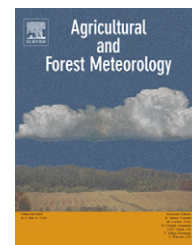


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# Isotopic CO<sub>2</sub> measurements of soil respiration over conventional and no-till plots in fall and spring

G. Drewitt, C. Wagner-Riddle, J. Warland\*

University of Guelph, Dept. of Land Resource Science, Guelph, ON, N1G 2W1, Canada

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## ABSTRACT

Soils and vegetation are the second largest global carbon reservoir. Carbon storage in soil can be increased by increasing carbon inputs and/or reducing decomposition rates. Reduced tillage practices have the potential to increase soil carbon storage by reducing decomposition of soil organic matter and/or crop residue. Isotope values ( $\delta^{13}\text{C}$ ) of soil respiration can help infer the contribution of soil carbon pools to the soil CO<sub>2</sub> flux, providing insight into the effects of tillage on residue decomposition. The objectives of this paper were to: (1) measure the isotope signatures of respired CO<sub>2</sub> from conventional tillage and no-till plots; (2) compare and contrast the two treatments in the fall and in the following spring before planting; and (3) compare the  $\delta^{13}\text{C}$  of soil respiration of the experimental plots with the surrounding region. Isotope soil CO<sub>2</sub> fluxes were measured using tunable diode laser spectroscopy and micrometeorological methods in a field experiment in Ontario, Canada. Measurements were made in fall following corn (a C<sub>4</sub> plant) harvest and again in spring prior to soybean emergence. Data were used to compute the  $\delta^{13}\text{C}$  value of respired CO<sub>2</sub> using both the flux ratio and Keeling plot methods. The large concentration footprint prevented the Keeling plots from discerning the treatment effect. In the conventional till plots, the respired  $\delta^{13}\text{C}$  value showed a stronger C<sub>4</sub> signature ( $-16.7 \pm 2.5\%$ ) compared to the no-till field ( $-20.2 \pm 2.7\%$ ) which had no soil incorporation of above-ground crop residue. This indicates more rapid decomposition of the 'new' residue in the conventional tillage treatment. Both treatments showed a decrease in the isotope ratio during the spring measurements ( $-20.6 \pm 3.7\%$  and  $-24.2 \pm 3.8\%$  for the conventional and no-till plots, respectively) which shows a depletion of the labile C<sub>4</sub> substrate and a shift in respired substrate towards the soil C<sub>3</sub> organic matter over the fall to spring period. For the fall, we estimate that 57 and 25% of the CO<sub>2</sub> flux originated from crop residue for the conventional and no-till systems, while in the spring the proportions had decreased to 22 and 0%, respectively.

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## 1. Introduction

Vegetation and soils are the second largest global reservoir of carbon (C). Carbon is added to this pool by photosynthesis, and is lost through respiration, and these opposing processes can respond differently to management practices. Carbon seques-

tration in soil can be achieved by increasing C inputs through changes in cropping systems (e.g. cover crops) or when soil management (e.g. reduced tillage) reduces residue or organic matter decomposition. Significant storage of C in no-tillage (NT) compared to conventional practices has been estimated from a global database of long-term experiments (West and

\* Corresponding author.

E-mail addresses: [gdrewitt@uoguelph.ca](mailto:gdrewitt@uoguelph.ca) (G. Drewitt), [cwagnerr@uoguelph.ca](mailto:cwagnerr@uoguelph.ca) (C. Wagner-Riddle), [jwarland@uoguelph.ca](mailto:jwarland@uoguelph.ca) (J. Warland).  
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Post, 2002). However, results from research focused on quantifying net soil C accumulation due to conversion to NT in Canada have been ambiguous, with sites in western Canada showing significant increases in soil C, while those in eastern Canada did not show significant increases (Vanden-Bygaart et al., 2003). NT in eastern Canada has been shown to increase C in the surface soil (0–10 cm), but reduce accumulation below this zone (Angers et al., 1997). It is the labile component of soil organic matter that changes most over the first years of NT (Gregorich et al., 1994). Due to the difficulties in measuring short-term changes in soil organic carbon (SOC) decomposition rates, studies quantifying SOC accumulation under NT vs. conventional tillage (CT) have involved long-term (>10 years) trials. Since this long-term accumulation is the net result of changes that occur in the short-term, clarifying the effects of management on the temporal dynamics (<1 year) of crop residue carbon (CRC) and SOC decomposition through continuous flux measurements is essential for understanding the contrasting regional results from long-term plots.

The analysis of the stable isotope  $^{13}\text{C}$  is a relatively new technique for studying the dynamics of SOC and quantification of C sequestration. Due to differences in photosynthetic efficiency coupled with kinetic discrimination during diffusion, plants incorporate  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  isotopologues differently during photosynthesis (Farquhar et al., 1989). Plants using the C3 pathway (most temperate crops) do not incorporate the  $^{13}\text{C}$  isotope as readily as plants using the C4 pathway, such as corn. The isotopic signature is typically measured using mass spectrometry as the  $^{13}\text{C}/^{12}\text{C}$  ratio relative to a standard and expressed as  $\delta^{13}\text{C}$ . If the SOC originated largely from C3 species, monitoring the  $\delta^{13}\text{C}$  of respired soil  $\text{CO}_2$  following a shift from C3 to C4 vegetation allows the quantification of the contributions of the sources of C substrate being oxidized, SOC vs. CRC (Rochette et al., 1999).

