

Interactive comment on “Use of the isotope flux ratio approach to investigate the C¹⁸O¹⁶O and ¹³CO₂ exchange near the floor of a temperate deciduous forest” by E. Santos et al.

Anonymous Referee #1

Received and published: 14 September 2011

General comments:

In summary, this paper presents measurements of vertical gradients in CO₂ isotopologues: ¹²C¹⁶O₂, ¹³C¹⁶O₂ and ¹²C¹⁸O¹⁶O from near the floor to above the canopy of a temperate deciduous forest. From those measurements, they applied the isotopic flux ratio (IFR) approach to calculate the isotope ratios of the near surface or soil CO₂ flux. The isotopic composition of the fluxes calculated using the IFR were then verified against two other methods: a modified Keeling plot approach (mKP) and a Lagrangian dispersion analysis (WT). They found that the variability in IFR fluxes agreed well with the mKP fluxes for d¹⁸O, but that there was not enough variability in d¹³C

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to produce a significant correlation, however, the mean d13C flux values were nearly identical using the two methods. The comparison with the WT approach was not as good, but it showed reasonable correlation during conditions of high canopy turbulence when WT conditions are more favorable. They also compared the d18O from the IFR with a model of soil CO₂ d18O flux and found that the model did not capture the half-hourly variability using a constant value for the activity of carbonic anhydrase in the soil. The main conclusions are that (1) the IFR works reasonably well in this setting and (2) that soil water d18O must be measured with increased temporal frequency and vertical resolution to make a meaningful comparison of the modeled d18O CO₂ soil flux with the IFR d18O flux. These methods have been previously published using data from different ecosystems, but the measurements themselves are still fairly novel, and this paper presents an incrementally important contribution to the field of ecosystem CO₂ flux isotopic tracer analysis. The subject is within the scope of BG and substantial conclusions were reached. The paper is generally well-written and organized, but can still be improved significantly by a few changes listed below.

Specific comments:

1. The authors refer several times to the diel variability in d18OF becoming more enriched in the daytime. I interpret this as less negative delta values. However, in Fig 8, I see more negative delta values for d18OF during daytime. I do not see evidence presented to support the authors' conclusions in this case. Please correct this error, or show more data to support enriched daytime d18OF.
2. p. 7673, line 4: Also cite 13C studies in addition to 18O studies, e.g. Giais, Francey, and Keeling publications.
3. In the supporting measurements section (p. 7679), please provide more details. How often did the auto chamber make measurements? Light or dark chamber? How was precipitation collected for isotope analysis? No measurement of the canopy air temperature? List the soil chamber model number as well.

4. Section 2.4, needs some work. Make it clear this goes into the IFR description immediately. I think this needs to be laid out a little differently. It's a little sloppy as is. First you should describe the ratio of the fluxes of the isotopologues ($RF = \text{heavy}/\text{light}$) to derive the δF of the ecosystem fluxes. $\delta F = \text{eqn 1}$. RF becomes eqn 2a. On line 21 'averaged vertical gradients'. The WT method description seems sloppy also. If Eqn 4 sums over j layers, why is it labeled as F_j ? Do you mean the cumulative flux for each species instead of for each layer (line 16)? I don't really understand how this method is applied and would appreciate more details either here or in the appendix.

5. The last paragraph in sec 3.3 doesn't seem to apply to the WT comparison. It's mostly a discussion of theory regarding the IFR method. It seems the IFR comparison with WT is somewhat tricky because IFR works better in stable (low u_{star}) conditions and WT works better when u_{star} is high. For that reason, this seems like a limited comparison and maybe not the best way to verify the IFR method.

6. Sec 3.4, third paragraph. $d_{18}O_R$ wasn't 'observed' in the study, it was modeled. $d_{18}O_F$ was observed. This argument seems contradictory as $d_{18}O_a$ increases during the daytime and $d_{18}O_F$ decreases during the daytime. Please explain. . .

