemical processes involved. Because of a non-linear feature in the light response of photosynthesis, the framework emphasizes that the efficiencies should be evaluated considering the diurnal course of incident PAR, rather than only calculating the efficiencies for the limiting-light condition. From the same reason, the scaling up from leaf to canopy level should account for the fact that different parts of the canopy receive different intensities of PAR. The analysis showed that the efficiency in converting a given amount of PAR to  $\text{CH}_2\text{O}$  at both leaf and canopy levels depends on daylength. For 15 h daylength, average energy conversion of a healthy green leaf in a day of  $20 \text{ MJ m}^{-2}$  solar radiation is  $\sim 2.8$  and  $3.8\%$  for a  $\text{C}_3$  and  $\text{C}_4$  plant, respectively. The equivalent energy conversion of a full canopy (LAI=7) is maximally  $\sim 4.7$  and  $5.6\%$ , respectively. These values may be decreased to  $4.2$  and  $5.1\%$ , respectively, because the vertical profile of photosynthetic resources (like N) is not fully acclimated with the PAR profile in a canopy. From a season-long growth perspective, incomplete PAR interception during early and late season could result in  $\sim 20$ – $25\%$  loss. Considering  $30\%$  loss due to crop respiration, energy conversion efficiency drops to  $\sim 2.2$  and  $3.0\%$  for  $\text{C}_3$  and  $\text{C}_4$  crops, respectively (Fig. 5). These estimations are comparable with the highest solar energy conversion efficiency reported for  $\text{C}_3$  ( $\sim 2.4\%$ ) and  $\text{C}_4$  ( $\sim 3.7\%$ ) crops based on solar radiation intercepted by the leaf canopy (Monteith, 1977; Beale & Long, 1995; Beale *et al.*, 1996). Our estimate corresponds to  $\sim 22$  and  $30 \text{ t ha}^{-1}$  biomass for a  $\text{C}_3$  and  $\text{C}_4$  crop, respectively, if the crop grows for 120 d and experiences an incoming solar radiation



**Fig. 5.** Indicative values for losses (%) estimated from our two-series framework to assess the efficiency of converting incident solar radiation into phytomass energy by present  $\text{C}_3$  (values outside brackets) and  $\text{C}_4$  (values inside brackets) crops under well-managed conditions. The value 12.3 of the first series represents the theoretical maximum efficiency (%) of leaf photosynthesis under limiting light (see the text). Values at the bottom of the first series refer to daily average efficiency (%) for uppermost leaves in a canopy. The calculations for this and the scaling up to canopy assume that total incident solar radiation =  $20 \text{ MJ m}^{-2} \text{ d}^{-1}$ , direct-light fraction = 0.5; daylength = 15 h, maximum LAI = 7  $\text{m}^2 \text{ m}^{-2}$ , canopy leaf-N =  $12 \text{ g m}^{-2}$ ,  $T = 25 \text{ }^\circ\text{C}$ , and atmospheric  $[\text{CO}_2] = 400 \text{ } \mu\text{mol mol}^{-1}$ . PPI, loss due to primary photosystem inefficiency; BEP, loss due to basal alternative  $\text{e}^-$  pathway; NPQ, loss due to non-photochemical quenching; AEP, loss due to additional alternative  $\text{e}^-$  pathway.

of  $20 \text{ MJ m}^{-2} \text{ d}^{-1}$  and the carbon fraction of biomass is 0.45 (with the caution that this fraction depends on crop species and organs; Penning de Vries *et al.*, 1989). The equivalent season-long radiation use efficiency (total crop biomass per unit intercepted solar radiation) is 1.22 and  $1.56 \text{ g MJ}^{-1}$  for a  $C_3$  and  $C_4$  crop, respectively, largely in line with the literature reports (Sinclair & Muchow, 1999).

## Routes to improve the solar energy use efficiency

In view of the steps where energy losses occur as discussed above, routes to improve solar energy use efficiency can be identified across leaf, canopy, and crop levels. Some of the routes have been much discussed in recent literature, and we summarize them here briefly.

