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Use of the isotope flux ratio approach to investigate the $C^{18}O^{16}O$ and $^{13}CO_2$ exchange near the floor of a temperate deciduous forest

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Abstract

Stable isotopologues of CO_2, such as $^{13}CO_2$ and $C^{18}O^{16}O$, have been used to study the CO_2 exchange between land and atmosphere. The advent of new measuring techniques has allowed near-continuous measurements of stable isotopes in the air. These measurements can be used with micrometeorological techniques, providing new tools to investigate the isotope exchange in ecosystems. The objectives of this study were to evaluate the use of the isotope flux ratio method (IFR) near the forest floor of a temperate deciduous forest and to study the temporal dynamics of $\delta^{18}O$ of CO_2 flux near the forest floor by comparing IFR estimates with estimates of $\delta^{18}O$ of net soil CO_2 flux provided by an analytical model. Mixing ratios of $^{12}C^{16}O_2$, $^{13}CO_2$ and $C^{16}O^{18}O$ were measured within and above a temperate deciduous forest, using the tunable diode laser spectroscopy technique. The half-hourly compositions of the CO_2 flux near the forest floor ($\delta^{13}C_F$ and $\delta^{18}O_F$) were compared with estimates provided by a modified Keeling plot technique (mKP) and by a Lagrangian dispersion analysis (WT analysis). The mKP and IFR $\delta^{18}O_F$ estimates showed good agreement (slope = 1.03 and correlation, $R^2 = 0.80$). The $\delta^{13}C_F$ estimates from the two methods varied in a narrow range of −32.7 and −23.1 ‰; the mean (±SE) mKP and IFR $\delta^{13}C_F$ values were −27.5 ‰ (±0.2) and −27.3 ‰ (±0.1), respectively, and were statistically identical ($p > 0.05$). WT analysis and IFR $\delta^{18}O_F$ estimates showed better correlation ($R^2 = 0.37$) when only turbulent periods ($u^* > 0.6\,m\,s^{-1}$) were included in the analysis. The large data capture (~95 % of half-hour periods evaluated) for the IFR in comparison with mKP (27 %) shows that the former provides new opportunities for studying $\delta^{18}O$-CO_2 flux dynamics within forest canopies. Values of $\delta^{18}O_F$ showed large temporal variation, with values ranging from −31.4 ‰ (DOY 208) to −11.2 ‰ (DOY 221). Precipitation events caused substantial variation (~8 ‰) in $\delta^{18}O_F$ over a period of approximately 24 h. A diel trend of $\delta^{18}O_F$ was observed, with more enriched values present during the daytime. Model simulations indicate that the activity of the carbon anhydrase enzyme was very variable during the evaluated period. These simulations indicate that more frequent sampling

BGD
8, 7671–7712, 2011

of $\delta^{18}O$ of soil water could improve the estimates of $\delta^{18}O$ of net soil CO_2 flux.

1 Introduction

Stable isotopes of CO_2 have been used to investigate the exchange of carbon dioxide between land and atmosphere (Farquhar et al., 1993; Yakir and Wang, 1996; Cuntz et al., 2003). Naturally occurring CO_2 isotopologues, such as $^{13}CO_2$ and $C^{18}O^{16}O$, have been used to study the uptake of CO_2 by oceans and land (Tans et al., 1993; Ciais et al., 1995), to investigate the exchange of CO_2 between ecosystems and atmosphere (Fung et al., 1997) and for partitioning the net CO_2 ecosystem exchange into photosynthetic and respiratory fluxes (Yakir and Wang, 1996; Bowling et al., 2001; Ogée et al., 2004; Zhang et al., 2006).

The isotopologue $^{13}CO_2$ has been used as a tracer in ecosystems where there is a contrast between the isotope compositions ($\delta^{13}C$) of growing plants and soil organic matter (Rochette et al., 1999; Griffis et al., 2005a). This contrast is commonly observed either when C_3 plants are growing in soil with organic carbon derived from C_4 residue or vice versa, and it is caused by differences in the photosynthetic isotopic discrimination between C_3 and C_4 plants (Farquhar et al., 1989). On the other hand, the use of $C^{18}O^{16}O$ as a tracer relies on differences in ^{18}O composition ($\delta^{18}O$) of CO_2 fluxes originating from soil and plant canopies, caused by the isotopic equilibration between CO_2 and liquid water in soils and leaf tissues (Gillon and Yakir, 2001). Differences in $\delta^{18}O$ between soil and foliage water pools arise as $H_2^{16}O$ evaporates more readily than $H_2^{18}O$ and due to different evaporation rates between water pools (Farquhar and Cernusak, 2005; Welp et al., 2008). Ogée et al. (2004) proposed the use of the two isotopologues for partitioning the net CO_2 ecosystem exchange into plant and soil components. The use of $C^{18}O^{16}O$ is particularly advantageous in established ecosystems where the $\delta^{13}C$ differences between plants and soil organic matter are not very large (Ogée et al., 2004; Griffis et al., 2005b).

BGD
8, 7671–7712, 2011

One of main challenges of using $C^{18}O^{16}O$ as a tracer in ecosystems is its large temporal dynamics (Griffis et al., 2005b; Wingate et al., 2010; Xiao et al., 2010), which is controlled by variables such as efficiency of the CO_2 hydration, kinetic fractionation, isotopic composition of water in the soil and foliage (Yakir and Sternberg, 2000; Seibt et al., 2006). Riley et al. (2003) observed that the rate of equilibration between CO_2 and water in soils could not be explained strictly by a physical model and proposed that the rate of CO_2 hydration is enhanced by the activity of carbonic anhydrase enzyme (CAE) in the soil. Soil chamber studies have shown that the effect of CAE varies in time and between sites, so additional studies are required to quantify the level of activity of the CAE in the soil in different biomes (Seibt et al., 2006; Wingate et al., 2008, 2010). Furthermore, chamber studies have brought new insights into mechanisms controlling the $C^{18}O^{16}O$ exchange in soils; however the use of soil chambers in ecosystem scale studies requires a very intensive sampling scheme to characterize the spatial heterogeneity of ecosystem fluxes (Law et al., 1999; Davidson et al., 2002). In addition, soil chambers can significantly affect the $C^{18}O^{16}O$ exchange between soil and air, requiring the use of soil diffusion models to correct for this effect (Seibt et al., 2006).

The advent of new measuring techniques, such as quantum cascade laser-based spectrometry (Tuzson et al., 2008; Kammer et al., 2011) and tunable diode laser absorption spectroscopy (Bowling et al., 2003b; Griffis et al., 2005b, 2008; Wingate et al., 2010) has allowed near-continuous measurements of CO_2 isotopologues in the air. These measurements can be combined with existing micrometeorological techniques, allowing the investigation of isotope exchange in spatial and temporal scales suitable for studying ecosystem biophysical processes (Griffis et al., 2007, 2010). Griffis et al. (2004) proposed the use of the isotope flux ratio method (IFR), based on gradient-diffusion theory, to determine the isotope composition of ecosystem respiration. This approach shows some advantages over the commonly used Keeling plot technique (KP) (Keeling, 1958), since it is theoretically less sensitive to changes in background atmospheric CO_2 mixing ratios and provides estimates of flux components that are consistent with the flux footprint (Griffis et al., 2004, 2007). The IFR method could be

BGD
8, 7671–7712, 2011

particularly helpful to study $C^{18}O^{16}O$ exchange since the conventional KP technique, with concentration data collected during large time intervals (several hours), is not as reliable for determining the ^{18}O composition of fluxes as when applied to ^{13}C measurements (Tans, 1998; Flanagan et al., 1999; Griffis et al., 2005b). The IFR method has been applied to investigate the isotope exchange above plant canopies. Studies have shown that the gradient-diffusion theory, in principle, is not suitable to study mass and energy exchange within plant canopies, due to the close proximity of sources/sinks and to the length scale of turbulent eddies inside plant canopies (Corrsin, 1974; Denmead and Bradley, 1987). However, it has been shown that the gradient-diffusion based approaches provide reasonable estimates of fluxes in the open trunk space of forests (Dolman and Wallace, 1991; Baldocchi and Meyers, 1991; Wu et al., 2001). According to the localized near-field theory of Raupach (1989a), a gas constituent that originates from sources at the ground inside a vegetation stand can be described by the gradient-diffusion model.

The use of the IFR method beneath plant canopies could bring new insights into mechanisms regulating the isotope exchange in ecosystems. In this study, near continuous measurements of $^{12}C^{16}O_2$, $^{13}CO_2$ and $C^{18}O^{16}O$, obtained using tunable diode laser absorption spectroscopy, were used for the first time with the IFR approach to study the isotopic exchange near the floor of a temperate deciduous forest. Thus the objectives of this study were:

1. To evaluate the use of the IFR method near the forest floor of a temperate deciduous forest by comparing its estimates of isotope composition of CO_2 flux with values provided by a modified KP technique (mKP) and the analytical Lagrangian dispersion analysis proposed by Warland and Thurtell (2000). The latter analysis takes into consideration the proximity of source and sinks and the length scale of turbulence within plant canopies.

