

# Response to interactive comment of anonymous Referee #3 on “First measurements of continuous $\delta^{18}\text{O}\text{-CO}_2$ with a Fourier Transform InfraRed spectrometer in Heidelberg, Germany”

We want to thank the referee for helpful comments and suggestions for changes and have revised the manuscript as described in the responses below.

General comments:

The paper entitled "First measurements of continuous  $\delta^{18}\text{O}\text{-CO}_2$  with a Fourier Transform InfraRed spectrometer in Heidelberg, Germany" describes the methodologies of using this type of FTIR and briefly goes into 2 cases studies that examine  $\text{d}18\text{O}$  measurements in Germany during the winter and summer. I thought the paper was generally well written, though it felt like some parts needed more clarification. The introduction was a little oversimplified, and did not mention any of the more recent studies that have examined the controls on  $\text{d}18\text{O}\text{-CO}_2$  variations. For example, there has been a couple of modeling studies that have shown that CA activity in soils may be more important than previously thought (Wingate et al., 2009; Buening et al. 2014). Also, the influence of RH is not mentioned here at all, but the latest papers suggest that it has a huge influence (Still et al. Welp et al. Buening et al). I think that section 4 had the potential to be the most intriguing part of the paper, but it was too brief and could have used a more rigorous analysis on the controls. The paper ends feeling a little bland, with a conclusion that sounds like "we have a continuous record of  $\text{d}18\text{O}\text{-CO}_2$ , but we still need more measurements to make any sense of the data". It seems like if there was an actual hypothesis that was tested, then it would strengthen the conclusion and the overall paper.

## Response

We agree that the interpretation of the  $\delta^{18}\text{O}\text{-CO}_2$  record is an intriguing part of the paper and we would have loved to be able to interpret the isotope data set quantitatively in terms of net and gross fluxes. However, this is out of the scope of this paper and, we feel, also out of the scope of the journal AMT. The aim of the present paper is to show that reliable  $\delta^{18}\text{O}\text{-CO}_2$  measurements are possible with our instrument and here we want to assess the accuracy, precision and stability of our  $\delta^{18}\text{O}$  measurements with the FTIR. This is what we have done in Sections 1-3 of our manuscript.

Still, in chapter 4 we wanted to show some examples of ambient air  $\delta^{18}\text{O}\text{-CO}_2$  signals and briefly discuss these. However, after their qualitative evaluation, we are not able to provide a comprehensive quantitative interpretation of the measured data set. This is because we do not yet have the means, e.g. a regional isotopic  $\text{CO}_2$  flux model and the exact isotopic composition of the water

and carbon reservoirs that play a crucial role on local scale  $\delta^{18}\text{O}$ -CO<sub>2</sub> variations in the atmosphere. As the referee has pointed out clearly, the parameters controlling the atmospheric  $\delta^{18}\text{O}$  are various and their interaction is complex. We agree that it might make sense to list the most important controls and we elaborate on this in the introduction and in section 4 of our revised manuscript. However, we do not feel that at this stage a rigorous analysis of all controls in all their complexity will add any more meaning or scientific input to the paper.

We also see how the manuscript might not have an exciting ending to it, but we fear that we cannot provide any other conclusion than “we have a continuous record of  $\delta^{18}\text{O}$ -CO<sub>2</sub>, but we still need more measurements of the end members and a regional model to make any sense of the data”. However, we appreciate the idea of using hypotheses (or questions) to structure our manuscript and make it more appealing.

In our revised manuscript, we have made it clear to the reader that the main questions are: 1. Is it possible to measure  $\delta^{18}\text{O}$ -CO<sub>2</sub> using a FTIR and if yes, how well can we measure it?  
2. Can we use the continuous record to disentangle the CO<sub>2</sub> (iso-) fluxes in our catchment area?

#### Specific comments:

1. page 6503, line 20: Is this true at every latitude? Recent studies have shown that it eventually changes sign to the north.

#### Response

Still et al., (2000), Cuntz et al. (2003) and Buenning et al., (2014) point out, that the strong depletion of precipitation and with that of leaf water in northern latitudes can lead to a depletion of retro-diffused CO<sub>2</sub> and deplete the atmospheric  $\delta^{18}\text{O}$ -CO<sub>2</sub> value. Nevertheless, for our measurement site in Central Europe we expect the discrimination during assimilation to be positive (Farquhar et al, 1993).

We have added this information in the revised manuscript.

2. Section 3.1 line 11: where is 1 permil taken from? The results below or is a reference needed?

#### Response

This is a value typical for our Heidelberg measurement site, as we know from our two years of continuous measurements. It can be seen in the results in Figures 6 and 7.

We have added this in the revised manuscript.