Recently, the tunable diode laser trace gas analyzer (TDLTGA) developed by Edwards et al. (2003) was modified to permit reliable, high frequency measurements of stable  $\text{CO}_2$  isotopologues in the field (Bowling et al., 2003). Griffis et al. (2005) used this instrument in combination with micrometeorological techniques to partition  $\text{CO}_2$  flux between ecosystem respiration and net ecosystem exchange over corn. The isotope signature of the respired  $\text{CO}_2$  allowed them to further partition respiration into heterotrophic and autotrophic components using a mass balance model. This work demonstrated the utility of these techniques for examining ecosystem carbon dynamics, and their potential to provide new information on soil carbon dynamics under NT vs. CT.

This study examines the effects of tillage on CRC decomposition in the fall and spring following a corn crop in a corn-soybean rotation. Two NT replicate plots and two CT replicate plots, managed as such for 6 years prior to the experiment, were instrumented with a  $\text{CO}_2$  isotope TDLTGA to measure vertical concentration gradients for the micrometeorological flux-gradient method. The isotopic signature of respired  $\text{CO}_2$  was determined from the ratio of the isotopic fluxes ( $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$ ) following Griffis et al. (2004). Keeling plots (Keeling, 1958) have been traditionally used to obtain  $\delta^{13}\text{C}$  of soil respiration. Schmid (1994) showed that the footprint of concentration measurements is much larger than the flux footprint. Griffis et al. (2007) showed that this results in a much

larger footprint for Keeling plot measurements than for the flux-ratio method of Griffis et al. (2004). This provided an opportunity to compare  $\delta^{13}\text{C}$  values from the treatment plots with the surrounding region by comparing data analysed by the flux-ratio method with Keeling plot analyses.

The specific objectives of this paper were to: (1) measure the isotope signatures of respired  $\text{CO}_2$  from NT and CT plots after a C4 crop; (2) compare and contrast the two treatments in the fall and in the following spring before planting; and (3) compare the  $\delta^{13}\text{C}$  of soil respiration of the experimental plots with the surrounding region.

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## 2. Methods

### 2.1. Site description

Measurements were made at the Elora Research Station located at 43°39'N, 80°25'W, 376 m asl in Southern Ontario, Canada. Detailed descriptions of the site can be found in McCoy et al. (2006) and Wagner-Riddle et al. (2007). Soil at the site is classified as Grey-Brown podzolic loam-till with imperfect to good drainage (Hoffman et al., 1963). Textural analysis shows that the soil is approximately 29% sand, 52% silt and 19% clay. The field used in this study is tile drained at a spacing of approximately 16 m and the land generally slopes towards the north at a 3% grade. The experimental plots are part of a long-term experiment comparing conventional-tillage (CT) agricultural practices against those considered best management practices, including NT. From January 2000 to April 2005, the CT management generally followed recommended guidelines for nitrogen application (OMAFRA, 2002), with moldboard tillage to 20 cm after harvest. The NT plots were managed by N fertilizer application according to soil nitrogen tests, no tillage of the soil with the crop planted directly into residue from the previous year, and the occasional use of cover crops (Jayasundara et al., 2007). Starting in May 2005, the NT plots were managed similarly to the CT plots, except for tillage which continued to be NT.

Two replicated plots, 100 m × 150 m each of both CT and NT were located within a larger field (~30 ha) which was planted with the same crop as the treatments. Between 1992 and 2000, the plots had a variety of C3 and C4 crops such as alfalfa, barley, canola, soybeans and corn. Beginning in 2000, the same crop was grown in all plots. The crop rotation starting in 2000 has been corn, soybeans, winter wheat, corn, soybeans and corn. Harvesting of grain corn and tillage of the conventionally managed plots was completed on 5 October 2005. Due to the difficulty of tilling while entire corn stalks were present, a mower was used to chop the stalks after grain harvesting, prior to fall tillage. Measurements reported in this study commenced on 10 October 2005 and continued until 30 May 2006, just after emergence of the soybean crop.

### 2.2. Carbon dioxide isotope measurements

A Tunable Diode Laser Trace Gas Analyzer (Model 100A, Campbell Scientific Incorporated (CSI), Logan, UT, USA, hereafter referred to as TGA) was used to measure concentrations and vertical concentration differences of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  above

the four plots between 10 October 2005 and 30 May 2006. A detailed description of the TGA can be found in Edwards et al. (2003) with the added ability to resolve isotopic concentrations as discussed in Bowling et al. (2003) and Griffis et al. (2004).

The isotopologues  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  were measured using the absorption lines at wavenumbers of 2293.881 and 2294.481  $\text{cm}^{-1}$ , respectively. The TGA was operated in a temperature-controlled trailer and the instrument enclosure was further insulated and temperature-controlled to protect it from temperature fluctuations. The 30 min standard deviation of air temperature inside the enclosure measured at 0.1 Hz (averaged from 10 Hz sampling) was typically less than 0.003 °C. Twice-weekly refilling of the liquid nitrogen cooled laser dewar induced a strong temperature perturbation ( $\sim 2^\circ\text{C}$ ) in the TGA enclosure which took 2–3 h to subside. Data collected during this equilibration time was excluded from further analysis. Reference gas with  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  concentrations of approximately 5000 and 50  $\mu\text{mol mol}^{-1}$  respectively was sent to the reference cell of the TGA at a flow rate of approximately 10  $\text{cm}^3 \text{min}^{-1}$ . The gap between the sample tube and the laser dewar was purged with nitrogen gas to prevent any absorption outside the sample tube.