### Leaf level

#### Increasing photochemical efficiency

The primary loss of the PSII photochemical efficiency appears unavoidable (Rutherford *et al.*, 2012). Although this efficiency for dark-adapted leaves ( $\Phi_{2DK}$ ) is still not known with certainty (Schansker *et al.*, 2014), it is believed to be  $\sim 0.85$  (Björkman & Demmig, 1987). PSII photochemical efficiency under limiting light ( $\Phi_{2LL}$ ) is often found to be lower than  $\Phi_{2DK}$  (e.g. Bernacchi *et al.*, 2003), but this difference is also uncertain (Schreiber *et al.*, 1995). Evidence from Gu *et al.* (2012) suggests some genetic variation in  $\Phi_{2LL}$ . Improving  $\Phi_{2LL}$  is beneficial, especially for lower leaves in the canopy.

#### Decreasing photorespiration

This has been the area under most active exploration to improve  $C_3$  leaf photosynthesis. Avenues include: improving Rubisco specificity factor  $S_{c/o}$  (Long *et al.*, 2006), improving mesophyll conductance for  $\text{CO}_2$  diffusion (Tholen *et al.*, 2012), enhancing the re-assimilation of photorespired  $\text{CO}_2$  (Busch *et al.*, 2013), engineering for photorespiratory bypass (Kebeish *et al.*, 2007), introducing cyanobacteria CCM into  $C_3$  leaves (Pengelly *et al.*, 2014; McGrath & Long, 2014), and transforming the full  $C_4$  mechanism into main  $C_3$  crops like rice and wheat (von Caemmerer *et al.*, 2012). However, each of these avenues has its own constraints to overcome (Long *et al.*, 2006).

#### Increasing $\theta$ by decreasing NPQ

The convexity factor  $\theta$  in the light response of  $e^-$  transport rate in Eqn (A4) in Supplementary Appendix A reflects the amount of absorbed light energy that has to be dissipated as heat via NPQ. The value of  $\theta$  ranges between 0 and 1, and a higher  $\theta$  will predict a lower NPQ when  $J_{\max}$  in Eqn (A4) is fixed. The factor may depend on growth environment (Ögren, 1993), as well as on genotype (Gu *et al.*, 2012). Commonly used values are 0.7–0.8, but a high  $\theta$  of 0.95 can be measured (Ögren, 1993).

#### Increasing leaf photosynthetic capacity

There is an opportunity to improve leaf photosynthetic capacity by optimizing N partitioning among the photosynthetic

apparatus (Terashima & Evans, 1988). Zhu *et al.* (2007) showed that rearrangement in N among photosynthetic proteins can result in a significant increase in photosynthetic capacity without any increase in total leaf N invested into the photosynthetic apparatus. Another way to improve leaf photosynthesis is to optimize the local photosynthetic capacity in terms of the light gradient inside a leaf (Farquhar, 1989). All these can potentially improve leaf  $V_{\text{cmax}}$  and  $J_{\text{max}}$ .

In addition, most of these photosynthetic parameters, which have widely been believed to be improved by genetic engineering as indicated above, were found to have significant variation among genotypes or accessions (e.g. Gu *et al.*, 2012; Driever *et al.*, 2014). Such natural variation in leaf photosynthesis, although not significantly correlated with seed yield or biomass, is a valuable resource that should be explored to improve crop productivity via conventional breeding (Gu *et al.*, 2014; Driever *et al.*, 2014).

### Canopy level

#### Improving canopy architecture and chlorophyll distribution

Improving canopy photosynthesis by exploring canopy architecture using different leaf inclinations has long been studied (e.g. Angus *et al.*, 1972). Manipulating leaf inclinations will change the value of  $k_L$  for light interception. It is recognized that reducing  $k_L$  when LAI is high and increasing  $k_L$  when LAI is low is advantageous for canopy photosynthesis. Erect upper leaves combined with more horizontal leaves at the bottom is most effective for canopy light interception (e.g. Long *et al.*, 2006). Another way, as an alternative to manipulating canopy architecture, is to manipulate the vertical distribution of chlorophyll in a canopy (Ort *et al.*, 2011), and its more uniform distribution will theoretically allow the light to be more evenly distributed through the canopy and will reduce the proportion of leaves that become light saturated.

#### Improving vertical distribution of photosynthetic resources

Once  $k_L$  is determined for a given canopy architecture and chlorophyll distribution, it is still possible to improve canopy photosynthesis by optimizing the vertical distribution of the remaining leaf N that is not used for the building up of chlorophyll. If the profile of the remaining leaf N in the canopy follows such a profile that the extinction coefficient for light-saturated photosynthesis capacity is equal to  $k_L$ ,  $A_{\text{canopy}}$  can be improved (Sands, 1995). However,  $k_L$  may change rapidly with sun track and sky conditions in the field, and it is impossible that a crop can adjust its N distribution in a canopy so quickly.

