Interactive comment on "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" by E. Santos et al.

Anonymous Referee #2

Received and published: 7 December 2011

We would like to thank the referee #2 for his/her comments. Our response to the comments is written bellow in blue.

This study shows high-frequency observations of stable isotopes in carbon dioxide in a forest canopy for two month. It tries to infer the isotopic composition of soil respiration from these measurements with three different methods. Finally, the study compares the preferred method with some model estimate of the isotopic flux signature.

My major concerns are the following:

The three methods are best, i.e. most reliable, at different times of the days or under different micrometeorological conditions. There is no discussion of the strengths and weaknesses of the different methods (there is admittedly a bit about IFR). For the WT method for example: one can safely say that dispersion theory inside the canopy might be o.k. for neutral and perhaps for unstable conditions; we have not understood it for stable conditions, though. At least this is what Finnigan and colleagues say. It is therefore questionable to apply the WT method under stable conditions, exactly when KP works best. There is no prove that IFR gives actually the right answer under turbulent conditions. The perfect result would have been if IFR compares favourable with KP at stable conditions and it compares well with WT in neutral conditions. u* therefore seems not the right indicator. Why not using L or z/L?

Response: Some of the advantages and weaknesses of IFR and KP methods were discussed in the introduction (**p. 7674 lines 25 to 29** and **p. 7675 lines 1 to 4**). We

highlighted that previous studies (Griffis, Tans, Flanagan, Ogée) have demonstrated that the traditional KP approach is not very reliable for determining $\delta^{18}O$ of CO_2 flux, even under stable conditions, which may allow large amplitude of CO_2 concentration to occur (see fig. 5 from Tans (1998) and discussion on **p. 7685 line 25 to 27** and **p. 7686 line 1 to 16**.).

We agree with the reviewer that there are some limitations with the WT analysis under stable conditions, when the poor mixing between canopy air layers is likely to affect the performance of this approach. This is the reason why we have used u^* as an indicator of the degree of turbulent mixing in the canopy. In addition, the Obukhov length (L), suggested by the referee, was indirectly used when we applied corrections for atmospheric stability, proposed by Leuning (2000) (**p. 7673 line 4 to 7**). These corrections minimize the atmospheric stability effects on the parameterizations of turbulence statistics. The WT analysis or other Lagrangian dispersion analysis could be a useful tool to study isotope exchange in ecosystems, but we acknowledge that the use of these tools still requires further investigation, perhaps using a larger dataset.

Although the relationship between WT analysis and IFR method estimates did not show the same agreement and precision as the relationship between the KP and IFR methods, we believe that there is no good reason to suspect that the IFR approach theory would not work well under turbulent conditions. Previous studies have shown that gradient diffusion theory, which is the basis of the IFR method, provides very good fluxes estimates under those conditions. In addition, studies conducted by Griffis et al. show good agreement between the IFR and KP methods over a wide range of atmospheric conditions.

So what to do now? If I am an experimenter: do I use IFR also if I have no laser, i.e. with flasks? Or is IFR only good with a fast laser system? And is IFR good under all conditions? I only have to measure close enough to the ground to have a gradient between the two heights?

Response: The use of the IFR method with flask data and additional evaluation on the ability of the gas sampling system to measure concentration gradients well above the

ground are important research topics, but they are beyond the scope of this study. These issues could be addressed in future studies.

The comparison with the d18O_R model is quite unsatisfactory. There are so many things that are not discussed but well in the literature. Examples are:

Why is there almost no diel cycle with fCA /= 1? In Seibt et al. (2006) you could well see the diel cycle of almost 10 permil, with CA activity. Do you use a diurnal cycle in temperature?

Response: Yes, we have used a diurnal cycle of temperature in the model calculations. However, the daily amplitude of soil temperature was quite small (~ 1 °C) in the forest. This could be one of the reasons why a clear daily pattern in modeled d18O of CO_2 flux was not observed in this study.

The soil water d18O, and therefore one of the major inputs, is hard to understand. How comes that DOY 211 is so much lighter at the top? Did you get a very light rain? Why was it so different to DOY 198, which had also a rain event before? What is the isotopic composition of the rain? How good are your fits?