2. To compare the $\delta^{18}O$ of CO_2 flux measured using the IFR near the forest floor with modeled $\delta^{18}O$ of soil CO_2 flux obtained using an analytical model (Tans, 1998;

BGD
8, 7671–7712, 2011

Amundson et al., 1998; Wingate et al., 2009). This model has been tested in chamber based studies and can be used to investigate the effect of environmental variables, such as the isotope composition of precipitation and the activity of soil CAE on the temporal dynamics of $\delta^{18}O$ of CO_2 flux near the forest floor (Wingate et al., 2010).

2 Materials and methods

2.1 Site description

The experiment was carried out in a deciduous forest at the Environment Canada research station at Borden, ON, Canada (44°19′ N, 79°56′ W) from June to September 2009. The approximately 100-yr old forest, consisting of natural re-growth on abandoned farmland, is composed of mixed hard-wood and coniferous species (Neumann and den Hartog, 1989). A survey conducted in 2006 indicates that red maple (*Acer rubrum* L.) is the most predominant tree species (52.2 %) followed by Eastern white pine (*Pinus strobes* L.) with 13.5 %, and large-tooth aspen (*Populus grandidentata* Michx.) and white ash (*Fraxinus americana* L.) (~7 % each) (Teklemariam et al., 2009). In July 2009 the stand height was approximately 22 m and the leaf area index (±SE) was 3.9 (±0.13) $m^2\ m^{-2}$.

The terrain at the site presents variations of elevation within 2 m, except for a 20 m deep and 40 m wide river valley located 1 km south from the 44 m sampling tower and a 6 km wide swamp located 5 km northeast from the tower (Lee et al., 1999). Textural analysis of soil cores indicated the occurrence of loamy sand soil at the site and an increase in the proportion of sand in the soil with depth (Table 1). The average carbon content was equal to 2.4 % by mass in the 0–10 cm layer.

BGD
8, 7671–7712, 2011

2.2 Measurements of mixing ratios of stable isotopes of carbon dioxide

Mixing ratios of the isotopologues, $^{12}C^{16}O_2$, $^{13}CO_2$ and $C^{18}O^{16}O$, were measured at 10 Hz within the forest canopy and above the forest using a sampling system connected to a tunable diode trace gas analyzer (TGA100A, Campbell Scientific, Logan, UT, USA; hereafter TGA), kept in a temperature controlled enclosure set up in a trailer. The TGA measures the mixing ratio of trace gases in the air by comparing the infrared absorption of sample and reference gas in a specific absorption line of the spectrum. Additional details about stable isotope measurements using the TGA can be found elsewhere (Bowling et al., 2003b; Lee et al., 2005; Griffis et al., 2005b).

The air was sampled using eight air intakes, set up within and above the forest canopy at 0.45, 1.45, 5.51, 9.65, 16.69, 20.77, 25.81 and 36.81 m (Fig. 1). In the first stage of the experiment (Day of year, DOY = 182 to 229) only the two closest intakes to the forest floor were sampled during weekends. On week days (Monday to Friday) measurements were taken above the forest; results related to these measurements will be presented in a future study. From DOY 237 to 260, all eight air intakes were sampled.

Each air intake consisted of a 1-m stainless tube with a rain diverter and mesh screen in one of its extremities. The other extremity of the tube was connected to a stainless filter (SS-4F-K4-7, 7 µm sintered element filter, Swagelok, OH, USA). In order to prevent condensation, the filter holder was heated using a 0.5 W heater connected to a 12 V DC power supply and a critical flow orifice located downstream of the filter was used to reduce the air pressure in the intake line. Approximately 40 m of polyethylene/aluminum tube (0.43 I.D., Synflex 1300, Aurora, OH, USA) directed the sample to a custom made manifold (Campbell Scientific).

The manifold was used to control the flow of ambient air from the air inlets and calibration gases through the TGA. The duration of each sampling cycle was 5 min, in which the system measured atmospheric and secondary calibration tank mixing ratios for each isotopologue. The sampling system manifold switched between air

BGD
8, 7671–7712, 2011

intakes every 15 s for 4 min, and then each of the two calibration tank was sampled for 30 s. The air was pulled continuously through all air intakes at a flow rate of approximately 600 $cm^3\,min^{-1}$ using a vacuum pump (RB0040, Bush Vac. Tec., Boisbriand, PQ, Canada). A sub-sample of the total flow was directed to the TGA at a flow rate of 200 $cm^3\,min^{-1}$ in order to maintain the TGA sample cell at approximately 1.8 kPa reducing the pressure broadening of the absorption line (Bowling et al., 2003b).

The secondary calibration tanks were compared weekly with two primary calibration standards obtained from the Stable Isotope Laboratory (SIL) at the Institute of Arctic and Alpine Research, University of Colorado, in cooperation with the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration. The calibration values for primary standard A were: CO_2 mixing ratio 360.62 µmol mol^{-1}, $\delta^{13}C$ −8.475 ‰ (±0.003 ‰) and $\delta^{18}O$ −1.037 ‰ (±0.006 ‰). Primary standard B consisted of CO_2 mixing ratio 545.77 µmol mol^{-1}, $\delta^{13}C$ −16.202 ‰ (±0.002 ‰) and $\delta^{18}O$ −11.861 ‰ (±0.007 ‰). The calibration of the secondary tanks followed the two point calibration procedure suggested by Bowling et al. (2003b). An example of corrected mixing ratios for secondary tanks and standard deviations, obtained during a weekly calibration, is shown in Table 2.

TGA measurements during tank calibration were also used to determine the time necessary to flush the TGA sampling cell after switching intakes (Fig. 2). The time required for the TGA to reach 95 % of the total response after switching between high (~545 µmol mol^{-1}) and low (~330 µmol mol^{-1}) $^{12}C^{16}O_2$ concentration tanks was ~4.5 s, which was the same time response obtained for $C^{18}O^{16}O$ and $^{13}CO_2$. Thus the mixing ratios of the two isotopologues for each intake and calibration tanks were extracted from the dataset, discarding 5 s after switching intakes. A total of 50 datapoints were discarded after switching intakes giving a total of 4800 datapoints per sampled height and 3000 datapoints per calibration cycle every 30 min when the TGA system was sampling the two intakes near the forest floor. High frequency sampling (10 Hz) allows for large number of measurements at each observation height and has the advantage of improving the precision of concentration difference measurements

BGD
8, 7671–7712, 2011

(Wagner-Riddle et al., 2005). The data were averaged into 5 min intervals and corrected using the measurements obtained from each calibration tank during each measuring cycle. The corrected data were used to calculate half-hour mean mixing ratios for each isotopologue. The isotope ratios of CO_2 in the air ($\delta^{13}C_a$ and $\delta^{18}O_a$) were expressed according to the delta notation, in reference to the Viena Peedee Belemnite (VPDB) scale, i.e. $[^{13}C]/[^{12}C] = 0.0111797$ and $[^{18}O]/[^{16}O] = 0.002088349077$ (Griffis et al., 2004, 2005b).

2.3 Supporting measurements

The temporal variation of half-hourly soil CO_2 flux was measured using one automated chamber (Li-8100, Li-Cor) with a 20 cm diameter. To correct the automated chamber measurements (F_{static}) for the effect of spatial heterogeneity of the soil flux, the net soil CO_2 flux (F_R) was measured weekly using a static chamber at 10 different points in an area adjacent to where the automated measurements were taken. A linear model ($F_R = 0.727 + 0.623F_{static}$, $R^2 = 0.88$, $p < 0.001$) was used to scale up the single-point soil chamber measurements, following Ohkubo et al. (2007). Measurements of F_R were used for modeling the $\delta^{18}O$ of net soil CO_2 flux (see Sect. 2.5).

Soil samples were taken weekly to determine the $\delta^{18}O$ of soil water ($\delta^{18}O_{sw}$) at 5, 10 and 50 cm depth. Liquid water from soil samples was extracted using the cryogenic vacuum extraction method (Ehleringer and Osmond, 1989). In addition, the $\delta^{18}O$ of precipitation water ($\delta^{18}O_{pw}$) was determined on an event basis. The $\delta^{18}O$ of soil and precipitation was determined using the CO_2 equilibration method on a gas bench auto sampler attached to a mass spectrometer (Delta Plus XL, Thermo Finnigan, Bremen, Germany) with precision of 0.1 ‰. The $\delta^{18}O$ of soil water and precipitation were expressed relative to the Vienna Standard Mean Ocean Water (VSMOW) in the delta scale. Profiles of $\delta^{18}O_{sw}$, used to model $\delta^{18}O$ of soil CO_2 flux (Sect. 2.5 and Appendix B), were obtained by fitting an exponential functions with e-foldings of 5 and 8 cm to measured $\delta^{18}O_{sw}$ (Fig. 3), as proposed by Wingate et al. (2008).

BGD
8, 7671–7712, 2011

Soil temperature (T_s) and water content (θ_w) were measured at 10 cm depth using thermocouples (105T, Campbell Scientific, Logan, UT, USA) and moisture probes (CS615-L, Campbell Scientific, Logan, UT, USA), respectively. The precipitation and air temperature were measured in an open pond area adjacent to the site using a tipping bucket rain gauge (Belfort, Baltimore, MD) and air temperature probe (HMP45A, Vaisala, Vantaa, Finland). The wind velocity components were measured at 33.4 m using a sonic anemometer (CSAT3, Campbell Scientific, Logan, UT, USA, Fig. 1).