### Crop level

#### Improve full canopy cover duration

This may be achieved by: (i) faster canopy closure ('early vigour'); and (ii) slower senescence ('stay-green'), as often emphasized for crop agronomic management. For example, Asseng *et al.* (2003) showed a 5–15% yield increase in wheat by early vigour by selecting for an increased specific leaf area. Borrell *et al.* (2014) showed that a delayed onset of senescence



(i.e. 'stay-green') of sorghum genotypes can enhance grain yield by modifying canopy development.

#### Reduced crop respiration

Although the efficiency of the respiratory systems seemed unaffected by plant breeding (Loomis & Amthor, 1999), it has been shown that there is heritable variation in the respiration rate within ryegrass, and a lower respiration rate resulted in higher-yielding lines (Wilson & Jones, 1982). Exploring avenues to decrease respiratory loss is especially important for a future warmer climate with high night temperatures.

#### Achievable energy conversion efficiency

Based on the above discussed routes for improvement, we conceive, in our personal opinion, that constraints along leaf, canopy, and crop levels are moderately ameliorated to an achievable level (Table 1). Maximum achievable energy conversion efficiency in annual C<sub>3</sub> crops depends on the extent to which photorespiration is suppressed by future breeding or engineering approaches. Given that this is an uncertainty, C<sub>c</sub> is assumed to be unchanged (Table 1). If all other potential avenues for improvement (Table 1) are incorporated, the maximum energy conversion efficiency can be calculated as 3.6 and 4.1%, respectively, for C<sub>3</sub> and C<sub>4</sub> crops under the same aforementioned conditions (Table 1). This would correspond to radiation use efficiency values of 1.75 and 2.00 g MJ<sup>-1</sup>, and would translate into biomass values of ~35.7 and 40.8 t ha<sup>-1</sup>, for C<sub>3</sub> and C<sub>4</sub> crops, respectively, if the crop grows for 120 d and experiences an incoming solar radiation of 20 MJ m<sup>-2</sup> d<sup>-1</sup>. This indicates that C<sub>3</sub> crop productivity could be considerably improved (being higher than that of the present C<sub>4</sub> crops) without recourse to the suppression of photorespiration. Greater improvements in C<sub>3</sub> than in C<sub>4</sub> species is again because C<sub>3</sub> species benefit more from most of the individual improvement avenues such as smaller  $k_L$  (Table 1), largely due to the more curvilinear nature of their photosynthetic light response. Note that these individual avenues are not equally important in improving the overall conversion efficiency and their relative importance may differ between C<sub>3</sub> and C<sub>4</sub> crops, as evidenced by the reduction percentage, relative to the overall 'achievable' efficiency, calculated from retaining the parameters one at a time at the default value (Table 1).

### Concluding remarks

Based on the linear single-series approaches, previous reports addressing 'the efficiency of converting solar energy to phytoenergy' mainly consider the losses in leaf photosynthesis under limiting light. Such approaches do not explicitly account for 'canopy enhancement', nor for the effects of day-length and canopy cover dynamics. We therefore developed a simple framework having two series, for leaf scale, and for canopy and crop scale, respectively.

Equations (2)–(6) were described for calculating each loss at the leaf level, based on a generalized analytical model for an e<sup>-</sup> transport-limited rate of leaf photosynthesis (Supplementary Appendix A), thereby heuristically generating new insights into

energy loss that were not revealed in the previous analyses. First, the model shows that the loss due to photosystem photochemical inefficiencies is not dependent only on  $\Phi_{1LL}$  and  $\Phi_{2LL}$  but also on  $f_{cyc}$ , and therefore that at a given set of values for  $\Phi_{1LL}$  and  $\Phi_{2LL}$  the loss due to photosystem photochemical inefficiencies ( $F_{ppi}$ ) is mathematically less in C<sub>4</sub> than in C<sub>3</sub> species because  $f_{cyc}$  is much higher in C<sub>4</sub> than in C<sub>3</sub> species. For the same reason, the loss due to NPQ ( $F_{npq}$ ) is higher in C<sub>3</sub> than in C<sub>4</sub> species (Fig. 1b). These results suggest that engaging cyclic e<sup>-</sup> transport helps to reduce the loss due to photosystem photochemical inefficiencies and NPQ. Secondly, a common practice to assess an overall conversion efficiency in previous analyses was to multiply the efficiencies of each step (e.g. Loomis & Williams, 1963; Monteith, 1972; Zhu *et al.*, 2008). Our analysis based on the analytical model suggests that this multiplication procedure is not always correct. The estimated energy conversion efficiencies up to the first two steps (i.e. 9.4% for C<sub>3</sub> species and 6.6% for C<sub>4</sub> species thus far) are the result of integrating the losses due to both photosystem inefficiencies  $F_{ppi}$  and basal alternative e<sup>-</sup> pathways  $F_{bep}$ , which cannot be the result of mathematical multiplication of  $(1-F_{ppi})$  and  $(1-F_{bep})$ . The multiplication rule is valid for the leaf level only if cyclic e<sup>-</sup> transport is absent, which may hold for C<sub>3</sub> species (Johnson, 2011) but certainly not for C<sub>4</sub> species (Yin & Struik, 2012).

