

#### 4.4 SEASONAL VARIATION IN THE ISOTOPE RATIO OF ECOSYSTEM RESPIRATION AND CANOPY-SCALE DISCRIMINATION IN A CORN-SOYBEAN ECOSYSTEM

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## 1. INTRODUCTION

There is increasing interest in combining micrometeorological and stable isotope techniques to study the cycling of carbon dioxide (CO<sub>2</sub>) between the land and atmosphere. These methods offer a new opportunity to gain greater process information at the field scale and can provide key biophysical parameters for scaling from leaf to region. The recent developments in tunable diode laser absorption spectroscopy (TDLAS) have provided a robust method for obtaining continuous long-term measurements of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> mixing ratios (Bowling et al., 2003) and fluxes (Griffis et al., 2004).

Quantification of the isotopic ratio of respiration ( $\delta^{13}C_R$ ) and canopy discrimination ( $\Delta$ ) can provide important biophysical parameters for inversion modeling, constraining carbon budgets, and understanding the impacts of land use change on carbon cycling. The objectives of this research were to use continuous micrometeorological and stable isotopomer measurements to: 1) quantify seasonal changes in the isotope ratio of respired carbon from a corn-soybean system; 2) examine the variation in source (C<sub>3</sub> vs C<sub>4</sub>) contribution to respiration; 3) interpret seasonal variations in NEE, and 4) obtain key biophysical parameters at the field scale for improving carbon inversion models.

## 2. METHODS

### 2.1 Study Site

Field research was conducted in the Upper Midwest, United States, at the University of Minnesota Rosemount Research and Outreach Center (RROC). RROC is located 20 km south of the St. Paul Campus (40° 45' N 93° 05' W). The experiment was conducted in a 17 ha agricultural field. The field was in soybean (*Glycine max*, C<sub>3</sub> photosynthetic pathway) production during 2002. The soybean crop was harvested and the field was tilled November 7, 2002 with a combination chisel plow/tandem disk. Corn (*Zea mays*, C<sub>4</sub> photosynthetic pathway) was planted into the field on May 2, 2003.

### 2.2 Eddy Flux Measurements

CO<sub>2</sub> flux measurements were made using a three-dimensional sonic anemometer-thermometer

(CSAT3, Campbell Scientific Inc., USA) and an open path infrared gas analyzer (LI-7500, LI-COR, USA). The height of the CSAT3 and LI-7500 were adjusted in relation to the changing canopy height in order to measure above the roughness sublayer and to maintain a similar flux footprint throughout the experiment. Further details regarding CO<sub>2</sub> flux calculations can be found in Griffis et al., (2004).

### 2.3 Trace Gas Measurement System

The stable isotopomers, <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>, were measured continuously using the TDLAS method (Trace Gas Analyzer, TGA100, Campbell Scientific Inc., USA). A detailed discussion of the methodology can be found in Bowling et al., (2003) and Griffis et al., (2004). Mixing ratios of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> were measured at two heights within the canopy and above the roughness sublayer. The height of the intakes varied through the season depending on the canopy height. Each sample inlet consisted of a Delrin filter holder with Teflon filter membranes (A-06623-32 and EW-02916-72, Cole Parmer, USA) followed by a critical flow orifice (D-7-BR, O'Keefe Controls Co., USA). The flow rate was set to 0.260 l min<sup>-1</sup> to maintain a TGA sample cell pressure of 2.0 kPa. Tubing (Dekabon Type 1300, Dekoron, USA) connected the inlets located at a micrometeorological tower to a custom manifold (Campbell Scientific, Inc., USA) and then to a Nafion Dryer (PD-200T-24-SS, Perma Pure Inc., USA) located just before the TGA. The TGA was housed in an instrument trailer located at the edge of the field. A rotary vane vacuum pump (RB0021, Busch Inc., USA) pulled the sample and calibration gases through the TGA sample cell. The manifold sequentially directed the flow from each of the selected intakes or calibration standards to the TGA sample cell.

### 2.4 Calibration and Measurement Cycle

The TGA controlled the sampling system, with its *Site Means* parameters set to cycle through four sample inlets and two calibration standards every two minutes as follows: 1) calibration using ~350 μmol mol<sup>-1</sup> CO<sub>2</sub> with known isotope ratio; 2) calibration using ~600 μmol mol<sup>-1</sup> CO<sub>2</sub> with known isotope ratio; 3) measurement of CO<sub>2</sub> mixing ratio above the canopy at a height z<sub>1</sub>; 4) measurement of

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CO<sub>2</sub> mixing ratio above the canopy at height  $z_2$ ; 5) measurement of CO<sub>2</sub> mixing ratio within the canopy at  $z_3$ , and 6) measurement of the mixing ratio of CO<sub>2</sub> within the canopy at  $z_4$ . Within each two minute cycle each sample and calibration inlet was sampled for 20 s. Calibration standards were obtained from the National Oceanic and Atmospheric Administration - Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL).  $\delta^{13}\text{CO}_2$  values are reported relative to the Vienna Pee Dee belemnite Scale.