2.4 Determining the $\delta^{18}O$ and $\delta^{13}C$ of CO_2 flux near the forest floor

Three methods were used to determine the isotope composition of CO_2 flux near the forest floor: IFR, mKP and WT. Griffis et al. (2004) proposed the use of the ratio between fluxes of heavier and lighter isotopologues to derive the isotope ratio of ecosystem fluxes:

$$\delta_F = \left(\frac{R_F}{R_{VPDB}} - 1\right) \cdot 1000 \quad (1)$$

where δ_F is the isotope ratio of the CO_2 flux (‰). R_F is the ratio between the heavier and lighter isotopologue fluxes (F^{heavy}/F^{light}) defined as F^{13}/F^{12} for $^{13}CO_2$ and $^{12}CO_2$ fluxes, or $0.5F^{18}/F^{16}$ for $C^{18}O^{16}O$ and $C^{16}O_2$ fluxes. Using the flux-gradient method to express CO_2 fluxes:

$$F^{heavy}/F^{light} = \frac{-\left(K\overline{\rho_a}/M_a\right) d\overline{[heavy]}/dz}{-\left(K\overline{\rho_a}/M_a\right) d\overline{[light]}/dz} \quad (2a)$$

where K is the eddy diffusivity, which was assumed to be the same for the heavier and lighter isotopologues, $\overline{\rho_a}$ is the mean density of dry air, M_a is the molar mass of dry air and $d\overline{[heavy]}/dz$ and $d\overline{[light]}/dz$ are the time averaged gradients of the heavy and light isotopologues measured simultaneously at the same height. For practical

BGD
8, 7671–7712, 2011

applications Eq. (2a) can be rewritten as:

$$F^{heavy}/F^{light} = \frac{\overline{[heavy]}_{z_2} - \overline{[heavy]}_{z_1}}{\overline{[light]}_{z_2} - \overline{[light]}_{z_1}} \quad (2b)$$

where $\overline{[heavy]}$ and $\overline{[light]}$ are the half-hour mean mixing ratios of isotopologues, measured at two heights ($z_1 = 0.45$ and $z_2 = 1.45$ m) near the forest floor. Large uncertainties in the estimates provided by the IFR method were observed when the gradient of $^{13}CO_2$ mixing ratio was smaller than 0.035 µmol mol^{-1} m^{-1}, which, considering the typical proportion of $^{13}CO_2$ in the air, corresponds to a gradient of CO_2 mixing ratio of approximately 5 µmol mol^{-1} m^{-1}. The same threshold was also observed by Griffis et al. (2005a). Hence, only half-hours in which the difference of CO_2 mixing ratio between two measurement heights was larger than 5 µmol mol^{-1} were used to calculate δ_F.

The isotope composition of CO_2 ($\delta^{18}O_F$ and $\delta^{13}C_F$) provided by the IFR approach was compared to $\delta^{18}O_F$ and $\delta^{13}C_F$ estimates derived using a mKP technique. Pataki et al. (2003) recommended the use of a minimum CO_2 mixing ratio range of 75 µmol mol^{-1} to minimize the errors of the conventional KP approach used with ^{13}C flask sampling data spanning long periods (hours). However, one of the main limitations of applying KP technique to ^{18}O is the high variability of $\delta^{18}O$ of source water in leaves and soil at short time scales (i.e. hours) (Bowling et al., 2003a; Ogée et al., 2004; Griffis et al., 2005b). In this study we attempted to minimize this problem by applying the KP method to derive $\delta^{18}O_F$ for half-hourly periods using 5 min values of CO_2 mixing ratios, $\delta^{18}O_a$ and $\delta^{13}C_a$ measured at 1.45 m above the forest floor (mKP). During half-hour periods, the threshold of mixing ratio (75 µmol mol^{-1}) for conventional flask-based Keeling plot is unlikely to be met, so in this study the half-hour Keeling plot data was screened based on an amplitude of mixing ratio (>25 µmol mol^{-1}) and R^2 values (>0.95). In addition, the type I regression was used to estimate the Keeling-plot intercept since some bias can be introduced with the type II (geometric) regression when the range of CO_2 mixing ratio is small (Zobitz et al., 2006).

BGD
8, 7671–7712, 2011

Estimates of $\delta^{18}O_F$ and $\delta^{13}C_F$ provided by the IFR method were also compared to the Lagrangian dispersion analysis proposed by Warland and Thurtell (2000) (hereafter, WT analysis). The WT analysis was used to infer half-hourly $^{12}C^{16}O_2$. $^{13}CO_2$ and $C^{18}O^{16}O$ fluxes near the forest floor. This formulation is based on Taylor's Lagrangian dispersion theory (Taylor, 1921) and assumes that the canopy is formed by several vertical source layers, each one with a specific value of source strength (S). Over time, each source layer releases a certain amount of matter or energy that is assumed to disperse in a Gaussian fashion. The vertical gradient of concentration (dC/dz) can then be obtained by adding the contributions from each source layer and is given by:

$$\left.\frac{dC}{dz}\right|_i = \sum_{j=1}^{m} \mathbf{M}_{ij} S_j \Delta z_j \tag{3}$$

where i and j are the concentration (C) and source (S) layer indices, respectively, Δz_j is the thickness of the source layer j with respect to the vertical coordinate (z) and $\mathbf{M}$ is the dispersion matrix, calculated using profiles of vertical wind velocity (σ_w) and Lagrangian time scale (T_L). Equation (3) can be also used to solve the inverse problem (i.e. S from C). Further details on WT analysis calculations are shown in Appendix A.

The cumulative flux (F_j) for each source layer is given by:

$$F_j = \sum_{j=1}^{m} S_j \Delta z_j \tag{4}$$

where m is the number of source layers, which was set to 4 in this study. The bottom source layer thickness ($\Delta z_1 = 1.4$ m) was set to match the two lowest concentration intake heights. Estimated $^{12}C^{16}O_2$, $^{13}CO_2$ and $C^{18}O^{16}O$ fluxes for the ground level source layer were converted to delta notation using Eq. (1).

BGD
8, 7671–7712, 2011

2.5 Modeling $\delta^{18}O$ of net soil CO_2 flux

The $\delta^{18}O$ of CO_2 flux obtained near the forest floor using the IFR approach was compared with estimates of $\delta^{18}O$ of net soil CO_2 flux ($\delta^{18}O_R$) obtained using an analytical model (Tans, 1998; Wingate et al., 2009). This formulation assumes isothermal and uniform soil water conditions to estimate $\delta^{18}O_R$, as follows:

$$\delta^{18}O_R = \delta^{18}O_{eq,s} + \varepsilon_{d,eff} + \left(\delta^{18}O_{eq,s} - \delta^{18}O_a\right) v_{inv} \frac{C_a}{F_R} \quad (5)$$

where $\delta^{18}O_{eq,s}$ (‰, VPDB) is the $\delta^{18}O$ of CO_2 in isotopic equilibrium with the soil water, $\varepsilon_{d,eff}$ is the effective isotopic fractionation during CO_2 diffusion in soil pores, C_a is the CO_2 molar concentration ($\mu mol\, m^{-3}$) obtained at 0.45 m above the forest floor and F_R is the soil CO_2 flux ($\mu mol\, m^{-2}\, s^{-1}$) measured using soil chambers (Sect. 2.3), v_{inv} ($m\, s^{-1}$) represents the rate at which CO_2 in a column of air exchanges its oxygen atoms with liquid water in the soil (Tans, 1998), which is given by:

$$v_{inv} = \sqrt{B\theta_w k_s D_{18}} \quad (6)$$

B is the Bunsen solubility coefficient for CO_2 (Weiss, 1974, $B = 1.739 \cdot \exp(-0.0390 \cdot T_s + 0.000236 \cdot T_s^2)$, θ_w is the soil water content ($m^3\, m^{-3}$), D_{18} is the effective diffusivity of $C^{18}O^{16}O$ in soil air, k_s is effective rate of oxygen isotope exchange between CO_2 and liquid water (s^{-1}), given by:

$$k_s = f_{CA} k_h \quad (7)$$

where f_{CA} is the relative increase in hydration resulting from the CAE in the soil (Riley et al., 2003; Seibt et al., 2006; Wingate et al., 2008) and k_h is the rate of oxygen isotope exchange between CO_2 and water, equal to $1/3 \cdot 0.037 \cdot \exp^{[0.118 \cdot (T_s - 25)]}$ (Skirrow, 1975; Wingate et al., 2008). Additional details on calculations of parameters used to model $\delta^{18}O_R$ are shown in Appendix B.