A similar argument can be made for the crop level that the present energy conversion efficiency cannot be the multiplicative result based on the higher 'achievable efficiency' and individual reduction percentages (Table 1). Our analysis also suggests that (i) canopy enhancement for energy conversion efficiency, (ii) the benefit from the optimum acclimation of N profile in canopy, and (iii) improvement in crop productivity from future improvement in leaf photosynthetic parameters and canopy architecture are all higher in C<sub>3</sub> than in C<sub>4</sub> species. These can be explained by the fact that the light response of C<sub>4</sub> leaf photosynthesis is more linear than that of C<sub>3</sub> leaf photosynthesis.

Focusing on only generic guiding principles, we have not dealt with specific aspects that contribute to the difference in radiation use efficiency among crop species (Sinclair & Muchow, 1999). Furthermore, there are several approximations. First, our framework is based on a model describing steady-state leaf photosynthesis. Leaves in the field experience continuously fluctuating environments. Secondly, we did not consider any feedback effect of crop sink size, or feedforward effect of past photosynthesis, on current photosynthesis. Both dynamic photosynthesis and feedback or feedforward effects would need more complicated models to predict. Thirdly, of the non-photosynthetic processes, only crop respiration was considered. We ignored the loss due to root exudates and shoot litters, due to its smaller importance (e.g. Loomis & Williams, 1963). Finally, crops under field conditions may be subject to (a)biotic stresses from poor management (Sinclair & Muchow, 1999). It is these stress factors that make a typical solar energy conversion efficiency of annual crops very low, considered to be even less than 1% (de Groot, 2008). Our analysis suggests that, under favourable conditions, the efficiency of present crops (Fig. 5), although indicative, can at least double this humble efficiency, and could potentially be higher than 4.0%.

## Supplementary data

Supplementary data are available at *JXB* online.

**Supplementary Appendix A.** A biochemical leaf photosynthesis model and its extended version.

**Supplementary Appendix B.** The model of de Pury & Farquhar (1997) for canopy photosynthesis.

**Supplementary Appendix C.** Equations based on Yin *et al.* (2003) to estimate daytime course of radiation and seasonal time course of LAI.

## Acknowledgements

This work was carried out within the Dutch research programme 'BioSolar Cells'. We thank two reviewers for their comments that enabled us to improve the paper accordingly.

