An improved isotopic method for partitioning net ecosystem-atmosphere CO₂ exchange

R. Wehr and S.R. Saleska

Abstract

Stable carbon isotopes can be used to partition the net ecosystem-atmosphere exchange (NEE) of carbon dioxide (CO₂) into its photosynthetic and respiratory components, but the method has not been generally adopted due to instrumental and theoretical limitations. Here, motivated by recently improved instrumentation, we extend the theory of isotopic flux partitioning to include photorespiration, foliar daytime ‘dark’ respiration, and other refinements, arriving at a general yet practical formulation from which all previous formulations can be derived as simplifying approximations. We use a full growing season of isotopic eddy covariance flux data from a temperate deciduous forest to demonstrate the method, quantify its uncertainties, and determine biases associated with previously published formulations. We find that when $\delta^{13}\text{C}$ of CO₂ is acquired with high precision (0.02‰ RMSE for 100 s integration times), the statistical uncertainty in the partitioned fluxes is comparable to that in NEE itself—i.e., as good as practicably possible. Assessable systematic uncertainty is $\pm 17\%$ of gross ecosystem production (GEP), due mostly to uncertainty in the isotopic fractionation by carboxylation. Additional, currently unquantifiable systematic uncertainty is associated with treating the canopy as a single “big leaf”. Both sources of systematic uncertainty could be greatly reduced by feasible supporting leaf-level measurements. Our extended theory corrects systematic biases in previous isotopic approaches, including overestimation (by 13 %) of GEP due to the omission of photorespiration. The partitioning determines the isotopic signature of photosynthesis, which we find to vary seasonally between -24 and -28 ‰ such that the isotopic disequilibrium between ecosystem carbon input and output remains stable at approximately -0.5 ‰ through most of the growing season. The key advantage of isotopic partitioning over standard, regression-based partitioning is that it enables controls on the ecosystem-scale

photosynthetic and respiratory fluxes to emerge from observations, without having to assume functional relations to environmental drivers *a priori*. As an example, we show how isotopic partitioning reveals certain large variations in daytime NEE to be caused by shifts in the flux tower sampling footprint between regions of high and low respiratory flux—a finding unobtainable by standard partitioning. For this reason, isotopic partitioning can be more precise than standard partitioning for quantifying environmental controls on NEE.

Keywords: carbon dioxide; net ecosystem exchange; partitioning; eddy covariance; isotope; forest

1. Introduction

The net ecosystem-atmosphere exchange of CO₂ (NEE) is routinely measured by eddy covariance at hundreds of tower sites around the world (Baldocchi, 2008; Luyssaert et al., 2009). NEE is the balance of ecosystem photosynthesis and ecosystem respiration, and most analyses of NEE involve partitioning it into these somewhat independent and somewhat coupled components. There being no means to measure each component directly, standard empirical flux partitioning (Lasslop et al., 2010; Reichstein et al., 2005; Stoy et al., 2006) works by prescribing the functional forms of the responses of ecosystem-scale photosynthesis and/or respiration to environmental drivers based on inferences drawn from leaf or soil-plot gas exchange measurements or from nighttime NEE. Isotopic flux partitioning (IFP) is an alternative that avoids such assumptions, instead identifying the photosynthetic and respiratory components of NEE by their distinct stable isotopic signatures—here ¹³C versus ¹²C. The ratio of ¹³C to ¹²C differs between photosynthesized and respired carbon chiefly because there is a strong

isotopic fractionation by photosynthesis that varies on timescales shorter than the mean age of the substrate for respiration. Isotopic partitioning has not seen general use because of limits on both the precision of *in situ* isotope measurements and the theory used to apply those measurements to the partitioning problem.

That theory has been developed through a succession of studies (Billmark and Griffis, 2009; Bowling et al., 2001; Fassbinder et al., 2012; Knohl and Buchmann, 2005; Lai et al., 2003; Ogée et al., 2003; Yakir and Wang, 1996; Zhang et al., 2006; Zobitz et al., 2008), as recently reviewed by Fassbinder et al. (2012). Motivated by recently developed spectroscopic technology for high-precision ^{13}C measurements in atmospheric CO_2 (Wehr et al., 2013), we elaborate the theory further, incorporating photorespiration, foliar daytime 'dark' respiration, and several other refinements to arrive at a general but practical formulation (Section 2) from which all previously published formulations can be derived as approximations. We then use a full growing season of isotopic eddy covariance measurements (Wehr et al., 2013) and supporting data from a temperate forest (Section 3) to demonstrate the partitioning, to quantify its uncertainties, and to quantify biases associated with previous formulations (Section 4). Appendix A provides some fundamental definitions; Appendix B provides a detailed accounting of the resistances, fractionations, and other input parameters we selected for our oak-dominated forest ecosystem; and Appendix C summarizes the differences between the present formulation and those previously published.

2. Isotopic Flux Partitioning Equations

96 The basic idea of isotopic flux partitioning(Bowling et al., 2001; Ogée et al., 2003;
 97 Yakir and Wang, 1996)is to determine the magnitudes of the photosynthetic and
 98 respiratory gross fluxes using their isotopic signatures and the isotopic composition
 99 and magnitude of their sum (i.e. NEE); that is, to solve the set of two equations
 100 describing the isotopic mass balance of CO₂ in the forest,

$$101 \quad F_N = F_A + F_{NR} \quad (1)$$

$$102 \quad \delta_N F_N = \delta_A F_A + \delta_{NR} F_{NR}, \quad (2)$$

103 for the unknowns F_A and F_{NR} , where the ecosystem-scale fluxes F and their isotopic
 104 compositions δ are labeled by the following subscripts: N for NEE, A for canopy net
 105 photosynthetic assimilation, and NR for non-foliar ecosystem respiration. In this
 106 article, δ is shorthand for $\delta^{13}\text{C}$, which is the ratio of ^{13}C to ^{12}C expressed as a relative
 107 difference from a standard material (see Appendix A).

108 Solving this pair of equations requires knowledge of the isotopic composition of NEE
 109 (δ_N), the isotopic signature of non-foliar ecosystem respiration (δ_{NR}), and the
 110 isotopic signature of net photosynthetic assimilation (δ_A). δ_N can be measured
 111 directly, and δ_{NR} can be obtained from a combination of soil chamber and nighttime
 112 Keeling plot measurements as detailed in Section 3.2. δ_A , however, cannot be
 113 measured at the ecosystem scale. Instead, the approach generally taken is to use our
 114 understanding of photosynthetic fractionation (also called discrimination) by
 115 individual leaves to express δ_A in terms of F_A , so that δ_A can be eliminated from the
 116 above equations (and thus solved for as part of the partitioning). In the original

117 formulation of this approach(Bowling et al., 2001), the link between δ_A and F_A
118 consisted simply of Fick's law for CO₂ diffusion through the leaf stomata,
119
$$F_A = -g_s(c_a - c_i), \quad (3)$$

120 and the well-known simplified equation for photosyntheticfractionation(Farquhar
121 et al., 1982),
122
$$\epsilon_A = \epsilon_s + (b - \epsilon_s) \frac{c_i}{c_a}, \quad (4)$$

123 along with an approximate definition of the photosynthetic fractionation,
124
$$\epsilon_A \approx \delta_a - \delta_A \quad (5)$$

125 (cf. the exact definition in Appendix A).In the above equations, g_s is the stomatal
126 conductance, c_i is the intercellular CO₂ concentration inside the leaf, c_a and δ_a are the
127 CO₂ concentration and isotopic composition of the air outside the leaf, ϵ_A is the
128 apparent isotopic fractionation of canopy net photosynthetic assimilation (often
129 written as Δ), ϵ_s is the fractionation associated with diffusion of CO₂ through the
130 stomata (4.4 ‰), and b is the apparent fractionation associated with fixation of
131 intercellular CO₂ (~27 ‰). Combining these equations eliminates c_i and ϵ_A and
132 gives δ_A in terms of F_A —provided that atmospheric CO₂ is measured, that stomatal
133 conductance can be determined (e.g. from measured ecosystem-scale heat and water
134 fluxes), and that ϵ_s and b are known constants. The above fractionation equation, Eq.
135 (4), neatly expresses the central fact that the fractionation by photosynthesis
136 depends on the relative rates of CO₂ diffusion and fixation, being weighted towards

137 the fractionation associated with whichever of those two processes is most limiting
 138 to the overall rate of assimilation (because diffusion limitation will cause c_i to
 139 approach zero while fixation limitation will cause c_i to approach c_a).

140 This basic approach for estimating the canopy-scale isotopic signature of
 141 photosynthesis (and the more comprehensive one we develop here below) relies on
 142 the assumption that our understanding of leaf-level photosynthetic
 143 fractionation(Farquhar et al., 1982) can be scaled directly to the canopy. This
 144 approach, in which the whole canopy is treated as a single “big leaf”, requires that the
 145 response of the distribution of leaves in the canopy to the distribution of
 146 environmental conditions that they experience can be approximated by the
 147 response of a single “big leaf” to the average environmental conditions. Such an
 148 approximation is insufficient for some analyses(De Pury and Farquhar, 1997), but
 149 big leaf approaches have nonetheless been shown to accurately capture key aspects
 150 of canopy photosynthesis(Amthor et al., 1994; Lloyd et al., 1995), and in this case,
 151 there are insufficient observational data at present to constrain a more complex
 152 dual- or multi-leaf model. Note, however, that carbon isotope discrimination has
 153 been considered in a multi-leaf framework before(Baldocchi and Bowling, 2003;
 154 Ogée et al., 2003).

155 Note that we depart from some of the notation inherited through the lineage of IFP
 156 studies, sacrificing continuity in favor of a standardized notation consistent with
 157 guidelines inCoplen(2011) (wherein, e.g., ε represents isotopic fractionation, leading
 158 us to use ε_A rather than Δ for photosynthetic fractionation). Our symbols and

159 notations are explained in Tables 1 and 2, and several key variables are defined in
160 Appendix A. Except in a few special cases, each property (e.g. fractionation) is given a
161 unique letter or symbol (e.g. ε), and the property is associated with specific sites
162 (e.g. above the canopy) or processes (e.g. dissolution) by subscripts. Superscripts 12
163 and 13 specify the carbon isotopes.

Symbol	Description	Units
F	flux(formally flux density) of CO ₂	mol m ⁻² s ⁻¹
H	flux(formally flux density) of sensible heat	W m ⁻²
E	flux(formally flux density) of water vapor	mol m ⁻² s ⁻¹
R	isotope atom ratio, ¹³ C/ ¹² C	--
δ	relative difference of R from R_{VPDB}	--
α	isotopic fractionation factor	--
ε	isotopic fractionation (= $\alpha - 1$)	--
c	concentration of CO ₂	mol m ⁻³
C	mole fraction of CO ₂ in air	mol mol ⁻¹
C_p	specific heat capacity of air	J kg ⁻¹ K ⁻¹
r	Resistance	s m ⁻¹
g	conductance(= 1/ r)	m s ⁻¹
e	vapor pressure	Pa
T	Temperature	K
P	air pressure	Pa
ρ	density of air	kg m ⁻³
γ	psychrometric constant	Pa K ⁻¹
λ	latent heat of vaporization of water	J mol ⁻¹
k_H	Henry's constant (= c_{ow}/c_i)	--

a	flux measurement height	m
h	canopy top height	m
Sc	Schmidt number for CO ₂	--
Sc_V	Schmidt number for water vapor	--
Pr	Prandtl number for air	--
Γ'_*	photocompensation point	mol mol ⁻¹
u	wind speed	m s ⁻¹
u_*	friction velocity	m s ⁻¹
χ	clear sky index	--
β	fraction of carboxylation performed by PEP-carboxylase	--

Subscript Meaning

PROCESSES

<i>N</i>	net ecosystem-atmosphere CO ₂ exchange (NEE)
<i>P</i>	gross photosynthesis (uptake is negative)
<i>PR</i>	Photorespiration
<i>DR</i>	foliar daytime 'dark' respiration
<i>A</i>	net foliar photosynthetic assimilation
<i>NR</i>	non-foliar (heterotroph, root, and stem) respiration
<i>e</i>	turbulent eddy 'diffusion'
<i>b</i>	leaf boundary layer diffusion of CO ₂
<i>bH</i>	leaf boundary layer diffusion of heat
<i>bV</i>	leaf boundary layer diffusion of water vapor
<i>s</i>	stomatal diffusion of CO ₂
<i>sV</i>	stomatal diffusion of water vapor
<i>d</i>	dissolution of CO ₂ in water
<i>hyd</i>	hydration of CO ₂
<i>m</i>	mesophyll diffusion of CO ₂
<i>wp</i>	mesophyll cell wall and plasmalemma diffusion of CO ₂
<i>ch</i>	chloroplast envelope and stroma diffusion of CO ₂
<i>f</i>	enzyme-catalyzed fixation of CO ₂
<i>Ru</i>	carboxylation by Rubisco

LOCATIONS

<i>a</i>	above the canopy, at flux measurement height
<i>h</i>	top of canopy
<i>n</i>	within the canopy
<i>u</i>	under the leaf boundary layer, outside the stomata
<i>i</i>	in the leaf intercellular airspace
<i>ow</i>	in the liquid lining the outside of the mesophyll cell walls
<i>c</i>	at the site of carboxylation
<i>L</i>	throughout the leaf

2.1. Carbon Isotope Mass Balance

We begin by expanding the terms of the mass balance of CO_2 in the forest air (Eq.(1)) to now explicitly include the photorespiration flux F_{PR} , the foliar daytime 'dark' respiration flux F_{DR} , and the non-foliar (mostly belowground) respiration flux F_{NR} :

$$F_N = F_P + F_{PR} + F_{DR} + F_{NR}. \quad (6)$$

All the fluxes F are at the ecosystem scale and are positive when directed into the atmosphere. We define gross ecosystem production by $\text{GEP} \equiv -(F_P + F_{PR})$, ecosystem respiration by $R_{\text{eco}} \equiv F_{DR} + F_{NR}$, and the canopy net CO_2 assimilation flux by $F_A \equiv F_P + F_{PR} + F_{DR}$.

Equation (6) applies to total CO_2 and to $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ individually, so that twice applying it leads to:

$$R_N F_N = R_P F_P + R_{PR} F_{PR} + R_{DR} F_{DR} + R_{NR} (F_N - F_P - F_{PR} - F_{DR}), \quad (7)$$

where the R are absolute ratios of ^{13}C to ^{12}C . Eq. (7) is exact if the fluxes refer to ^{12}C , and is a good approximation if they refer to total carbon, i.e. as written (Tans et al., 1993). Because the proportional differences between the isotopic ratios R_N , R_P , R_{PR} , R_{DR} , and R_{NR} are less than about 10 ‰, the maximum proportional error in any term in Eq. (7) when all the ^{12}C fluxes are replaced with total C fluxes is less than about 0.1 ‰.

There are 9 variables in Eq. (7), only 3 of which (R_N , F_N , R_{NR}) are measured here. To solve for the remaining variables, we require five additional equations in F_P , R_P , F_{PR} , R_{PR} , F_{DR} , and R_{DR} , the derivation of which is the subject of Sections 2.2 and 2.3.

2.2. Photorespiration and Foliar Daytime 'Dark' Respiration

We have no means to measure F_P , F_{PR} , and F_{DR} independently, and because photorespiration (F_{PR}) and foliar daytime 'dark' respiration (F_{DR}) fractionate the carbon isotopes (i.e. $R_P \neq R_{PR} \neq R_{DR}$) (Ghashghaie et al., 2003; Igamberdiev et al., 2004; Lanigan et al., 2008; Tcherkez, 2006; Tcherkez et al., 2004; 2010), we cannot simply wrap them into net assimilation and ignore them. Fortunately, the published literature provides a useful empirical understanding of photorespiration and foliar daytime 'dark' respiration.