BGD
8, 7671–7712, 2011

3 Results and discussion

3.1 Environmental conditions and temporal dynamics of CO_2 isotopes in the air near the forest floor

Rainfall was well-distributed throughout the experiment with the largest daily totals occurring at the end of July (DOY = 207) and beginning of August (DOY 221) (Fig. 4a). The total precipitation from July to September was 190 mm, which was above the long-term average (144 mm) from 1989 to 2006 for a nearby weather station (Egbert, Environment Canada, 2009). The daily average air temperature during the experiment was slightly cooler (17.5 °C) than the long-term average (17.8 °C). Air temperature reached its maximum in August (DOY 229) and then presented a downward trend until the end of the period (Fig. 4a). Average soil temperature at 10 cm was equal to 22 °C over the study period. Large precipitation events and good drainage favoured by sandy soil at the site (Table 1) contributed to the occurrence of significant variability in the soil water content throughout the season, with soil water content ranging from 0.08 to 0.18 $m^3\ m^{-3}$ at 10 cm depth (Fig. 4b). The half-hourly soil CO_2 flux (F_R) showed similar temporal variation as the soil water content. Higher values of F_R ($\sim 6.5\ \mu mol\ m^{-2}\ s^{-1}$, DOY 205) were observed when soil water content values were high while smaller magnitudes of soil respiration ($3.1\ \mu mol\ m^{-2}\ s^{-1}$, DOY 220) were observed during dry periods (Fig. 4c).

The ensemble averaged CO_2 mixing ratio (86 days), $\delta^{18}O_a$ and $\delta^{13}C_a$ obtained near the forest floor show a distinct diurnal pattern (Fig. 5). The CO_2 mixing ratio reached its minimum ($379\ \mu mol\ mol^{-1}$) in the early afternoon (13:30 h EST), and its maximum ($465\ \mu mol\ mol^{-1}$) at 07:00 h EST. Data points during liquid nitrogen refilling time were excluded from this figure. Conversely, $\delta^{18}O_a$ became less negative reaching its maximum value (−0.39 ‰) in the early afternoon and minimum (−2.63 ‰) in the morning. Values of $\delta^{13}C_a$ showed a similar daily trend as $\delta^{18}O_a$, with values ranging from −11.01 to −7.94 ‰. The causes of this daily pattern of $\delta^{18}O_a$ and $\delta^{13}C_a$ are the

BGD
8, 7671–7712, 2011

intense mixing of air combined with the enrichment of the air in $^{13}CO_2$ and $C^{18}O^{16}O$ during the daytime and the buildup of relatively more depleted CO_2 originated from the soil during low turbulence conditions in the nighttime (Griffis et al., 2004, 2005b; Seibt et al., 2006).

3.2 Comparison between isotope flux ratio and Keeling plot approaches

The comparison between $\delta^{18}O_F$ and $\delta^{13}C_F$ estimated using the mKP and IFR methods is shown in Fig. 6. The averages of mKP standard error of intercept were equal to 0.9 ‰ and 1.3 ‰ for $\delta^{18}O_F$ and $\delta^{13}C_F$, respectively. Only 17 % ($\delta^{18}O_F$) and 24 % ($\delta^{13}C_F$) of the half-hours analyzed met the criteria used to screen the mKP estimates (CO_2 range >25 µmol mol^{-1} and $R^2 > 0.95$). The intercept error was much larger (3.4 and 3.7 ‰, for $\delta^{18}O_F$ and $\delta^{13}C_F$, respectively) when R^2 was not used to screen mKP data. Conversely, 95 % of the half-hour intervals met the criterion used to screen the IFR data obtained close to the forest floor, i.e. difference of CO_2 mixing ratio between the two air intakes near the forest floor was larger than 5 µmol mol^{-1}. The estimates of $\delta^{18}O_F$ provided by the IFR method showed good correlation ($R^2 = 0.80$) and agreement (slope = 1.03) with estimates of $\delta^{18}O_F$ obtained using the mKP technique. The regression analysis coefficients were not significant for $\delta^{13}C_F$ ($P < 0.01$). This can be explained by the relative large uncertainties in mKP and IFR estimates in comparison to the small range of $\delta^{13}C_F$ values observed for this ecosystem. The mean (±SE) mKP and IFR $\delta^{13}C_F$ values were −27.5 ‰ (±0.2) and −27.3 ‰ (±0.1), respectively, both within the range of values reported for soil respiration of C_3 ecosystems (Buchmann et al., 1997; Bowling et al., 2005), which provides evidence supporting the validity of these methods inside the forest. A student t-test showed that the two estimates for $\delta^{13}C_F$ were not different statistically ($P > 0.05$).

The KP approach has been widely used to determine the $^{13}CO_2$ composition of ecosystem respiration (Pataki et al., 2003). However, previous studies have shown that this approach may not be reliable for inferring the $\delta^{18}O$ of CO_2 flux (Flanagan

BGD
8, 7671–7712, 2011

et al., 1997; Ogée et al., 2004; Griffis et al., 2005b). Tans (1998) demonstrated that the use of KP approach to estimate $\delta^{18}O_R$ could lead to significant error due the ^{18}O exchange between CO_2 in the air and soil water, which is also known as abiotic flux or non-respiratory invasion flux (F_{inv}) (Miller et al., 1999; Riley, 2005), defined as the product of v_{inv} (Eq. 6) and C_a. Tans (1998) showed that the magnitude of the error in the derived $\delta^{18}O_R$ using the KP approach is proportional to F_{inv}/F_R. His simulations indicate that an error of 3‰ could occur in $\delta^{18}O_F$, derived using the KP approach, when F_{inv}/F_R was 0.5 and an error of 9‰ would be expected for $F_{inv}/F_R = 2$. In this study the ratio between modeled F_{inv} and measured F_R, was calculated for half-hour periods in which $\delta^{18}O_F$ was obtained using the mKP approach (Fig. 6). The average F_{inv}/F_R for these periods was 0.13 and the maximum value for this ratio was 0.19. The good agreement between the IFR and mKP $\delta^{18}O_F$ estimates is encouraging, but we acknowledge that the magnitude of F_{inv} could be larger due to the activity of the enzyme carbon anhydrase in the soil (Eq. 7). The effect of this enzyme on the CO_2 hydration in the soil is not fully understood and shows large temporal and spatial variation (Seibt et al., 2006; Wingate et al., 2008, 2010).

3.3 Isotope flux ratio and WT analysis comparisons

Estimates of $\delta^{18}O_F$ and $\delta^{13}C_F$ obtained using the IFR were compared with $\delta^{18}O_F$ and $\delta^{13}C_F$ obtained using the WT analysis (Fig. 7). This comparison was only performed for a 23 day period (DOY 237 to 260), when the eight air intakes were sampled continuously within and above the forest canopy. The regression analysis coefficients were not significant ($P > 0.05$) for the relationships between $\delta^{18}O_F$ and $\delta^{13}C_F$ obtained using IFR and mKP methods. Santos et al. (2011) observed that the WT analysis yielded spurious estimates of CO_2 flux for the lowest source layer in a corn canopy. They hypothesize that the poor performance of the WT analysis was observed when the flows above and within the canopy were decoupled due to poor mixing within the corn canopy. In this study the regression analysis coefficients for the relationship between

BGD
8, 7671–7712, 2011

WT analysis and IFR $\delta^{18}O_F$ were significant ($y = -9.9 + 0.28x$, $R^2 = 0.37$, $P < 0.01$) when only half-hour periods with friction velocity (u_*) $\geq 0.6\,m\,s^{-1}$ were included. The mean difference between $\delta^{13}C_F$ estimated by mKP and IFR methods was not statistically significant based on a Student t-test ($P > 0.05$), as observed by for the comparisons between mKP and IFR methods.

A concern that is generally raised when using gradient-diffusion based methods is the occurrence of counter-gradient fluxes within canopies. Corrsin (1974) observed that a description of the turbulent exchange of scalars using the gradient-diffusion theory is only feasible if the length scale of turbulence is much smaller than the distance over which the gradient of concentration of the transported scalar changes. Wilson (1989) demonstrated that near elevated sources, such as plant canopies, there is substantial changes in gradients of concentration of transported entities over distances much smaller than the length scale of turbulence, expressed by $\sigma_w T_L$, leading to counter-gradient fluxes in some situations. Raupach (1987) used a Lagrangian homogeneous-turbulence formulation to demonstrate how counter-gradient fluxes arise in plant canopies. Their results showed that counter-gradient fluxes are expected to occur when the transported entity source profile strength shows an intense and localized peak in the foliage well above the ground; however, their simulations do not indicate the occurrence of counter-gradient fluxes in the trunk space near the ground. Wilson (1989) observed that the magnitudes of σ_w and T_L are small in relation to the gradient of concentration near the surface (Fig. A1), so the gradient-diffusion theory is suitable to investigate the transport of scalars near ground-level sources. Furthermore, previous studies have confirmed the suitability of gradient-diffusion based methods to study scalar exchange in the open trunk space of forests (Dolman and Wallace, 1991; Baldocchi and Meyers, 1991; Wu et al., 2001). These studies and the results obtained here indicate that the IFR is suitable to investigate the isotope exchange in the trunk space near the forest floor.