## References

- Allen JF.** 2003. Cyclic, pseudocyclic and noncyclic photophosphorylation: new links in the chain. *Trends in Plant Science* **8**, 15–19.
- Amthor JS.** 2010. From sunlight to phytomass: on the potential efficiency of converting solar radiation to phyto-energy. *New Phytologist* **188**, 939–959.
- Angus JF, Jones R, Wilson JH.** 1972. A comparison of barley cultivars with different leaf inclinations. *Australian Journal of Agricultural Research* **23**, 943–957.
- Anten NPR, Schieving F, Werger MJA.** 1995. Patterns of light and nitrogen distribution in relation to whole canopy carbon gain in  $C_3$  and  $C_4$  mono- and dicotyledonous species. *Oecologia* **101**, 504–513.
- Archontoulis SV, Vos J, Yin X, Bastiaans L, Danalatos NG, Struik PC.** 2011. Temporal dynamics of light and nitrogen vertical distributions in canopies of sunflower, kenaf and cynara. *Field Crops Research* **122**, 186–198.
- Archontoulis SV, Yin X, Vos J, Danalatos NG, Struik PC.** 2012. Leaf photosynthesis and respiration of three bioenergy crops in relation to temperature and leaf nitrogen: how conserved are biochemical model parameters among crop species? *Journal of Experimental Botany* **63**, 895–911.
- Asada K.** 1999. The water-water cycle in chloroplasts: Scavenging of active oxygens and dissipation of excess photons. *Annual Review of Plant Physiology and Plant Molecular Biology* **50**, 601–639.
- Asseng S, Turner NC, Botwright T, Condon AG.** 2003. Evaluating the impact of a trait for increased specific leaf area on wheat yield using a crop simulation model. *Agronomy Journal* **95**, 10–19.
- Baker NR, Harbinson J, Kramer DM.** 2007. Determining the limitations and regulation of photosynthetic energy transduction in leaves. *Plant, Cell and Environment* **30**, 1107–1125.
- Beale CV, Bint DA, Long SP.** 1996. Leaf photosynthesis in the  $C_4$ -grass *Miscanthus x giganteus*, growing in the cool temperature climate of southern England. *Journal of Experimental Botany* **47**, 267–273.
- Beale CV, Long SP.** 1995. Can perennial  $C_4$  grasses attain high efficiencies of radiant energy conversion in cool climates? *Plant, Cell and Environment* **18**, 641–650.
- Bellasio C, Griffiths H.** 2014. Acclimation of  $C_4$  metabolism to low light in mature maize leaves could limit energetic losses during progressive shading in a crop canopy. *Journal of Experimental Botany* **65**, 3725–3736.
- Bernacchi CJ, Pimentel C, Long SP.** 2003. *In vivo* temperature response functions of parameters required to model RuBP-limited photosynthesis. *Plant, Cell and Environment* **26**, 1419–1430.
- Berndes G, Hoogwijk M, van den Broek R.** 2003. The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass and Bioenergy* **25**, 1–28.
- Björkman O, Demmig B.** 1987. Photon yield of  $O_2$  evolution and chlorophyll fluorescence characteristics at 77 K among vascular plants of diverse origins. *Planta* **170**, 489–504.
- Boote KJ, Loomis RS.** 1991. The prediction of canopy assimilation. In: Boote KJ, Loomis RS, eds. *Modeling crop photosynthesis—from biochemistry to canopy*. Crop Science Society of America Special Publication Number 19. Madison, Wisconsin, 109–140.
- Borrell AK, Oosterom EJ, Mullet JE, George-Jaeggli B, Jordan DR, Klein PE, Hammer GL.** 2014. Stay-green alleles individually enhance grain yield in sorghum under drought by modifying canopy development and water uptake patterns. *New Phytologist* **203**, 817–830.
- Buckley TN, Cescatti A, Farquhar GD.** 2013. What does optimization theory actually predict about crown profiles of photosynthetic capacity when models incorporate greater realism? *Plant, Cell and Environment* **36**, 1547–1563.
