We would like to thank Dr. Manning for his careful reading of the manuscript and helpful and constructive comments. The reviewer comments are shown below in *blue italics*, with our responses in regular black font.

Comments on Petrenko et al 2020, "An improved method for atmospheric ^{14}CO 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 ^{14}CO. Some key points are:

- *the quality of ^{14}CO 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 ^{14}CO 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 ^{14}CO 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 ^{14}C 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 ^{14}C 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.

In the revised manuscript, we will add the Poluianov et al (2016) reference. We note that the main focus of this paper is on the analytical techniques, rather than on interpretation of the ^{14}CO results and their implications for atmospheric OH and the ^{14}C production scheme used in models. Considering this, we would prefer to keep the discussion of atmospheric ^{14}C production relatively brief.

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 ^{14}C 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.

We thank Dr. Manning for pointing this out. However, again, we would prefer to keep the focus of this manuscript on the analytical techniques. The qualitative comparison to prior Barbados measurements is used in the manuscript to support the overall argument that our technique produces reliable results. An in-depth quantitative comparison would require the consideration of changes in atmospheric ^{14}C production as Dr. Manning points out, as well as a chemistry – transport model. We feel that such an analysis is beyond the scope of this paper.

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 ^{14}C production rates and their spatial distribution.

These two references will be added in the revised manuscript.

lines 96-97: determination of a global average ^{14}C 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.

This reference will be added to the revised manuscript.

line 98: this is a minor point but there are other estimates of the ^{14}CO 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}CO production is not quite the same as ^{14}C production.

While the Mak et al. (1994) study we cited used 93% for this value, some other studies have used a slightly different value of 95% (Jockel and Brenninkmeijer, 2002; Krol et al., 2008). In the revised manuscript, we will add the Jockel and Brenninkmeijer reference and give a 93 – 95% range for the ^{14}CO yield.

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.

Thanks!

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}CO 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?

Unfortunately, these records were not kept, and the routing / aircraft information for past shipments is not available from FedEx (the carrier for all our samples). See also the response to Reviewer 1 point 8. Our best estimates for in situ ^{14}CO production in the canisters during Hawaii → Rochester shipping come from Blanks 9 and 10 (see Table S2), as these blanks were collected in a single day (rather than with a week in between canister half-fills, as was the case for most samples and blanks). These blanks yielded ^{14}CO values of 1.15 and 0.74 molecules / cm^3 STP, and were already discussed in the original manuscript (middle paragraph on p. 11).

The storage time at Rochester is short (typically on the order of 1 week), but has varied by ± 1 week. However, the laboratory building is at an altitude of only ≈150 m a.s.l.. Further, the received sample and blank canisters are stored on the basement level of a 5-story building, which provides added shielding from cosmic rays. In situ ^{14}CO production in sample canisters during storage at Rochester should therefore be negligible compared to in situ production during aircraft transport and the ≈1 week storage at the Mauna Loa observatory (3397 m a.s.l.).

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.

Please see our response regarding the Barbados – Mauna Loa results comparison in the general comments section above.

lines 304 – 311 again: while MLO and Ragged Point Barbados have similar latitudes their altitudes are different and local cosmogenic ^{14}CO 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}CO concentrations.

This again is a valid point. However, again, we are not attempting to do a detailed quantitative comparison of our Mauna Loa and prior Barbados ^{14}CO results. Our preference would therefore be to leave such a detailed comparison (which would consider changes in atmospheric 14C production, site altitude, ^{14}CO transport, etc) for a future study.

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

Yes, in the revised manuscript we will clarify that in situ ^{14}CO production in the canisters during aircraft shipment from Hawaii to Rochester appears to be larger than in situ production during storage at MLO.

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?

Please see the detailed response to point 6 from Reviewer 1, which posed very similar questions. Briefly, the consistently low CO mole fractions measured in the blanks indicate that any effects from the canisters (memory, outgassing) would be negligible for sample ^{14}CO.

References

Poluianov, S.V., Kovaltsov, G.A., Mishev, A.L., and Usoskin, I.G., 2016: Production of cosmogenic isotopes ^{7}Be, ^{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.

References (beyond those in the original manuscript and those given by Dr. Manning above):

Krol, M.C., Meirink, J.F., Bergamaschi, P., Mak, J.E., Lowe, D., Jockel, P., Houweling, S., Rockmann, T., 2008. What can (CO)-C-14 measurements tell us about OH? *Atmospheric Chemistry and Physics* 8, 5033-5044.