Photorespiration is the dominant component of daytime foliar CO_2 production, with photorespiratory carbon loss equal to about one fifth the net photosynthetic carbon gain in C_3 plants (Bauwe et al., 2010). The photorespiratory flux is known to depend on the available light, the temperature, and the O_2 and CO_2 concentrations at the site of carboxylation (Sharkey, 1988). In particular, Equations (4), (5a), and (8) of Sharkey (1988) can be used to write:

$$F_{PR} = -F_P G^{\text{c}} / C_c, \quad (8)$$

where $C_c = (c_c / k_H) / c_{\text{air}}$ is the gas-phase equivalent molar mixing ratio of chloroplast CO_2 to (wet) air and G^{c} is the photocompensation point expressed as a gas-phase equivalent molar mixing ratio of CO_2 to (wet) air. Here c_c is the

208 concentration of CO₂ at the site of carboxylation in the chloroplast, k_H is Henry's
 209 constant, and c_{air} is the moles of (wet) air per unit volume in the forest canopy. An
 210 expression for c_c/k_H is derived in Section 2.3, and an empirical formula for G_c^{c} as a
 211 function of temperature under ambient O₂ is provided in Appendix B6. The
 212 measured temperature and pressure at flux measurement height can be used to
 213 calculate a sufficiently accurate c_{air} via the ideal gas law.

214 The carbon isotope fractionation by photorespiration has been considered in detail
 215 by Tcherkez(2006), whose Equation (B2) is, in our notation:

$$216 \quad R_{PR} = \frac{a_0}{1+a_1(F_{PR}/F_P)} R_P, \quad (9)$$

217 where

$$218 \quad a_0 = \frac{2(1+\epsilon)}{(2+g)}; \quad a_1 = \frac{2(1+\epsilon)(1+g)}{(2+g)} - 1 \quad (10)$$

219 and where, in turn, $\epsilon \sim 1 \text{ ‰}$ is a parameter (not strictly a fractionation, unlike
 220 elsewhere in this article) that depends on the fractionation by aldolase and
 221 transketolase, and $g \sim 22 \text{ ‰}$ is the fractionation by glycine
 222 decarboxylase(Tcherkez, 2006). These values are discussed in Appendix B8.

223 Having established equations for the flux and isotopic composition of
 224 photorespiration, we turn to foliar daytime 'dark' respiration, which has not been
 225 well described by measurement or theory. At this point, even the substrate is
 226 uncertain; however Tcherkez et al. (2010) have reported that the substrate for foliar
 227 'dark' respiration in the light is similar to that in the dark—though the metabolic

228 pathway (and hence fractionation) differs—and Nogués et al. (2004) have reported
 229 that the substrate for foliar ‘dark’ respiration after the cessation of illumination is
 230 not composed of recent photosynthates. Nonetheless, the isotopic fractionation by
 231 daytime ‘dark’ respiration is generally defined by assuming that the substrate has
 232 the same isotopic composition as recent net assimilates—that, for example, is the
 233 way in which the fractionation parameter e is defined in the full discrimination
 234 equation of Farquhar et al. (1982). Based on that assumption, foliar ‘dark’
 235 respiration in the dark is thought to discriminate against ^{12}C (by up to 6 ‰), while
 236 foliar ‘dark’ respiration in the light is thought to discriminate against ^{13}C (by about
 237 5 ‰) (Tcherkez et al., 2010; 2004).

238 Fortunately for IFP, foliar daytime ‘dark’ respiration should be much smaller than
 239 photorespiration, and is inhibited by sunlight in some species (Hurry et al., 2005;
 240 Pärnik and Keenberg, 2007)—though it is unknown whether such inhibition occurs
 241 in the oak leaves considered here. Xu and Griffin (2008) estimated mean nightly
 242 foliar respiration for the period from June to October in dry and mesic oak stands
 243 in New York State (from a model) and reported $45 \text{ mmol m}^{-2} \text{ night}^{-1}$ for the dry
 244 stand and $101 \text{ mmol m}^{-2} \text{ night}^{-1}$ for the mesic stand, which correspond to about 1.5
 245 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ and $3.5 \mu\text{mol m}^{-2} \text{ s}^{-1}$, respectively. Given our June-to-October mean
 246 nighttime NEE of $5.2 \mu\text{mol m}^{-2} \text{ s}^{-1}$, Xu and Griffin (2008)’s findings would suggest
 247 that foliar respiration accounts for one quarter to one half of our nighttime NEE. For
 248 the partitioning presented in this article, we simply assume that foliar daytime ‘dark’
 249 respiration is one quarter of nighttime R_{eco} . Thus F_{DR} is calculated as:

$$F_{DR} = 0.25 R_{eco}^*, \quad (11)$$

where R_{eco}^* is R_{eco} for the same wind direction as F_{DR} , obtained from a whole-season Loess-smoothing of nighttime NEE versus wind direction.

We also make the usual assumption that the substrate for daytime 'dark' respiration has the same isotopic composition as recent net photosynthates, in which case,

$$R_{DR} = R_A / \alpha_{DR} = \left(\frac{R_P F_P + R_{PR} F_{PR} + R_{DR} F_{DR}}{F_P + F_{PR} + F_{DR}} \right) / \alpha_{DR}, \quad (12)$$

where α_{DR} is the fractionation factor for daytime 'dark' respiration (see Appendix B8), and where in the expansion of R_A , we have replaced ^{12}C fluxes by total C fluxes as in Eq. (7). Rearranging Eq. (12) to isolate R_{DR} , and then inserting Eq. (9) to eliminate R_{PR} , yields:

$$R_{DR} = \frac{F_P + \frac{\alpha_0}{1 + \alpha_1 (F_{PR}/F_P)} F_{PR}}{\alpha_{DR} (F_P + F_{PR} + F_{DR}) - F_{DR}} R_P. \quad (13)$$

The errors resulting from the assumed substrate composition and rate for daytime 'dark' respiration should be small given the low sensitivity of IFP to F_{DR} and R_{DR} (Section 4.4).

2.3. CO₂ Transport and Fixation within the Leaf

Two tasks remain: (1) deriving the final equation, which must relate the gross photosynthetic flux F_P to its isotopic composition R_P , and (2) deriving an expression for c_c/k_H to insert into Eq. (8). Both tasks require us to consider the series of diffusive and biochemical processes by which leaves assimilate atmospheric CO₂. We

depict those processes in Figure 1, adapted from Tholen et al.(2012). To reach the site of carboxylation (subscript c) in the chloroplast, CO_2 from the canopy air (n) must diffuse through: the leaf boundary layer (b), the stomata (s), the mesophyll cell wall and plasmalemma (wp), and the chloroplast envelope and stroma (ch). Along the way, CO_2 passing from the intercellular air space to the cell wall must dissolve in water according to Henry's constant k_H . Simultaneously, photorespiration and foliary daytime 'dark' respiration are producing CO_2 , which is injected into the cytosol (y) by the mitochondria, partway along the transport pathway. Each of these processes has its own isotope-specific rate constant.

Figure 1. Schematic diagram of CO_2 production, consumption, and transport in and around the leaf. The various r are resistances to CO_2 transport, the various c are CO_2 concentrations, and the various F are CO_2 fluxes. Subscripts are explained in Table 2. Adapted from Tholen et al. (2012).

Approximating the CO_2 transport as one-dimensional, Fick's Law (Eq. (A1)) defines a resistance r to the diffusion of each isotope through each component of the leaf. We

follow Tholen et al. (2012) in assuming that the resistances of the intercellular air space (i) and the cytosol (y) are much less than those of the cell wall, plasmalemma, chloroplast envelope, and stroma (an uncertain but necessary assumption given the present state of knowledge: see Evans and Caemmerer, 1996; Flexas et al., 2008; Gillon and Yakir, 2000; Mott and O'Leary, 1984; Parkhurst and Mott, 1990). Thus the total mesophyll resistance is $r_m \approx r_{wp} + r_{ch}$, and we can write the following equations for diffusion against the component resistances r_{wp} and r_{ch} :

$$c_y - c_c = -r_{ch} F_P \quad (14)$$

$$c_{ow} - c_y = -r_{wp} F_A = -r_{wp} (F_P + F_{PR} + F_{DR}), \quad (15)$$

where c_{ow} is the concentration just outside the cell wall, in solution. This concentration is related to c_i by Henry's Law:

$$c_{ow} = k_H c_i, \quad (16)$$

where Henry's constant k_H is about 0.8 but is different for each isotope. Eq. (16) assumes that exchange of CO_2 across the gas-liquid interface is very much faster than diffusion of CO_2 in air or water (a good assumption according to Siegenthaler and Munnich, 1981).

Similarly, for the gas-phase diffusion path, we can write:

$$c_n - c_i = -(r_b + r_s) F_A = -(r_b + r_s) (F_P + F_{PR} + F_{DR}). \quad (17)$$

Eqs. (14-17) can be combined to yield:

$$\frac{c_c}{k_H} = c_n + (r_b + r_s + x_{wp} + x_{ch})F_P + (r_b + r_s + x_{wp})(F_{PR} + F_{DR}), \quad (18)$$

where we have introduced the gas-phase equivalent resistance $x = r/k_H$. At this point it is useful to introduce the abbreviations,

$$r_1 = r_b + r_s + x_{wp} + x_{ch} \quad (19)$$

$$r_2 = r_b + r_s + x_{wp}, \quad (20)$$

and to use Eq. (A3) to define $a_1 \circ r_1^{13}/r_1^{12}$ and $a_2 \circ r_2^{13}/r_2^{12}$. Because Eqs. (14-20) apply separately to each isotope as well as to total CO₂, we have:

$$a_1 = \frac{a_b r_b^{12} + a_s r_s^{12} + a_d a_{wp} x_{wp}^{12} + a_d a_{ch} x_{ch}^{12}}{r_b^{12} + r_s^{12} + x_{wp}^{12} + x_{ch}^{12}} \quad (21)$$

and likewise for a_2 , where

$$a_d \circ k_H^{12}/k_H^{13} \quad (22)$$

is the (equilibrium) fractionation for dissolution of CO₂. Combining Eqs. (A3) and (18-22) yields:

$$R_P = \frac{R_c}{a_f} = \frac{1}{a_d a_f} \times \frac{c_n^{13} + a_1 r_1^{12} R_P F_P^{12} + a_2 r_2^{12} (R_{PR} F_{PR}^{12} + R_{DR} F_{DR}^{12})}{c_n^{12} + r_1^{12} F_P^{12} + r_2^{12} (F_{PR}^{12} + F_{DR}^{12})}, \quad (23)$$

where α_f is the fractionation factor for CO₂ fixation (Appendix B7). Replacing the ¹²C quantities with total C quantities, as in Eq. (7), gives:

$$R_P = \frac{c_n^{13} + a_2 r_2 (R_{PR} F_{PR} + R_{DR} F_{DR})}{a_d a_f (c_n + r_1 F_P + r_2 F_{PR} + r_2 F_{DR}) - a_1 r_1 F_P}. \quad (24)$$

319 Inserting Eq. (9) and Eq. (13) into Eq. (24) eliminates R_{PR} and R_{DR} :

$$320 \quad R_P = \frac{c_n^{13}}{\alpha_d \alpha_f (c_n + r_1 F_P + r_2 F_{PR} + r_2 F_{DR}) - \alpha_1 r_1 F_P - \frac{\alpha_2 r_2 \alpha_0 F_{PR}}{1 + \alpha_1 F_{PR} / F_P} - \frac{\alpha_2 r_2 (F_P + \alpha_0 F_{PR} / (1 + \alpha_1 F_{PR} / F_P)) F_{DR}}{\alpha_{DR} (F_P + F_{PR} + F_{DR}) - F_{DR}}} \cdot (25)$$

321 Having obtained the desired expression relating R_P to F_P , let us go back and complete
 322 the expression for F_{PR} by inserting Eq. (18) for c_c/k_H into Eq. (8). The result is a
 323 quadratic equation for F_{PR} ,

$$324 \quad r_2 F_{PR}^2 + (r_1 F_P + r_2 F_{DR} + c_n) F_{PR} + F_P G_*^{\ell} c_{\text{air}} = 0, \quad (26)$$

325 the physically meaningful root of which is always

$$326 \quad F_{PR} = \frac{-(r_1 F_P + r_2 F_{DR} + c_n) + \sqrt{(r_1 F_P + r_2 F_{DR} + c_n)^2 - 4 r_2 F_P G_*^{\ell} c_{\text{air}}}}{2 r_2}. \quad (27)$$

327 The values of the fluxes retrieved by isotopic partitioning depend on the values of
 328 the resistances and fractionations used in the above equations. Best estimates of
 329 those resistances and fractionations based on the literature are discussed in
 330 Appendix B.

331 **2.4. Numerical Solution of the Equations**

332 With F_N , R_N , and R_{NR} measured, and using the parameterization described in
 333 Appendix B, Eqs. (7), (9), (11), (13), (25), and (27) form a system of six equations in
 334 six unknowns (F_P , R_P , F_{PR} , R_{PR} , F_{DR} , and R_{DR}), which when solved, give the desired
 335 fluxes of photosynthesis ($GEP = -(F_P + F_{PR})$) and whole-ecosystem respiration ($R_{\text{eco}} =$

336 $F_{DR} + F_{NR}$). We solve this system numerically rather than analytically. The procedure,
337 depicted in Figure 2, is as follows:

- 338 1) Prescribe F_{DR} using Eq. (11).
- 339 2) Guess F_P .
- 340 3) Calculate F_{PR} from Eq. (27).
- 341 4) Calculate R_P from Eq. (25).
- 342 5) Calculate R_{PR} from Eq. (9).
- 343 6) Calculate R_{DR} from Eq. (13).
- 344 7) Calculate R_N from Eq. (7). Call this value R_N^* .
- 345 8) Compute $d = (R_N^* - R_N)^2$, where R_N is the measured value.
- 346 9) Repeat steps 2-8, adjusting F_P to minimize d .
- 347 10) Calculate F_{NR} from Eq. (6) using the optimized fluxes and ratios from step 9.

Figure 2.Flowchart depicting numerical solution of the IFP equations.

Care must be taken in the particulars of the minimization because the equations typically admit multiple solutions (~75 % of the time) and sometimes none at all (~25 % of the time). When there are multiple solutions, a plot of d versus F_P will reveal more than one dip to zero (within computational machine precision), but in our experience, only one of the corresponding F_P values is plausible, the others being either near zero, substantially positive (whereas uptake fluxes are defined negative), or of an absurdly large magnitude. For the temperate forest dataset used here (Section 3), the plausible value could always be selected as the most negative value less negative than $-100 \mu\text{mol m}^{-2} \text{s}^{-1}$.

When there is no solution to the partitioning equations, due either to measurement error (most likely noise in δ_N) or to the violation of one or more assumptions, a plot

of d versus F_p will reveal a broad minimum well above computational machine zero (e.g. 10^{-9} , well above 10^{-16}), and it is necessary to choose whether to accept that minimum as the best approximate solution or to reject the data point entirely. Rejection might seem conservative but would itself induce a bias because, as it happens, error that pushes F_p to lesser magnitudes is much more likely to cause the exact solution to vanish than is error that pushes F_p to greater magnitudes. The biases involved in accepting or rejecting best approximate solutions are described in Section 4.3.

Note that the above considerations apply equally to the previously published IFP methods, which admitted no exact solution roughly as often as did the full theory presented here.

3. Measurements

The measurements used here span May through October 2011 at the Harvard Forest Environmental Measurements Site (Goulden et al., 1996; Urbanski et al., 2007; Wofsy et al., 1993), situated in a temperate deciduous forest dominated by red oak and red maple but also including hemlock, white pine, and red pine, in Massachusetts, U.S.A. For calculations of the leaf boundary layer and mesophyll resistances, we treat all leaves at the site as oak leaves; given the sensitivity of the partitioning to these resistances (Section 4.4), this approximation should introduce a proportional error in GEP of at most a few percent.