A pair of air intakes was located near the center of each trial plot adjacent to ongoing  $\text{N}_2\text{O}$  flux-gradient measurements. The intake tubes were terminated with an inverted-funnel and mesh screen to prevent ingress of debris or insects. The intake tubes were connected to a pair of one-way solenoid valves (Model 8020, Asco Valve, Brantford, ON, Canada). The solenoid valves were connected with a Tee (Swagelok Co, Sonolon OH, USA) followed by a 1  $\mu\text{m}$  air filter (Model 1235, Pall Corporation, Mississauga, ON, Canada) before a common, 9.5 mm diameter internal diameter (i.d.) tube (Synflex 1300, St-Gobain Performance Plastics, Wayne, NJ, USA) that extended to the instrument trailer. The tubing from each plot to the instrument trailer was 150 m long.

A vacuum pump (Model RB0040, Busch Vacuum Technics, Boisbriand, PQ, Canada) drew sample air from the four plots continuously into a single common bypass manifold. Flow through each tube was adjusted with a flow meter and maintained at approximately 20  $\text{L min}^{-1}$ . A subsample from each of the four sample tubes was drawn from an in-line Tee union and 1.0 mm i.d. stainless steel tube connected to a second solenoid-valve manifold assembly which was controlled by a datalogger (Model CR1000, Campbell Scientific Incorporated). The sample manifold was also directly connected to four tanks of  $\text{CO}_2$ -in-air mixtures used for calibration of the TGA (described below). Air from one of the 8 intake ports of the sample manifold was selected and drawn through an in-line air dryer (Model PD 200T 24, Perma Pure Inc., NJ, USA) to remove water vapour from the sample air. Flow through the analyzer was controlled by a mass flow controller (MC series 16, Alicat Scientific, Tucson, AZ, USA) which was set to deliver air to the TGA at a rate of 200  $\text{cm}^3 \text{min}^{-1}$ . This flow rate had the desirable effect of maintaining relatively low pressure inside the TGA ( $\sim 200$  Pa) which reduced pressure broadening of the absorption lines (Bowling et al., 2003). Flow from the sample manifold to the TGA was maintained with a second vacuum pump (Model RB0021, Busch). Variation in pressure inside the TGA was entirely due to short-term fluctuations in the pump's performance and not caused by any systematic difference in

**Table 1 –  $\text{CO}_2$  concentrations ( $\pm$  standard deviation) and  $\delta^{13}\text{C}$  ( $\pm$  standard error) values of gold standard tanks used in this study for working tank inter-calibration as reported by laboratory analysis.**

| Tank designation | $\text{CO}_2$ ( $\mu\text{mol mol}^{-1}$ ) | $\delta^{13}\text{C}$ (‰) |
|------------------|--|---------------------------|
| Gold Std. A      | 545.76 $\pm$ 0.01                          | –16.192 $\pm$ 0.002       |
| Gold Std. B      | 320.37 $\pm$ 0.03                          | –8.426 $\pm$ 0.002        |

the pressure caused by the flow controller and sample manifold valves. Typically, the mean difference in pressure between the sampling of the upper and lower intakes and the calibration tanks during a half-hour period was less than 1 Pa.

The TGA concentration measurements were calibrated by regularly measuring tanks with known concentrations of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$ . A linear fit of observed vs. known tank concentrations was used to develop a gain and offset factor to correct the measurements as described in Bowling et al. (2003). The tanks used for these regular calibrations were designated as “working standards”. Every 5 min during measurements, the sample manifold switched to draw air from the two working standards for 30 s each. These working standards were compared weekly against tanks that had a precisely known concentration of both  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  (referred to as the “gold standards”, specifications of which are provided in Table 1). These weekly inter-comparison tests consisted of switching the sampling manifold to sequentially measure each of the four tanks (two working standard and two gold standards) for 1 min each. The 4 tank inter-comparisons were generally performed for 90–120 min. The gold standard tanks were purchased from the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA) and calibrated by the Stable Isotope Laboratory at INSTAAR, University of Colorado. The two-stage regulators on the working and gold standard tanks (Series 312, Controls Corporation of America, Virginia Beach, VA, USA) were set to maintain the same delivery pressure to the mass flow controller as the sample lines drawn from the bypass manifold.

In this paper, we follow the recommendations proposed in Coplen (1994) that the  $\delta^{13}\text{C}$  of the current isotopic standard (NBS19) is considered 1.00195 times that of the the Vienna PeeDee Belemnite standard ( $R_{\text{VPDB}}$ ). Based on measurements of NBS19 reported in Zhang and Li (1990), we used the value of  $R_{\text{VPDB}} = 0.0111797$  as outlined in Appendix 1 of Griffis et al. (2004). The weekly inter-comparison of the two working tanks against the two gold standards provided a means of evaluating the performance of the TGA and an indication of the precision of the  $\delta^{13}\text{C}$  measurement. The measurement of the calibration tanks resulted in a sample gain and offset for the gold standards which was then applied to calculate the concentration of the working tanks. The standard deviation of these  $\delta^{13}\text{C}$  measurements was always less than 0.1‰. From these weekly comparisons and an evaluation of the limits of precision discussed in Bowling et al. (2005) we conservatively estimate a precision of 0.15‰ for our half hourly  $\delta^{13}\text{C}$  measurements.

