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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimation of the fossil-fuel component in atmospheric CO based on radiocarbon measurements at the Beromünster tall tower, Switzerland" *by* Tesfaye A. Berhanu et al.

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This paper describes a two-year times series of CO2, CO and 14CO2 measurements from a rural tall tower in Switzerland, and examines enhancements in these species relative to a Jungfraujoch high altitude (nominally free troposphere) background, including calculating fossil fuel CO2 using the 14CO2 observations. They clearly demonstrate that both fossil fuel and biogenic signals contribute to the observed CO2 enhancement over their chosen background. They observe higher CO to CO2ff ratios than might have

been expected from Swiss emissions, and also see a significant difference between the CO to CO2ff and the CO to CO2 ratios.

This paper is well written, clear and easy to follow, and well organized into sensible sections. The methodology and data quality appear to be sound (although note a few specific comments). The results are interesting and well worthy of publication in ACP, however, some additional effort is needed to sufficiently interpret many of the results, particularly the CO emission ratios. A major point is that the authors implicitly assume that they are observing Swiss sources, whereas the choice of high altitude background means that they are likely observing a much larger European footprint, which changes much of the interpretation. For this reason, I recommend major revision, but expect that the revisions should be straight-forward.

Specific comments: Abstract line 18. Please specify here that 212.5 m is the highest sampling level on the tower.

Line 69. 14C production is not only in the lower stratosphere, perhaps "upper atmosphere" would be a better phrase.

Line 72. Please reference the papers that observed and explain this trend.

Lines 82 to 84. Clarify why the biosphere is enriched in 14C relative to the atmosphere (bomb 14C that was absorbed is now being released back to the atmosphere). Also, should be "bomb tests" and "nuclear industries", not "the bomb tests" and "the nuclear industries".

Line 85. "separation" not "to separate".

Line 86. "better constrains" not "to better constrain"

Line 89. I think you mean the uncertainty in the contribution of other sources such as nuclear power.

Line 95. Turnbull et al. 2014 doesn't talk about additional tracers. Perhaps you meant

to refer to Turnbull et al 2006 or 2011?

Lines 98 to 104. Variability in the source emission ratio of CO to CO2 (or CO2ff) is likely a very important contribution. This may cause both spatial and temporal variations, e.g. Turnbull et al., 2015, Vogel et al., 2010.

Lines 165 to 167. Is this leakage at the point of sample collection (at the tower), or do you mean leakage that occurred when extracting the CO2 in the lab? Please clarify. If the leak was during the CO2 extraction, then the blank tests described in lines 170-171 are sufficient, but if the leak occurred during air collection at the tower, how can you be sure that the problem was completely resolved, and that there isn't a small remaining leak (small enough that it wouldn't be obvious from your CO2 mixing ratio calculation, but perhaps still large enough to influence the 14C results)?

Section 2.3. 14C measurement. Some more detail of the 14C data quality should be included in this section: How was the reported 14C uncertainty determined? Simply from 14C counting statistics, or is some measure of uncertainty from sample processing or long-term repeatability considered as well? Are any reference materials measured for quality control (other than the primary standards and blanks), to assess the short and long-term data quality of the atmospheric samples? At least part of the sample preparation could be assessed by examining the scatter of the 3 targets of each material averaged to determine the final 14C content. Is the 13C correction done using online AMS 13C values, or using offline IRMS 13C values? Previous work has shown quite clearly that using offline IRMS 13C values can cause substantial wheel-to-wheel biases in AMS 14C results (eg Graven et al 2007) and even with online correction, wheel-to-wheel variability may be observed. Is the offset between your measurements and the Heidelberg lab's measurements based entirely on the small (5 sample) intercomparison exercise described by Hammer et al 2016? It seems rather bold to assume that a single set of measurements (presumably in a single wheel) is sufficient to characterize the inter-laboratory offset over the long-term. This is a key point, since an offset of 2.1 ‰ in Δ14C translates to a bias in calculated CO2ff of 0.8 ppm, or 20% of the mean ob-

served CO2ff signal! And which direction is the offset? Further, in the Hammer paper, the individual labs are held anonymous. It would be appropriate to identify which lab number in the Hammer paper corresponds to your facility (so that readers can see for themselves the offset and it's variability).

Line 196. I believe Meijer and Zondervan (1996) did a similar analysis earlier than the Levin et al work.

Lines 216-223. The authors should also refer to Turnbull et al (2009) and Miller et al (2012) where the heterotrophic respiration bias is discussed in more detail and spatially and temporally explicit bias corrections are estimated. It may be clearer to write equations 3 and 4 in a different form to clarify how the corrections (heterotrophic respiration and NPP) that are applied.

Lines 231-233. Be clear that the very large contribution identified by Vogel et al is for a reactor that is very close to the measurement site, and that reactor in question is a CANDU type, which are known to produce much more 14C than almost any other reactor type.

Lines 237-250. When measuring compared to the Jungfraujoch background, which is essentially a free troposphere background, your observations will represent some sort of continental-scale signal, not just the local signal. Is the model domain used to determine the NPP correction sufficient to capture all the NPP emissions that might be observed in your observations? Please include some discussion of this. A figure showing the model domain and influence functions would be helpful.

Lines 251-256. Are you able to provide the NPP 14C emission data (perhaps in the supplementary material)? I can imagine this would be of interest to some readers.

Equation 5. Please explain more clearly how this value is calculated. How is dCff determined in this case? And what is Anuc?