3.1. Eddy Fluxes

The isotopic CO₂ flux measurements were acquired using a quantum cascade laser spectrometer (QCLS) and have been described in detail elsewhere (Wehr et al., 2013). The sensible heat and water fluxes were measured by the long-term HF-EMS eddy flux system (Goulden et al., 1996; Urbanski et al., 2007; Wofsy et al., 1993). Flux measurements were sparse in May owing to inclement weather and associated power outages.

3.2. The Isotopic Signature of Non-Foliar Respiration

We obtained the isotopic signature of non-foliar respiration, δ_{NR} , from nighttime Keeling plots (i.e. plots of δ versus $1/C$, in which the y-intercept is the respiratory source signature). For each night, we constructed a Keeling plot using all values of C and δ measured by the QCLS at all 7 sampling heights on the HF-EMS tower, including inlets at 0.2 and 1.0 m above ground (Wehr et al., 2013). An example Keeling plot from the night of May 25-26 is shown in Figure 3. The vast majority of the variation in C and δ in the Keeling plot came from their vertical gradients rather than temporal variation. We confirmed by a simple multilayer isotopologue eddy diffusion simulation (designed specifically for our site and conditions) that the intercept of such a Keeling plot is very close to the isotopic signature of belowground respiration and is almost uninfluenced by canopy respiration. For example, if canopy respiration is 25 % of the total ecosystem respiration and its signature is 4 ‰ different from the belowground signature, the Keeling plot intercept is still within 0.2 ‰ of the belowground signature. This insensitivity to canopy respiration is due to the fact that the Keeling plot intercept is dominated by the high-CO₂

measurements near the ground (as is clear from Fig. 3), which are dominated in turn by belowground-respired CO_2 . Thus our Keeling plot intercepts should not be significantly contaminated by foliar respiration. The intercepts were interpolated in time using a Loess filter, rejecting extreme points, to obtain δ_{NR} for each flux measurement point.

Figure 3. An example Keeling plot used to determine the isotopic signature of non-foliar respiration through the night of May 25-26, 2011. Inlets near the ground (red) exert a dominant influence on the y-intercept.

There are two key assumptions implicit in this approach. The first is that δ_{NR} may vary from day to day but not hourly, so that it does not change significantly during the night and it does not differ systematically between night and day. This assumption is supported by our preliminary measurements of the isotopic composition of the soil surface CO_2 efflux in automated chambers at the HF-EMS, made in August 2012 (unpublished data); these measurements put an upper limit of 0.25 ‰ on peak-to-peak diel variation in the isotopic signature of belowground respiration (which translates into a proportional error of less than 1% in

421 GEPretrieved by IFP), consistent with recent results in a subalpine conifer forest
 422 (Bowling et al., 2015). Previously, Betson et al. (2007) put an upper limit of about
 423 1 ‰ on said variation in a boreal forest.

424 The second assumption is that δ_{NR} does not vary spatially, i.e. with the tower
 425 footprint. To get an indication of the impact of footprint motion on δ_{NR} , we computed
 426 the flux-weighted isotopic composition of nighttime NEE in three wind sectors
 427 chosen according to the magnitude of nighttime NEE: 0-180° (a low flux sector),
 428 180-260° (a moderate flux sector), and 260-360° (a high flux sector). The flux
 429 weighting, which reduced the influence of highly uncertain values near zero NEE,
 430 was accomplished by taking δ_N as the slope of a linear fit to a plot of I_N^{13} versus F_N ,
 431 with the fit forced through the origin. The resulting values of nighttime δ_N were: -
 432 26.8 ± 0.7 ‰ (0-180°), -26.0 ± 0.6 ‰ (180-260°), and -26.6 ± 0.3 ‰ (260-360°). All
 433 these values fall within one standard error of the seasonal mean δ_{NR} as determined
 434 by Keeling plots at the tower, which was -26.5 ± 0.1 ‰. Given the possible spread of
 435 δ_N across our three wind sectors, we estimate the uncertainty in δ_{NR} due to spatial
 436 variation at about ± 0.5 ‰ (1 standard deviation). The uncertainty in δ_{NR} due to our
 437 Keeling plot approach is less than that. As we will see in Section 4.4, a 0.5 ‰ error
 438 in δ_{NR} would cause a 0.2 ‰ error in δ_A and a 2 % error in GEP (8 % in R_{eco}). A caveat
 439 regarding this directional analysis is that nighttime NEE includes foliar respiration,
 440 the influence of which is suppressed in our estimates of δ_{NR} . Nonetheless, as non-
 441 foliar respiration should be the larger component of total respiration (Wofsy et al.,

1993; Xu and Griffin, 2008), spatial variation in δ_{NR} is unlikely to be significantly greater than that in nighttime δ_N .

3.3. Leaf Area Index

Leaf area index (LAI) is used in the calculation of the leaf boundary layer conductance (Eq.(B4)) and mesophyll conductance (Eq.(B14)), and in the parameterization of stomatal conductance when evaporation is non-negligible (Eq.(B12)). We estimate LAI here from plant area index (PAI), measured optically at several plots in the tower footprint on a monthly basis (as part of routine HF-EMS operations) and interpolated to our 40-minute time grid. We adjust observed PAI to LAI by accounting for the wood fraction and the evergreen and deciduous LAI components, as follows. True PAI is the sum of the wood area index (WAI) and the leaf area index (LAI), the latter of which is the sum of the evergreen leaf area index (ELAI) and the deciduous leaf area index (DLAI); however, as LAI increases, optically measured PAI (hereafter PAI^*) approaches LAI because leaves mask branches (Breda, 2003; Kucharik et al., 1998). Thus, to a practical approximation, PAI^* varies between LAI in the summer and $WAI + ELAI$ in the winter. Accordingly, we rescale the conventional calculation of DLAI so that:

$$LAI = \frac{PAI_{max}^* - ELAI}{PAI_{max}^* - PAI_{min}^*} (PAI^* - PAI_{min}^*) + ELAI \quad (49)$$

where PAI_{max}^* is the summertime peak PAI^* (roughly equal to peak LAI) and PAI_{min}^* is the wintertime minimum PAI^* (roughly equal to $WAI + ELAI$). The second bracket in Eq. (49) is the conventional calculation of DLAI, and the first bracket is our

rescaling factor. Because we do not have measurements of ELAI and WAI separately, we specify $ELAI = WAI = PAI_{min}^*/2$, a rough approximation. At the HF-EMS in 2011, $PAI_{max}^* = 5.1$ and $PAI_{min}^* = 1.9$, but PAI^* was greater than 3 throughout the measurement period reported here.

3.4. Data Filtering

Following previous work at this site (Urbanski et al., 2007), only flux measurements for which the friction velocity (u_*) exceeded 0.17 were used. In addition, for the calculation of stomatal conductance via Eq. (B10) in Appendix B, it was necessary to exclude those rare daytime measurements for which either the water flux or the leaf-air vapor pressure difference was negative (in which case there is no transpiration). For IFP, it was further necessary to exclude those rare measurements for which the stomatal conductance calculated via Eq. (B10) was negative (due to measurement noise). Finally, we restricted IFP to measurements for which $PAR > 50 \mu E m^{-2} s^{-1}$ because the isotopic composition of the photosynthetic flux becomes noisy as that flux approaches zero (and is undefined when that flux is zero).

4. Results and Discussion

4.1. Demonstration: The Seasonal Patterns of Isotopic Discrimination and Disequilibrium

In order for IFP to work, the isotopic signature of net photosynthetic assimilation, δ_A , must be distinct from (i.e. out of equilibrium with) that of non-foliar respiration,

484 δ_{NR} . For an individual eddy flux measurement, that is almost always the case because
 485 of the relatively large (several ‰) diurnal variation of δ_A and the relative constancy
 486 (<0.25 ‰) of δ_{NR} . In addition, our results (Figure 4) confirm that even at the seasonal
 487 timescale, there is a small but distinct isotopic disequilibrium ($D = \delta_{NR} - \delta_A$), stable at
 488 roughly -0.5 ‰ through most of the growing season but with high values (> 0) at
 489 the start and slightly low values (-1 ‰) at the end. The sign (which is opposite to
 490 that expected from the Suess effect), approximate magnitude, and relatively high
 491 early-season values of D are consistent with recent measurements in a subalpine
 492 conifer forest (Bowling et al., 2014), although those measurements indicated a late-
 493 season increase in D rather than the slight decrease found here. Several plausible
 494 explanations for persistent negative D were discussed in that study, including post-
 495 photosynthetic fractionation leading to sequestration of isotopically enriched
 496 carbon in wood or soil (Bowling et al., 2014). Note that none of the systematic
 497 uncertainties considered in Section 4.4 is likely to account for a bias in D of 0.5 ‰.

498 Though offset by the disequilibrium, the seasonal pattern of δ_{NR} (which describes the
 499 ecosystem carbon output) closely matches that of δ_A (which describes the ecosystem
 500 carbon input) with no resolvable time lag (Fig. 4), indicating that most respired
 501 carbon has resided in the ecosystem for less than a week. The match between these
 502 patterns also substantiates the IFP results because δ_A is an output of IFP while δ_{NR} is
 503 an independent measurement (Section 3.2). (Although the IFP calculation
 504 takes δ_{NR} as an input, the value of δ_A determined by IFP is hardly influenced by the

value of δ_{NR} : a 0.5 ‰ change in δ_{NR} causes only a 0.1 ‰ change in δ_A , as shown in Section 4.4).

Fig. 4 also shows the close correspondence of the apparent fractionation by net photosynthetic assimilation, ϵ_A (commonly called discrimination), and the intercellular CO₂ mole fraction, consistent with the basic idea of stomatal influence expressed in Eq. (4).

Figure 4. Seasonal cycles of: the isotopic composition of CO₂ in the canopy airspace, δ_n ; the apparent fractionation by net photosynthetic assimilation (i.e. the discrimination), ϵ_A ; the isotopic signatures of net photosynthetic assimilation, δ_A , and non-foliar respiration, δ_{NR} ; the isotopic disequilibrium, D ; and the intercellular CO₂ mole fraction, C_i . The dark lines connect flux-weighted means (including all daylight hours) for each 10-day bin, except in the case of δ_{NR} , where the lines connect simple means for each bin including all nighttime hours (because δ_{NR} is derived from nighttime Keeling plots rather

than daytime flux measurements). The light shaded bands around the dark lines show the standard errors in the flux-weighted means calculated according to the ratio variance approximation recommended in (Gatz and Smith, 1995) (or just the standard error in the mean for δ_{NR}), based on the variability within each bin. Hatched areas indicate periods of leaf expansion and senescence, during which some parameters used for isotopic partitioning might not be valid.

4.2. Demonstration: Precision and Ecosystem Heterogeneity

We partitioned 1042 independent NEE measurements over the 2011 growing season (Figure 5), but to reveal the characteristics of IFP, we focus on 3 illustrative days in August 2011 (Figure 6). We note two broad features of interest.

Figure 5. Individual eddy covariance measurements of NEE (black) partitioned into GEP (green, inverted) and R_{eco} (brown). All partitioned flux measurements from 2011 are shown.

First, the variability in daytime R_{eco} from IFP is similar in magnitude and character to that in nighttime NEE, suggesting that the precision of the isotopically partitioned fluxes is similar to that of NEE itself. Indeed, taking all July measurements together, the standard deviation of daytime R_{eco} to the southwest of the tower was $5.8 \mu\text{mol m}^{-2} \text{s}^{-1}$, compared to $5.3 \mu\text{mol m}^{-2} \text{s}^{-1}$ for July nighttime NEE in the same quadrant.

We conclude that the variability in daytime R_{eco} and GEP derived almost entirely from variability in measured NEE rather than from the isotopic partitioning.

Figure 6. NEE (black points) and isotopically partitioned GEP (green points, inverted) and R_{eco} (brown points) over 3 days in August 2011, smoothed to 2 hours (i.e. 3 points). Also shown are wind direction (top panel), PAR (yellow shading, inverted), and GEP (pink lines) and R_{eco} (blue lines) estimated by standard partitioning based on nighttime NEE and temperature. Missing points were filtered out by one of the criteria discussed in Section 3.4.

Second, the measured respiration—day or night—depends strongly on wind direction, a coarse indicator of the tower sampling footprint. The dependence is strong (Figure 7): certain areas to the northwest of the tower exhibited respiratory fluxes that were on average 3 times greater than areas to the southwest. This directional variation in respiration violates the eddy covariance assumption of a horizontally homogeneous ecosystem (which cannot be fully satisfied at any real site) and therefore probably induces errors in NEE. Additionally, it causes further (and likely larger) errors in standard NEE partitioning because that partitioning is based on 4- or 6-day regression windows and therefore blends the different tower footprints together. Thus standard R_{eco} is virtually flat through the

day (Fig. 6), and the variations in NEE due to footprint motion are mistakenly attributed entirely to GEP—which therefore behaves erratically with respect to environmental drivers, as is most evident on the morning of Aug 11 in Fig. 6, when standard GEP is strongly anti-correlated with PAR.

IFP, on the other hand, captures the directional variation in respiration because it partitions each flux measurement independently. From the perspective of one interested in whole-ecosystem (i.e. spatially integrated) R_{eco} and GEP, IFP correctly partitions the meteorological noise in NEE while standard partitioning does not. IFP reveals that GEP was also greater to the northwest than to the southwest, but the proportional variation was less than 20 % (not shown).

Figure 7. Nighttime NEE (black), daytime R_{eco} estimated by isotopic flux partitioning (brown), and daytime R_{eco} estimated by standard partitioning based on nighttime NEE and temperature (blue) versus wind direction, over the entire growing season. Dark lines are bin means while light shaded regions indicate ± 1 standard error in the mean based on variability within the bin.

Standard partitioning based on light-response curves (Lasslop et al., 2010) can be even more severely corrupted by footprint motion because the method interprets footprint-related variations in measured daytime NEE as being light-related, and can thereby arrive at unrealistic light-response curves. In the days surrounding August 11, for example, this method exaggerated GEP and R_{eco} by a factor of 2, putting R_{eco} at about $35 \mu\text{mol m}^{-2} \text{s}^{-1}$ all day (not shown). More subtle errors of the same kind would bias estimates of GEP and R_{eco} without being detectable, absent the isotopic flux measurements.

We should point out that August 11 is the most extreme day in the dataset in terms of footprint motion and of disagreement between standard and isotopic partitioning; August 10 and 12 are more typical of the northwest quadrant.

4.3. Biases due to the Structure of the Equations

Because the partitioning equations are nonlinear, normally distributed error in the measured variables can translate into skewed error and therefore bias in GEP. For the instrumentation that acquired the data used here (Section 3), the only measured variable with non-negligible random error was δ_N , and the bias due to that error turned out to be negligible. We estimated the bias as follows.

For each eddy flux measurement in July, we determined the response of GEP to the value of δ_N (all else being equal) by rerunning the partitioning calculation using a range of values of δ_N rather than the actual measured value. The shape of this response curve depends on other variables such as the magnitude of NEE, so that it

589 varies from one eddy flux measurement to the next. We then used the resulting
 590 response function for each eddy flux measurement to map normally distributed
 591 error in δ_N onto GEP for that measurement. We centered the distribution of error in
 592 δ_N on an approximate true δ_N estimated as the flux-weighted average of
 593 all δ_N measurements within ± 2 hours of the measurement under consideration, and
 594 we set the standard deviation of the error in δ_N as $14.2(\text{NEE}^{-0.955}) + 0.215$, which is
 595 a close description of the random instrument error based on the characterization
 596 method detailed in Wehr et al. (2013); as NEE increases, error in δ_N decreases.
 597 Finally, for each flux measurement, we computed the bias as the difference between
 598 the mean of the resulting GEP distribution and the 'true' GEP calculated from the
 599 approximate true δ_N .