### 2.3. Micrometeorological measurements

The site at the Elora Research Station was extensively instrumented to obtain micrometeorological measurements

of mass and energy fluxes from the treatment plots. Half hourly eddy covariance measurements of CO<sub>2</sub> and H<sub>2</sub>O flux and turbulence statistics such as friction velocity ( $u_*$ ) were obtained at the site using a pair of sonic anemometers (model CSAT-3, CSI) and two open-path CO<sub>2</sub>/H<sub>2</sub>O gas analyzers (Model 7500, LI-COR Inc., Lincoln, NE, USA). The  $u_*$  data were used in computing eddy diffusivity values, the other data from the eddy covariance systems are not discussed in this paper. Two masts, each with four cup anemometers (F460, Climatronics Corp., Newton, PA, USA) were placed in one of each of CT and NT plots at 0.5, 1.0, 1.5 and 2.2 m above ground. These measured profiles of wind speed were used to iteratively calculate roughness length ( $z_0$ ) and displacement height ( $d$ ) as well as provide an estimate of  $u_*$  when the sonic anemometers were not operating due to inclement weather or sensor failure.

Half-hourly vertical differences of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> concentrations were calculated over each of the four plots in sequential order (i.e. one flux measurement from each plot every 2 h). The switching frequency of the upper and lower intake solenoid valves was established during the TGA installation by sending nitrogen gas through one of the intakes. This induced a very large gradient and allowed the response of the various plumbing components of the gas analyzer system to be optimized. In particular, the lag between the upper and lower intake sample arrival at the TGA and the number of samples to omit from the concentration measurement was determined in this manner. The temporal lag for samples to arrive from the intakes in the field was approximately 17 s while approximately 5 s of data were omitted from each measurement to ensure the TGA was adequately flushed of the previous sample. A sampling duration of 15 s per intake was determined to be the best compromise between system equilibration and the ability to capture the temporal behavior of vertical CO<sub>2</sub> gradients. All of the 10 Hz data output from the TGA was stored and archived for analysis. Time series of the half hourly data were examined during periods of large CO<sub>2</sub> gradients to verify the correct operation of pumps and the timing sequences of the plumbing system. During selected periods the intakes were placed at the same height to determine if there was any bias between the upper and lower intake measurements. These were usually performed during field operations such as planting or harvesting and revealed that there was no detectable difference between intakes.

The intake heights were positioned to be away from the roughness sublayer but close enough to provide a representative flux measurement when considering the size of the plots and the upwind micrometeorological fetch. Difference in concentration between the upper and lower intakes is increased by maximizing their vertical separation which ensures the measured concentration difference is greater than the instrument resolution. However, this will also increase the degree of mismatch of source areas or flux-footprints between the two intakes. Following the measurement protocol reported in Wagner-Riddle et al. (2007) for continuous N<sub>2</sub>O flux measurements, intakes were separated by a distance of 50 cm in both the CT and NT plots. The lower intakes were placed at a height of 40 cm in the CT plots and at a height of 60 cm in the NT plots. The reason for the difference was due to the presence of leftover corn stubble and vertically oriented corn stalks (~20 cm high) in the NT plots. In this

study, flux data were removed from further analysis if the aerodynamic fetch was less than 60 m, based on measurements of the plot dimensions, intake location, and wind direction. This arbitrary cut-off was selected as a compromise between removing an excessive number of measurements and providing a minimum 50:1 fetch.

Half hourly fluxes of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> were calculated using the flux-gradient technique as described in Wagner-Riddle et al. (1996) and given by the following equation:

$$FCO_2 = \frac{u_* k \rho_{ma} \Delta C}{\ln((z_2 - d)/(z_1 - d))} \quad (1)$$

where  $FCO_2$  is the flux of <sup>12</sup>CO<sub>2</sub> or <sup>13</sup>CO<sub>2</sub> in units of  $\mu\text{mol mol}^{-2} \text{s}^{-1}$ ,  $\Delta C$  the concentration difference of the respective isotopologue density between the two intakes at heights  $z_2$  and  $z_1$  in units of  $\mu\text{mol mol}^{-1}$ ,  $k$  the von Kármán's constant, and  $\rho_{ma}$  is the molar density of air. Monin-Obukhov stability corrections were not applied as discussed in detail below. This equation assumes that the turbulent Schmidt number is unity, meaning that the turbulent diffusivities for momentum and passive scalars are the same (Flesch et al., 2002). To ensure adequate turbulence for a representative flux measurement and to neglect storage of CO<sub>2</sub> in the air column between the two intakes, all fluxes measured at  $u_* < 0.1 \text{ m s}^{-1}$  were discarded, as done in Griffis et al. (2004). As the focus of this study was on  $\delta^{13} \text{C}$  values of respired CO<sub>2</sub>, further QA/QC and gap-filling were not applied, and since measurements were confined to the non-growing season, no attempt was made to calculate net ecosystem exchange.

As shown in Griffis et al. (2004), the isotope ratios of respired <sup>13</sup>CO<sub>2</sub> ( $\delta^{13} \text{C}_r$ ) can be inferred by comparison of the ratio of the isotopologue fluxes expressed by:

$$\delta^{13} \text{C}_r = \left( \frac{F^{13} \text{CO}_2 / F^{12} \text{CO}_2}{R_{VPDB}} - 1 \right) \times 1000 \quad (2)$$

This method of calculating  $\delta^{13} \text{C}_r$  is very appealing since it takes advantage of many of the desirable qualities of micrometeorological measurements such as an integrated measure over the flux footprint. As shown by Schmid (1994) and discussed extensively by Griffis et al. (2007), the flux footprint is of order 10–100 m, while the concentration footprint, used in a Keeling plot, is about 20 × larger.