Section 2.4.3. CO:CO2 ratios. The choice of Jungfraujoch as background could be

problematic for CO, since CO has a relatively short lifetime of 1-2 months, the free troposphere may be depleted in CO relative to surface sites, biasing the ratio high.

Lines 281-283. Production of CO from oxidation of VOCs may be important too.

Lines 299-302. You say here that spikes in CO2 happened mainly in winter, but what stands out in the figure is the large and highly variable CO2 values in the summer of 2015!

Lines 303 – 305. Please show the raw 14C data as well as the corrected data. For CO and CO2, you make smooth curve fits to the Jungfraujoch background data, but it appears that the Jungfraujoch 14C data is used without smoothing. From figure 4, it is clear that Jungfraujoch experiences significant periods of polluted air – how would the results change if a smooth curve fit was used for the Jungfraujoch 14C background, or if another site was used (e.g. Niwot Ridge, which is essentially similar to Jungfraujoch in 14C, but the nature of the 14C sampling there allows exclusion of pollution events to reveal a clean air signal)?

Lines 319-320. How do you account for uncertainty in the interlaboratory offset, biosphere and NPP corrections? These are large corrections, so some measure of the uncertainty in these values should be propagated into the final CO2ff uncertainty.

Lines 322-332. This is a nice demonstration of the influence of farfield emissions – can you show the modelled influence function or trajectory?

Lines 340-343. These wildly varying CO2bio values during summer 2015 are quite peculiar and need further investigation and explanation. Is there any chance of a CO2 instrument problem during this time? It is hard to imagine how a swing from +10 to -10 ppm and back again in CO2bio could occur over a short period simply due to harvesting, and some more thought should be put into possible explanations for this.

Section 3.2. I was concerned that the use of Jungfraujoch background for CO would bias RCO high, but your comparison with using a constructed background from

Beromünster gives me some confidence that this is not a significant problem, although it could be the explanation for the slight difference in RCO for the two difference background choices.

The comparison with bottom-up inventories in section 3.3 needs to be done using RCO, not the CO:CO2 ratio, unless you also include a biogenic CO2 bottom-up estimate.

To interpret the observed RCO, you need to also consider: 1. How large are the non-fossil sources of CO for Switzerland and Europe (eg wood burning, VOC oxidation)? Could these explain the higher-than-expected RCO? Wood burning tends to be inefficient and produce high RCO values. 2. The effective footprint that the tower is "seeing" is crucial to interpreting the observed enhancements and ratios. The choice of Jungfraujoch as background means that the effective footprint is likely to include much of Europe, and certainly a much larger area than just Switzerland. Some estimate of the actual footprint should be made, either for each individual sample (or a few example days), or at least a generalized footprint, and consider the emission sources for the whole footprint. I'd suspect that RCO would be much higher in other parts of Europe and could be causing the higher-than-expected ratios. 3. You may also want to compare with Popa et al (2014) for recent Swiss traffic RCO.

Section 3.3 This section needs significant revision to address the key point that CO:CO2 ratios (as opposed to CO:CO2ff) ratios incorporate all CO2 sources and are therefore not directly related to only anthropogenic sources. In summer, and possibly spring and autumn, this ratio is essentially nonsensical, since the biogenic fluxes strongly dominate over the fossil fuel CO2 flux. Miller et al (2012) showed very clearly that even though CO:CO2 correlations may be strong in winter, they give very different slopes than CO:CO2ff correlations. Several studies have demonstrated that at the continental scale, the biogenic and fossil fuel fluxes are roughly equal in magnitude (Miller et al 2012, Turnbull et al 2015, Turnbull et al 2011b). This can readily explain the observed difference between CO:CO2 and CO2ff, and indeed the calculated CO2ff and CO2bio values also show this. In this light, the comparison of bottom-up anthropogenic

CO:CO2 emission ratio should be with the observed CO:CO2ff ratio; bottom-up biogenic CO2 flux estimates are also needed to makes the comparison with observed CO:CO2 valid.

Section 3.4. Some assessment of the uncertainty in applying a single RCO value should be included here. It seems quite likely that variability in RCO through time could be driving the apparently odd results shown in figure 5. It not simply diurnally varying RCO values (as mentioned in line 418), but likely variability depending on the varying atmospheric transport bringing different emission sources (with possibly wildly varying RCO) to the site.

I don't understand how you get to figure 6 from figure 5. Figure 5 looks like a jumble of random noise, yet figure 6 looks clean and interpretable. Is figure 6 just averaging of the data shown in figure 5? The text states that during winter, the CO2bio values are mostly close to zero or positive; this is not at all obvious from figure 5. It may simply be that the scale of figure 5 makes it difficult to see what is going on. Perhaps taking a small (1 week?) section and zooming in on it would make it clear.

At the end of this section, there's a discussion of differences between different levels of the tower, but no data is shown or discussed from the lower levels. Be clear as to what data is used here and if it is CO2 data from different levels of the tower, that data should be discussed in the methods section.

Figure 2. Please show the raw 14C data as well as the corrected data. And if possible, include the actual measured values as supplemental material or point to the data archive.

Figure 3. Show the CO:CO2ff values as points, not just the line of fit.

Figure 4. Please add the 14C-based CO2ff values as points on plot c.

Figure 5. Please add a plot to show a short time period (a couple of example weeks) so that the reader can clearly see the diurnal variability. This plot is hard to look at

because there are so many data points scrunched together.

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