3. Section 3.2, lines 23-24: How does Figure 7 show this. Some clarification is need here. And where does 1/5 come from? 0.27permil of 1 permil is not 1/5th, or am I reading this wrong?

#### Response

Figure 7 (and 6) only shows a typical diurnal variation in Heidelberg. It is in the order of about 1 ‰. Therefore an intermediate measurement precision (called reproducibility in the submitted manuscript) of 0.27 ‰ is about 1/4th of the expected signal.

We have changed this in the revised manuscript.

4. Section 4, line 18: fast equilibration needs a reference

#### Response

We have added the reference Francey and Tans (1987) for the fast equilibration in leaves and Wingate et al. (2009) for an accelerated equilibration with soils.

5. Section 4, lines 18-19: "18O signature of soil respired" is this different than what was said in the previous statement. It sounds the same.

#### Response

It is the same. We have removed the previous sentence.

6. Page 6512 line 6: 5 permil change in d18O-CO2 is large though.

#### Response

For a quantitative analysis, it is necessary to include the invasion flux. For the summer period, we only want to make the point, that the isotopic composition of the water reservoirs change, which is reflected in the atmospheric  $\delta^{18}\text{O-CO}_2$ . For the winter period, the uncertainty in isotopic signature of soil and leaf respiration and photosynthesis in our catchment area are in the same order as the invasion flux itself. We acknowledge that it must not be neglected in a qualitative data analysis, but in the light of the high uncertainty of our end members, we neglect to discuss explicitly the effect of the invasion flux on our atmospheric  $\delta^{18}\text{O-CO}_2$  measurement.

7. Page 6512 line 9: You mean invasion flux?

Response

We cannot estimate the magnitude of this effect for our catchment area without intensive sampling and isotopic CO<sub>2</sub> flux modelling. Therefore, we do not consider the invasion flux explicitly, but we are aware that the invasion flux will introduce a feedback on net soil CO<sub>2</sub> isofluxes and with that on the “apparent” soil respiration signature (Seibt et al., 2006).

We have rephrased this in the revised manuscript.

8. Page 6513, equations 3-5: These equations are little sloppy (words rather than symbols), and the variables are not defined very well.

Response

We have changed this in the revised manuscript.

9. Page 6513, Lines 14-16: Why are these values so low? Are these not the atmospheric values?

Response

These are the Keeling intercepts (source signatures) derived from the atmospheric records. They lie in the range, which we would expect from literature. For  $\delta^{13}\text{C}$ , a value of -25 ‰ could originate from coal combustion as well as from biospheric fluxes whereas a value of -28 ‰ is typical for oil or petrol combustion (Widory and Javoy, 2003; Mook, 1994; Kaul, 2008). For  $\delta^{18}\text{O}$ , a wintertime value of -28 ‰ is typical for wood or natural gas burning (Schumacher et al., 2011) and a value of -12 ‰ is a typical soil respiration CO<sub>2</sub> value in our region (Neubert, 1998).

10. Page 6514, Lines 14-15: But they would still deplete the signal, no?

Response

Yes, both would deplete the signal as can be seen in Figure 7a and b. This is the reason why we chose to use  $\Delta\delta$ , i.e. the difference between the measured  $\delta$ -value and the constructed delta value (Figure e and f).

11. Page 6514, I think this paper would be more interesting with some additional measurements of atmospheric data. For instance, Does RH or temperature change during the d18O-CO<sub>2</sub> fluctuations. Is there a change in wind direction that would maybe

bring in more pollution and more depleted d18O? I would find this type of analysis very interesting, and I think it would greatly strengthen the paper.