### 3. RESULTS

#### 3.1 Seasonal Variation in $\delta^{13}\text{CO}_2$

Half-hourly variations in  $\delta^{13}\text{CO}_2$  showed a distinct diurnal and seasonal pattern (Fig. 1). During late May to early June (DOY 140 to DOY 160) the surface layer was relatively depleted in  $^{13}\text{CO}_2$  due to the accumulation of respired CO<sub>2</sub> in the surface layer. During the early spring and late fall the  $\delta^{13}\text{CO}_2$  of the well-mixed ( $u_* > 0.1 \text{ m s}^{-1}$ ) surface layer was approximately -8.5‰. Following leaf emergence (DOY 168), daytime photosynthesis ( $P_g$ ) caused the surface layer air to become enriched in  $^{13}\text{CO}_2$ . During the daytime, when  $P_g$  was large and atmospheric mixing strong,  $\delta^{13}\text{CO}_2$  reached -6.3‰ during early August (DOY 225). Fig. 1 illustrates that during stable nighttime conditions the accumulated CO<sub>2</sub> in the surface layer resulted in large negative  $\delta^{13}\text{CO}_2$  values, often less than -12‰. These values became more negative (lighter) when respired CO<sub>2</sub> accumulated in the stable nocturnal boundary layer. The onset of senescence is evident after DOY 250 as the  $\delta^{13}\text{CO}_2$  became relatively depleted in  $^{13}\text{CO}_2$ .

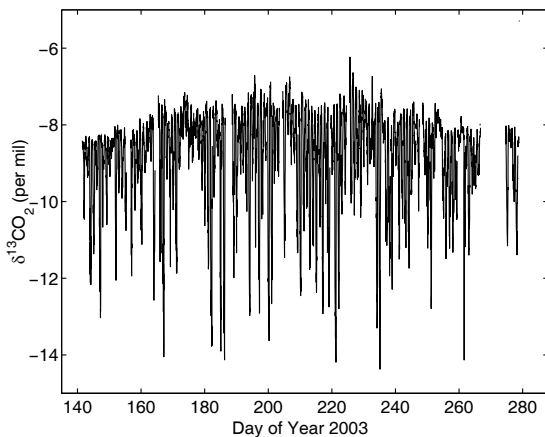


Fig. 1. Seasonal variation of half-hourly  $\delta^{13}\text{CO}_2$  measured above a corn-soybean rotation ecosystem using the TDLAS technique. Data are shown for the corn (C<sub>4</sub>) phase of the rotation during 2003.

#### 3.2 Isotope Ratio of Ecosystem Respiration and Ecosystem Discrimination

Previous measurements at this site showed considerable day-to-day variation in the isotope ratio of non-growing season respiration ( $\delta^{13}\text{C}_R$ ) with values characteristic ( $\delta^{13}\text{C}_R = -26.41\text{‰}$ ) of the C<sub>3</sub> soybean crop that was grown in 2002 (Griffis et al., 2004). These initial measurements ended in November 2002. When measurements resumed during spring 2003,  $\delta^{13}\text{C}_R$  varied from about -28 to -18‰ from DOY 140 to DOY 170 and rapidly increased (became heavier) as the corn canopy developed and  $P_g$  increased (Fig. 2). During full canopy  $\delta^{13}\text{C}_R$  varied from about -16 to -10‰.  $\delta^{13}\text{C}_R$  rapidly became more negative as the corn canopy senesced. Large variations were observed during early spring and late fall when CO<sub>2</sub> fluxes were small. Canopy-scale  $\Delta$  (data not shown) showed a similar seasonal pattern illustrating the strong isotopic disequilibrium associated with this C<sub>3</sub>-C<sub>4</sub> rotation ecosystem. During full canopy  $\Delta$  varied from about +10 to +16‰ indicating that  $\delta^{13}\text{C}_R$  adjusted rapidly to the recently fixed CO<sub>2</sub>.

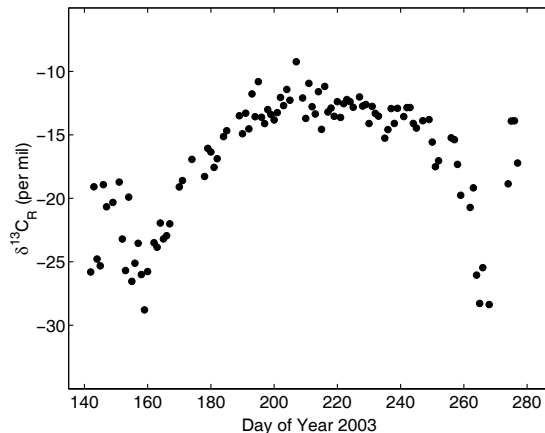


Fig. 2. Seasonal variation of nighttime  $\delta^{13}\text{C}_R$  above a corn-soybean rotation ecosystem.  $\delta^{13}\text{C}_R$  was estimated from the nighttime flux ratio,  $^{13}\text{CO}_2/^{12}\text{CO}_2$ . Data are shown for the corn (C<sub>4</sub>) phase of the rotation during 2003.