An issue of significant note concerns the use of the flux of CO<sub>2</sub> as opposed to the gradient measurement ( $\Delta c$ ). Griffis et al. (2004, 2007) stated that, as the eddy diffusivities cancel, use of either measure should produce identical estimates of  $\delta^{13} \text{C}_r$ . This is true for a single measurement or for a constant eddy diffusivity (i.e. over periods ~1 h), however in practice a linear regression between  $F^{13} \text{CO}_2$  and  $F^{12} \text{CO}_2$  measured over many hours or days is used to estimate the ratio from the slope. This is essentially an averaging operation, and since the sum of products is not equal to the product of sums, the use of  $\Delta c$  to determine  $\delta^{13} \text{C}_r$  fails. Because of this issue, accurate determination of the eddy diffusivity becomes important. Noise in this estimate reduces the precision of the final  $\delta^{13} \text{C}_r$ . It is for this reason that we chose to neglect the standard stability corrections, which can introduce considerable noise into the eddy diffusivity estimate. All our measurements were made close to the surface during the colder parts of the year,

conditions in which the stability corrections are expected to be minor. We recognize that this may not be the most satisfactory solution to the problem, however correct determination of the eddy diffusivity for isotope work is beyond the scope of the present work.

#### 2.4. Keeling plots

The most widely used method to study isotopic signatures of ecosystem respiration is the Keeling plot approach (Keeling, 1958; Pataki et al., 2003). This method assumes that the background air has a constant CO<sub>2</sub> isotopic composition and concentration. Any measured changes in concentration and  $\delta^{13}\text{C}$  are contributed by ecosystem respiration derived from a source with an assumed constant  $\delta^{13}\text{C}$ . Although it requires only the measurement of a range of CO<sub>2</sub> concentrations, a number of conditions must be met and some of the assumptions may not be justified in certain cases. One difficulty is the fact that a sufficient range of concentrations must be measured to obtain a meaningful linear regression (Pataki et al., 2003; Zobits et al., 2006). The use of continuous spectroscopic measurements with a TGA can partially address this concern. The assumption that background composition is static also may be questioned when air is contaminated with CO<sub>2</sub> of fossil fuel combustion plumes. Collecting measurements far away from urban areas or nearby sources is important although regional transport of urban-influenced air may be difficult to avoid at times.

One challenge in interpreting Keeling plot measurements is attempting to relate them to respiration from a particular source area. The area contributing to a concentration measurement above a surface is much larger than that contributing to a flux measurement (Schmid, 1994). Griffis et al. (2007) combined the use of a flux and concentration footprint model and demonstrated that the Keeling plots represent a source area roughly 20× greater in extent than the flux-ratio measurements in an agricultural setting.

In this paper, we present  $\delta^{13}\text{C}_r$  results from Keeling plots, calculated using <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> concentration data from the lower air intakes, during the fall and spring which were computed using Model 1 ordinary least-squares regression as recommended in Zobits et al. (2006). We use the Keeling plot estimates of  $\delta^{13}\text{C}_r$  to describe processes that are general to the research station and surrounding lands, and the results from the flux-ratio method to describe the specific treatments being examined. Comparison of the two methods allows some distinction to be made between generally occurring processes at this site and those specific to the NT and CT treatments under study. We expect that the  $\delta^{13}\text{C}$  values measured by the Keeling plot technique should be identical over the two treatments, since the majority of the source will be outside of the treatment area, and represent an integration of the research station lands. However, data have been presented according to the treatment over which they were collected to verify this hypothesis.

Obtaining concentration measurements under well-mixed, turbulent conditions prevents the accumulation of CO<sub>2</sub> near the ground thereby limiting the range of concentrations measured. Measurements during cooler temperatures lead to a reduction in fluxes which usually results in a relatively small

range in concentrations near the surface. This low range in the Keeling plot data can dramatically increase the uncertainty in the calculated value of  $\delta^{13}\text{C}_r$ , and lead to a significant negative bias in  $\delta^{13}\text{C}_r$ , as discussed in Zobits et al. (2006). To maximize the range of CO<sub>2</sub> concentrations in this study, measurements of concentrations were not filtered based on any  $u_z$  criteria.

#### 2.5. Fall vs. spring

To compare the temporal change of respired carbon isotopic signature from the two treatments, data was split into two distinct periods when the trial plots were free of vegetation and CO<sub>2</sub> flux was derived only from decomposition of soil organic matter and crop residue. The first period ('fall') started after fall tillage and continued until a large winter storm event that left the fields snow covered (10 October 2005–2 December 2005). The second period ('spring') started when the 5 cm depth soil temperature indicated a thaw (1 April 2006) and progressed until the soybean crop emerged from the soil (30 May 2006). Between 2 May 2006 and 10 May 2006 the TGA was shut down due to power failures and planting operations. Data over winter (December 3–March 31) were collected sporadically, and are not discussed because of a low signal-to-noise ratio due to small CO<sub>2</sub> fluxes during winter conditions.

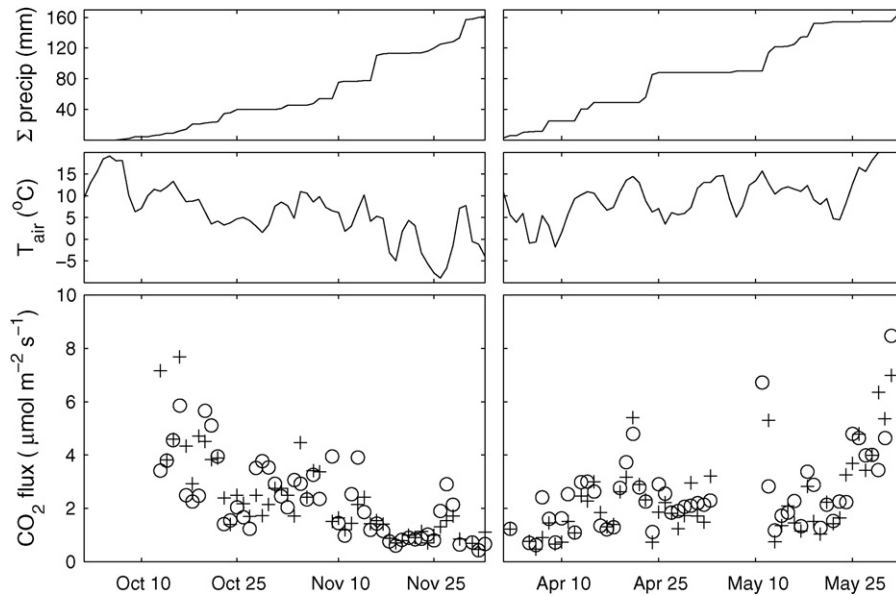
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### 3. Results and discussion