Technical corrections:

title and throughout: I think the authors should be consistent in how they denote the isotopologues throughout the manuscript. For example, if ^{16}O and ^{12}C are implied, they should appear as: CO_2 , $C^{18}O_2$, and $^{13}CO_2$.

p. 7672 line 13: '... were calculated by IFR and compared with estimates...' line 22: $d_{18}O-CO_2$ not defined line 26: I see lower values of $d_{18}O_F$ during the daytime in Fig 8. line 27: 'carbon' should be 'carbonic'. 'very variable' is awkward.

p. 7673 line 17-19: I don't like how this sentence is worded. The 'differences' in soil and leaf ^{18}O fluxes are not 'caused' by the isotopic equilibration between CO_2 and H_2O . They are caused by the evaporative enrichment of leaf water as you describe in

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the next sentence. Please reword. line 22: Welp et al is not an appropriate citation here. Perhaps something more classic like Craig and Gordon? line 22-23: Actually it would be using three isotopologues including $^{12}\text{C}^{16}\text{O}_2$. Perhaps say 'using carbon and oxygen isotope tracers'.

p. 7674 line 3: Also add varying environmental conditions to the list. line 12: Cite chamber studies, e.g. Powers and McDowell et al 2010

p. 7675 line 13: Consider changing 'inside' to 'below'.

p. 7676 line 13: 'most predominant' is redundant. line 16: comma after 2009 line 21: delete 'the occurrence of' line 22: 'average soil carbon'

p. 7677 line 4: 'tunable diode laser' line 17: list the size and ID of the stainless tubing.

p. 7678 line 9: CMDL is now ESRL/GMD. Please correct. line 12-14: Equal signs missing?

p. 7680 line 10: Make clear this goes into the IFR description immediately.

p. 7681 line 11: 'The isotopic composition of the soil CO_2 flux ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$)...' line 23: consider changing 'amplitude' to 'range' or 'span'.

p. 7683 line 1: $\delta^{18}\text{O}$ line 12: 'in the soil via abiotic soil invasion...' line 19: CAE not defined.

p. 7684 line 23: Max looks like 9:00 to me, not 7:00. line 24: refill time 10-11am

p. 7685 line 1: Entrainment of air enriched in ^{13}C and ^{18}O . line 2: CO_2 depleted in the heavy isotopes

p. 7686 line 10: Fig 6 does not show this. What fCA was used in these calculations?

p. 7687 lines 1-5: Don't you mean WT instead of mKP here?

p. 7689 line 8: Again, I see a decrease rather than an increase on those days. Day 220 is not shown in full. Otherwise, yes, higher fCA is needed to improve the model

agreement. A general comment here is that the possibility of diel cycle soil water d18O is not discussed as a possible cause of the variability in the d18OF. Changes in fCA may not be the only possible explanation.

p. 7691 line 7-8: Again, I just don't see it... line 10: '...soil water d18O sampling scheme...'

p.7692 line 7: '...used to quantify sigma_w and TL...'

p. 7693 line 14: please define 'r'.

p. 7694 line 11: '... converted into the VPDB scale using eq B1.'

Table 1: In footnotes, these are mean values of multiple core samples right? Is there a standard deviation or error on the texture?

Fig 2: I find it odd that the symbols are larger than the error bars. Consider using smaller symbols, or state that the error bars are smaller than the symbols.

Fig 4: No gaps in FR due to data quality screening?

Fig 5: This figure would benefit from longer/major tick marks at the labeled hours so it's easier to determine the times in the middle and upper panels. A few minor ticks would be good in the upper panel CO2 axis.

Fig 6 & 7: Pick consistent axis labels for the different d18OF products, e.g. IFR d18OF (permil), WT d18OF (permil) and mKP d18OF (permil). You might consider using both abbreviations and full descriptions (e.g. modified Keeling plot) in the figure captions.

Fig 6: There is no need to have the scale of the x- and y- axes of d13C match those of d18O. You can zoom in some more. Label y-axis as 'IFR'?

Fig 7: y-axis label should be the same as in Fig 6.

Interactive comment on Biogeosciences Discuss., 8, 7671, 2011.