Reply to the referee comments by Jocelyn Turnbull

We wish to thank Jocelyn Turnbull for her very thoughtful comments and suggestions to improve the manuscript. Our answers and proposed changes are given below with the original comments printed in black and our replies in blue.

This paper outlines a strategy for collection of flask samples at the ICOS atmospheric stations. To my knowledge this is the most careful, detailed strategy available for utilizing combined in situ and flask greenhouse gas measurements together. The paper discusses the reasons for using flask samples (quality checks on in situ measurements, measurement of additional species that are not or cannot be measured in situ). They discuss the strategy for when to collect flasks, and how to collect flasks, and the reasons that integrated sampling is useful. This is a very nice paper, and I recommend publication with minor revisions as detailed below.

Specific comments:

Edit for English grammar is needed throughout, but particularly in the introduction.

We will check English grammar (again) in the revised version of our manuscript.

Abstract Line 33. The intent of this phrase is unclear. *(Phrase: "In order to have a maximum chance to also sample ffCO2 emission areas, additional flasks need to be collected on all other days in the afternoon."*

The likelihood to sample flasks that are significantly (by about 6 ‰ (2 sigma)) "contaminated" by ffCO2 is low, as ICOS stations are located far away from anthropogenic emissions. In order to "catch" ffCO2 events, which can be used in dedicated inversions we thus have to sample flasks frequently and check afterwards, using the continuous CO measurements at the stations, which flasks should indeed be kept for 14CO2 analysis.

We will add text to make this issue more clear already in the abstract.

Abstract Line 36. This is explained in the paper text, but it is unclear in the abstract why 4-5ppm is important.

We will add the explanation i.e. including after 4-5ppm ", *that allows ffCO2 estimates with an uncertainty below 30%"*

Line 224. Six not sic

Thanks

Line 246-248. This method differs somewhat from the Turnbull 2012 approach, which used a 15L integrating volume. In the ICOS case, the 3L flask itself is being used as the integrating volume. It would be helpful to see the weighting function that is used and a discussion of any impact the smaller integrating volume might have on the final integrated sample. This could be added as supplementary material.

An almost constant weighting of the sample concentration over the one-hour sampling time is achieved by the temporal modulation of the sample flow f(t) [SLPM] passing a flask, which acts at the same time as mixing volume V given in liter STP.

The flow rate f is changed according to $f(t) = V/(t - t_0)$ over time t. Since the flow rate at the start time t_0 in a 1/time function would be infinite, which is not possible in reality, a 30 minute flushing phase at maximum flow rate precedes the averaging phase to ensure the complete air exchange in the flask.

The concentration $c_F(t)$ in the flask is determined by the ambient air concentration $c_A(t)$ and can be described as time series using sufficiently small time steps Δt:

$$c_F(t + \Delta t) = \frac{c_F(t) \cdot (V - f(t) \cdot \Delta t) + c_A(t) \cdot (f(t) \cdot \Delta t)}{V} \approx c_F(t) + c_A(t) \cdot \frac{f(t) \cdot \Delta t}{V}$$

The resulting weight of the ambient air concentration w_{c_A} at time step t_n in the flask depends on two factors:

$$w_{c_A}(t_n) \sim c_A(t_n) \cdot \frac{f(t_n) \cdot \Delta t}{V} \cdot \prod_{i=n+1}^{E} \left(1 - \frac{f(t_i) \cdot \Delta t}{V}\right)$$

the weight at the moment when the ambient air portion enters the flask and a weight reduction factor caused by dilution with sampled air entering the flask at later times. The reduction is calculated by multiplication of the respective dilution steps from t_n to the sampling end time t_E.

Figure 1 shows an example flow and weighting function over time from a sampling event. The weight functions are calculated from the respective flow controller and pressure sensor measurements for each single sampling event.