- Busch FA, Sage TL, Cousins AB, Sage RF.** 2013.  $C_3$  plants enhance rates of photosynthesis by reassimilating photorespired and respired  $CO_2$ . *Plant, Cell and Environment* **36**, 200–212.
- Cannell MGR, Thornley JHM.** 2000. Modelling the components of plant respiration: Some guiding principles. *Annals of Botany* **85**, 45–54.
- Carpita NC, McCann MC.** 2008. Maize and sorghum: genetic resources for bioenergy grasses. *Trends in Plant Science* **13**, 415–420.
- Cheng L, Fuchigami LH, Breen PJ.** 2001. The relationship between photosystem II efficiency and quantum yield for  $CO_2$  assimilation is not affected by nitrogen content in apple leaves. *Journal of Experimental Botany* **52**, 1865–1872.
- de Groot H.** 2008. Harnessing solar energy for the production of clean fuels. In: van Keulen H, van Laar HH, Rabbinge R, eds. *40 Years Theory and Model at Wageningen UR—on the occasion of the 40th anniversary of the inaugural address of C.T. de Wit in 1968*. Wageningen University and Research Centre, The Netherlands, 5–7.
- de Pury DGG, Farquhar GD.** 1997. Simple scaling of photosynthesis from leaves to canopies without the errors of big-leaf models. *Plant, Cell and Environment* **20**, 537–557.
- DeLucia EH, Gomez-Casanova N, Greenberg JA, Hudiburg TW, Kantola IB, Long SP, Miller AD, Ort DR, Parton WJ.** 2014. The theoretical limit to plant productivity. *Environmental Science & Technology* **48**, 9471–9477.
- Dohleman FG, Heaton EA, Leahey ADB, Long SP.** 2009. Does greater leaf-level photosynthesis explain the larger solar energy conversion efficiency of *Miscanthus* relative to switchgrass. *Plant, Cell and Environment* **32**, 1525–1537.
- Dohleman FG, Long SP.** 2009. More productive than maize in the Midwest: how does *Miscanthus* do it? *Plant Physiology* **150**, 2104–2115.
- Driever SM, Baker NR.** 2011. The water-water cycle in leaves is not a major alternative electron sink for dissipation of excess excitation energy when  $CO_2$  assimilation is restricted. *Plant, Cell and Environment* **34**, 837–846.
- Driever SM, Lawson T, Andralojc PJ, Raines CA.** 2014. Natural variation in photosynthetic capacity, growth, and yield in 64 field-grown wheat genotypes. *Journal of Experimental Botany* **65**, 4959–4973.
- Ehleringer J, Pearcy RW.** 1983. Variation in quantum yield for  $CO_2$  uptake among  $C_3$  and  $C_4$  plants. *Plant Physiology* **73**, 555–559.
- Emerson R.** 1958. The quantum yield of photosynthesis. *Annual Review of Plant Physiology* **9**, 1–24.
- Farquhar GD, von Caemmerer S, Berry JA.** 1980. A biochemical model of photosynthetic  $CO_2$  assimilation in leaves of  $C_3$  species. *Planta* **149**, 78–90.
- Farquhar GD.** 1989. Models of integrated photosynthesis of cells and leaves. *Philosophical Transactions of the Royal Society, London B* **323**, 357–367.
- Gifford RM.** 1995. Whole plant respiration and photosynthesis of wheat under increased  $CO_2$  concentration and temperature: long-term vs. short-term distinctions from modelling. *Global Change Biology* **1**, 385–396.
- Gifford RM.** 2003. Plant respiration in productivity models: conceptualisation, representation and issues for global terrestrial carbon-cycle research. *Functional Plant Biology* **30**, 171–186.
- Goudriaan J, Kropff MJ, Rabbinge R.** 1991. Mogelijkheden en beperkingen van biomassa als energiebron. *Energie Spectrum* **6**, 171–176.
- Goudriaan J, van Laar HH.** 1994. *Modelling potential crop growth processes*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Gu J, Yin X, Stomph TJ, Struik PC.** 2014. Can exploiting natural genetic variation in leaf photosynthesis contribute to increasing rice productivity? A simulation analysis. *Plant, Cell and Environment* **37**, 22–34.