Response: p. 7679 line 25: "Profiles of $\delta^{18}O_{sw}$, used to model δ18O of soil CO2 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)."

now reads:
"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). The mean absolute difference between measured and estimated $\delta^{18}O_{sw}$ ranged from 0.25‰ (DOY 198) to 0.53‰ (DOY 211). Lighter $\delta^{18}O_{sw}$ values close to the soil surface on DOY 211 were a result of a precipitation event on DOY 206 with $\delta^{18}O_{sw}$ = -14.64‰."

Did you check your soil water isotopes with a model? There are quite a few: Isolsm, Musica, Sispat, Soil-Litter-Iso, ...

Response: $\delta^{18}O$ of soil water showed good correlation with $\delta^{18}O$ of precipitation water values found at our site. The complete $\delta^{18}O$ soil and precipitation water data set will be presented in more details in a manuscript that is being prepared. The soil water sampling and analysis followed the procedures described by Welp et al. (2008). So, $\delta^{18}O_{sw}$ measurements are reliable, although a more frequent soil sampling scheme could improve model estimates (**p. 7690 line 6 to 11**).

There is quite a discussion in the literature if the simple model you are using is actually valid or if one has to use a multi-layer model in order to understand the d18O in CO2 signal. The discussion was under the topic "setting point depth" between Riley, Miller, Yakir and others.
So I think the conclusion that fCA was variable during the evaluated period is not very robust, to say the least.

Response: We acknowledge that complex depth-integrated numerical models can yield a better description of the impact of profiles of forcing variables, such as soil temperature and water content, on $\delta^{18}O_R$. However, simple analytical models are more suitable to investigate the effect of several forcing variables on $\delta^{18}O_R$ signal (see Tans 1998, Riley et al. 2005 and Wingate et al. 2010), which was one of the goals of this study. The analytical model used in this study was assessed in previous studies (see Wingate et al. 2009; Wingate et al. 2010) and provided robust estimates of $\delta^{18}O_R$. The conclusion about the behavior of f_{CA} in this paper is in agreement with the results obtained in previous papers (Seibt et al. 2006; Wingate et al. 2009; Wingate et al. 2010), so we respectfully disagree with the reviewer regarding the robustness of the model used in estimating the $\delta^{18}O_R$ signal.

Miscellaneous comments (unsorted):

1. What was modified at Keeling plots? It looks to me that regular Keeling plots are done. The time scale differs from the one in Pataki et al. (2003) and the recommended range is differently. But Keeling did not say anything about it. I find the term "modified Kelling Plot" very misleading.

Response: We used the term "modified Keeling plot (mKP)" to emphasize to the reader that the data used in this study did not range from several hours, as commonly shown in previous studies (Flannagan, Griffis, etc). We decided to emphasize this point because these studies have shown that the traditional Keeling plot approach is not reliable to determine the $C^{18}OO$ composition of CO_2 flux due to the variability of the source composition during the day.

p. 7681 line 18 to 20
"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)."

now reads

"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). In this study we adopted the term mKP to designate the modified Keeling plot approach to emphasize that the period and range of CO_2 mixing ratio were different than what is usually used in the literature."

2. How do you come from 0.035 ppm 13CO2 and a VPDB of 0.011 to a CO2 mixing ratio of 5 ppm? 0.035/0.011 is close to 3.2?

Response:

p. 7681 line 8

"approximately 5 µmol mol^{-1} m^{-1}. The same threshold was observed by Griffis et al.(2005a). Hence, only half-hours in which the difference of CO_2 mixing ratio between two measurement heights was large than 5 µmol mol^{-1} were used to calculate δ_F."

Now reads:

"approximately 3.2 µmol mol^{-1} m^{-1}. The same threshold was observed by Griffis et al.(2005a). To minimize the IFR method uncertainties, 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."

3. Please explain better the observed diel cycle of atmospheric isotopes.

Response:

p. 7684 line 27 and p. 7685 lines 1 to 4:

The causes of this daily pattern of $\delta^{18}O_a$ and $\delta^{13}C_a$ are the 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).

now reads:

The main reason for this daily pattern of $\delta^{18}O_a$ and $\delta^{13}C_a$ is the expansion of daytime boundary layer and entrainment of more isotope enriched air from atmospheric above morning surface inversion. During nighttime there is a buildup of relatively more depleted CO_2 originated from the soil due to low turbulence conditions (Griffis et al., 2004, 2005b; Seibt et al., 2006).