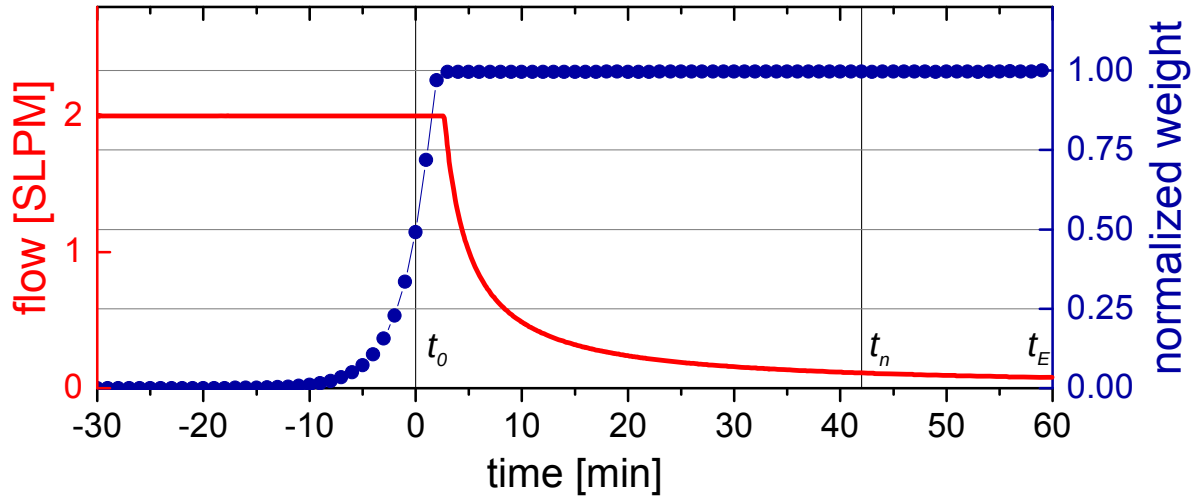

Fig. 1: Flow-rate and respective weighting function from a sampling event using a 3 liter flask.

For the results originally presented in Figs. 3 and 4 of the manuscript we used a slightly different weighting function (i.e. according to Turnbull et al., 2012) than described above. Re-evaluation of the comparison data for Heidelberg with the algorithm shown above did not significantly change the outcome (slightly improved it). The more correct evaluation method described here will be applied for all Heidelberg and Hohenpeißenberg comparison data and presented in the revised version of the manuscript.

Unfortunately, we are not in the position to discuss the impact a small integrating volume may have as we did not make any respective experiments. Up until now we are confident that it has no impact at all.

A comprehensive description of the suggested universal 1/t approach is currently in preparation and will be published together with a more detailed description of the flask sampler itself and its potential applications (Eritt et al., in preparation). This will also concern description of the possibility of more elaborated sampling strategies, such as triggering through trajectory forecasts. In the current manuscript we will thus limit description of sample integration to a minimum and point the reader to a more elaborate upcoming paper.

Line 255. I'm guessing that this is because the flask itself is used as the integrating volume? If that is correct, please say so explicitly.

Not exactly: In order to sample two flasks exactly in parallel, one needs two flow controllers (independent of the fact that the flow rate through the flask is changed during integrated sampling (Fig. 1) or not). This is mainly due to slightly different flow resistances of tubing and valves when flushing the 24 different flasks, as was mentioned in lines 255 ff of the manuscript.

Line 271. Is there enough air for all these analyses in a single flask?

The 3 Liter flasks are pressurized to 1.7 bar abs, thus providing a total sample volume of 5100 ml STP. The following volumes (STP) are consumed by the different analyses in the FCL:

GHG (duplicate analysis): 120 ml,
Stable isotope ratios of CO2: 600 ml,

O2/N2: 150ml.

The remaining sample volume for the 14C AMS analysis is, thus, about 4100 ml. In practice, the volumes analysed for 14CO2 vary between 1000 ml and 5500 ml with a median of 4200 ml. This variation is caused by the use of smaller flask sizes and by the fact that not for all flasks all analyses were yet conducted before CO2 extraction for AMS analysis. The AMS error for a single sample is composed of the counting error and the uncertainty of the calibration, which is determined using oxalic acid standards and blanks according to Wacker et al. (2010). For sample volumes larger than 2500 ml our mean AMS error is (1.9±0.4) ‰. For sample volumes smaller than 2500 ml the AMS error increases to about 3‰ for sample volumes of 1500 ml only.