600 The resulting bias estimates when including or excluding best approximate
 601 solutions to the partitioning equations (Section 2.4) are plotted versus the absolute
 602 magnitude of NEE in Figure 8. The bias estimates for individual eddy flux
 603 measurements are subject to variability associated with environmental conditions
 604 as well as with error in our approximate true δ_N , and so we have used a Loess filter
 605 to smooth them versus the magnitude of NEE. The smoothed curves show that the
 606 bias in GEP when including best approximate solutions is between zero and -
 607 $0.3 \mu\text{mol m}^{-2} \text{s}^{-1}$ for all values of NEE; the overall mean is $-0.2 \mu\text{mol m}^{-2} \text{s}^{-1}$ (-1% of the
 608 July daytime mean GEP). When excluding approximate solutions, GEP is biased
 609 positively at low magnitudes of NEE by up to $1 \mu\text{mol m}^{-2} \text{s}^{-1}$, with an overall mean of
 610 $+0.4 \mu\text{mol m}^{-2} \text{s}^{-1}$ (+2% of the July daytime mean GEP). We therefore chose to

accept best approximate solutions, thereby reducing bias and allowing the partitioning of more flux measurements.

Note that we have been considering random measurement error rather than total variability: as discussed in Section 4.2, there is large variability in measured NEE that is responsible for most of the variability in the retrieved fluxes, but most of that variability is not erroneous from the perspective of IFP, because it is caused by changes in the flux tower sampling footprint and, during the day, by changes in cloud cover—both of which affect the real fluxes of CO₂, water, and heat observed at the tower.

Figure 8. Bias in GEP resulting from normally distributed measurement error in δ_N coupled with the nonlinear nature of the partitioning equations, as a function of the absolute magnitude of NEE, when best approximate solutions are included (grey circles, black line) or excluded (pink triangles, red line). The points are bias estimates for each of the individual flux measurements in July, 2011, and the lines are smoothings versus the absolute magnitude of NEE, made using a Loess filter.

4.4. Systematic Uncertainties

627 Because IFP depends on the complex interaction of many input parameters, we
 628 quantified its systematic uncertainty in terms of the sensitivity of whole-season
 629 mean GEP and δ_A to adjustment of each input parameter, all else being equal. The
 630 results are reported in Figure 9, which includes each of the substantially uncertain
 631 input parameters described in Appendix B (e.g. the fractionation by Rubisco, e_{Ru}) as
 632 well as: the rates and signatures of photorespiration and foliar daytime ‘dark’
 633 respiration; the measured isotopic signature of non-foliar respiration; the measured
 634 isotopic composition of NEE; and the measured eddy fluxes of CO₂, water vapor, and
 635 sensible heat. Adjustments of the input parameters also affected the diurnal and
 636 seasonal patterns of GEP and δ_A somewhat, but the impact on their means was
 637 dominant. The magnitude of each variable’s adjustment was chosen in the spirit of
 638 the standard error; that is, we judged that errors of the chosen magnitudes were
 639 fairly probable but errors of more than twice those magnitudes were improbable.
 640 Unfortunately, the literature usually presents no means for a more rigorous
 641 approach.

642 The bases for our judgments were as follows: $e_{Ru} + 2 \text{ ‰}$ and $\beta + 0.03$, the
 643 distributions of published values across (a limited number of) species; $r_{bH} \times 1.5$, the
 644 uncertainty reported in McNaughton and Van den Hurk (1995) for the amalgamated
 645 coefficient 150 in Eq. (B4); $r_m \times 1.2$, the uncertainty reported in Warren and Dreyer
 646 (2006); $g - 4 \text{ ‰}$, the range of values reported in Tcherkez (2006) for the
 647 photorespiratory fractionation f and for fractionation by glutamate
 648 decarboxylase (this adjustment is negative because the preferred value is at the top

649 of the reported range); $G^c \times 1.1$, the discrepancy between the measurements of
 650 Jordan and Ogren(1984) and Brooks and Farquhar (1985); $F_{DR} \times 1.5$, estimates of
 651 foliar dark respiration(Xu and Griffin, 2008) and of its inhibition by sunlight(Atkin
 652 et al., 1998; Hurry et al., 2005; Pärnik et al., 2007); $e_{DR} + 1 \text{ ‰}$, the
 653 uncertaintyreported inTcherkez et al.(2010) (but those measurements were for
 654 sunflower); $\delta_{NR} + 0.5 \text{ ‰}$, our determination of spatial heterogeneity surrounding the
 655 EMS tower (Section 3.2). For the flux measurements, we arbitrarily adjusted the
 656 values up by 5 %, though such errors are not particularly likely. For δ_N , we
 657 arbitrarily adjusted the value up by 0.5 ‰, in keeping with δ_{NR} . In the case of the
 658 water flux E , the error could be imagined as methodological or as due to the
 659 presence of evaporation in the total water flux. The parameters are ordered in the
 660 figure according to the magnitude of the effect on GEP.

Figure 9. Sensitivity analyses: responses of growing season mean δ_A and GEP to adjustments in various IFP input parameters (red) and measured quantities (blue).

Previous IFP studies have stressed r_s and r_m as leading sources of uncertainty (Bowling et al., 2001; Knohl and Buchmann, 2005; Ogée et al., 2003; Zobitz et al., 2008). Although IFP is highly sensitive to r_s , it does not appear in Fig. 9 because it is derived from other parameters in the figure (E , H , r_{bH} , r_e , e_a , and T_a). And although IFP is also sensitive to r_m , Fig. 9 indicates that the parameters contributing the greatest uncertainty to GEP are the fractionation by Rubisco ϵ_{Ru} and the proportion of carboxylation done by PEP-carboxylase β , both of which concern the isotopic fractionation by carboxylation and have never before been considered as a source of error. The leaf boundary layer resistance r_{bH} is also important. The

uncertainties associated with the rates and isotopic signatures of photorespiration and daytime 'dark' respiration are less than a few percent of GEP – much smaller than the error induced by neglecting photorespiration entirely (see Fig. 10below). Combining all the systematic literature parameter uncertainties in Fig. 9in a simple sum-of-squares error approach gives an overall proportional systematic uncertainty in GEP of $\pm 17\%$. If the fractionation by carboxylation (e_{Ru} and β) were known precisely, that uncertainty would drop to $\pm 7\%$. This approach assumes that the parameters are non-interacting, which is not quite true. For δ_A , the overall absolute systematic uncertainty is $\pm 0.3\text{ ‰}$ ($\pm 0.1\text{ ‰}$ if e_{Ru} and β were known precisely).

The systematic uncertainty associated with the big-leaf canopy approximation underlying the IFP equations in Section 2 (and all simplifications thereof) cannot be quantified without knowing how the sources and sinks of $^{13}\text{CO}_2$, $^{12}\text{CO}_2$, light, water, and heat are distributed throughout the canopy. Leaf-level measurements distributed through the canopy would be valuable for testing the big-leaf approximation and implementing a multi-leaf version of IFP. Error due to this approximation might be correlated with PAR and time of day or season via the sun angle and the diffuse light fraction, but with sufficient data, these variations could be constrained by analyzing periods of completely diffuse light and identical canopy structure.

In addition to estimating systematic uncertainties, we can use sensitivity analyses to ask what is gained by the extended theoretical framework presented here. Thus in Figure 10, we present the biases (relative to the full model presented here) induced

in GEP and δ_A by using the simplified theoretical formulations of Bowling et al. (2001), Ogée et al. (2003), and Knohl and Buchmann (2005) (but always using the same stomatal conductance, determined by our method described in Appendix B4). We also present the bias induced by neglecting photorespiration in particular. The original isoflux-based IFP formulation (Bowling et al., 2001), which lacked boundary layer and mesophyll resistances, gives a bias of +67 % of GEP (i.e. GEP was systematically too high compared to what would be estimated by the approach here), while the more recent formulations (Knohl and Buchmann, 2005; Ogée et al., 2003) give biases of +2 % and +14 % of GEP. All previous formulations neglect photorespiration, which in itself biases GEP by +13 %, but the overall biases in the more recent formulations are similar to or less than +13 % because other approximations and errors fortuitously balance the neglect of photorespiration for this dataset; for example, neglecting foliar daytime ‘dark’ respiration biases GEP by -3 % (not shown). Each simplified formulation also gives a bias of between -0.1 and -0.3 ‰ in δ_A . Because none of the major systematic uncertainties in the full theory (those related to e_{Ru} , β , r_{bH} , and r_m) is removed by any of the simplifications, the full theory is preferable—at least when applied to a deciduous oak forest. (Assigning a parameter a value well outside the range of uncertainty in that parameter, e.g. $G^c = 0$, does not change the uncertainty; it merely guarantees some minimum bias associated with that parameter.)

Figure 10. Sensitivity analyses: responses of growing season mean δ_A and GEP to three simplifications of the IFP theory (B-2001 = Bowling et al., 2001; O-2003 = Ogée et al., 2003; K-2005 = Knohland Buchman, 2005), to the neglect of photorespiration in particular (No PR), and to use of the EC/flask approximation to the isotopic composition of NEE (EC/flask).

The final column in Fig. 10 shows the biases resulting from the EC/flask approximation (Bowling et al., 2001) used by most IFP studies (Bowling et al., 2001; Knohl and Buchmann, 2005; Lai et al., 2003; Ogée et al., 2003; Zobitz et al., 2008) in place of direct measurements of the isotopic flux. Our method for simulating the EC/flask method has been described elsewhere (Wehr et al., 2013). For our temperate forest dataset, the EC/flask approximation biases GEP by +14 % and biases δ_A by +1.1 ‰, which is roughly equal to the seasonal mean isotopic disequilibrium and therefore non-negligible. We therefore recommend that direct flux measurements be used instead of the EC/flask approximation.

The bias induced in the diel cycle of non-foliar respiration (F_{NR}) by three of the simplifying formulations (Bowling et al., 2001; Knohl and Buchmann, 2005; Ogée et al., 2003) is presented in Figure 11. Because the respiratory flux is smaller than the photosynthetic flux, the +14 % bias in GEP associated with the formulation in Knohl and Buchmann (2005), for example, corresponds to a rough tripling of midday non-foliar respiration. The results from the full theory suggest, intriguingly, that daytime ecosystem respiration is less than nighttime ecosystem respiration, consistent with leaf-level studies reporting that foliar respiration is inhibited by light (Heskel et al., 2013). However, confirmation of that possibility at the ecosystem scale would require a reduction in the systematic uncertainty of the partitioning, to less than about $1 \mu\text{mol m}^{-2} \text{s}^{-1}$ ($\sim 6\%$ of GEP), which would depend in particular on reducing the uncertainties associated with the big-leaf approximation and the isotopic fractionation by carboxylation. Those uncertainties could both be reduced by feasible site-specific leaf-level measurements, as could uncertainty in the mesophyll conductance.

Even without a reduction in those *a priori* uncertainties, IFP can be used to study temporal patterns with much greater certainty than means or sums, because the systematic uncertainties in Fig. 9 have only minor (and quantifiable) effects on many temporal patterns in GEP and δ_A . As noted above, with sufficient data, even the as-yet unquantifiable effect of the big-leaf approximation can be rendered time-invariant by restricting analysis to periods of highly diffuse light and nearly identical canopy structure. It may thereby prove possible to constrain the overall uncertainty

in IFPa *posteriori* by validation against infrequent instantaneous or time-integrated estimates of GEP or daytime R_{eco} .

Figure 11. Growing season mediandiel cycles of non-foliar respiration to the southwest of the flux tower, as determined by the present IFP formulation and the three previously published simplifications from Fig. 10, along with nighttime NEE. Also shown for comparison are: growing season median air temperature, PAR, and diffuse light fraction.

5. Conclusion

We have presented an extended formulation of isotopic flux partitioning from which all previously published formulations can be derived as simplifying approximations, and demonstrated the method using data from a temperate deciduous forest. The statistical uncertainty in GEP and R_{eco} was found to be negligible compared to variability in NEE itself, while the assessable systematic uncertainty was $\pm 17\%$ of gross ecosystem production. Systematic uncertainty in the isotopic composition of canopy net photosynthates was $\pm 0.3\%$. Neglect of photorespiration in previously

published formulations was found to bias GEPhigh (by 13 %), but that bias
wassometimes offset by other approximations and errors. Some bias due to the
approximation of the canopy as a 'big leaf' should be common to this and all
previous formulations but cannot be estimated at present,for lack of data describing
the canopy heterogeneity.

The partitioning revealed that the isotopic signature of ecosystem non-leaf
respiration closely tracked the signature of carbon supply from the leaves,
indicating that most respired carbon had resided in the ecosystem for less than a
week. The disequilibrium between carbon input and output was stable on the
seasonal timescale through most of the growing season, agreeing with recently
published measurements but contradicting the prevalent idea that the
disequilibrium results from the Suess effect.

Our results illustrateda key practical advantage over standard non-isotopic
partitioning, which is the ability to partition individual flux measurements and
thereby reduce errors and biases due to changes in the flux tower sampling
footprint. The fundamental advantage, however, is that isotopic flux partitioning
does not prescribe the behaviors of ecosystem-scale photosynthesis or respiration,
which one is therefore free to discover. In the temperate forest studied here,
isotopic partitioning suggested that daytime ecosystem respiration was less than
nighttime ecosystem respiration, consistent with inhibition of leaf respiration by
light, though confirmation of that possibility would require a reduction in the
systematic uncertainty of the partitioning.

The measurements most likely to reduce that uncertainty are measurements of the fractionation by carboxylation and of the mesophyll resistance, in relevant species, and measurements constraining canopy heterogeneity sufficiently to enable a multi-leaf isotopic partitioning framework. Regardless of its systematic uncertainty, isotopic flux partitioning allows for the investigation of temporal patterns and thereby offers a unique window into the controls on ecosystem photosynthesis and respiration. Isotopic partitioning would be especially powerful in concert with complementary and potentially corroborating methods such as H₂O-CO₂ correlation analysis (Scanlon and Kustas, 2010), carbonyl sulfide flux analysis (Billesbach et al., 2014; Wohlfahrt et al., 2011), sun-induced fluorescence (Joiner et al., 2013), soil chambers, and leaf chambers.

Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Science, Terrestrial Ecosystem Science (TES) Program (Award #DE-SC0006741).

802 **Appendix A. Definitions**

803 The conductance g (m s^{-1}) and resistance $r \equiv 1/g$ (s m^{-1}) to CO_2 transport between
804 point z_1 and point $z_2 > z_1$ are defined by Fick's law of diffusion:

$$805 \quad F \equiv -g(c(z_2) - c(z_1)), \quad (\text{A1})$$

806 where F is the net flux ($\text{mol m}^{-2} \text{s}^{-1}$) in the positive z direction and $c(z)$ is the
807 concentration (mol m^{-3}) at point z . Because we employ the convention that fluxes
808 into the atmosphere are positive, the photosynthetic flux is negative.

809 The relative isotopic composition δ of a substance or flux is defined as:

$$810 \quad \delta \circ \frac{R}{R_{\text{VPDB}}} - 1, \quad (\text{A2})$$

811 where R is the ratio of ^{13}C atoms to ^{12}C atoms in the substance or flux, and R_{VPDB} is
812 the ratio of ^{13}C atoms to ^{12}C atoms in the Vienna Pee Dee Belemnite standard
813 material. We follow Griffis et al. (2004) in using the value $R_{\text{VPDB}} = 0.0111797$, but the
814 choice of R_{VPDB} has no effect on IFP so long as it is consistent.

815 The isotopic fractionation factor α (also called the isotope effect) for an irreversible
816 process such as diffusion or carboxylation is defined as:

$$817 \quad \alpha \circ \frac{k^{12}}{k^{13}} = \frac{R_{\text{source}}}{R_{\text{product}}} \text{ (for a reaction)} = \frac{g^{12}}{g^{13}} \text{ (for diffusion)}, \quad (\text{A3})$$

818 where k^{12} and k^{13} are the isotope-specific rate constants for the process.