4. Why is $z_1=1.4$ m? The measurement is at 1.4 m and it is not representative for 0-1.4 m. It should be more direction $z_1=2.8$ m (or less).

Response: We did not understand the referee's comment.

5. You give error bars for the Keeling estimates but not for the other methods? Any error estimates?

Response: The IFR method provides a single estimate of isotope composition of flux for each half-hour period, so a half-hour variance can not be calculated. The mKP was based on regression analysis using 5 min means obtained over each half-hour.

Minor comments are (unsorted):

1. Be consistent with $O=16O$, $C=12C$.

Response:
This was already modified as suggested by referee #1.

2. I think that CA for carbonic anhydrase is well established and there is no need for CAE as further abbreviation.
Response: We replaced CAE for CA in:
p. 7674 lines: 8 and10
p. 7676 line 4
p. 7683 line 19
p. 7688 line 25
p. 7689 line 25

3. The short names IFR and mKP denote a method while WT denote two authors. WT should be replaced to something like LD to also reflect a method rather than names.

Response: The terms "WT analysis" or "WT model" have been already used in previous studies (Wohlfart, 2004; Qiu and Warland, 2006 and Santos et al. 2011) and refer to a specific approach in LD analysis. The term 'Keeling' also refers to an author's name and we prefer to use WT.

4. Symbols in the appendix are not defined or defined in the main text. This makes it hard to read.

Response: Symbols were defined as variables were mentioned in the text. We are not sure about which symbols the referee is referring to.

5. Please follow CIAAW recommendations: delta definition equations should avoid extraneous numerical factors, such as the factor of 1000.

Response:
p. 7680 line 14

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

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:

now reads:

$$\delta_F = \frac{R_F}{R_{VPDB}} - 1 \tag{1}$$

where δ_F is the isotope ratio of the CO_2 flux, reported in parts per thousand (‰) in this study. 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:

6. Griffis et al. (2005b) is no good reference for VPDB-CO2 of 18O. You should emphasize, though, that you use the VPDB of Griffis et al. (2004) for 13C. This is not the "usual" VPDB.

Response:
p. 7679 line 5

"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)."
now reads:

"in reference to the Viena Peedee Belemnite (VPDB) scale, i.e. $[^{13}C]/[^{12}C] = 0.0111797$, which differs from the Chicago Peedee Belemnite ($[^{13}C]/[^{12}C] = 0.112372$) by approximately 5‰, and $[^{18}O]/[^{16}O] = 0.002088349077$ (Griffis et al., 2004; Allison et al. 1995)."

7. Already at the time of Griffis et al. (2004), I was wondering why there is no credit given to Langendorfer et al. (2002) who used a gradient method in a forest with 18O isotopes.

Response: Langendorfer et al. (2002) did not use the IFR method. They used the flux gradient method.

8. Zoom into 13C-plots. Does not have to be the same as 18O.
Response: This was already modified as suggested by referee #1.

9. Each plot states that it is Borden, ON, Canada. This might be slightly redundant.

Response: plot captions were changed.

10. Why are the days different in Fig 4 and Fig 5?

Response: Because concentration profile measurements, required to use WT analysis, were only taken from DOY = 237 to 260.

11. The scales in Fig 6 and 7 should eb the same for each isotope, i.e. why is Fig 7 going up to +10?

Response: Because there was more noise in the IFR and WT analysis comparisons, so a scale ranging from -40 to 0‰ would not include all the data.

12. Something is fishy with Eq. (4) and I do not know where I need it in the manuscript.

Response: We are not sure what the reviewer means by 'fishy'. This is a well-established approach.

13. What are the numbers -14.64, -7.36 and -1.8 in Fig. 8?
Response:
Please see **p. 7711, Fig. 8 label:**
"arrows indicate precipitation events with respective isotope composition of precipitation expressed in the VSMOW scale."