Seasonal dynamics and partitioning of isotopic CO_2 exchange in a C_3/C_4 managed ecosystem

T.J. Griffis [a,*], J.M. Baker [a,b], J. Zhang [a]

[a] *Department of Soil, Water, and Climate, University of Minnesota-Twin Cities, Borlaug Hall,*
1991 Upper Buford Circle, St. Paul, MN 55108, USA
[b] *USDA-ARS, St. Paul, MN, USA*

Abstract

Ecosystem-atmosphere fluxes of $^{12}CO_2$ and $^{13}CO_2$ are needed to better understand the impacts of climate and land use change on ecosystem respiration (F_R), net ecosystem CO_2 exchange (F_N), and canopy-scale photosynthetic discrimination (Δ). We combined micrometeorological and stable isotope techniques to quantify isotopic fluxes of $^{12}CO_2$ and $^{13}CO_2$ over a corn–soybean rotation ecosystem in the Upper Midwest United States. Results are reported for a 192-day period during the corn (C_4) phase of the 2003 growing season. The isotopomer flux ratio, $d^{13}CO_2/d^{12}CO_2$, was measured continuously using a tunable diode laser (TDL) and gradient technique to quantify the isotope ratios of F_R (δ_R) and F_N (δ_N). Prior to leaf emergence δ_R was approximately $-26‰$. It increased rapidly following leaf emergence and reached an average value of $-12.5‰$ at full canopy. δ_R decreased to pre-emergence values following senescence. δ_N also showed strong seasonal variation and during the main growing period averaged $-11.6‰$. δ_R and δ_N values were used in a modified flux partitioning approach to estimate canopy-scale Δ and the isotope ratio of photosynthetically assimilated CO_2 (δ_P) independent of calculating canopy conductance or assuming leaf-scale discrimination factors. The results showed substantial day-to-day variation in Δ with an average value of 4.0‰. This flux-based estimate of Δ was approximately 6‰ lower than the Keeling mixing model estimate and in better agreement with leaf-level observations. These data were used to help constrain and partition F_R into its autotrophic (F_{Ra}) and heterotrophic (F_{Rh}) components based on the numerical optimization of a mass balance model. On average F_{Ra} accounted for 44% of growing season F_R and reached a maximum of 59% during peak growth. The isotope ratio of F_{Rh} (δ_{Rh}), was $-26‰$ prior to leaf emergence, and became increasingly ^{13}C enriched as the canopy developed indicating that recent photosynthate became the dominant substrate for microbial activity. Sensitivity analyses substantiated that F_{Rh} had a major influence on the seasonal pattern of δ_R, δ_N and the isotopic disequilibrium of the ecosystem. These data and parameter estimates are critical for validating and constraining the parameterization of land surface schemes and inverse models that aim to estimate regional carbon sinks and sources and interpreting changes in the atmospheric signal of $\delta^{13}CO_2$.

* Corresponding author. Tel.: +1 612 625 3117; fax: +1 612 625 2208.
 E-mail address: tgriffis@umn.edu (T.J. Griffis).

1. Introduction

It is well recognized that isotopic CO_2 flux measurements between the ecosystem and atmosphere are needed to better constrain regional estimates of net ecosystem CO_2 exchange (F_N) (Lloyd and Farquhar, 1994; Fung et al., 1997; Buchmann et al., 1998; Randerson et al., 2002; Lai et al., 2004) and the partitioning of F_N into gross photosynthesis (F_P) and ecosystem respiration (F_R) (Yakir and Wang, 1996; Bowling et al., 2001). In particular, better estimates of the isotope ratios of F_N (δ_N), F_R (δ_R), and canopy-scale photosynthetic discrimination (Δ) against $^{13}CO_2$ are needed to improve our current understanding of the global carbon cycle and its sensitivity to climate variation and land use change. The need for improved isotope exchange studies at the ecosystem scale has been highlighted by Fung et al. (1997) who demonstrated that a 3‰ overestimate of Δ in carbon cycle inversion models could result in an underestimate of 0.7 Gt C y^{-1} in the terrestrial carbon sink.