819 The isotopic fractionation ε is defined as:

$$e^{\circ} \alpha - 1 = \frac{\delta_{\text{source}} - \delta_{\text{product}}}{1 + \delta_{\text{product}}} \text{ (for a reaction) ,} \quad (\text{A4})$$

and should not be approximated as $\delta_{\text{source}} - \delta_{\text{product}}$ (as it has been in all IFP studies to date). That approximation induces a proportional error in ε equal to δ_{product} , which is about -30 ‰ in the case of the apparent fractionation of net photosynthesis. The corresponding absolute error is -0.7 ‰, which is not negligible. Moreover, the exact definition, Eq. (A4), is tractable. Note that the alternative definitions $\alpha^{\circ} R_{\text{product}}/R_{\text{source}}$ and $e^{\circ} 1 - \alpha$ have also been used (e.g. Lee et al., 2009), and were acknowledged by Farquhar et al.(1989), but only the definitions used here are consistent with Farquhar et al. (1989) and Coplen(2011).

Appendix B. Values for the Resistances, Fractionations, and other Input Parameters

The published literature provides values or empirical formulae for all those parameters that are required to solve our system of equations but that we do not measure. In this appendix, we describe the best estimates available for each. In Section 4.4, we test the sensitivity of IFP to these parameters according to their estimated uncertainties.

B1. Canopy CO₂ Concentration, Vapor Presssure, and Temperature

The concentration and isotopic composition of CO₂ in the canopy (c_n and δ_n) are determined from the same measurements used to determine the canopy CO₂ storage (iso-)flux for the calculation of F_N and δ_N (Wehr et al., 2013). In particular, c_n and δ_n are averages of measurements at 12, 18, and 24 m on the flux tower, which span the region of maximum light absorption determined by G. G. Parker in 1998 (unpublished data), and which were meant to represent the region of peak photosynthetic assimilation.

From the within-canopy and above-canopy CO₂ measurements, it is possible to define a turbulent eddy transport resistance r_e by assuming that turbulent eddy transport functions as a gradient-driven diffusion process (Raupach and Thom, 1981), and treating the canopy as a single thin layer. In that situation, one can use Fick's Law, Eq. (A1), to write:

$$c_n = c_a + r_e F_e \quad (\text{B1})$$

where F_e is the CO₂ eddy flux (i.e. without storage). Applying the same resistance r_e to heat and water vapor (i.e. assuming the same eddies transport all scalar quantities indiscriminately, with differences in their source/sink distributions neglected, in keeping with a single-thin-layer canopy) allows us to calculate the canopy airspace temperature T_n and vapor pressure e_n , which will be necessary to calculate leaf temperature and thence stomatal resistance in Eqs. (B8-B9), below.

The sign of r_e calculated from Eq. (B1) was sometimes negative, indicating counter-gradient transport (Raupach and Thom, 1981), which we did not forbid. To reduce the impact of sampling noise in the canopy CO₂ concentrations (which are only measured for a few minutes out of every 40 minutes), we smoothed r_e to 2 hours. By using canopy CO₂ measurements from the tower, we are assuming that the flux-gradient relationships at the tower are the same as those in the eddy flux sampling footprint at the same moment in time; some statistical error should be associated with this assumption, and possibly some systematic error as well.

B2. Leaf Boundary Layer Resistance

The leaf boundary layer resistance r_b varies with leaf size, shape, orientation, distribution, and density, as well as with wind speed and with the relative importance of forced and free convection near the leaf surface. It has been studied both in wind tunnels and in the field, but owing to the complexities of its spatial and temporal variability, it remains only roughly predictable, with models requiring empirical adjustments (Massman, 1999; McNaughton and Hurk, 1995; see Schuepp, 1993). The most reasonable formulation for r_b , in our estimation, is that of

872 McNaughton and Van den Hurk(1995). It begins with the Pohlhausen equation for
 873 heat transfer to or from a flat plate (see Schuepp, 1993), which gives, for double-
 874 sided transfer:

$$875 \quad r_{bH} = 150\sqrt{L/u} \quad (B2)$$

876 where r_{bH} is the boundary layer resistance to heat transfer (different from the
 877 corresponding resistance to CO₂ transfer, as explained below), L is the plate
 878 dimension (m), u is the wind speed (m s⁻¹) just outside the boundary layer, and the
 879 amalgamated constant 150 has units of s^{1/2} m⁻¹. McNaughton and Van den
 880 Hurk(1995) then make assumptions concerning the variation of wind speed and
 881 heat flux with height in order to obtain a suitable flux-weighted average boundary
 882 layer resistance to apply to the big-leaf canopy. Following the derivation in
 883 McNaughton and Van den Hurk(1995) except in retaining u and avoiding the
 884 unhelpful division by u_* , we obtain:

$$885 \quad r_{bH} = \frac{150}{LAI} \sqrt{\frac{L}{u_h}} \int_0^1 \exp\left(-\frac{\alpha}{2}(1-z)\right) f(z) dz \quad (B3)$$

886 where LAI is the leaf area index, L is now the characteristic leaf dimension (we use
 887 0.1 m, typical for our site), u_h is the mean wind speed at the top of the canopy, z is
 888 height divided by canopy top height, $f(z)$ is the vertical profile of the heat source
 889 normalized such that $\int_0^1 f(z) dz = 1$, and α is the extinction coefficient (not a
 890 fractionation factor) for the assumed exponential wind profile:

$$\frac{u(z)}{u_h} = \exp\left(\frac{\alpha}{h}(z - 1)\right). \quad (\text{B4})$$

The wind speed at the top of the canopy can be obtained from Eq. (B4) with z set to correspond to flux measurement height a :

$$u_h = u_a \left/ \exp\left(\frac{\alpha}{h} \frac{a}{h} - 1\right) \right., \quad (\text{B5})$$

where h is the canopy top height. For canopies with leaf area indices of 0.6, 2, 4, and 9, McNaughton and Van den Hurk(1995) suggest $\alpha = 1, 2, 3$, and 4, respectively, which corresponds to the exponential relationship $\alpha = 4.39 - 3.97 \exp(-0.258 \times \text{LAI})$, which we use to calculate α for our site. From late June through the end of August, while $5.0 < \text{LAI} < 5.1$, we obtain $\alpha = 3.3$. For $f(z)$, we replace the assumptions in McNaughton and Van den Hurk(1995) with the assumption that $f(z)$ is identical to the normalized profile of light absorption, which was measured at our site by G. G. Parker in 1998 (unpublished data). We adjust $f(z)$ to account for diel and seasonal variation in the solar zenith angle, which has a small ($\sim 20\%$) effect on r_{bH} at dawn and dusk but a negligible effect on IFP. The integration over the assumed vertical profiles of wind and heat flux in Eq. (B3) is our only departure from the assumption of a big-leaf canopy; the flux-weighted average r_{bH} obtained from Eq. (B3) is assumed to apply to all leaves equally.

The boundary layer resistances for heat (r_{bH}), CO_2 (r_b), and water vapor (r_{bV}) are related by (see Hicks et al., 1987 but also Eq. (47), below):

$$r_b = N \frac{Sc \bar{\theta}^n}{\bar{\theta} Pr} r_{bH} \quad (B6)$$

$$r_{bV} = N \frac{Sc_V \bar{\theta}^n}{\bar{\theta} Pr} r_{bH} \quad (B7)$$

where Sc is the Schmidt number for CO_2 (≈ 1.05), Sc_V is the Schmidt number for water vapor ($= Sc/1.57$), Pr is the Prandtl number for air (≈ 0.71), $N = 1$ for amphistomatous leaves (i.e. leaves with stomata on both sides of the leaf, so that heat, water, and CO_2 are all transferred from both sides), and $N = 2$ for hypostomatous leaves (i.e. leaves with stomata predominantly on the underside of the leaf, so that heat is transferred from both sides while water and CO_2 are transferred from only one side). The red oak and red maple trees that dominate our Harvard Forest site are hypostomatous ($N=2$). The empirical exponent n accounts for the fact that transfer through the boundary layer is partly turbulent and is assigned the approximate value $2/3$, applicable to most gases (Hicks et al., 1987; Lamaud et al., 1994). The constant 1.57 relating Sc_V to Sc is the ratio of the binary diffusion coefficient of H_2O in air to that of CO_2 in air, as determined from their molecular masses and the molecular mass of air.

Previous IFP studies that considered the boundary layer (Billmark and Griffis, 2009; Knohl and Buchmann, 2005; Ogée et al., 2003; Zobitz et al., 2008) calculated the boundary layer resistance as a function of a constant Stanton number B (i.e. $r_{bH} = 1/u_* B$), which is not a simplification but rather a misinterpretation. The Stanton number is a dimensionless number representing the ratio of the heat flux into a fluid

to the thermal capacity of the fluid, and is defined in general as $B \equiv h/\rho_a C_p u \equiv 1/r_{bH} u$, where h is the heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$) and u is the fluid velocity (m s^{-1}). Owen and Thomson (1963) proposed that the characteristic wind speed in the canopy should be u_* and thereby *defined* the Stanton number for all subsequent canopy exchange literature. Thus $r_{bH} = 1/u_* B$ does not express a proportionality between r_{bH} and u_* ; B is merely a dimensionless form of r_{bH} that varies between sites, with time, and even with u_* (Massman, 1999; McNaughton and Hurk, 1995; Schuepp, 1993). For typical daytime conditions, B as calculated for our site based on the model of McNaughton and Van den Hurk (1995) (Appendix B2) varies roughly between 1/8 and 1/2 and is nearly inversely proportional to u_* . Under the same conditions, r_{bH} itself only varies between about 8 and 12 s m^{-1} . Thus, assuming a constant r_{bH} would be more accurate than assuming a constant B .

B3. Leaf Temperature

Given r_{bH} , and assuming that the internal leaf temperature T_L (K) is the same as the leaf surface temperature, Fick's Law (Eq. (A1)) for thermal diffusion gives

$$T_L = \frac{H r_{bH}}{r_a C_p} + T_n \quad (\text{B8})$$

where H is the net heat flux (W m^{-2}), T_n is the canopy airspace temperature (K), ρ_a is the density (kg m^{-3}) of air and C_p is the specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$) of (wet) air.

B4. Stomatal Resistance

The stomatal resistance to CO_2 , derived from the stomatal resistance to water vapor r_{sV} , is a highly influential parameter in IFP, since it is among the most significant and most variable of the resistance terms that set the isotopic fractionation by photosynthesis. When the measured net water vapor flux E ($\text{mol m}^{-2} \text{s}^{-1}$) is entirely transpiration, i.e. when evaporation from soil and canopy surfaces is negligible and the water flux is positive, r_{sV} can be obtained from E once r_e , r_{bV} , and T_L have been calculated. Assuming that air inside the leaf is saturated with water vapor, Fick's Law (Eq. (A1) again) for diffusion of water vapor gives

$$r_{sV} = \frac{e_{\text{SAT}}(T_L) - e_n}{RT_n E} - r_{bV} \quad (\text{B9})$$

where $e_{\text{SAT}}(T_L) = e_i$ is the saturation vapor pressure (Pa) at temperature T_L , e_n is the vapor pressure (Pa) in the canopy airspace, and $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ is the molar gas constant (not an isotope ratio here). The stomatal resistances to H_2O and CO_2 are related by $r_s = 1.57 r_{sV}$ and the saturation vapor pressure is given by the following empirical formula (World Meteorological Organization, 2008):

$$e_{\text{SAT}}(T) = 611.2 \exp \left(\frac{17.62(T - 273.15)}{T - 30.03} \right) \quad (\text{B10})$$

with T in Kelvin (note that this formula is provided in hPa and $^{\circ}\text{C}$ in the cited source).

Unfortunately evaporation is often non-negligible at the HF-EMS; evaporation from soil and canopy surfaces contributes substantially to the measured water flux but has no bearing on stomatal conductance, so that r_s from Eq. (B9) is often an underestimate. Canopy surface wetness can result in large evaporative water fluxes

969 but typically lasts less than a few daylight hours after the cessation of rain or dew, a
970 fact confirmed by the direct leaf surface water measurements of Klemm et al. (2002)
971 as well as by our own simple experiment. Our experiment consisted of thoroughly
972 wetting a few isolated leaves placed under an awning on a cool (18°C), completely
973 overcast day, with the leaf exposed to only 50 % of the sky and with rain continuing
974 to fall around (but not on) the leaf; even under these unfavorable conditions, all
975 water had evaporated from the leaf surface within about 3 hours.

976 Soil and ground surface water usually results in smaller evaporative fluxes but is
977 longer lived, lasting a day or two after a large rain in hot, dry periods (e.g. late July
978 2011) and several days or more after a large rain in cold, wet periods (e.g. May
979 2011).

980 Our approach to calculating g_s in periods with non-negligible evaporation is adapted
981 from Knohl and Buchmann(2005):a function is fit to EC-derived g_s in periods with
982 negligible evaporation and used to extrapolate g_s into wet periods.For the function,
983 Knohl and Buchmann(2005) used a stomatal conductance model (Collatz et al.,
984 1991) in which g_s depends on the net photosynthetic assimilation flux F_A , the CO₂
985 molar mixing ratio to dry air at the leaf surface, and the relative humidity at the leaf
986 surface. Because F_A was unknown, Knohl and Buchmann(2005) modeled it as a
987 saturating function of PAR, which introduced some circularity in their analysis.
988 Instead, we use an entirely empirical function of leaf area index (LAI),
989 photosynthetically active radiation (PAR), the leaf-air water vapor difference (LVD),

and the clear sky index χ (i.e. the ratio of observed PAR to the PAR that would have been observed for the same solar zenith angle under clear skies):

$$g_s = \text{LAI}(b_0 e^{b_1 \text{LVD}} e^{b_2 \chi}) \text{PAR} \quad (\text{B11})$$

where b_0 , b_1 , and b_2 are fitted parameters. Transpiration predicted by this function was able to closely reproduce ($r^2 = 0.94$) the measured water flux in manually selected evaporation-free periods throughout the entire growing season using a single set of fitted parameters b_0 , b_1 , b_2 . The r^2 was not appreciably improved by using a curvilinear response to PAR (a Michaelis-Menten function converged to linearity in the fitting), nor by adding dependencies on T_L or soil water content (the fitted scaling factors converged to constants), nor by adding an offset representing stomatal conductance in the dark (the offset converged to $5 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$). The observed linear response of g_s to PAR contradicts the common assumption of a saturating response but agrees with some recent sap flux measurements (Schäfer, 2011).

A comparison of our g_s function to EC-derived g_s during a week including rain is shown in Figure B1. Evaporation following the rain events on 7/18 contaminated Eq. (B9) and caused its EC-derived g_s to surge above g_s from Eq. (B11) (which was fitted to evaporation-free periods only) for about a day in this example, which is from July, when soils were driest. In May, September, and October, when near-surface soil moisture was 40 % higher, substantial evaporation sometimes persisted for two or three days following rain. The fact that a single set of fit parameters could reproduce the entire season, including both moist and dry soil periods, suggests that

g_s was not significantly affected by soil water in 2011 and that the increased water flux generally observed in the day or two following rain was due to increased evaporation rather than transpiration. Thus use of Eq. (B11) to extrapolate g_s into periods with non-negligible evaporation appears justified. Doing so increased the number of NEE measurements we could safely partition from 337 to 1042. We did not extrapolate to periods with higher ($>31^\circ\text{C}$) or lower ($<18^\circ\text{C}$) temperatures or with lower volumetric soil water contents ($<19\%$) than were represented in the evaporation-free periods used to fit Eq. (B11). The mean difference between GEP with and without use of the fitted g_s function in evaporation-free periods over the whole growing season was $-0.06\ \mu\text{mol m}^{-2}\text{ s}^{-1}$, which was a proportional difference of -0.3% . The root-mean-square difference was $2.5\ \mu\text{mol m}^{-2}\text{ s}^{-1}$, which was 14% of the corresponding mean GEP and is attributable mostly to point-to-point meteorological noise in the g_s from Eq. (B9), as evident in Fig. B1.