#### 3.1. CO<sub>2</sub> fluxes

To provide a general context for the measurements of  $\delta^{13}\text{C}_r$ , daily fluxes of CO<sub>2</sub> for the two treatments, measured during the fall and spring using the flux-gradient method, are shown in Fig. 1. Also shown are the air temperature and precipitation during the measurements. Fluxes followed the expected pattern, decreasing as soil temperature decreased in the fall and gradually increasing again in the spring. There were just over 160 mm of precipitation during the fall measurements. There was relatively little snow during the fall with the exception of about 8 cm on the ground that fell on 23 and 24 November. Precipitation during the spring measurements was predominantly rain with the exception of approximately 2 cm of snow on the plots between April 5 and 6. Planting of the fields occurred on May 9–10. Following planting, a relatively large flush of CO<sub>2</sub> occurred from both pairs of NT and CT plots on May 11. Prior to planting, the CT field was disked which disturbed the soil, possibly increasing aeration and incorporating crop residue into the soil. Further, on May 11, 28.5 mm of precipitation were recorded. Likely, the emission peak on this day is due to the combination of tillage and precipitation. The air sampling system on the NT plots was not fully functional on May 11, so the effects of tillage vs. precipitation cannot be separated.

Because the isotopic analyses presented below depend on a range of flux or concentration values to produce a reliable estimate of the regression slope or intercept, Fig. 2 shows histograms of CO<sub>2</sub> flux separated by treatment and period of measurement. The seasonal-averaged fluxes from the four plots were 1.84  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , with maximum half-hourly fluxes of 16.3 and 19.1  $\mu\text{mol m}^{-2} \text{s}^{-1}$  from CT (fall and spring,

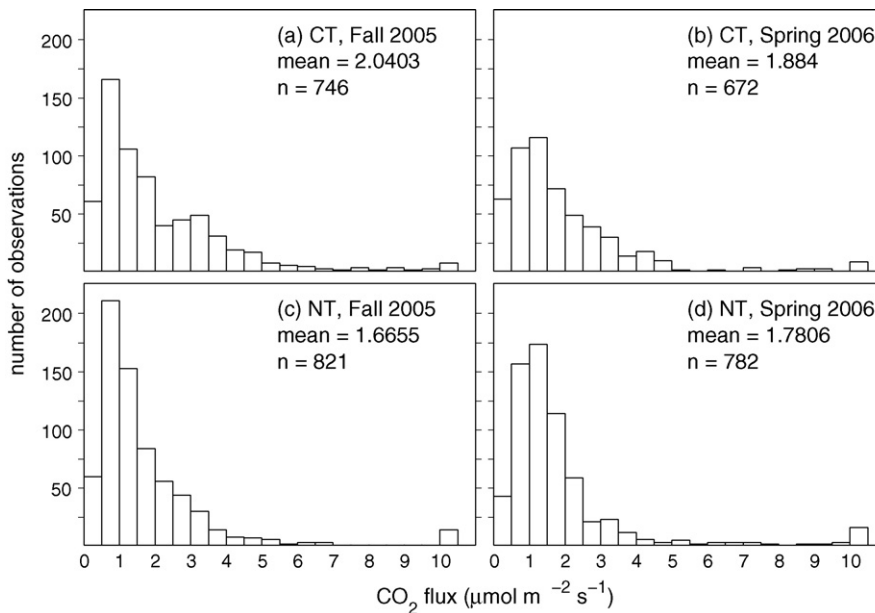


**Fig. 1 – Time series of cumulative daily precipitation (top), mean daily air temperature (middle) and mean daily CO<sub>2</sub> fluxes (bottom) during fall, 2005 and spring, 2006. Each daily CO<sub>2</sub> flux measurement represents the average of a minimum of 10 half hourly measurements averaged over two replicate treatments. Conventional tillage (CT) denoted by × and no-tillage (NT) by +.**