- Gu J, Yin X, Stomph TJ, Wang H, Struik PC.** 2012. Physiological basis of genetic variation in leaf photosynthesis among rice (*Oryza sativa* L.) introgression lines under drought and well-watered conditions. *Journal of Experimental Botany* **63**, 5137–5153.
- Hammer GL, Wright GC.** 1994. A theoretical analysis of nitrogen and radiation effects on radiation use efficiency in peanut. *Australian Journal of Agricultural Research* **45**, 575–589.
- Harley PC, Thomas RB, Reynolds JF, Strain BR.** 1992. Modelling photosynthesis of cotton grown in elevated CO<sub>2</sub>. *Plant, Cell and Environment* **15**, 271–282.
- Hikosaka K.** 2014. Optimal nitrogen distribution within a leaf canopy under direct and diffuse light. *Plant, Cell and Environment* **37**, 2077–2085.
- Johnson GN.** 2011. Physiology of PSI cyclic electron transport in higher plants. *Biochimica et Biophysica Acta* **1807**, 384–389.
- Kebeish R, Niessen M, Thiruveedhi K, Bari R, Hirsch H-J, Rosenkranz R, Stähler N, Schönfeld B, Kreuzaler F, Peterhänsel C.** 2007. Chloroplastic photorespiratory bypass increases photosynthesis and biomass production in *Arabidopsis thaliana*. *Nature Biotechnology* **25**, 593–599.
- Kromdijk J, Griffiths H, Schepers HE.** 2010. Can the progressive increase of C<sub>4</sub> bundle sheath leakiness at low PFD be explained by incomplete suppression of photorespiration? *Plant, Cell and Environment* **33**, 1935–1948.
- Kubien DS, Whitney SM, Moore PV, Jesson LK.** 2008. The biochemistry of Rubisco in *Flaveria*. *Journal of Experimental Botany* **59**, 1767–1777.
- Long SP, Postl WF, Bolhár-Nordenkamp HR.** 1993. Quantum yields for uptake of carbon dioxide in C<sub>3</sub> vascular plants of contrasting habitats and taxonomic groupings. *Planta* **189**, 226–234.
- Long SP, Zhu X-G, Naidu SL, Ort DR.** 2006. Can improvement in photosynthesis increase crop yields? *Plant, Cell and Environment* **29**, 315–330.
- Loomis RS, Amthor JS.** 1999. Yield potential, plant assimilatory capacity, and metabolic efficiencies. *Crop Science* **39**, 1584–1596.
- Loomis RS, Williams WA.** 1963. Maximum crop productivity: an estimate. *Crop Science* **3**, 67–72.
- McGrath JM, Long SP.** 2014. Can the cyanobacterial carbon-concentrating mechanism increase photosynthesis in crop species? A theoretical analysis. *Plant Physiology* **164**, 2247–2261.
- Monteith JL.** 1972. Solar radiation and productivity in tropical ecosystems. *Journal of Applied Ecology* **9**, 747–766.
- Monteith JL.** 1977. Climate and the efficiency of crop production in Britain. *Philosophical Transactions of the Royal Society London* **281**, 277–294.
- Moreau D, Allard V, Gaju O, Le Gouis J, Foulkes MJ, Martre P.** 2012. Acclimation of leaf nitrogen to vertical light gradient at anthesis in wheat is a whole-plant process that scales with the size of the canopy. *Plant Physiology* **160**, 1479–1490.
- Murchie EH, Lawson T.** 2013. Chlorophyll fluorescence analysis: a guide to good practice and understanding some new applications. *Journal of Experimental Botany* **64**, 3983–3998.
- Ögren E.** 1993. Convexity of the photosynthetic light-response curve in relation to intensity and direction of light during growth. *Plant Physiology* **101**, 1013–1019.
- Ort DR, Zhu X, Melis A.** 2011. Optimizing antenna size to maximize photosynthetic efficiency. *Plant Physiology* **155**, 79–85.
- Pengelly JLL, Forster B, von Caemmerer S, Badger MR, Price GD, Whitney S M.** 2014. Transplastomic integration of a cyanobacterial bicarbonate transporter into tobacco chloroplasts. *Journal of Experimental Botany* **65**, 3071–3080.
- Penning de Vries FWT, Jansen DM, ten Berge HFM, Bakema A.** 1989. *Simulation of ecophysiological processes of growth in several annual crops*. IRRRI, Los Baños, The Philippines, and Pudoc, Wageningen, The Netherlands.
- Piedade MT, Junk WJ, Long SP.** 1991. The productivity of the C<sub>4</sub> grass *Echinochloa polystachya* on the Amazon floodplain. *Ecology* **72**, 1456–1463.
- Piedade MT, Long SP, Junk WJ.** 1994. Leaf and canopy photosynthetic CO<sub>2</sub> uptake of a stand of *Echinochloa polystachya* on the Central Amazon floodplain. Are the high potential rates associated with the C<sub>4</sub> syndrome realized under the near-optimal conditions provided by this exceptional natural habitat? *Oecologia* **97**, 193–201.
- Rutherford AW, Osyczka A, Rappaport F.** 2012. Back-reactions, short-circuits, leaks and other energy wasteful reactions in biological electron transfer: Redox tuning to survive life in O<sub>2</sub>. *FEBS Letters* **586**, 603–616.
- Ruuska SA, Badger MR, Andrews TJ, von Caemmerer S.** 2000. Photosynthetic electron sinks in transgenic tobacco with reduced amounts of Rubisco: little evidence for significant Mehler reaction. *Journal of Experimental Botany* **51**, 357–368.