Figure B1. Time series of stomatal conductance (top panel) and of the water vapor flux (bottom panel) as calculated by eddy covariance (black lines) and by the fitted function described in the text (red lines). Also shown are precipitation (blue) and PAR (filled yellow).

1029 We add a few technical notes. First, rather than fitting a function to EC-derived g_s
 1030 directly, we used Eq. (B9) to convert g_s into transpiration, and fit that to measured E .
 1031 The idea was to do the fitting in terms of the measured variable so that the
 1032 measurement noise would be normally distributed and not bias the fit. Second, we
 1033 selected evaporation-free periods in which to fit our function manually rather than
 1034 by algorithm because we did not expect the soil hydrology to be sufficiently
 1035 described by any simple function of our measured variables (e.g. time, net radiation,
 1036 soil moisture at 15 cm). We began by selecting periods several days after
 1037 precipitation and excluding most mornings, when canopy dew evaporation was
 1038 plausible. It was clear from an initial fit of our empirical function that g_s responded
 1039 consistently to PAR throughout much of this provisional evaporation-free period;
 1040 the presence or absence of dew evaporation became fairly obvious on many
 1041 mornings, as did the presence or absence of soil or surface water evaporation on
 1042 many days. We cropped or expanded our evaporation-free periods accordingly for
 1043 the final version of the fit, allowing us to include more morning data in particular.
 1044 Third, though the shape of the response of g_s to PAR, LVD, and χ did not change with
 1045 wind direction, the magnitude of the response did, consistent with a directional
 1046 variation in LAI. So, LAI for our calculations (including Eq. (B11)) was inferred for
 1047 each wind direction as follows: (i) the fitting of Eq. (B11) was initially restricted to
 1048 the relatively homogeneous sector from 210-240° (containing 114 points), (ii) the
 1049 ratio of g_s from Eq. (B9) to fitted g_s from Eq. (B11) was calculated for all
 1050 evaporation-free data (376 points), (iii) the natural logarithm of that ratio was
 1051 smoothed versus wind direction using a Loess filter, and (iv) the exponential of the

result was multiplied by the site-average LAI to obtain LAI as a smoothly varying function of wind direction (the 376 available points were enough to resolve directional variation with a resolution of around 15° in the data-rich sectors to the west of the tower). The Loess smoothing was done on the logarithm of the ratio so that the result would be a geometric mean (rather than an arithmetic mean), as is appropriate when averaging ratios. The g_s calculation was then repeated using the new direction-dependent LAI as input; one such iteration of the calculation was enough to obtain sufficient convergence in LAI and g_s . The direction-dependent LAI was also used as input to the rest of the IFP calculations.

B5. Mesophyll Resistance

Recent studies have increasingly emphasized the importance of the mesophyll resistance in regulating leaf and canopy scale photosynthesis (Gu and Sun, 2014). The gas-phase equivalent canopy-scale mesophyll resistance $x_m = x_{wp} + x_{ch}$ is considered to vary with LAI and leaf temperature. We convert it to units of s m^{-1} from the mesophyll conductance reported in flux units (g_m^* , in $\text{mol m}^{-2} \text{s}^{-1}$ rather than m s^{-1}) as:

$$x_m = \frac{1}{g_m^*} \frac{P_a}{RT_L} \quad (\text{B12})$$

where $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is again the molar gas constant (not an isotope ratio), and where

$$g_m^* = \text{LAI} \times 0.188 \times \exp\left(-0.5 \frac{\ln((T_L - 273.15)/28.8)}{0.610}\right) \quad (\text{B13})$$

between 10°C and 35°C, with T_L in Kelvin (Warren, 2006). The reported uncertainty in Eq. (B13) at the reference temperature of 25°C is $\pm 0.034 \text{ mol m}^{-2} \text{ s}^{-1}$, or about $\pm 20 \%$ (Warren, 2006). Though Eq. (B13) was obtained for *Quercus canariensis* rather than *Quercus rubra* (both deciduous oaks), it gives $g_m^g = 0.183$ at 25°C (LAI = 1), in good agreement with the value $g_m^g = 0.175 \pm 0.016 \text{ mol m}^{-2} \text{ s}^{-1}$ reported for *Quercus rubra* at 25°C (Manter and Kerrigan, 2004). Note that Eq. (B13) assumes that the population of leaves responds like a single ‘big leaf’, and if some of the aggregate canopy leaf mesophyll is ‘wasted’ in the shade, Eq. (B13) should overestimate the effective conductance.

A number of studies have reported that mesophyll conductance varies substantially and rapidly in response to environmental conditions, and is tightly correlated with stomatal conductance (see Flexas et al., 2008); however, Tholen et al. (2012) recently pointed out that because photorespiration and foliar daytime ‘dark’ respiration inject CO_2 into the cytosol (partway through the mesophyll diffusive pathway), the mesophyll conductance measured in those studies is not the true conductance but rather an *apparent* one. Tholen et al. (2012) moreover showed that this apparent conductance will covary with stomatal conductance even when the true mesophyll conductance is constant. Thus it is unclear how the mesophyll resistance varies on short timescales and there is little basis for modeling that variation. For the same reason, the dependence on temperature in Eq. (B13) may be

underestimated by 12 % or more (Tholen et al., 2012); however, the results of IFP are not sensitive to whether Eq. (B13) or a fixed mesophyll conductance is used.

We divide the total mesophyll resistance x_m into x_{wp} and x_{ch} according to ^{18}O measurements in oak (*Quercus robur*, not *Quercus rubra*) by Gillon and Yakir (2000), who found $g_{ch}/g_{wp} = 3.2$, i.e. $x_{wp} = 0.76x_m$ and $x_{ch} = 0.24x_m$.

B6. Photocompensation Point

The photocompensation point, used in the calculation of the photorespiration flux (Eq.(8)), depends on temperature and O_2 concentration. We know of no temperature-dependent measurements in red oak or red maple, but measurements in *Q. canariensis* (Warren, 2006) agreed well with a function (Brooks and Farquhar, 1985) describing *S. oleracea* (spinach) leaves between 15 and 30°C at ambient (21 %) O_2 :

$$G_*^{\text{f}} = 42.7 + 1.68(T_L - 298.15) + 0.0012(T_L - 298.15)^2 \quad (\text{B14})$$

where T_L is in K and G_*^{f} is in $\mu\text{mol mol}^{-1}$. Using spinach data (Jordan and Ogren, 1984), a second, similar equation was derived (Brooks and Farquhar, 1985), putting the photocompensation point about 5 % higher than does Eq. (B14) except under rare cold conditions ($T_L < 15^\circ\text{C}$), when the discrepancy is greater.

B7. Kinetic Fractionation by CO_2 Fixation

We turn now to the fractionations, beginning with $\epsilon_f = \alpha_f - 1$, the fractionation by fixation of CO_2 with respect to dissolved CO_2 in the chloroplast. Most CO_2 in C_3 plants

1112 is fixed by ribulose 1,5-bisphosphate carboxylase-oxygenase (Rubisco), but some is
 1113 fixed by phosphoenolpyruvate(PEP) carboxylase (Farquhar and Richards, 1984;
 1114 Lloyd and Farquhar, 1994). Letting β denote the molar fraction of fixed carbon that
 1115 is fixed by PEP carboxylase, we can write

$$1116 \quad a_f = \frac{a_{Ru} a_{PEP}^*}{b a_{Ru} + (1 - b) a_{PEP}^*} \quad (B15)$$

1117 where a_{Ru} is the fractionation factor for Rubisco carboxylation and a_{PEP}^* is the
 1118 fractionation factor for PEP carboxylation, both with respect to dissolved CO₂ in the
 1119 chloroplast. Measurements of β have put it between 0 and 0.15 (Douthe et al., 2012;
 1120 Lloyd and Farquhar, 1994), with variation between species—e.g. 0.02 for wheat and
 1121 0.04 for radish (Caemmerer and Evans, 1991)—and no measurements in oak of
 1122 which we are aware. We somewhat arbitrarily use $\beta = 0.05$.

1123 The fractionation for Rubisco carboxylation, $e_{Ru} = a_{Ru} - 1$, is commonly taken to be
 1124 constant at 29 ‰ following Roeske and O’Leary (1984), and that is the value we use
 1125 here. However, there is in fact very little data on how e_{Ru} might vary with species or
 1126 environmental conditions at the precision level desired for the present analysis
 1127 (~ 1 ‰). As summarized in McNevin et al. (2007), most measurements of e_{Ru} for C₃
 1128 plants have used Rubisco from *S. oleracea* (spinach) *in vitro*, for which the reported
 1129 values range from 26.4 ± 0.6 ‰ (the value at pH 9.0 in Roeske and O’Leary, 1984) to
 1130 30.3 ± 0.8 ‰ (Guy et al., 1993), with some suggestion that pH influences the value
 1131 but conflicting indications as to the direction of that influence. Most early
 1132 measurements were called into question by Roeske and O’Leary (1984) on account

1133 of problems with the method used, known as the combustion method. One early
 1134 study using the combustion method (Estep et al., 1978) reported a very strong
 1135 influence ($\sim 10\text{ ‰}$) of the metal cofactor used for enzyme activation on e_{Ru} , an issue
 1136 which appears not to have been explicitly investigated since, using improved
 1137 methods. The only *in vitro* measurements for C_3 species other than spinach are
 1138 McNevin et al. (2007)'s measurement for tobacco ($27.4 \pm 0.9\text{ ‰}$), a measurement
 1139 for cotton ($27.1 \pm 3.5\text{ ‰}$) (Wong et al., 1979), and a measurement for soybean
 1140 ($28.3 \pm 1.5\text{ ‰}$) (Christeller et al., 1976), the latter two of which used the combustion
 1141 method. Christeller et al. (1976) is also the only study to have examined the
 1142 temperature-dependence of e_{Ru} in C_3 plants, which was a rather large $+0.22\text{ ‰/°C}$
 1143 between 15°C and 35°C , though Christeller et al. (1976) did not consider this trend
 1144 significant and the results might be questionable in any case due to use of the
 1145 combustion method. Christeller et al. (1976) did not report any uncertainties, and
 1146 their coefficient was reported as -0.22 ‰/°C because they considered the difference
 1147 between source and product $\delta^{13}\text{C}$ rather than the actual fractionation defined by
 1148 Eq. (A4). *In vivo* measurements of the combined fractionation due to Rubisco and
 1149 PEP carboxylase by von Caemmerer and Evans (1991) have suggested that $e_{Ru} >$
 1150 31 ‰ for wheat, and that e_{Ru} differs by at least 4 ‰ between wheat and radish,
 1151 although no uncertainties in these values were reported and they should be
 1152 somewhat in error because they did not take into account the fact that consumption
 1153 of CO_2 by photosynthesis and release of CO_2 by foliar respiration are not collocated
 1154 (Tholen et al., 2012).

1155 The fractionation for PEP carboxylation relative to dissolved CO₂ can be broken
 1156 down further if we assume that carbonic anhydrase is plentiful enough that
 1157 dissolved CO₂ and bicarbonate are always in equilibrium in the chloroplast. In that
 1158 case, we can write

$$1159 \quad \alpha_{\text{PEP}}^* = \alpha_{\text{hyd}} \alpha_{\text{PEP}} \quad (\text{B16})$$

1160 where α_{hyd} is the equilibrium fractionation factor of hydration (i.e. the ¹³C/¹²C ratio
 1161 of the dissolved CO₂ divided by that of the bicarbonate) and α_{PEP} is the kinetic
 1162 fractionation factor of PEP carboxylase with respect to dissolved bicarbonate. The
 1163 reported range for α_{PEP} is 2.0-2.5 ‰ (O'Leary, 1981), and as variation within this
 1164 range does not much affect IFP, we simply use 2.25 ‰. For the fractionation by CO₂
 1165 hydration, which is known to be dependent on temperature, we use the following
 1166 empirical formula (Mook et al., 1974):

$$1167 \quad \epsilon_{\text{hyd}} = -(9866 \pm 230)/T_L + (24.12 \pm 0.78) \text{‰} \quad (\text{B17})$$

1168 with T_L in Kelvin.

1169 We found that ϵ_f was between 26.9 and 27.3‰ throughout the growing season.

1170 **B8. Kinetic Fractionations by Photorespiration and Daytime 'Dark'**

1171 **Respiration**

1172 Kinetic fractionation by photorespiration depends on the parameter ϵ and on the
 1173 fractionation by glycine decarboxylase (g) in Eq. (10). The parameter ϵ , which
 1174 relates to the fractionations by aldolase and transketolase, is on the order of

1 %₀₀(Tcherkez, 2006) and its precise value is of only minor importance to IFP (we use 1 %₀₀). Fractionation by glycine decarboxylase is dominant, and Tcherkez(2006) suggests the value $g = 22$ %₀₀. This value corresponds to $f \sim 11$ %₀₀, where f is the apparent photorespiratory fractionation relative to the isotopic composition of recent assimilates, i.e. the same f appearing in the much used equation of Farquhar et al. (1982) for the apparent fractionation by net photosynthetic assimilation of atmospheric CO₂. Published measurements of f have been scattered about 10 %₀₀, as discussed in Tcherkez(2006), and $g = 18$ %₀₀ seems plausible as well.

The fractionation by daytime ‘dark’ respiration ε_{DR} (defined relative to a substrate with the same isotopic composition as recent net photosynthetic assimilates) has been theoretically predicted at 5.5 %₀₀(Tcherkez et al., 2004) and estimated from gas exchange measurements at 5 ± 1 %₀₀(Tcherkez et al., 2010). We use $\varepsilon_{DR} = 5$ %₀₀, i.e. $\alpha_{DR} = 1.005$ in Eq. (13).

B9. Equilibrium Fractionation by Dissolution

The equilibrium fractionation by dissolution of CO₂ in water is also dependent on (leaf) temperature, according to another empirical function (Mook et al., 1974):

$$\varepsilon_d = -(373 \pm 70)/T_L + (0.19 \pm 0.23)\text{‰} \quad (\text{B18})$$

with T_L in Kelvin once again. This formula gives $\varepsilon_d = 1.04$ %₀₀ $\pm$ 0.04 %₀₀ at 30°C, in good agreement the value $\varepsilon_d = 1.1 \pm 0.1$ %₀₀ measured by O’Leary (1984).

B10. Kinetic Fractionations by Diffusion

1195 The kinetic fractionations by diffusion through the leaf boundary layer, the stomata,
1196 and the mesophyll are: $\varepsilon_b = 2.9 \text{ ‰}$ (Farquhar et al., 1989), $\varepsilon_s = 4.4 \text{ ‰}$ (Farquhar et al.,
1197 1989), and $\varepsilon_{wp} = \varepsilon_{ch} = \varepsilon_m = 0.7 \text{ ‰}$ (O'Leary, 1984). Here we are assuming that the
1198 fractionation for diffusion through the cell wall and plasmalemma (ε_{wp}), as well as
1199 that for diffusion through the chloroplast envelope and stroma (ε_{ch}), is simply the
1200 fractionation for diffusion of CO₂ through water (0.7 ‰).