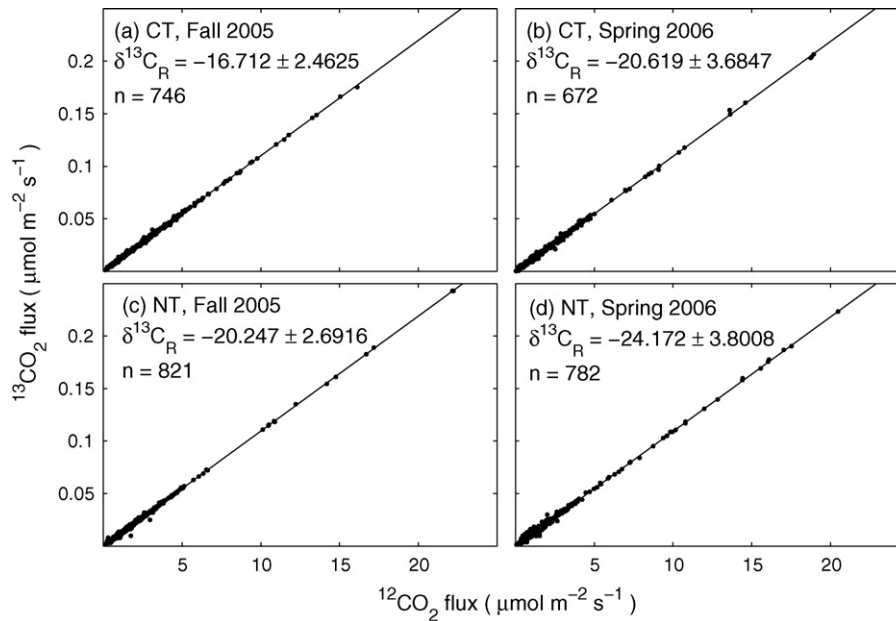
respectively) and 23.9 and 23.1  $\mu\text{mol m}^{-2} \text{s}^{-1}$  from NT (fall and spring, respectively). These data are positively skewed, with a few large fluxes but the bulk of measurements less than about 2  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . Though it is expected that fluxes will be small during these time periods, the heavy weighting towards low values shown in Fig. 2 increases the error in the regression used to estimate  $\delta^{13}\text{C}_r$ , presented below.

**3.2. CO<sub>2</sub> isotopic fluxes**

Half-hourly isotopic fluxes are shown in Fig. 3 for the fall and spring measurements over the CT and NT plots. Following the flux ratio method of Griffis et al. (2004), the slope of the regression line between  $F^{13}\text{CO}_2$  and  $F^{12}\text{CO}_2$  represents the average  $\delta^{13}\text{C}_r$ . In the fall,  $\delta^{13}\text{C}_r$  from the NT plots was about



**Fig. 2 – Frequency histogram of measured half-hourly flux ( $u_s > 0.1 \text{ m s}^{-1}$ ) in conventional (CT) and no-till (NT) plots during fall, 2005 and spring, 2006. Fluxes greater than 10.5  $\mu\text{mol m}^{-2} \text{s}^{-1}$  are retained in the last data bin. The maximum half-hourly fluxes were 16.3 and 19.1  $\mu\text{mol m}^{-2} \text{s}^{-1}$  from CT (fall and spring, respectively) and 23.9 and 23.1  $\mu\text{mol m}^{-2} \text{s}^{-1}$  from NT (fall and spring, respectively).**

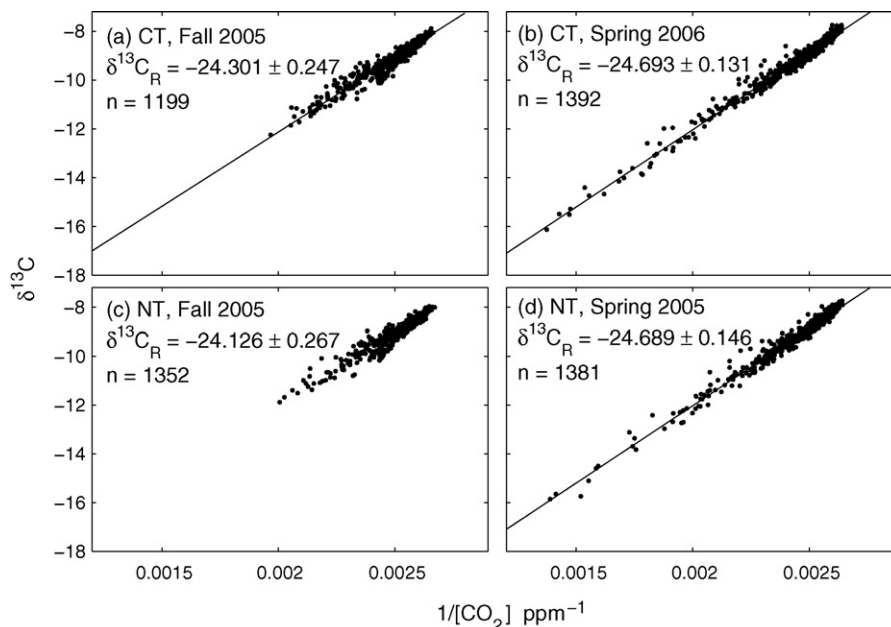


**Fig. 3 – Linear regression of  $^{12}\text{CO}_2$  vs.  $^{13}\text{CO}_2$  flux determined by the flux-gradient method.  $\delta^{13}\text{C}_r$  is estimated from the slope of the line according to the methodology of Griffis et al. (2004).**

3.5‰ lower than the CT plot ( $-20.25\%$  vs.  $-16.71\%$ ). The same difference in  $\delta^{13}\text{C}_r$  between treatments was seen in the spring. However, in both treatments, there was a notable drop in  $\delta^{13}\text{C}_r$  of about 4‰ from fall to spring. Thus there was a significant treatment effect which was seen in both fall and spring, as well as a drop in  $\delta^{13}\text{C}_r$  from fall to spring that was treatment-independent. The less negative  $\delta^{13}\text{C}_r$  for CT indicates a stronger signature associated with the corn residue added in fall after crop harvest. The consistent decrease of approximately 4‰ between fall and spring for both treatments could be accounted for by a gradual depletion of the labile corn

C4 substrate and more of the C3 dominated soil organic substrate being used for respiration.