In summary: Yes, there is enough air in the flasks for precise analysis of all currently envisaged components.

Line 395. This is a very nice demonstration of the utility of flask measurements in quality control. It is worth emphasizing in the conclusions that fast turnaround on the flask measurements AND speedy analysis of the results is needed to achieve outcomes like this.

Yes, Jocelyn, you are right. We will mention this in the conclusions !

Lines 468-469. I understand the motivation to measure 14C when the signals are large, but I wonder if this biased sampling methodology will be a headache in the end. If flask samples are biased towards high ffCO2 values, then the observed emission ratios might also be biased. For example, Turnbull et al 2011 measured 14C and CO from flasks collected in South Korea. The high ffCO2 values were associated with air masses coming from (nearby) Korea, which had low CO:ffCO2 ratios. Lower ffCO2 values were associated with air masses coming from China, which meant the ffCO2 signals were diluted. However, these Chinese samples had much higher CO:ffCO2 ratios. I could imagine a similar scenario in Europe. A secondary concern is that this data will presumably be shared across the wide ICOS network, and if these many and varied users are not aware of the deliberate sampling bias, there is a risk of misinterpretation of the results.

This is a valid point and totally correct: We have indeed to make sure that the flask sample results are used in a proper way. It is, however, not our aim to determine CO/ffCO2 ratios and then use those for e.g. estimating continuous ffCO2 concentrations as in Vogel et al. (2010). Here CO is only used as indicator for potentially high ffCO2 concentrations at the time of flask sampling. We expect that this dedicated sampling has advantages when the results are used in regional inversions to estimate the ffCO2 component. If we always measure 14C-based ffCO2 signals at the detection limit, this increases the uncertainty of the results and we may not meet our primary aim 3 to determine the ffCO2 component. As presented in Fig. 7, we collect, in addition to the flasks, two-week integrated 14CO2 samples, which sample all footprints and will thus provide representative results.

We will add a corresponding note in the revised manuscript.

Line 479-480. References please.

We will add the following references:

Gamnitzer et al., 2006; Turnbull et al., 2006 ; Levin and Karstens, 2007 ; Vogel et al., 2010 ; Turnbull et al., 2011.

Lines 525-527. I would argue that the 14C analysis would be most important in summer when the biospheric signals are larger and 14C is going to be even more critical for partitioning the fossil fuel and biospheric signals. This could be motivation to work towards higher precision 14C measurement capability.

Again Jocelyn Turnbull is very right and we are all working hard towards this aim (summer ffCO2 estimates and better precision in 14C analysis). It is clear and in fact it was on purpose NOT to design the ICOS network for monitoring ffCO2 emissions but to monitor European ecosystem fluxes and their changes as a first priority. We are thus happy to see that our original ICOS network design was successful in measuring only small fossil fuel CO2 concentrations. Our first step and currently realistic aim with flask sampling is trying to constrain winter time ffCO2 (emissions). The ongoing two-week integrated 14CO2 sampling at the ICOS stations provides whole-year representative data, also covering the vegetation period.

Lines 546-547. In this case, will there be sufficient air remaining for a high precision 14C analysis?

Yes, there is enough air in the flasks for precise analysis of all currently envisaged components (see our comment above).

Lines 553-555. Absolutely.

This is in fact our main concern and we hope that the modelling community (and funding agencies) will be able to support this aim soon.

Lines 557-558. The NOAA tall tower network has an analogous flask program used for the same three goals. They collect flasks every 3 days (I think), but don't use integrated sampling. A point of difference would be that ICOS has taken a more thoughtful approach to design a sampling strategy to maximise the information from a minimum number of flasks.

We will take up this comment in our conclusions.

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