- Sands PJ.** 1995. Modelling canopy production. I. Optimal distribution of photosynthetic resources. *Australian Journal of Plant Physiology* **22**, 593–601.
- Schansker G, Tóth SZ, Holzwarth AR, Garab G.** 2014. Chlorophyll a fluorescence: beyond the limits of the Q<sub>A</sub> model. *Photosynthesis Research* **120**, 43–58.
- Schreiber U, Hormann H, Neubauer C, Klughammer C.** 1995. Assessment of photosystem II photochemical quantum yield by chlorophyll fluorescence quenching analysis. *Australian Journal of Plant Physiology* **22**, 209–220.
- Sinclair TR, Muchow RC.** 1999. Radiation use efficiency. *Advances in Agronomy* **65**, 215–265.
- Sinclair TR, Murphy CE Jr., Knoerr KR.** 1976. Development and evaluation of simplified models for simulating canopy photosynthesis and transpiration. *Journal of Applied Ecology* **13**, 813–829.
- Taiz L, Zeiger E.** 2010. *Plant physiology*. Sinauer Associates, Sunderland, MA.
- Terashima I, Evans JR.** 1988. Effects of light and nitrogen nutrition on the organization of the photosynthetic apparatus in spinach. *Plant and Cell Physiology* **29**, 143–155.
- Tholen D, Boom C, Zhu X-G.** 2012. Opinion: Prospects for improving photosynthesis by altering leaf anatomy. *Plant Science* **197**, 92–101.
- Ubierna N, Sun W, Cousins AB.** 2011. The efficiency of C<sub>4</sub> photosynthesis under low light conditions: assumptions and calculations with CO<sub>2</sub> isotope discrimination. *Journal of Experimental Botany* **62**, 3119–3134.
- Verhoeven AS, Demmig-Adams B, Adams WW III.** 1997. Enhanced employment of the xanthophyll cycle and thermal energy dissipation in spinach exposed to high light and N stress. *Plant Physiology* **113**, 817–824.
- von Caemmerer S.** 2000. *Biochemical models of leaf photosynthesis*. CSIRO Publishing, Collingwood, Australia.
- von Caemmerer S, Evans JR, Hudson GS, Andrews TJ.** 1994. The kinetics of ribulose-1,5-bisphosphate carboxylase/oxygenase in vivo inferred from measurements of photosynthesis in leaves of transgenic tobacco. *Planta* **195**, 88–97.
- von Caemmerer S, Quick WP, Furbank RT.** 2012. The development of C<sub>4</sub> rice: current progress and future challenges. *Science* **336**, 1671–1672.
- Wilson D, Jones JG.** 1982. Effect of selection for dark respiration rate of mature leaves on crop yields of *Lolium perenne* cv. S23. *Annals of Botany* **49**, 313–320.
- Yin X, Belay DW, van der Putten PEL, Struik PC.** 2014. Accounting for the decrease of photosystem photochemical efficiency with increasing irradiance to estimate quantum yield of leaf photosynthesis. *Photosynthesis Research* **122**, 323–335.
- Yin X, Goudriaan J, Lantinga EA, Vos J, Spiertz JHJ.** 2003. A flexible sigmoid function of determinate growth. *Annals of Botany* **91**, 361–371 [erratum: *Annals of Botany* **91**, 753].
- Yin X, Harbinson J, Struik PC.** 2006. Mathematical review of literature to assess alternative electron transports and interphotosystem excitation partitioning of steady-state C<sub>3</sub> photosynthesis under limiting light. *Plant, Cell and Environment* **29**, 1771–1782 [erratum: *Plant, Cell and Environment* **29**, 2252].
- Yin X, Struik PC.** 2012. Mathematical review of the energy transduction stoichiometries of C<sub>4</sub> leaf photosynthesis under limiting light. *Plant, Cell and Environment* **35**, 1299–1312.
- Yin X, Sun Z, Struik PC, van der Putten PEL, van Ieperen W, Harbinson J.** 2011. Using a biochemical C<sub>4</sub>-photosynthesis



model and combined gas exchange and chlorophyll fluorescence measurements to estimate bundle-sheath conductance of maize leaves differing in age and nitrogen content. *Plant, Cell and Environment* **34**, 2183–2199.

**Yin X, van Laar HH.** 2005. *Crop systems dynamics: an ecophysiological simulation model for genotype-by-environment interactions*. Wageningen Academic Publishers, Wageningen, The Netherlands.

**Yin X, van Oijen M, Schapendonk AHCM.** 2004. Extension of a biochemical model for the generalized stoichiometry of electron transport limited C<sub>3</sub> photosynthesis. *Plant, Cell and Environment* **27**, 1211–1222.

**Yuan JS, Tiller KH, Al-Ahmad H, Stewart NR, Neal Stewart jr C.** 2008. Plants to power: bioenergy to fuel the future. *Trends in Plant Science* **13**, 421–429.

**Zhu X-G, de Sturler E, Long SP.** 2007. Optimizing the distribution of resources between enzymes of carbon metabolism can dramatically increase photosynthetic rate: a numerical simulation using an evolutionary algorithm. *Plant Physiology* **145**, 513–526.

**Zhu X-G, Long SP, Ort DR.** 2008. What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? *Current Opinion in Biotechnology* **19**, 153–159.