Appendix C. Relation to Previous Formulations

Aside from a few minor errors, all isoflux-based IFP formulations (Billmark and Griffis, 2009; Bowling et al., 2001; Fassbinder et al., 2012; Knohl and Buchmann, 2005; Lai et al., 2003; Ogée et al., 2003; Zhang et al., 2006; Zobitz et al., 2008) can be obtained from that presented here under various simplifying approximations. The following three approximations were made by all previous IFP studies. First, photorespiration and foliar daytime ‘dark’ respiration were neglected by assuming $R_P = R_{PR} = R_{DR}$ or, equivalently, $F_{PR} = F_{DR} = 0$ ($F_{PR} = 0 \Leftrightarrow G_*^{\mathcal{C}} = 0$), in which case F_P becomes F_A , and our decomposition $r_m = r_{wp} + r_{ch}$ becomes superfluous. Second, constant values were used (rather than temperature-dependent functions) for the fractionations by dissolution (ε_d) and carboxylation (ε_f), which are sometimes (Bowling et al., 2001; Lai et al., 2003; Zhang et al., 2006) bundled along with the fractionation by mesophyll transport in the single constant parameter b , as in Eq. (4). Finally, photosynthetic fractionation was approximated by Eq. (5), $\varepsilon_A \approx \delta_a - \delta_A$, which introduces non-trivial error, as discussed in Appendix A.

In other approximations, the previous formulations differ from each other. First, all but one formulation (Fassbinder et al., 2012) used an inverted Penman-Monteith (PM) equation (Monteith, 1965) to determine the stomatal resistance, rather than the Fick’s law formulation used here (Eqs. (B9-B11)). The PM equation was derived to predict evaporation in the absence of sensible heat flux measurements; it too is based on Fick’s Law but it uses energy balance and some approximations to eliminate the sensible heat flux as a variable. When sensible heat flux is

measured(as at every eddy flux site), it is more accurate and straightforward to use
 Eqs. (B9-B11). Second, all but one formulation(Fassbinder et al., 2012), which was in
 a chamber study not involving turbulent eddies, calculated the turbulent eddy
 transport resistance from the momentum analog of Eq. (B1), which requires the
 poor assumption that the wind speed falls to zero in the canopy airspace, outside
 the leaf boundary layer. Third, all but two formulations (Fassbinder et al., 2012;
 Zobitz et al., 2008) considered the isotopic compositions of the within-canopy and
 above-canopy air to be the same ($\delta_h = \delta_a$), which is inconsistent with ecosystem
 source/sink isotopic fractionation. Fourth, only one formulation (Zhang et al., 2006),
 which was intended for C_4 plants, explicitly considered PEP carboxylase. Fifth, one
 formulation (Fassbinder et al., 2012) took the net apparent fractionation by
 diffusion from the canopy air to the chloroplast to be 4.4 ‰, which is the value
 strictly appropriate only to the stomatal portion of the pathway. Sixth, some
 formulations (Bowling et al., 2001; Lai et al., 2003; Zhang et al., 2006) neglected the
 boundary layer and mesophyll resistances ($r_b = r_m = 0$), while one (Fassbinder et al.,
 2012) included the mesophyll but not the boundary layer, and the rest (Billmark
 and Griffis, 2009; Knohl and Buchmann, 2005; Ogée et al., 2003; Zobitz et al., 2008)
 included both but calculated the boundary layer resistance as a function of a
 constant Stanton number B , which is an error discussed in Appendix B2.
 Finally, it should be noted that none of the previous formulations considered
 hypostomatous leaves (i.e. leaves with stomates on only the leaf underside, such as
 those of red oak and red maple, which dominate the canopy of Harvard Forest and
 many other forests), which require $N = 2$ in Eqs. (B6-B7).

1246 **References**

- 1247 Amthor, J.S., Goulden, M.L., Munger, J.W., Wofsy, S.C., 1994. Testing a mechanistic
1248 model of forest-canopy mass and energy exchange using eddy correlation:
1249 carbon dioxide and ozone uptake by a mixed oak-maple stand. *Aust J Plant*
1250 *Physio.* 21, 623–651.
- 1251 Atkin, O.K., Evans, J.R., Siebke, K., 1998. Relationship between the inhibition of leaf
1252 respiration by light and enhancement of leaf dark respiration following light
1253 treatment. *Aust J Plant Physio.* 25, 437–443. doi:10.1071/PP97159
- 1254 Baldocchi, D.D., 2008. “Breathing” of the terrestrial biosphere: lessons learned from
1255 a global network of carbon dioxide flux measurement systems. *Aust. J. Bot.* 56,
1256 1–26. doi:10.1071/BT07151
- 1257 Baldocchi, D.D., Bowling, D.R., 2003. Modelling the discrimination of ^{13}C above
1258 and within a temperate broad-leaved forest canopy on hourly to seasonal time
1259 scales. *Plant*.
- 1260 Bauwe, H., Hagemann, M., Fernie, A.R., 2010. Photorespiration: players, partners and
1261 origin. *Trends in Plant Science* 15, 330–336. doi:10.1016/j.tplants.2010.03.006
- 1262 Betson, N.R., Göttlicher, S.G., Hall, M., Wallin, G., Richter, A., Högberg, P., 2007. No
1263 diurnal variation in rate or carbon isotope composition of soil respiration in a
1264 boreal forest. *Tree Physiology* 27, 749–756.
- 1265 Billesbach, D.P., Berry, J.A., Seibt, U., Maseyk, K., Torn, M.S., Fischer, M.L., Abu-Naser,
1266 M., Campbell, J.E., 2014. Growing season eddy covariance measurements of
1267 carbonyl sulfide and CO_2 fluxes: COS and CO_2 relationships in Southern Great
1268 Plains winter wheat. *Agricultural and Forest Meteorology* 184, 48–55.
1269 doi:10.1016/j.agrformet.2013.06.007
- 1270 Billmark, K.A., Griffis, T.J., 2009. Influence of Phenology and Land Management on
1271 Biosphere-Atmosphere Isotopic CO_2 Exchange, in: *Phenology of Ecosystem*
1272 *Processes*. Springer New York, New York, NY, pp. 143–166. doi:10.1007/978-1-
1273 4419-0026-5_6
- 1274 Bowling, D.R., Ballantyne, A.P., Miller, J.B., Burns, S.P., Conway, T.J., Menzer, O.,
1275 Stephens, B.B., Vaughn, B.H., 2014. Ecological processes dominate the ^{13}C land
1276 disequilibrium in a Rocky Mountain subalpine forest. *Global Biogeochemical*
1277 *Cycles* 28, 352–370. doi:10.1002/2013GB004686
- 1278 Bowling, D.R., Egan, J.E., Hall, S.J., Risk, D.A., 2015. Environmental forcing does not
1279 induce diel or synoptic variation in carbon isotope content of forest soil
1280 respiration. *Biogeosciences Discuss.* 12, 6361–6404. doi:10.5194/bgd-12-6361-
1281 2015
- 1282 Bowling, D.R., Tans, P.P., Monson, R.K., 2001. Partitioning net ecosystem carbon
1283 exchange with isotopic fluxes of CO_2 . *Global Change Biol* 7, 127–145.
- 1284 Breda, N.J.J., 2003. Ground-based measurements of leaf area index: a review of
1285 methods, instruments and current controversies. *Journal of Experimental*
1286 *Botany* 54, 2403–2417. doi:10.1093/jxb/erg263
- 1287 Brooks, A., Farquhar, G.D., 1985. Effect of temperature on the CO_2/O_2 specificity of
1288 ribulose-1,5-bisphosphate carboxylase/oxygenase and the rate of respiration in
1289 the light. *Planta* 165, 397–406.

1290 Caemmerer, von, S., Evans, J.R., 1991. Determination of the Average Partial Pressure
 1291 of CO₂ in Chloroplasts from Leaves of Several C₃ Plants. *Aust J Plant Physio.* 18,
 1292 287–305.

1293 Christeller, J.T., Laing, W.A., Troughton, J.H., 1976. Isotope Discrimination by
 1294 Ribulose 1,5-Diphosphate Carboxylase. *Plant Physiology* 57, 580–582.

1295 Collatz, G.J., Ball, J.T., Grivet, C., Berry, J.A., 1991. Physiological and environmental
 1296 regulation of stomatal conductance, photosynthesis and transpiration: a model
 1297 that includes a laminar boundary layer. *Agricultural and Forest Meteorology* 54,
 1298 107–136.

1299 Coplen, T.B., 2011. Guidelines and recommended terms for expression of stable-
 1300 isotope-ratio and gas-ratio measurement results. *Rapid Communications in*
 1301 *Mass Spectrometry* 25, 2538–2560.

1302 De Pury, D.G.G., Farquhar, G.D., 1997. Simple scaling of photosynthesis from leaves
 1303 to canopies without the errors of big-leaf models. *Plant Cell and Environment*
 1304 20, 537–557. doi:10.1111/j.1365-3040.1997.00094.x

1305 Douthe, C., Dreyer, E., Brendel, O., Warren, C.R., 2012. Is mesophyll conductance to
 1306 CO₂ in leaves of three Eucalyptus species sensitive to short-term changes of
 1307 irradiance under ambient as well as low O₂? *Functional Plant Biology* 39, 435–
 1308 448. doi:10.1071/FP11190

1309 Estep, M.F., Tabita, F.R., Parker, P.L., Van Baalen, C., 1978. Carbon Isotope
 1310 Fractionation by Ribulose-1,5-Bisophosphate Carboxylase from Various
 1311 Organisms. *Plant Physiology* 61, 680–687.

1312 Evans, J.R., Caemmerer, von, S., 1996. Carbon dioxide diffusion inside leaves. *Plant*
 1313 *Physiology* 110, 339–346.

1314 Farquhar, G., O'Leary, M.H., Berry, J.A., 1982. On the relationship between carbon
 1315 isotope discrimination and the intercellular carbon dioxide concentration in
 1316 leaves. *Aust J Plant Physio.* 9, 121–137.

1317 Farquhar, G.D., Ehleringer, J.R., Hubick, K.T., 1989. Carbon isotope discrimination
 1318 and photosynthesis. *Annual Review of Plant Physiology and Plant Molecular*
 1319 *Biology* 40, 503–537.

1320 Farquhar, G.D., Richards, R.A., 1984. Isotopic Composition of Plant Carbon Correlates
 1321 With Water-Use Efficiency of Wheat Genotypes. *Aust J Plant Physio.* 11, 539–
 1322 552. doi:10.1071/PP9840539

1323 Fassbinder, J.J., Griffis, T.J., Baker, J.M., 2012. Evaluation of carbon isotope flux
 1324 partitioning theory under simplified and controlled environmental conditions.
 1325 *Agricultural and Forest Meteorology* 153, 154–164.

1326 Flexas, J., Ribas Carbó, M., Diaz-Espejo, A., Galmés, J., Medrano, H., 2008. Mesophyll
 1327 conductance to CO₂: current knowledge and future prospects. *Plant* 31, 602–
 1328 621.

1329 Gatz, D.F., Smith, L., 1995. The standard error of a weighted mean concentration—I.
 1330 Bootstrapping vs other methods. *Atmospheric Environment* 29, 1185–1193.
 1331 doi:10.1016/1352-2310(94)00210-C

1332 Ghashghaie, J., Badeck, F.-W., Lanigan, G., Nogués, S., Tcherkez, G., Deléens, E., Cornic,
 1333 G., Griffiths, H.G., 2003. Carbon isotope fractionation during dark respiration and
 1334 photorespiration in C₃ plants. *Phytochemistry Reviews* 2, 145–161.

1335 Gillon, J.S., Yakir, D., 2000. Internal Conductance to CO₂ Diffusion and C₁₈O

- Discrimination in C3 Leaves. *Plant Physiology* 123, 201–213.
- Goulden, M.L., Munger, J.W., Fan, S.-M., Daube, B.C., Wofsy, S.C., 1996. Measurements of carbon sequestration by long-term eddy covariance: methods and a critical evaluation of accuracy. *Global Change Biol* 2, 169–182.
- Griffis, T.J., Baker, J.M., Sargent, S.D., Tanner, B.D., Zhang, J., 2004. Measuring field-scale isotopic CO₂ fluxes with tunable diode laser absorption spectroscopy and micrometeorological techniques. *Agricultural and Forest Meteorology* 124, 15–29.
- Gu, L., Sun, Y., 2014. Artefactual responses of mesophyll conductance to CO₂ and irradiance estimated with the variable J and online isotope discrimination methods. *Plant Cell and Environment* 37, 1231–1249. doi:10.1111/pce.12232
- Guy, R.D., Fogel, M.L., Berry, J.A., 1993. Photosynthetic Fractionation of the Stable Isotopes of Oxygen and Carbon. *Plant Physiology* 101, 37–47.
- Hicks, B.B., Baldocchi, D.D., Meyers, T.P., Hosker, R.P., Jr., Matt, D.R., 1987. A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. *Water, Air, and Soil Pollution* 36, 311–330.
- Hurry, V., Igamberdiev, A.U., Keerberg, O., Pärnik, T., Atkin, O.K., Zaragoza-Castells, J., Gardeström, P., 2005. Respiration in Photosynthetic Cells: Gas Exchange Components, Interactions with Photorespiration and the Operation of Mitochondria in the Light, in: Lambers, H., Ribas-Carbo, M. (Eds.), *Plant Respiration*. Springer-Verlag, Berlin/Heidelberg, pp. 43–61. doi:10.1007/1-4020-3589-6_4
- Igamberdiev, A.U., Mikkelsen, T.N., Ambus, P., Bauwe, H., Lea, P.J., Gardeström, P., 2004. Photorespiration contributes to stomatal regulation and carbon isotope fractionation: a study with barley, potato and *Arabidopsis* plants deficient in glycine decarboxylase. *Photosynthesis Research* 81, 131–152.
- Joiner, J., Guanter, L., Lindstrot, R., Voigt, M., Vasilkov, A.P., Middleton, E.M., Huemmrich, K.F., Yoshida, Y., Frankenberg, C., 2013. Global Monitoring of Terrestrial Chlorophyll Fluorescence from Moderate-Spectral-Resolution Near-Infrared Satellite Measurements: Methodology, Simulations, and Application to GOME-2. doi:10.5194/amt-6-2803-2013
- Jordan, D.B., Ogren, W.L., 1984. The CO₂/O₂ specificity of ribulose 1,5-bisphosphate carboxylase/oxygenase. *Planta* 161, 308–313. doi:10.1007/BF00398720
- Klemm, O., Milford, C., Sutton, M.A., Spindler, G., van Putten, E., 2002. A climatology of leaf surface wetness. *Theor Appl Climatol* 71, 107–117.
- Knohl, A., Buchmann, N., 2005. Partitioning the net CO₂ flux of a deciduous forest into respiration and assimilation using stable carbon isotopes. *Global Biogeochemical Cycles* 19, GB4008. doi:10.1029/2004GB002301
- Kucharik, C.J., Norman, J.M., Gower, S.T., 1998. Measurements of branch area and adjusting leaf area index indirect measurements. *Agricultural and Forest Meteorology* 91, 69–88.
- Lai, C.-T., Schauer, A.J., Owensby, C., Ham, J.M., Ehleringer, J.R., 2003. Isotopic air sampling in a tallgrass prairie to partition net ecosystem CO₂ exchange. *Journal of Geophysical Research* 108, 4566. doi:10.1029/2002JD003369
- Lamaud, E., Brunet, Y., Labatut, A., Lopez, A., Fontan, J., Druilhet, A., 1994. The Landes experiment: Biosphere-atmosphere exchanges of ozone and aerosol