BGD
8, 7671–7712, 2011

3.4 Comparison between isotope flux ratio estimates and modeled $\delta^{18}O_R$

The $\delta^{18}O_F$ estimated by the IFR approach near the forest floor was compared with modeled $\delta^{18}O_R$ (Eq. 5) to investigate the impact of environmental variables on the temporal dynamics of $\delta^{18}O_F$ during four selected periods (Fig. 8). These periods were selected because all the measurements required for modeling $\delta^{18}O_R$ were available and the sampling system was being used exclusively to measure the air intakes near the forest floor, resulting in a larger number of data points for each intake and consequently improving the ability of the TGA to measure concentration differences between air intakes (Wagner-Riddle et al., 2005).

The comparisons between $\delta^{18}O_F$ and modeled $\delta^{18}O_R$ rely on the assumption that the variation in $\delta^{18}O_F$ is mainly caused by $\delta^{18}O_R$ dynamics. This was considered a valid assumption since flux ratio measurements were obtained near the ground and the vegetation in the forest understorey was sparse. Estimated values of $\delta^{18}O_F$ using the IFR method ranged from −31.4 ‰ (DOY 208) to −11.2 ‰ (DOY 221). Large variations in $\delta^{18}O_F$ were observed on DOY 206 to 208, when precipitation events caused a reduction in $\delta^{18}O_F$ of approximately 8 ‰ from nighttime periods of DOY 207 to 208. A diurnal variation in $\delta^{18}O_F$ was observed on DOY 213, 220 and 221, with more depleted $\delta^{18}O_F$ present during daytime.

Wingate et al. (2010) also observed more depleted $\delta^{18}O_R$ values in the daytime in a Maritime pine stand which were synchronized with variations in $\delta^{18}O_a$ and F_R. In this study, diel cycles of $\delta^{18}O_a$ (Fig. 5) were also observe near the forest floor. Seibt et al. (2006) suggested that the ambient air invasion into the soil was responsible for the $\delta^{18}O_R$ diel cycle observed in a temperate *Picea sitchensis* plantation, and that this cycle could be amplified by acceleration of CO_2 hydration associated with soil CAE activity. This also seems to be a plausible explanation for the diel $\delta^{18}O_R$ trends observed in this study.

BGD
8, 7671–7712, 2011

The mean differences between $\delta^{18}O_F$ and modeled $\delta^{18}O_R$ over the whole period were equal to 4.2, 0.53 and 4.8 ‰ for $f_{CA} = 1$, 20 and 100, respectively (Fig. 8). Wingate et al. (2010) observed that a temporally uniform $f_{CA} = 70$ improved the agreement between modeled $\delta^{18}O_{sw}$ and estimated form the oxygen composition of the net CO_2 flux obtained during a 20 day period. Our results show that the use of $f_{CA} = 20$ could minimize the differences between $\delta^{18}O_F$ and modeled $\delta^{18}O_R$ over the whole period. However, the use of a single value of f_{CA} over the whole period could not explain diel variations in $\delta^{18}O_F$. The daytime enrichment in $\delta^{18}O_F$ (DOY 200, 213 and 220), for example, required larger values of f_{CA} to improve the daytime agreement between modeled and measured values when compared to the f_{CA} values used for the nighttime. Seibt et al. (2006) used a multi-layer model to study the temporal dynamics of $\delta^{18}O_R$ in a *P. sitchensis* plantation. Their results also indicate large temporal variation of f_{CA}, requiring the use of f_{CA} values ranging from 80 to 1000 for soil's top layer to match chamber observations during three sampling campaigns. The use of large values of f_{CA} results in shallower z_{eq} (see Appendix B). In this study typical values of z_{eq} were 7, 1.5 and 0.6 cm for $f_{CA} = 1$, 20 and 100, respectively. We acknowledge that the extrapolation of $\delta^{18}O_{sw}$ beyond the sampling depths could lead to errors in $\delta^{18}O_R$ estimates, especially when large gradients of $\delta^{18}O_{sw}$ were observed close to the soil surface (DOY 211, Fig. 3). An arbitrary reduction of 2 ‰ (VSMOW) in $\delta^{18}O_{sw}$ resulted in a decrease of ~4 ‰ (VPDB) in $\delta^{18}O_R$ values, assuming $f_{CA} = 100$. Thus, more superficial soil sampling could be beneficial when using this model for estimating $\delta^{18}O_R$.

On DOY 220 to 222 an upward trend in $\delta^{18}O_F$ values was observed, however this trend was not captured by the $\delta^{18}O_R$ model. Wingate et al. (2008) observed that besides the effect of the CAE, an evaporative enrichment of 3 ‰ in $\delta^{18}O_{sw}$ values was required to improve the agreement between modeled $\delta^{18}O_R$ and soil chamber observations during a 3 day period in a Mediterranean soil. In this study, an enrichment of ~2.5 ‰ (VSMOW) in $\delta^{18}O_{sw}$ from DOY 220 to 222 (before precipitation event) would

BGD
8, 7671–7712, 2011

be necessary to improve the agreement between modeled $\delta^{18}O_R$ and measured $\delta^{18}O_F$ for a constant $f_{CA} = 20$.

Large disagreement between modeled $\delta^{18}O_R$ and $\delta^{18}O_F$ was observed after precipitations events, which was likely due to changes in $\delta^{18}O_{sw}$. A decrease of approximately 5 ‰ in $\delta^{18}O_{sw}$ would be required to match measured with modeled $\delta^{18}O_R$ values on the nighttime of DOY 208, assuming a constant $f_{CA} = 20$. These results show that changes in $\delta^{18}O_{sw}$ caused by precipitation events are unlikely to be properly represented by the weekly soil sampling scheme performed in this study. The proper characterization of $\delta^{18}O_{sw}$ would require more frequent soil sampling or $\delta^{18}O_{sw}$ modeling approaches that take the $\delta^{18}O$ of precipitation into consideration (Braud et al., 2005; Wingate et al., 2010).

4 Conclusions

The IFR and mKP methods showed very good agreement (slope = 1.03) and good correlation ($R^2 = 0.80$) when used to estimate half-hourly $\delta^{18}O_F$. The mean (±SE) mKP and IFR $\delta^{13}C_F$ values were −27.5 ‰ (±0.2) and −27.3 ‰ (±0.1), respectively, both within the range of values reported for soil respiration of C_3 ecosystems (Bowling et al., 2005), which provides evidence supporting the validity of these methods inside the forest. The comparisons between IFR and mKP techniques are encouraging as they show that the IFR method can be used to study the isotope exchange near the forest floor. The large data capture (~95 % of half-hour periods evaluated) for the IFR method compared to the mKP method provides new opportunities for the study of $\delta^{18}O$-CO_2 flux dynamics within forest canopies.

The coefficients of the regression analysis between WT analysis and IFR were not significant ($P > 0.05$). However, better correlation ($R^2 = 0.37$) between WT analysis and IFR $\delta^{18}O_F$ was obtained when only turbulent periods ($u^* \geq 0.6\,m\,s^{-1}$) were included in the analysis. During low turbulence periods, the decoupling between above

BGD
8, 7671–7712, 2011

and within canopy flows could be one of the reasons for the poor agreement between the two methods. Further investigation on the use of the WT analysis to study the isotope exchange in ecosystems is still necessary.

The $\delta^{18}O$ of CO_2 flux near the forest floor showed large temporal variation, with values ranging from −31.4 ‰ (DOY 208) to −11.2 ‰ (DOY 221). Precipitation events caused substantial variation (~8 ‰) in $\delta^{18}O_F$ over a period of approximately 24 h. A diel trend of $\delta^{18}O_F$ was also observed, with more enriched values being observed during the daytime. The use of a single value of f_{CA} over the whole period could not explain the diel variation of $\delta^{18}O_F$. The results also show the importance of a frequent soil sampling scheme for the accuracy of modeled $\delta^{18}O_R$ values.

Appendix A

WT analysis and turbulence statistics calculations

Warland and Thurtell (2000) used a dispersion matrix (**M**) to relate the concentration profile with the source strength distribution of transported scalars within plant canopies (Eq. 3). The dispersion matrix **M** is calculated using turbulence statistics at source and concentration measurement heights, and is given by:

$$\mathbf{M}_{ij} = \begin{cases} \dfrac{-\left[1-\exp\left(\dfrac{-(z_i-z_j)^2}{2\Delta z_j^2}\right)\right]}{2\sigma_{wi}L_{Li}\left[1-\exp\left(-\sqrt{\dfrac{\pi}{2}}\dfrac{(z_i-z_j)}{(L_{Li}+L_{Lj})/2}\right)\right]} + G_{ij} & \text{for } z_i > z_j \\ G_{ij} & \text{for } z_i = z_j \\ \dfrac{\left[1-\exp\left(\dfrac{-(z_i-z_j)^2}{2\Delta z_j^2}\right)\right]}{2\sigma_{wi}L_{Li}\left[1-\exp\left(-\sqrt{\dfrac{\pi}{2}}\dfrac{(z_j-z_i)}{(L_{Li}+L_{Lj})/2}\right)\right]} + G_{ij} & \text{for } z_i < z_j \end{cases} \quad \text{(A1)}$$

