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

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ABSTRACT

Stable carbon isotopes can be used to partition the net ecosystem–atmosphere exchange (NEE) of carbon dioxide (CO_2) 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 $\delta^{13}C$ of CO_2 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 ±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.

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1. Introduction

The net ecosystem–atmosphere exchange of CO_2 (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 ^{13}C *versus* ^{12}C. The ratio of ^{13}C to ^{12}C 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

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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

The basic idea of isotopic flux partitioning (Bowling et al., 2001; Ogée et al., 2003; Yakir and Wang, 1996) is to determine the magnitudes of the photosynthetic and respiratory gross fluxes using their isotopic signatures and the isotopic composition and magnitude of their sum (i.e. NEE); that is, to solve the set of two equations describing the isotopic mass balance of CO_2 in the forest,

$$F_N = F_A + F_{NR} \tag{1}$$

$$\delta_N F_N = \delta_A F_A + \delta_{NR} F_{NR}, \tag{2}$$

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

Solving this pair of equations requires knowledge of the isotopic composition of NEE (δ_N), the isotopic signature of non-foliar ecosystem respiration (δ_{NR}), and the isotopic signature of net photosynthetic assimilation (δ_A). δ_N can be measured directly, and δ_{NR} can be obtained from a combination of soil chamber and nighttime Keeling plot measurements as detailed in Section 3.2. δ_A, however, cannot be measured at the ecosystem scale with the required time resolution. Instead, the approach generally taken is to use our understanding of photosynthetic fractionation (also called discrimination) by individual leaves to express δ_A in terms of F_A, so that δ_A can be eliminated from the above equations (and thus solved for as part of the partitioning). In the original formulation of this approach (Bowling et al., 2001), the link between δ_A and F_A consisted simply of Fick's law for CO_2 diffusion through the leaf stomata,

$$F_A = -g_s(c_a - c_i), \tag{3}$$

and the well-known simplified equation for photosynthetic fractionation (Farquhar et al., 1982),

$$\varepsilon_A = \varepsilon_s + (b - \varepsilon_s)\frac{c_i}{c_a}, \tag{4}$$

along with an approximate definition of the photosynthetic fractionation,

$$\varepsilon_A \approx \delta_a - \delta_A \tag{5}$$

(cf. the exact definition in Appendix A). In the above equations, g_s is the stomatal conductance, c_i is the intercellular CO_2 concentration inside the leaf, c_a and δ_a are the CO_2 concentration and isotopic composition of the air outside the leaf, ε_A is the apparent isotopic fractionation of canopy net photosynthetic assimilation (often written as Δ), ε_s is the fractionation associated with diffusion of CO_2 through the stomata (4.4‰), and b is the apparent fractionation associated with fixation of intercellular CO_2 (~27‰). Combining these equations eliminates c_i and ε_A and gives δ_A in terms of F_A—provided that atmospheric CO_2 is measured, that stomatal conductance can be determined (e.g. from measured ecosystem-scale heat and water fluxes), and that ε_s and b are known constants. The above fractionation equation, Eq. (4), neatly expresses the central fact that the fractionation by photosynthesis depends on the relative rates of CO_2 diffusion and fixation, being weighted toward the fractionation associated with whichever of those two processes is most limiting to the overall rate of assimilation (because diffusion limitation will cause c_i to approach zero while fixation limitation will cause c_i to approach c_a).

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

Note also that we depart from some of the notation inherited through the lineage of IFP studies, sacrificing continuity in favor of a standardized notation consistent with guidelines in Coplen (2011) (wherein, e.g., ε represents isotopic fractionation, leading us to use ε_A rather than Δ for photosynthetic fractionation). Our symbols and notations are explained in Tables 1 and 2, and several key variables are defined in Appendix A. Except in a few special cases, each property (e.g. fractionation) is given a unique letter or symbol (e.g. ε), and the property is associated with specific sites (e.g. above the canopy) or processes (e.g. dissolution) by subscripts. Superscripts 12 and 13 specify the carbon isotopes.

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}:

$$F_N = F_P + F_{PR} + F_{DR} + F_{NR}. \tag{6}$$

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