## Response

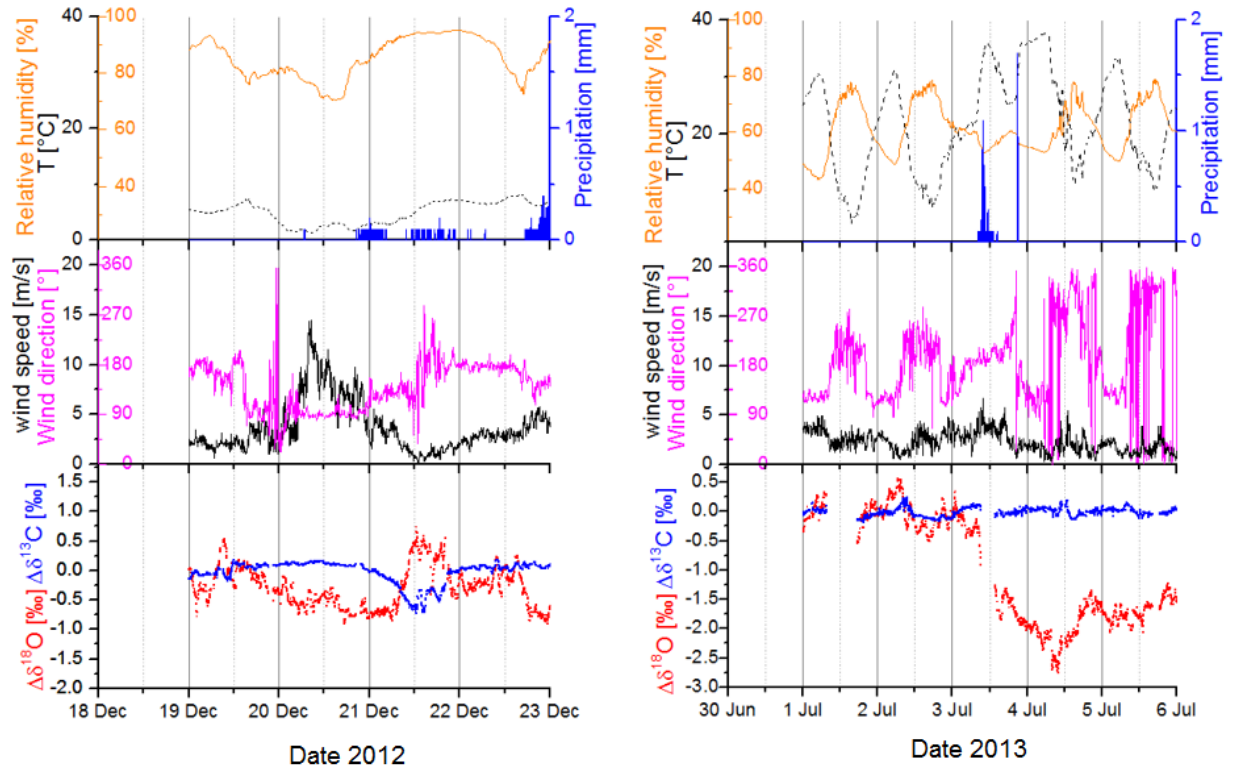


Figure R1: Upper panels: Relative humidity (orange), temperature (dashed) and precipitation (blue) in December 2012 (left) and July 2013 (right). Middle panels: Wind speed (black) and wind direction (magenta). Lower panels:  $\Delta\delta^{13}\text{C}$  (blue) and  $\Delta\delta^{18}\text{O}$  (red).

In winter (left panel of Figure R1), the  $^{13}\text{C}$  and  $^{18}\text{O}$  records are not correlated with relative humidity and temperature. The precipitation during these five days was only small, so that no correlation could be observed. The concentration build-up during the pollution event on the 21<sup>st</sup> of December 2012 is most likely due to an atmospheric inversion (low wind speed). At the same time, the wind direction changed slightly from east ( $90^\circ$ ) to south-east ( $90\text{-}180^\circ$ ). Thus, the change in  $\Delta\delta^{18}\text{O}$  and  $\Delta\delta^{13}\text{C}$ , which is in line with a  $\text{CO}_2$  increase, is most likely due to the increase of the source component in the ambient air and a small change in the footprint.

In summer, one can see that relative humidity, temperature, wind direction and  $\Delta\delta^{18}\text{O}$  show diurnal variations. The phasing between relative humidity and  $\Delta\delta^{18}\text{O}$  and between temperature and  $\Delta\delta^{18}\text{O}$  is not constant. Also the change in wind

direction is not clearly correlated to  $\Delta\delta^{18}\text{O}$ . From this, it is not clear, if one of the parameters and if yes, which one, is driving the variation of  $\Delta\delta^{18}\text{O}$ .

As discussed in the manuscript, a striking decrease in  $\Delta\delta^{18}\text{O}$ , which is not accompanied by a change in  $\Delta\delta^{13}\text{C}$ , follows the precipitation event on 3<sup>rd</sup> of July 2013, which must have changed the isotopic content of soil and leaf water. This, in turn, will have an influence on soil and leaf respiration and also on the soil invasion  $^{18}\text{O}$  isoflux.

We are very content to carefully have looked into correlations between the environmental parameters and the isotopologue variation. We think the fact that there is no significant correlation to the environmental parameters is important for the reader, but the plot will probably rather confuse than provide useful information. Nevertheless, we will give the reader more information about the meteorological conditions during the discussed periods and we will add this to our revised manuscript.

12. Page 6515, lines 6-7:  $\delta^{18}\text{O}$  of vapor has also been found recently to have a strong influence, but that's not mentioned anywhere in the paper.

Response

We have included this in the revised manuscript.

13. Technical corrections: 6508 Line 22: MS has already been defined.

Response

We have changed this in the revised manuscript.

## References

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