BGD
8, 7671–7712, 2011

where L_L the Lagrangian length scale, given by $L_L = \sigma_w T_L$, z_i and z_j are the heights of the concentration measurements i and of the source layer j, respectively, and $\mathbf{G}_{ij}$ represents the image source, specified to create a reflecting boundary (Warland and Thurtell, 2000), as follows:

$$G_{ij} = \frac{-\left[1 - \exp\left(\frac{-(z_i+z_j)^2}{2\Delta z_j^2}\right)\right]}{2\sigma_{wi}L_{Li}\left[1 - \exp\left(-\sqrt{\frac{\pi}{2}}\frac{(z_i+z_j)}{(L_{Li}+L_{Lj})/2}\right)\right]} \quad \text{(A2)}$$

The parameterizations of turbulence statistics proposed by Leuning et al. (2000) and Styles et al. (2002) were used to σ_w and T_L profiles, respectively (Fig A1). Leuning et al. (2000) used exponential and non- rectangular hyperbolic functions to describe the profile of σ_w as follows:

$$\frac{\sigma_w}{u_*} = c_1 e^{c_2 z/h} \quad \text{for} \quad z < 0.8h \quad \text{(A3a)}$$

$$\frac{\sigma_w}{u_*} = \frac{(az/h+b) + d_1\sqrt{(az/h+b)^2 - 4\theta abz/h}}{2\theta} \quad \text{for} \quad z \geq 0.8h \quad \text{(A3b)}$$

where u_* is the friction velocity, obtained using sonic anemometer set up at 33.4 m (Sect. 2.3), h is the canopy height, $c_1 = 0.2$, $c_2 = 1.5$, $a = 0.85$, $b = 0.4$, $d_1 = -1$ and $\theta = 0.98$. The σ_w profile obtained used these equations are in agreement with turbulence measurements, reported by Raupach (1989b) and obtained for seven different canopies (two corn and forest canopies and three wind tunnel models).

Styles et al. (2002) proposed the following function to describe the profile of T_L within and just above plant canopies:

$$T_L = c_4 \frac{1 - \exp(-c_3 \cdot z/h)}{1 - \exp(-c_3)} \frac{h}{u_*} \quad \text{(A4)}$$

BGD
8, 7671–7712, 2011

where c_3 and c_4 are fitted coefficients. We adopted values for c_3 (= 4.86) and c_4 (= 0.10) obtained by Haverd et al. (2009) used an optimization procedure to improve the agreement between modeled and measured concentration profiles of temperature, water vapour and CO_2 concentration in a temperate Eucalyptus forest. The parameterizations of turbulence statistics described above were developed under neutral atmospheric conditions, so atmospheric stability functions proposed by Leuning (2000) were used to correct the profiles of σ_w and T_L for non-neutral conditions.

Equation (3) needs to be integrated to be used with discrete measurements. This integration was performed using the trapezoidal rule from the concentration measurement height (z_j) to the reference height (z_r = 36.81 m), reducing the sensitivity of the source to small gradients between adjacent heights when solving the inverse problem (Qiu and Warland, 2006), as follows:

$$C_r - C_i = \sum_{i=1}^{n-1} \sum_{j=1}^{m} \frac{1}{2} \left(\mathbf{M}_{ij} + \mathbf{M}_{(i+1)j} \right) S_j \Delta z_j \Delta z_i \tag{A5}$$

where C_r and C_i are the concentrations at z_r and z_i, respectively, m (= 4) is the number of source layers, and n (= 8) is and the number of concentration measurement heights. The use of redundant concentration data ($n > m$) reduces source strength uncertainties originated from errors in the concentration or turbulence statistics profiles (Raupach, 1989b). In the present study a layer thickness Δz_i = 0.01 m was used in Eq. (A5), following Qiu and Warland (2006). $C^{16}O_2$ and $C^{18}O^{16}O$ source strengths were inferred within the forest canopy using concentration measurements obtained when the TGA sampling system was set to sample eight air intakes within and above the forest canopy (Sect. 2.2).

BGD
8, 7671–7712, 2011

Appendix B

Calculation of parameters used to model $\delta^{18}O$ of soil CO_2 flux

The isotope composition of CO_2 in isotopic equilibrium with the soil water (Brenninkmeijer et al., 1983), used in Eq. (5), was calculated as follows:

$$\delta^{18}O_{eq,s} = \delta^{18}O_{sw} + \frac{17604}{(T_s + 273.16)} - 17.93 \quad \text{(B1)}$$

where $\delta^{18}O_{sw}$ is the isotopic composition of soil water at the equilibration depth (z_{eq}), $z_{eq} = 2\sqrt{2\ln 2 D_{18}/k_s B\theta_w}$, which is defined as the shallowest depth at which full isotopic equilibration between water and CO_2 molecules occurs (Wingate et al., 2009). $\delta^{18}O_{sw}$ profiles were obtained as described in Sect. 2.3 and were converted into the VPDB scale.

The effective kinetic fractionation ($\varepsilon_{d,eff}$) was calculated following Wingate et al. (2009) and is given by:

$$\varepsilon_{d,eff} = \varepsilon_d \left\{ 1 - \frac{z_1}{z_0} \left[1 - \exp\left(-z_0/z_1\right) \right] \right\} \quad \text{(B2)}$$

where ε_d is the full kinetic fractionation during CO_2 diffusion in soil pores, equal to −8.7‰ (Tans, 1998), $z_1 = \left(2\sqrt{2\ln 2}\right)^{-1} z_{eq}$ and z_0 is the soil column depth over which uniform CO_2 production occurs, assumed to be equal to 0.15 m in this study (Riley et al., 2003).

The effective diffusivity of $C^{18}O^{16}O$ in soil air is given by $D_{18} = D_s \alpha_d$, with $\alpha_d = 1 + \varepsilon_d/1000$, and D_s the diffusivity of CO_2 in soil air (Moldrup et al., 2003), as follows:

$$D_s = D_{25}\theta_a^2 \left(\frac{\theta_a}{\theta_{sat}}\right)^{\frac{3}{b}} \left(\frac{T_s + 273.16}{T_{25}}\right)^n \quad \text{(B3)}$$

BGD
8, 7671–7712, 2011

where D_{25} is the molecular diffusivity of CO_2 ($1.4 \times 10^{-5}\,m^2\,s^{-1}$) at 298 K, θ_a is the proportion of soil pores filled with air, $\theta_a = \theta_{sat} - \theta_w$, where θ_{sat} is the soil water content at saturation estimated to be $0.46\,m^3\,m^{-3}$ at the site (Saxton and Willey, 2006), b is the soil water retention parameter, determined to be equal to 6.2 in this study (Cosby et al., 1984), $T_{25} = 298$ K and n is 1.5 (Bird et al., 2002).

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BGD
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BGD
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BGD
8, 7671–7712, 2011

Table 1. Textural composition and organic carbon content of the soil at a deciduous forest in Borden, ON, Canada.

Depth (cm)	Texture (%)[1]			C (%)[2]
	Sand	Silt	Clay	
0–10	87.1	8.2	4.6	2.40 (±0.03)
10–15	90.5	6.5	3.0	0.66 (±0.03)
15–30	95.1	3.3	1.6	0.63 (±0.02)
30–45	95.3	3.3	1.3	0.53 (±0.02)
45–60	96.8	2.4	0.8	0.52 (±0.02)

[1] Soil texture analysis was obtained from three soil cores.
[2] Soil carbon content from nine soil cores. Numbers in brackets are ±1 standard deviation.

BGD
8, 7671–7712, 2011

Table 2. CO_2 isotopologues mixing ratio (± mean standard error) of secondary calibration tanks obtained during weekly calibration on day of year 188.

Tank	Mixing ratio ($\mu mol\,mol^{-1}$)		
	$^{12}CO_2$	$^{13}CO_2$	$C^{18}O^{16}O$
1	327.142 (±0.007)	3.4973 (±0.0001)	1.32671 (±0.00003)
2	542.701 (±0.007)	5.9483 (±0.0001)	2.22550 (±0.00003)

Number of observations = 5625.

BGD
8, 7671–7712, 2011

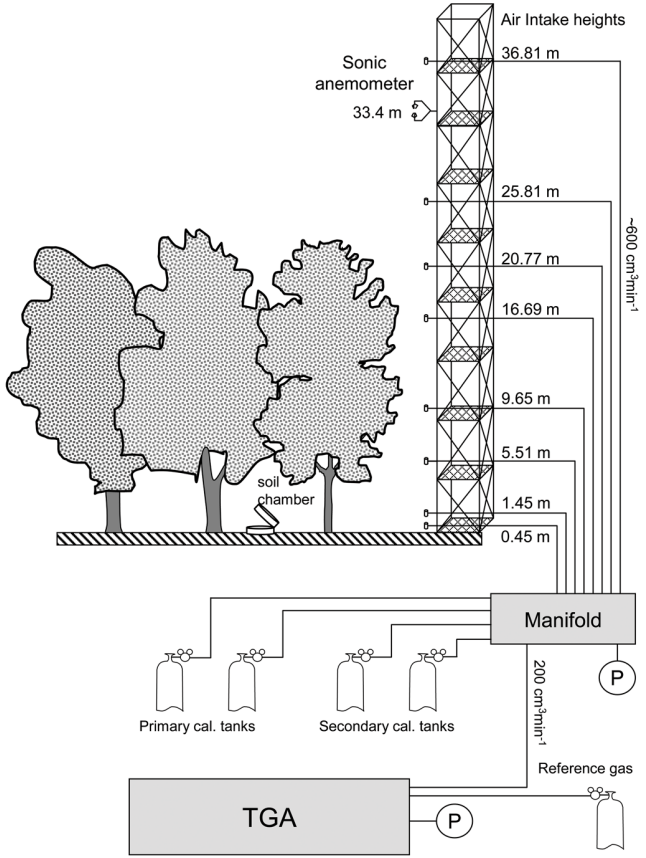

Fig. 1. Experimental set up used to study $C^{16}O_2$ and $C^{18}O^{16}O$ exchange in a temperate deciduous forest in Borden, ON, Canada. TGA denotes tunable diode laser; P shows placement of vacuum pumps. Placements of the automatic soil chamber used to measure the soil CO_2 flux and sonic anemometer are also shown.