Detailed mass spectrometry measurements of  $\delta^{13}\text{C}$  of the various organic pools in the soil at this site will be the subject of another publication. Preliminary data indicate that the  $\delta^{13}\text{C}$  of corn tissue at this site was typically about  $\delta^{13}\text{C}_{\text{CRC}} = -12\%$  for the corn cobs, leaves and stalks, in agreement with C4 vegetation as determined by Deines (1980). In contrast, soil samples with all roots excluded were in the range of  $\delta^{13}\text{C}_{\text{SOC}} = -22$  to  $-24\%$  which might be considered a composite of occasional C4 crops ( $\delta^{13}\text{C} \approx -12\%$ ) and C3 vegetation ( $\delta^{13}\text{C} \approx -28\%$ ).



**Fig. 4 – Keeling plot results with estimated  $\delta^{13}\text{C}_r$  for the two treatments in fall and spring.**

We used a simple mixing model,  $\delta^{13}C_r = f_{SOC} \times \delta^{13}C_{SOC} + f_{CRC} \times \delta^{13}C_{CRC}$ , where  $\delta^{13}C_{SOC}$  and  $\delta^{13}C_{CRC}$  are the values for the two substrates contributing to the  $CO_2$  flux, to derive the fraction of C stemming from SOC and CRC. We estimate that a larger proportion of measured  $CO_2$  flux in fall originated from CRC in CT compared to NT (57% vs. 25%). In spring this proportion had decreased to 22% for CT and 0% for NT. This indicates that incorporation of corn residue resulted in more rapid decomposition under CT compared to residue placement on the soil surface in NT plot. However, change in carbon storage over 25 years was not significantly different in long-term conventional vs. no-tillage plots adjacent to our experimental site (Deen and Kataki, 2003), in agreement with other results for cool, humid conditions of eastern Canada (Angers et al., 1997). This suggests that the short-term effect we observed is not sustained in the long-term, and likely followed by increased residue decomposition rates under NT compared to CT. Our short-term effect was observed over November, approximately 1 month after fall ploughing, and in April to May, before planting of the next crop. Micrometeorological measurements after soybean emergence yielded net  $CO_2$  fluxes (data not shown), but partitioning the heterotrophic components (SOC and CRC) of soil respiration was not possible due to the additional contribution from plants. We speculate that the higher summer soil moisture conditions associated with no-till at this site (McCoy et al., 2006) may promote CRC decomposition during the summer months, offsetting any decreases in decomposition rates observed in fall and spring.

### 3.3. Keeling plots

Calculated values of  $\delta^{13}C_r$  from the Keeling plots (Fig. 4) showed that, as expected, there was very little difference between the CT and NT measurements in the fall or in the spring, indicating that the concentration footprint was much larger than the treatment area. However, it is apparent that there was a slight decrease in  $\delta^{13}C_r$  of approximately 0.3‰ between the fall and spring. The slight reduction in  $\delta^{13}C_r$  from fall to spring, similar to the decrease in the flux ratio method data which is plot-specific, might be explained by a shift in substrate used for respiration in the local agroecosystems. However, the order-of-magnitude smaller decrease is consistent with the differing footprint area ( $\sim 20\times$ , Griffis et al., 2007). Much of the land in the area is in corn/soybean rotation, with corn grown in 2005 in the fields immediately surrounding the treatment plots. Because decomposition of C4 CRC is not evident in these data, these results suggest that the Keeling plot footprint was dominated by other local landuses, including soybean, grass and woodlot.

## 4. Conclusions

This paper examined  $^{12}CO_2$  and  $^{13}CO_2$  fluxes from two replicated conventional and no-tillage agricultural treatments in the fall and spring following the corn year of a typical corn-soybean-wheat rotation. Measurements of isotope  $CO_2$  flux were obtained over bare soil post-harvest in the fall of 2005 and prior to planting in the spring of 2006. The trace gas analyzer sampling system used a mass flow controller to subsample air drawn from the four plots to measure

concentrations and vertical gradients. Estimated precision of the half hourly  $\delta^{13}C$  was 0.15‰.

In the conventional till plots, where above-ground crop residue was incorporated into soil, the respired  $CO_2$  signature showed a stronger C4 signature ( $-16.7 \pm 2.5\%$ ) compared to the no-till field ( $-20.2 \pm 2.7\%$ ) where crop residue was left on the soil surface. This indicates a larger contribution of CRC to the soil respiration flux in the CT treatment. Both treatments showed a decrease in the isotopic signature during the spring measurements ( $-20.6 \pm 3.7\%$  and  $-24.2 \pm 3.8\%$  for the conventional and no-till plots, respectively) which indicates a depletion of the labile C4 substrate and a shift in respired substrate towards the soil C3-derived organic matter. For the fall, we estimate that 57 and 25% of the  $CO_2$  flux originated from crop residue for the conventional and no-till systems, while in the spring the proportions had decreased to 22 and 0%, respectively. These results suggest that NT will increase C storage, contradicting previous studies in eastern Canada. However, it may be that, under NT, decomposition increases at some time subsequent to the measurement periods reported here.

Analysis of  $\delta^{13}C_r$  using Keeling plots showed no difference between the two treatments since the footprint of concentration measurements extended well beyond the study area. The Keeling plots showed a similar decrease in  $\delta^{13}C_r$  from fall to spring as the flux-ratio method, though the decrease was of smaller magnitude. The difference of one order of magnitude is consistent with estimates of the ratio of flux to concentration footprint size. These results support the conclusions of Griffis et al. (2007), who demonstrated the difficulties in directly comparing  $\delta^{13}C_r$  estimates from Keeling plots with micrometeorological flux measurements.

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