1382 particles above a pine forest. *Journal of Geophysical Research* 99, 16–511–16–
 1383 521.
 1384 Lanigan, G.J., Betson, N., Griffiths, H., Seibt, U., 2008. Carbon Isotope Fractionation
 1385 during Photorespiration and Carboxylation in *Senecio*. *Plant Physiology* 148,
 1386 2013–2020. doi:10.1104/pp.108.130153
 1387 Lasslop, G., Reichstein, M., Papale, D., Richardson, A.D., Arneth, A., Barr, A., Stoy, P.C.,
 1388 Wohlfahrt, G., 2010. Separation of net ecosystem exchange into assimilation and
 1389 respiration using a light response curve approach: critical issues and global
 1390 evaluation. *Global Change Biol* 16, 187–208.
 1391 Lee, X., Griffis, T.J., Baker, J.M., Billmark, K.A., Kim, K., Welp, L.R., 2009. Canopy-scale
 1392 kinetic fractionation of atmospheric carbon dioxide and water vapor isotopes.
 1393 *Global Biogeochemical Cycles* 23, 1–15. doi:10.1029/2008GB003331
 1394 Lloyd, J., Farquhar, G.D., 1994. ^{13}C discrimination during CO_2 assimilation by the
 1395 terrestrial biosphere. *Oecologia* 99, 201–215. doi:10.1007/BF00627732
 1396 Lloyd, J., Grace, J., Miranda, A.C., Meir, P., Wong, S.C., Miranda, H.S., Wright, I.R., Gash,
 1397 J.H.C., McIntyre, J., 1995. A simple calibrated model of Amazon rainforest
 1398 productivity based on leaf biochemical properties. *Plant Cell and Environment*
 1399 18, 1129–1145.
 1400 Luyssaert, S., Inglis, I., Jung, M., 2009. Global forest ecosystem structure and
 1401 function data for carbon balance research. doi:10.3334/ORNLDAAAC/949
 1402 Manter, D.K., Kerrigan, J., 2004. A/Ci curve analysis across a range of woody plant
 1403 species: influence of regression analysis parameters and mesophyll
 1404 conductance. *Journal of Experimental Botany* 55, 2581–2588.
 1405 doi:10.1093/jxb/erh260
 1406 Massman, W.J., 1999. A model study of kBH–1 for vegetated surfaces using
 1407 “localized near-field” Lagrangian theory. *Journal of Hydrology* 223, 27–43.
 1408 doi:10.1016/S0022-1694(99)00104-3
 1409 McNaughton, K.G., Hurk, B., 1995. A “Lagrangian” revision of the resistors in the two-
 1410 layer model for calculating the energy budget of a plant canopy. *Boundary-Layer*
 1411 *Meteorology* 74, 261–288.
 1412 McNevin, D.B., Badger, M.R., Whitney, S.M., Caemmerer, von, S., Tcherkez, G.G.B.,
 1413 Farquhar, G.D., 2007. Differences in Carbon Isotope Discrimination of Three
 1414 Variants of D-Ribulose-1,5-bisphosphate Carboxylase/Oxygenase Reflect
 1415 Differences in Their Catalytic Mechanisms. *Journal of Biological Chemistry* 282,
 1416 36068–36076. doi:10.1074/jbc.M706274200
 1417 Monteith, J., 1965. Evaporation and environment. *Symp. Soc. Exp. Biol* 19, 205–234.
 1418 Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation
 1419 between dissolved bicarbonate and gaseous carbon dioxide. *Earth and Planetary*
 1420 *Science Letters* 22, 169–176. doi:10.1016/0012-821X(74)90078-8
 1421 Mott, K.A., O’Leary, M.H., 1984. Stomatal Behavior and CO_2 Exchange Characteristics
 1422 in Amphistomatous Leaves. *Plant Physiology* 74, 47–51.
 1423 Nogués, S., Tcherkez, G., Cornic, G., Ghashghaie, J., 2004. Respiratory Carbon
 1424 Metabolism following Illumination in Intact French Bean Leaves Using $^{13}\text{C}/^{12}\text{C}$
 1425 Isotope Labeling. *Plant Physiology* 136, 3245–3254.
 1426 O’Leary, M.H., 1984. Measurement of the Isotope Fractionation Associated with
 1427 Diffusion of Carbon Dioxide in Aqueous Solution. *The Journal of Physical*

1428 Chemistry 88, 823–825.
 1429 O'Leary, M.H., 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20, 553–
 1430 567. doi:10.1016/0031-9422(81)85134-5
 1431 Ogée, J., Peylin, P., Ciais, P., Bariac, T., Brunet, Y., Berbigier, P., Roche, C., Richard, P.,
 1432 Bardoux, G., Bonnefond, J., 2003. Partitioning net ecosystem carbon exchange
 1433 into net assimilation and respiration using ^{13}C measurements: a cost-
 1434 effective sampling strategy. *Global Biogeochemical Cycles* 17, 1070.
 1435 Owen, P.R., Thomson, W.R., 1963. Heat transfer across rough surfaces. *J. Fluid Mech.*
 1436 15, 321–334. doi:10.1017/S0022112063000288
 1437 Parkhurst, D.F., Mott, K.A., 1990. Intercellular Diffusion Limits to CO_2 Uptake in
 1438 Leaves. *Plant Physiology* 94, 1024–1032.
 1439 Pärnik, T., Ivanova, H., Keerberg, O., 2007. Photorespiratory and respiratory
 1440 decarboxylations in leaves of C_3 plants under different CO_2 concentrations and
 1441 irradiances. *Plant Cell and Environment* 30, 1535–1544. doi:10.1111/j.1365-
 1442 3040.2007.01725.x
 1443 Pärnik, T., Keerberg, O., 2007. Advanced radiogasometric method for the
 1444 determination of the rates of photorespiratory and respiratory decarboxylations
 1445 of primary and stored photosynthates under steady-state photosynthesis.
 1446 *Physiol Plant* 129, 34–44.
 1447 Raupach, M., Thom, A.S., 1981. Turbulence in and above Plant Canopies. *Annual*
 1448 *Review of Fluid Mechanics* 13, 97–129.
 1449 Reichstein, M., Falge, E., Baldocchi, D.D., Papale, D., Aubinet, M., Berbigier, P.,
 1450 Bernhofer, C., Buchmann, N., Gilmanov, T., Granier, A., Grünwald, T., Havrankova,
 1451 K., Ilvesniemi, H., Janous, D., Knohl, A., Laurila, T., Lohila, A., Loustau, D.,
 1452 Matteucci, G., MEYERS, T., Miglietta, F., Ourcival, J.-M., Pumpanen, J., Rambal, S.,
 1453 Rotenberg, E., Sanz, M., Tenhunen, J., Seufert, G., Vaccari, F., Vesala, T., Yakir, D.,
 1454 Valentini, R., 2005. On the separation of net ecosystem exchange into
 1455 assimilation and ecosystem respiration: review and improved algorithm. *Global*
 1456 *Change Biol* 11, 1424–1439. doi:10.1111/j.1365-2486.2005.001002.x
 1457 Roeske, C.A., O'Leary, M.H., 1984. Carbon isotope effects on enzyme-catalyzed
 1458 carboxylation of ribulose biphosphate. *Biochemistry* 23, 6275–6284.
 1459 doi:10.1021/bi00320a058
 1460 Scanlon, T.M., Kustas, W.P., 2010. Partitioning carbon dioxide and water vapor fluxes
 1461 using correlation analysis. *Agricultural and Forest Meteorology* 150, 89–99.
 1462 doi:10.1016/j.agrformet.2009.09.005
 1463 Schäfer, K.V.R., 2011. Canopy Stomatal Conductance Following Drought,
 1464 Disturbance, and Death in an Upland Oak/Pine Forest of the New Jersey Pine
 1465 Barrens, USA. *Frontiers in plant science* 2, 1–7. doi:10.3389/fpls.2011.00015
 1466 Schuepp, P., 1993. Leaf boundary layers. *New Phytologist* 125, 477–507.
 1467 Sharkey, T.D., 1988. Estimating the rate of photorespiration in leaves. *Physiol Plant*
 1468 73, 147–152. doi:10.1111/j.1399-3054.1988.tb09205.x
 1469 Siegenthaler, U., Munnich, K., 1981. $^{13}\text{C}/^{12}\text{C}$ Fractionation during CO_2 transfer from
 1470 Air to Sea, in: Bolin, B. (Ed.), *Carbon Cycle Modelling*. John Wiley, New York, pp.
 1471 249–257.
 1472 Stoy, P.C., Katul, G.G., Siqueira, M.B.S., Juang, J.-Y., Novick, K.A., Uebelherr, J.M., Oren,
 1473 R., 2006. An evaluation of models for partitioning eddy covariance-measured net

- ecosystem exchange into photosynthesis and respiration. *Agricultural and Forest Meteorology* 141, 2–18. doi:10.1016/j.agrformet.2006.09.001
- Tans, P., Berry, J., Keeling, R., 1993. Oceanic $^{13}\text{C}/^{12}\text{C}$ Observations: A New Window on Ocean CO_2 Uptake. *Global Biogeochemical ...*
- Tcherkez, G., 2006. Viewpoint: How large is the carbon isotope fractionation of the photorespiratory enzyme glycine decarboxylase? *Functional Plant Biology* 33, 911. doi:10.1071/FP06098
- Tcherkez, G., Farquhar, G., Badeck, F., Ghashghaie, J., 2004. Theoretical considerations about carbon isotope distribution in glucose of C_3 plants. *Functional Plant Biology* 31, 857. doi:10.1071/FP04053
- Tcherkez, G., Schäufele, R., Nogués, S., Piel, C., Boom, A., Lanigan, G., Barbaroux, C., Mata, C., Elhani, S., Hemming, D., Maguas, C., Yakir, D., Badeck, F.W., Griffiths, H., Schnyder, H., Ghashghaie, J., 2010. On the $^{13}\text{C}/^{12}\text{C}$ isotopic signal of day and night respiration at the mesocosm level. *Plant Cell and Environment* 33, 900–913. doi:10.1111/j.1365-3040.2010.02115.x
- Tholen, D., Ethier, G., Genty, B., Pepin, S., Zhu, X.-G., 2012. Variable mesophyll conductance revisited: theoretical background and experimental implications. *Plant Cell and Environment* 35, 2087–2103. doi:10.1111/j.1365-3040.2012.02538.x
- Urbanski, S., Barford, C., Wofsy, S., Kucharik, C., Pyle, E., Budney, J., McKain, K., Fitzjarrald, D., Czikowsky, M., Munger, J.W., 2007. Factors controlling CO_2 exchange on timescales from hourly to decadal at Harvard Forest. *Journal of Geophysical Research* 112, G02020. doi:10.1029/2006JG000293
- Warren, C., 2006. Temperature response of photosynthesis and internal conductance to CO_2 : results from two independent approaches. *Journal of Experimental Botany* 57, 3057–3067. doi:10.1093/jxb/erl067
- Wehr, R., Munger, J.W., Nelson, D.D., McManus, J.B., Zahniser, M.S., Wofsy, S.C., Saleska, S.R., 2013. Long-term eddy covariance measurements of the isotopic composition of the ecosystem–atmosphere exchange of CO_2 in a temperate forest. *Agricultural and Forest Meteorology* 181, 69–84. doi:10.1016/j.agrformet.2013.07.002
- Wofsy, S.C., Goulden, M.L., Munger, J.W., Fan, S.-M., Bakwin, P., Daube, B.C., Bassow, S., Bazzaz, F., 1993. Net exchange of CO_2 in a mid-latitude forest. *Science* 260, 1314–1317.
- Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A., Loreto, F., 2011. Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: potential and limitations. *Plant Cell and Environment* 35, 657–667. doi:10.1111/j.1365-3040.2011.02451.x
- Wong, W.W., Benedict, C.R., Kohel, R.J., 1979. Enzymic Fractionation of the Stable Carbon Isotopes of Carbon Dioxide by Ribulose-1,5-bisphosphate Carboxylase. *Plant Physiology* 63, 852–856.
- World Meteorological Organization, 2008. Guide to Meteorological Instruments and Methods of Observation (No. WMO-No. 8). World Meteorological Organization, Geneva.
- Xu, C.-Y., Griffin, K.L., 2008. Scaling foliar respiration to the stand level throughout the growing season in a *Quercus rubra* forest. *Tree Physiology* 28, 637–646.

1520 Yakir, D., Wang, X., 1996. Fluxes of CO₂ and water between terrestrial vegetation
 1521 and the atmosphere estimated from isotope measurements. *Nature* 380, 515–
 1522 517.
 1523 Zhang, J., Griffis, T.J., Baker, J.M., 2006. Using continuous stable isotope
 1524 measurements to partition net ecosystem CO₂ exchange. *Plant Cell and*
 1525 *Environment* 29, 483–496. doi:10.1111/j.1365-3040.2005.01425.x
 1526 Zobitz, J.M., Burns, S.P., Reichstein, M., Bowling, D.R., 2008. Partitioning net
 1527 ecosystem carbon exchange and the carbon isotopic disequilibrium in a
 1528 subalpine forest. *Global Change Biol* 14, 1785–1800. doi:10.1111/j.1365-
 1529 2486.2008.01609.x
 1530

Table 1.Key to symbols.

Symbol	Description	Units
F	flux (formally flux density) of CO ₂	mol m ⁻² s ⁻¹
H	flux (formally flux density) of sensible heat	W m ⁻²
E	flux (formally flux density) of water vapor	mol m ⁻² s ⁻¹
R	isotope atom ratio, ¹³ C/ ¹² C	--
δ	relative difference of R from R_{VPDB}	--
α	isotopic fractionation factor	--
ε	isotopic fractionation (= $\alpha - 1$)	--
c	concentration of CO ₂	mol m ⁻³
C	mole fraction of CO ₂ in air	mol mol ⁻¹
C_p	specific heat capacity of air	J kg ⁻¹ K ⁻¹
r	Resistance	s m ⁻¹
g	conductance(= 1/ r)	m s ⁻¹
e	vapor pressure	Pa
T	Temperature	K
P	air pressure	Pa
ρ	density of air	kg m ⁻³
γ	psychrometric constant	Pa K ⁻¹
λ	latent heat of vaporization of water	J mol ⁻¹
k_H	Henry's constant (= c_{ow}/c_i)	--

a	flux measurement height	m
h	canopy top height	m
Sc	Schmidt number for CO ₂	--
Sc_V	Schmidt number for water vapor	--
Pr	Prandtl number for air	--
Γ'_*	photocompensation point	mol mol ⁻¹
u	wind speed	m s ⁻¹
u_*	friction velocity	m s ⁻¹
χ	clear sky index	--
β	fraction of carboxylation performed by PEP-carboxylase	--

Table 2. Key to subscripts.

Subscript Meaning

PROCESSES	
<i>N</i>	net ecosystem-atmosphere CO ₂ exchange (NEE)
<i>P</i>	gross photosynthesis (uptake is negative)
<i>PR</i>	Photorespiration
<i>DR</i>	foliar daytime ‘dark’ respiration
<i>A</i>	net foliar photosynthetic assimilation
<i>NR</i>	non-foliar (heterotroph, root, and stem) respiration
<i>e</i>	turbulent eddy ‘diffusion’
<i>b</i>	leaf boundary layer diffusion of CO ₂
<i>bH</i>	leaf boundary layer diffusion of heat
<i>bV</i>	leaf boundary layer diffusion of water vapor
<i>s</i>	stomatal diffusion of CO ₂
<i>sV</i>	stomatal diffusion of water vapor
<i>d</i>	dissolution of CO ₂ in water
<i>hyd</i>	hydration of CO ₂
<i>m</i>	mesophyll diffusion of CO ₂
<i>wp</i>	mesophyll cell wall and plasmalemma diffusion of CO ₂
<i>ch</i>	chloroplast envelope and stroma diffusion of CO ₂
<i>f</i>	enzyme-catalyzed fixation of CO ₂
<i>Ru</i>	carboxylation by Rubisco

LOCATIONS

<i>a</i>	above the canopy, at flux measurement height
<i>h</i>	top of canopy
<i>n</i>	within the canopy
<i>u</i>	under the leaf boundary layer, outside the stomata
<i>i</i>	in the leaf intercellular airspace
<i>ow</i>	in the liquid lining the outside of the mesophyll cell walls
<i>c</i>	at the site of carboxylation
<i>L</i>	throughout the leaf

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure B1