BGD
8, 7671–7712, 2011

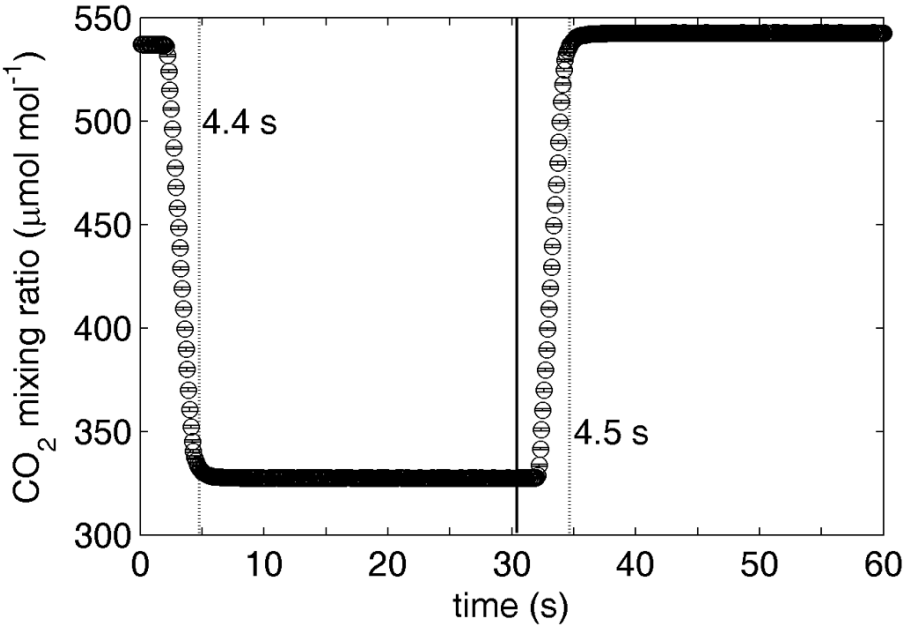

Fig. 2. Average $^{12}C^{16}O_2$ mixing ratios (±1 standard deviation) measured during switching between secondary calibration standards at 10 Hz ($n = 44$). The solid vertical line indicate the times (0 and 30 s) when the TGA sampling system switched from low (327 µmol mol^{-1}) to high (~543 µmol mol^{-1}) concentration calibration tanks and dotted lines indicate the times (4.4 and 4.5 s) after switching air intakes at which TGA readings reached 95 % of the total response.

BGD
8, 7671–7712, 2011

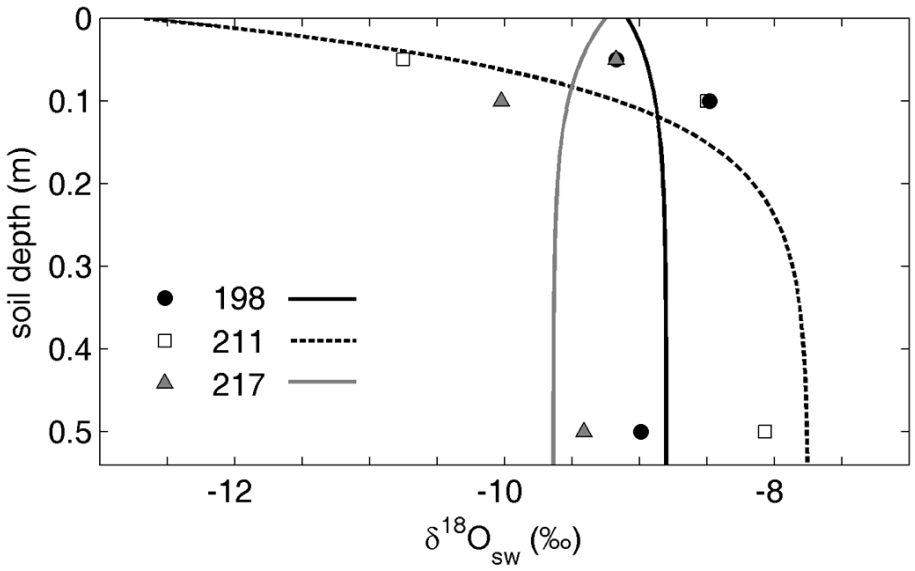

Fig. 3. Measured (symbols) and fitted (lines) profiles of ^{18}O values for soil water ($\delta^{18}O_{sw}$) for three sampling dates (Day of year, DOY = 198, 211 and 217) in a temperate deciduous forest in Borden, ON, Canada. Here $\delta^{18}O_{sw}$ is expressed in the VSMOW scale and was sampled at three depths: 0.05, 0.10 and 0.50 m. Fitted curves are exponential functions with e-foldings of 5 cm (DOY = 198 and 217) and 8 cm (DOY = 211).

BGD
8, 7671–7712, 2011

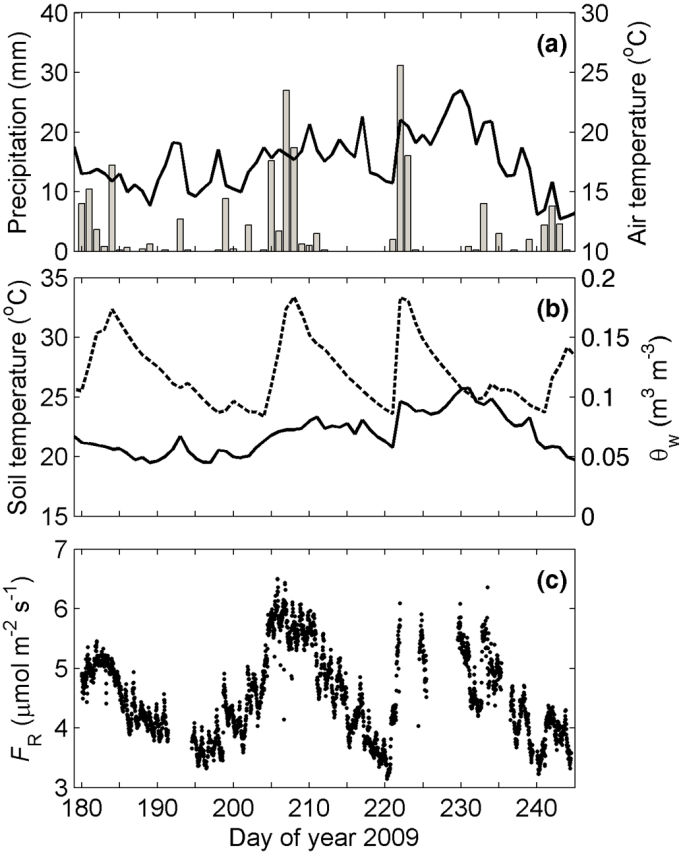

Fig. 4. (a) Daily total precipitation (bars) and mean air temperature (solid line), **(b)** daily mean soil temperature (solid line) and mean soil volumetric water content (θ_w, dashed line) at 10 cm depth, **(c)** half-hourly soil CO_2 flux (F_R) in Borden, ON, Canada. The gaps observed in F_R data were caused by automatic soil chamber failure.

BGD
8, 7671–7712, 2011

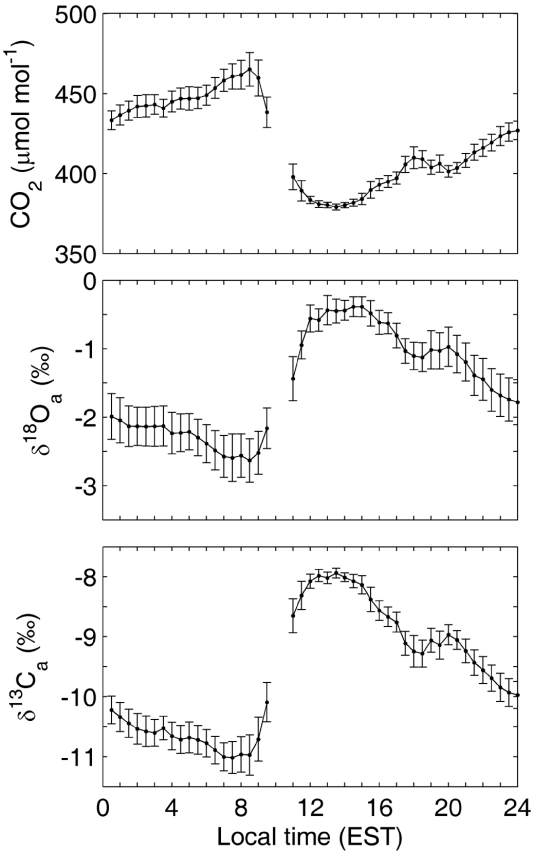

Fig. 5. Ensemble half-hourly average of CO_2 mixing ratio and isotopic compositions of CO_2 ($\delta^{18}O_a$ and $\delta^{13}C_a$, VPDB scale) in the air at 1.45 m above the floor of a deciduous temperate forest in Borden, ON, Canada from day of the year 188 to 274 in 2009. The error bars indicate ±1 mean standard error. Data from 09:00 to 10:00 (EST) was discarded due to liquid nitrogen filling time, which resulted in fewer data points than the remaining hours of the day.