#### 3.3 Partitioning Ecosystem Respiration

The rapid increase in  $\delta^{13}\text{C}_R$  (heavier signal) as the corn canopy developed indicates that recent CO<sub>2</sub> assimilation by corn dominated  $R_E$ . The shift in a source characteristic of C<sub>3</sub> soybean residue to that of a C<sub>4</sub> corn canopy is likely driven by autotrophic respiration and the microbial decomposition of fresh residue and exudates. We partitioned  $R_E$  into its C<sub>3</sub> ( $R_3$ ) and C<sub>4</sub> ( $R_4$ ) components using the isotopic mass balance equation,

$$R_E \delta^{13}C_R = R_3 \delta^{13}C_3 + R_4 \delta^{13}C_4 \quad (1)$$

where,  $\delta^{13}C_3$ ,  $\delta^{13}C_4$  and  $\delta^{13}C_R$  are the isotope ratios of respired carbon for the soybean, corn and  $R_E$ , respectively. Since  $R_3 = R_E - R_4$ , equation 1 is easily solved for the unknown,  $R_4$ . We used daily values of  $\delta^{13}C_R$  at the canopy-scale, using the TDLAS method, and measured vertical profiles of the isotopic ratio of corn leaves ( $\delta^{13}C_4$ ) through the experimental period using a stable isotope ratio mass spectrometer (Micromass Ltd., UK). The average isotope ratio of the leaf samples was -11.7‰. Fig. 3 shows the seasonal variation in the partitioning of  $R_E$  into  $R_4$ . As expected, the respiration contribution from corn increased rapidly as the canopy developed. This analysis indicates that approximately 75 to 95% of  $R_E$  resulted from  $R_4$  during the peak growing period (DOY 200 to DOY 230). The non-growing season fraction of  $R_4$  ranged from 25 to 45%.

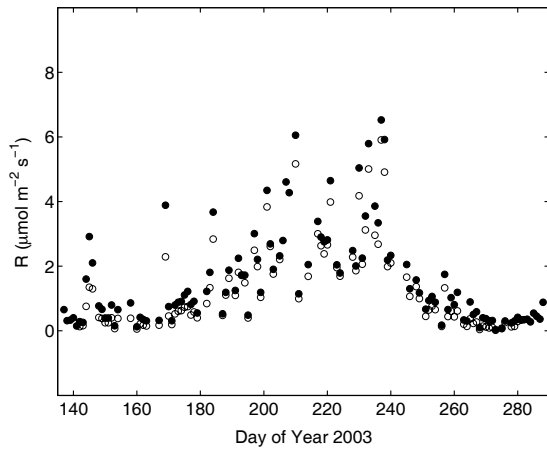


Fig. 3. Daily ecosystem respiration (closed symbols) measured using the eddy covariance technique and partitioned into the  $C_4$  contribution (open symbols) using a mixing model (Equation 1).

#### 4. DISCUSSION AND CONCLUSIONS

Continuous measurements of the stable isotopomers,  $^{12}CO_2$  and  $^{13}CO_2$ , combined with micrometeorological measurements of net ecosystem  $CO_2$  exchange (NEE) can provide unique process information for better understanding the cycling of  $CO_2$  between the land and atmosphere. As expected, we observed strong seasonal variation in  $\delta^{13}CO_2$ ,  $\delta^{13}C_R$  and  $\Delta$  for a corn-soybean rotation ecosystem in the Upper Midwest, United States. The seasonal variation of these variables was highly correlated with phenology – showing rapid changes following leaf emergence and senescence. Quantifying the daily and seasonal variation of these key variables at the field scale and relating them to other environmental

factors, such as leaf area index, will help to extend local studies to the region and should be of great benefit to the regional inversion carbon modeling community (Fung et al., 1997).

Understanding the biophysical controls on NEE at the field scale is required for evaluating land management techniques and improving/validating climate-carbon models. We combined atmospheric measurements of field-scale  $\delta^{13}C_R$  and stable isotope ratio assays of canopy leaves to parameterize a simple mass balance mixing model to better understand changes in  $R_E$ . We found that  $C_4$  respiration was 25 to 45% of  $R_E$  during the non-growing season. However, during mid-summer, when the corn canopy was fully developed, the contribution from  $C_4$  respiration increased to as much as 95%. Results from this mixing model analysis, combined with the strong temporal correlation between  $\Delta$  and  $\delta^{13}C_R$  indicate that during the growing season  $R_E$  is dominated by recently fixed  $CO_2$ . This evidence further supports the recent observations of Högberg et al., (2001).

#### ACKNOWLEDGEMENTS

This research was supported by the Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG02-03ER63684 and the University of Minnesota, Grant-in-Aid-of-Research, Artistry and Scholarship Program (TJG).

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