

Comments on Petrenko *et al* 2020, “An improved method for atmospheric ¹⁴CO measurements

Martin Manning, New Zealand Climate Change Research Institute, Victoria University of Wellington

General comments

This paper gives a well organised summary of what is clearly a significant improvement in our ability to determine atmospheric oxidation rates by using the tracer ¹⁴CO. Some key points are:

- the quality of ¹⁴CO concentrations is now well established for air samples significantly smaller than have been used previously, e.g. the air samples used here are five to ten times smaller than used in other studies ;
- while some aspects of the sample treatment are similar to that done in previous studies, the description of the complete process from air collection to correction of AMS measurements is very well set out;
- recognition that “blank” samples stored in cylinders can have cosmogenic ¹⁴CO production continuing to occur inside them is a point that is only considered implicitly in other papers on this tracer;
- there is a thorough treatment of corrections and uncertainties in the final results and the quality of analysis is shown through admission that there are still some issues to be resolved, e.g. variation in blanks covered in lines 334 – 337.

My only significant concern with the paper is its very brief coverage of what is known about ¹⁴CO production rates. While the Kovaltsov *et al*, 2012, paper is cited, most readers will miss the point that this was a major advance by Ilya Usoskin’s group as it has resolved a long-standing difference between model derived ¹⁴C production rates and estimates based on radiocarbon dating. Also, it was followed up by Poluianov *et al*, 2016 (see references below) which showed that a significant amount of ¹⁴C production occurs above the 10 hPa level in the atmosphere as has been expected by some experts in high energy physics, and has not been reflected at all in papers such as Masarik & Beer, 1999.

Similarly, Usoskin’s group regularly update their estimates of monthly changes in the average cosmic ray modulation strength (Phi) which is the primary cause for changes in ¹⁴C production rate. See <http://cosmicrays oulu.fi/phi/phi.html> and <http://cosmicrays oulu.fi/phi/Phi Table 2017.txt>. This data source could be used to quantify the level of agreement between periods 1996-97 and 2017-18 that are used in section 3.

Despite these comments I would recommend that this paper be published after the authors have considered some suggestions made below.

Specific comments

line 88: As noted above, I would recommend that this sentence be expanded to cover the two references Kovaltsov *et al* and Poluianov *et al* which have set out much more detailed estimates for ¹⁴C production rates and their spatial distribution.

lines 96-97: determination of a global average ¹⁴C production rate needs global coverage for data on the solar modulation of cosmic ray activity. I would recommend Usoskin *et al*, 2011, (see below) as a reference to be added here.

line 98: this is a minor point but there are other estimates of the ¹⁴CO production yield, e.g. by Jöckel and Brenninkmeijer, and these vary over a small range of about 93 – 96%. It is another small

source of uncertainty as it can vary with altitude and mean the vertical distribution of ^{14}C production is not quite the same as ^{14}C production.

lines 150 – 291: while there may be more detail in this section than some readers will follow, I would like to say that it is a very good summary of the range of issues that have to be dealt with in order to have precision in the results.

lines 184 – 187: presumably records are kept of the flight used to transport the sample from Honolulu, but do these use the same type of aircraft and so are expected to be at similar altitudes during the flight. Also have there been any estimates of in situ ^{14}C production during shipping to the University of Rochester by doing repeated shipping of a blank test sample? And will the storage time at Rochester vary between samples?

lines 266 – 267: as mentioned in my general comments, I think this is a very important point.

lines 304 – 311: to quantify my general comments on comparing periods 1996-97 and 2017-18, <http://cosmicrays.oulu.fi/phi/phi.html> shows that the cosmogenic modulation potential averaged over 1996 – 1997 was 506 MV and over 2017-18 was 456 MV. The weaker modulation effect in 2017-18 increases the global average production rate by 4% when the Kovaltsov *et al* production rates are used, and the Poluianov *et al* rates have very similar global averages.

lines 304 – 311 again: while MLO and Ragged Point Barbados have similar latitudes their altitudes are different and local cosmogenic ^{14}C production rates will be about 20 times larger at MLO. This is well recognised by rapid removal of the MLO samples to lower altitudes but also leaves a question about comparing the atmospheric observations at different altitudes. So, I would suggest adding the point that this comparison is valid because rapid vertical mixing in the troposphere means there are only small vertical gradients in ^{14}C concentrations.

331 – 337: does this comparison of the two different values for blanks lead to a conclusion?

374 – 377: following on from that last question, have surface effects in the canisters been considered and have they been treated to avoid variations in forms of carbon becoming attached to the interior surface?

References

Poluianov, S.V., Kovaltsov, G.A., Mishev, A.L., and Usoskin, I.G., 2016: Production of cosmogenic isotopes ^7Be , ^{10}Be , ^{14}C , ^{22}Na , and ^{36}Cl in the atmosphere: Altitudinal profiles of yield functions. *Journal of Geophysical Research: Atmospheres*, 121, 8125-8136.

Usoskin, I.G., Bazilevskaya, G.A., and Kovaltsov, G.A., 2011: Solar modulation parameter for cosmic rays since 1936 reconstructed from ground-based neutron monitors and ionization chambers. *J. Geophys. Res.*, 116, A02104, doi:10.1029/2010JA016105.