BGD
8, 7671–7712, 2011

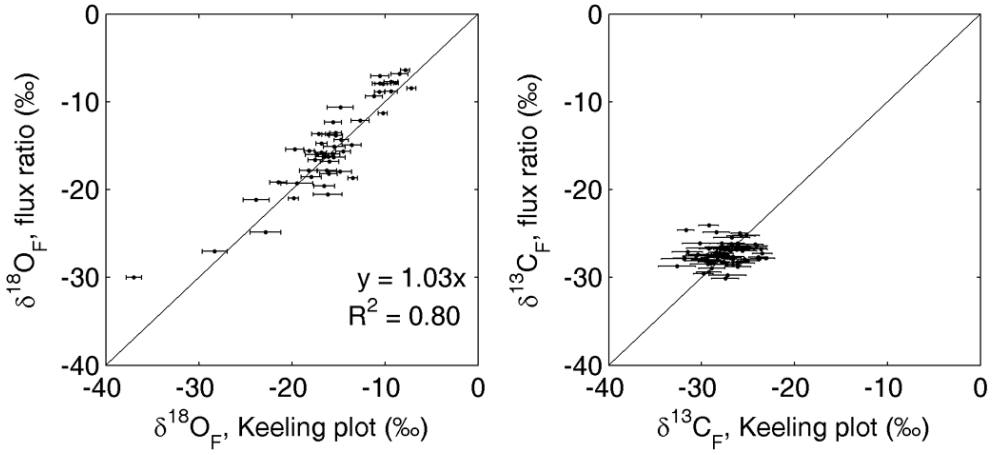

Fig. 6. Relationship between half-hourly isotopic ratios of the CO_2 flux near the forest floor ($\delta^{18}O_F$, $\delta^{13}C_F$) estimated using Keeling plot (± standard error of intercept) and isotopologue ratio method in the understory of a deciduous forest at Borden, ON, Canada.

BGD
8, 7671–7712, 2011

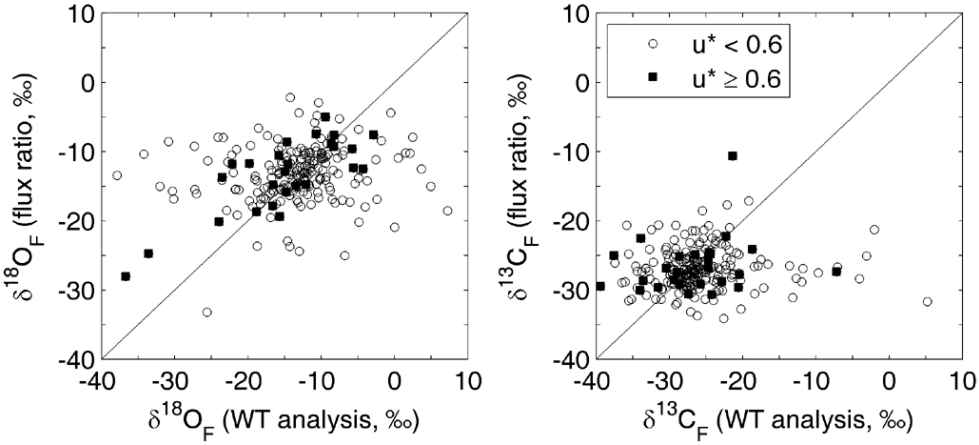

Fig. 7. Relationship between half-hourly isotopic ratios of the CO_2 flux near the forest floor ($\delta^{18}O_F$ and $\delta^{13}C_F$) estimated using a Lagrangian dispersion analysis (WT analysis) and flux ratio method in the understory of a deciduous forest at Borden, ON, Canada. u^* is the friction velocity ($m\,s^{-1}$).

BGD
8, 7671–7712, 2011

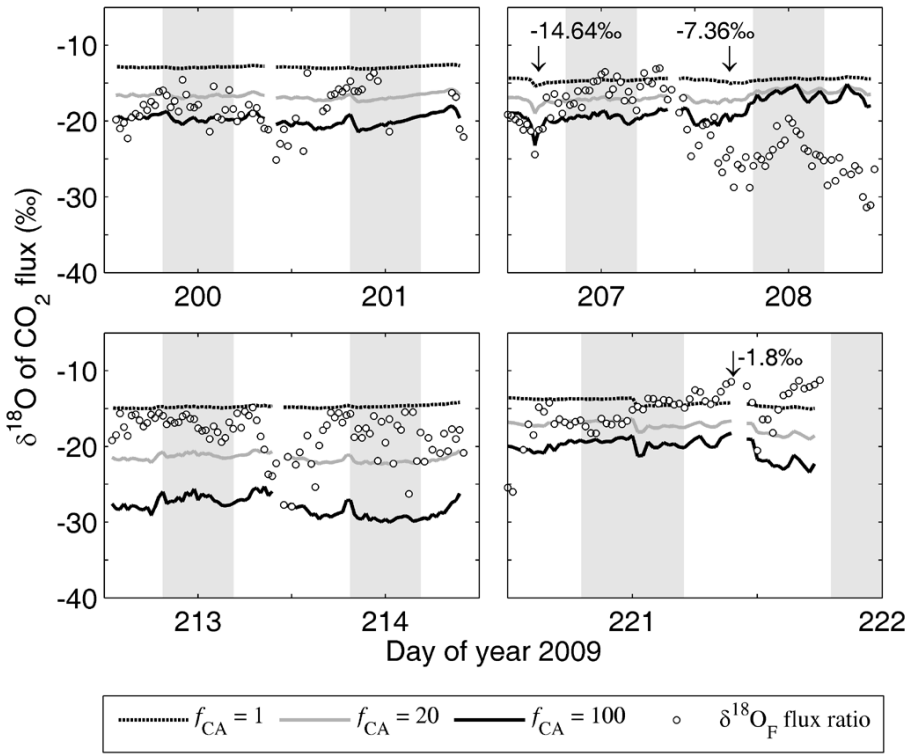

Fig. 8. Time series of $C^{18}O^{16}O$ compositions ($\delta^{18}O$) of CO_2 flux near the forest floor obtained using the isotope flux ratio method (open circles) and modeled $\delta^{18}O$ of net soil CO_2 flux (lines) according to Wingate et al. (2009) using three values for the relative increase in hydration due to the enzyme carbonic anhydrase activity in the soil (f_{CA}, Eq. 7) in a temperate deciduous forest at Borden, ON, Canada. The $\delta^{18}O$ of CO_2 flux is expressed in the VPDB scale. Shaded areas in the graph indicate nighttime periods and arrows indicate precipitation events with respective isotope composition of precipitation expressed in the VSMOW scale.

BGD
8, 7671–7712, 2011

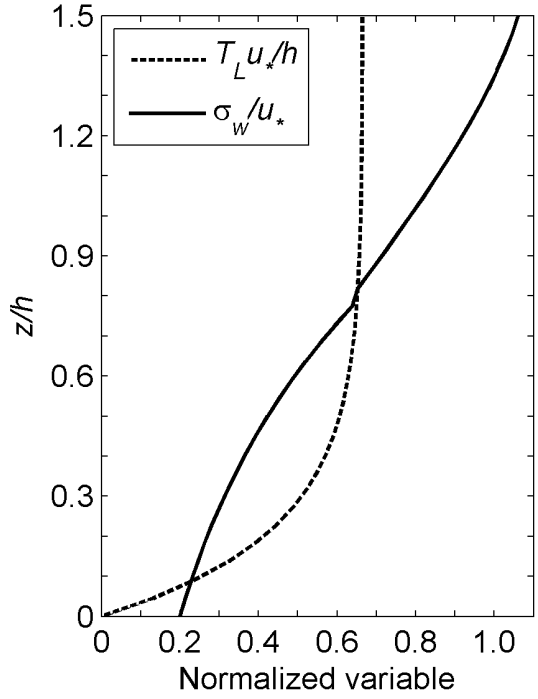

Fig. A1. Normalized profiles of Lagrangian time scale (T_L) and standard deviation of vertical wind velocity (σ_w), calculated using the parameterizations proposed by Styles et al. (2002) and Leuning (2000), respectively.

BGD
8, 7671–7712, 2011