Canopy-scale photosynthetic discrimination is often approximated from the mixing model, $\Delta_b = \delta^{13}C_a - \delta_R$, independent of direct flux measurements (Flanagan et al., 1996; Bakwin et al., 1998). In the above equation, $\delta^{13}C_a$ is defined as the isotope ratio of CO_2 in the surface layer and δ_R is obtained from a Keeling plot (Keeling, 1958). Using a similar definition, Buchmann et al. (1998) defined the parameter ecosystem discrimination, $\Delta_e = (\delta^{13}C_a - \delta_R)/(1 + \delta_R)$, with $\delta^{13}C_a$ referenced with respect to the free atmosphere, to infer changes in ecosystem discrimination caused by photosynthesis. Ideally, these estimates could be used as a suitable surrogate for Δ (Yakir and Sternberg, 2000). However, if an ecosystem is not in isotopic equilibrium (i.e. the isotope ratio of photosynthesis (δ_P) $\neq$ isotope ratio of ecosystem respiration (δ_R)), this approach cannot be expected to yield the true physiological Δ. For instance, Buchmann and Ehleringer (1998) found that Δ_e was 13.2‰ for an alfalfa (*Medicago sativa* L.) C_3 canopy and 13.8‰ for a C_4 corn (*Zea mays* L.) canopy. Contrary to observations from leaf-level experiments, weaker C_4 discrimination ($\sim$4‰) was not observed when using this mixing model approach—illustrating the strong influence of land use history on δ_R and the approximation of Δ. Consequently, the above approaches may not provide the best parameterization

for regional carbon models because disequilibrium is likely to be the norm as a result of seasonal climate variation, changes in phenology, historical differences in the isotopic composition of soil organic matter and disturbance factors related to land use change. The example above describes an extreme case, yet it highlights the need for a more mechanistic approach, especially when considering that managed agricultural ecosystems represent 12% of the land surface—an area approximately the size of South America (Leff et al., 2004). Furthermore, agricultural ecosystems are highly productive and can, therefore, have a significant influence on ecosystem-atmosphere CO_2 exchange.

Quantifying the isotope ratio of F_R (δ_R) has been the subject of numerous studies (Keeling, 1958; Flanagan et al., 1999; Pataki et al., 2003; Griffis et al., 2004a). Flask-based measurements and the Keeling mixing model have been used as an effective tool to estimate δ_R for a broad range of ecosystems represented in carbon cycle inversion models. Bowling et al. (2002) examined the seasonal variation in δ_R among six coniferous forests over a period of 3 years. Significant differences in δ_R were observed among the forest types, ranging from −33.1 to −23.1‰. Pronounced seasonal variation in δ_R was observed at only the Douglas fir (*Pseudotsuga menziesii*) stand, ranging from −33.0 to −24.5‰. This strong variation was linked to changes in the isotope ratio of assimilated CO_2 in response to changing stomatal conductance caused by precipitation events and variations in vapor pressure deficit. Ometto et al. (2002) also examined seasonal variation in δ_R in forest and pasture ecosystems in the Amazon Basin of Brazil. Seasonal variation in δ_R was minimal at their Manaus forest site, but varied significantly (−29 to −26‰) at the Santarém forest, which experienced strong variations in precipitation. In pastures that replaced clear cut forests, δ_R was enriched by 10‰ and showed strong variation following fire events. In agricultural ecosystems, δ_R values for corn (*Z. mays*) have been reported as −21.6‰ (Buchmann and Ehleringer, 1998) and −20.0‰ (Yakir and Wang, 1996). These values reveal the influence of C_3 crop production in previous years. The differences in δ_R among sites result from the complex interaction of land use history and physiological response to climatic variations. Studies have begun examining the short-term variation in δ_R and its coupling to recently assimilated CO_2 (McDowell et al.,