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

Comments on “An improved method for atmospheric 14CO measurements” by Petrenko et al.

General comments:

This manuscript describes an improved method for the collection of atmospheric samples used for the determination of ^{14}CO concentration, which serves as a useful tracer in characterizing the variability of atmospheric hydroxyl radical concentration. Since CO is present only in trace quantities in atmospheric samples, isotopic measurements, especially ^{14}CO measurements demand collection of larger air samples in order to enable measurements with acceptable uncertainties. Such large volume samplings can be both logistically challenging and expensive. Further, performing radiocarbon measurements on small samples (10-50 µgC) poses additional challenge both during graphitization and measurement. Through the methods described in this manuscript, following solutions have been presented: 1) use of a logistically attractive sample volume, 2) amplifying the mass of carbon present in the sample through dilution with high CO containing air to enable more precise measurements than possible in earlier work and 3) demonstrates the importance and the need of procedural blank sampling together with the actual sample collection.

The manuscript is very well written and falls within the scope of the journal AMT. I would recommend this manuscript for publication with some very minor clarifications.

Specific comments:
1. Page 6 Line 167: What pressures do you use during the “pressure-flush” step?

≈25 psig (this is somewhat variable as the pressure builds very quickly when the vent valve is closed). This detail will be added to the revised manuscript.

2. Page 6 Line 181: The use of italicized Latin forms should be consistent throughout the manuscript (see page 5 line 138).

All instances of “in situ” will be italicized in the revised manuscript

3. Page 7 Line 196: Please specify the amount of gas used up during the CRDS measurement.

This is ≈800 cm^3 STP; we will add this information to the revised manuscript

4. Page 7 Line 197: Was this ^{14}C-depleted high CO-in-air prepared in-house or purchased through a commercial vendor?

This custom gas mixture was purchased from Praxair. We will include this detail in the revised manuscript.

5. Page 7 Line 218: Please provide a part number/manufacturers details if purchased through a commercial vendor.

This was Schimadzu part no. 630-00996-00, we will add this detail to the revised manuscript

6. Page 11 Line 326-331: What part of this variability that you observe in your procedural blank could be due to memory from the canister itself? Do you clean the canisters in a special way and perform some sort of possible outgassing test? Could you please comment on this?

The stainless steel canisters have been electropolished at the time of manufacturing, which helps to clean and passivate the surface; the fact that the canisters are electropolished is already mentioned in the manuscript (end of 1st paragraph in section 2.1). Prior to being reused, the canisters are evacuated to 0.25 torr and leak-tested overnight. The best indicator that we have for a lack of significant "memory" from the canisters themselves is the consistently low CO mole fraction measured in the blanks (3.7 ± 1.8 (1σ) nmol mol^{-1} see also response to point 8 below). Following the dilutions with the high-CO, ^{14}C-depleted gas, the mean CO mole fraction in the sample and blank canisters was 512 ± 36 (1σ) nmol mol^{-1} for the ≈22 µgC samples and 1134 ± 19 (1σ) nmol mol^{-1} for the ≈50 µgC samples. Assuming that the observed CO in the blanks is originating from canister "memory", this memory would represent <1 % of the CO present in the canister prior to the evacuation. Further, following the dilution the ^{14}C activity of CO in the sample canisters is much lower than that of typical atmospheric CO. Assuming 3.7 nmol mol^{-1} of CO with a typical (after dilutions for ≈22 µgC samples) ^{14}C activity of 60 pMC is added via canister "memory", this translates to 0.07 ^{14}CO molecules / cm^3 STP – which is much smaller than the variability between the blanks and similar to the estimated 1σ uncertainty for blank ^{14}CO (see Table S2 in the original manuscript).

That said, it is much more likely that the small amount of CO observed in the blanks is due to a combination of CO outgassing from the KNF N145 pump used in the sampling system and from the sample canisters. The observed blank CO mole fractions are consistent with those expected based on sampling system and canister tests conducted in our laboratory prior to this and other projects that used the same equipment. Blank 13 was the only blank for which the preceding sample in the same canister was a ≈50 µgC sample with calculated CO mole fraction of 1112 nmol mol^{-1} following the dilution; for other blanks the preceding sample or blank in the same canister was ≈22 µgC in size with diluted CO mole fractions of ≈500 nmol mol^{-1}. CO mole fraction measured in Blank 13 (3.6 nmol mol^{-1}) is not anomalous compared to other blanks, arguing against a canister CO memory effect.

The sampling canisters outgas CO at a rate of 1 – 3 nmol mol^{-1} per month as determined in tests associated with prior projects. However, again, CO outgassing at this rate would not affect the sample ^{14}CO results significantly.

In the revised manuscript, we will add information regarding canister evacuation in between samples, as well as a brief statement that the consistently low CO mole fraction in the blanks rules out the possibility of significant ^{14}CO interference from canister memory or outgassing. We will also add measured CO mole fractions for the blanks to Table S2.

7. Figure 2: In a plot that covers a large dynamic range, it is common to display a residual to the fit which makes visualization of the distribution of your dataset around the fit very easy. Could you please include this?

This will be added to Figure 2 in the revised manuscript.

8. Figure 3: If one looks at your data carefully, there is a noticeable correlation (although weak) between the ^{14}CO content measured in the blanks vs. the blank-corrected samples collected on the same day. Could you please comment on why this is the case?

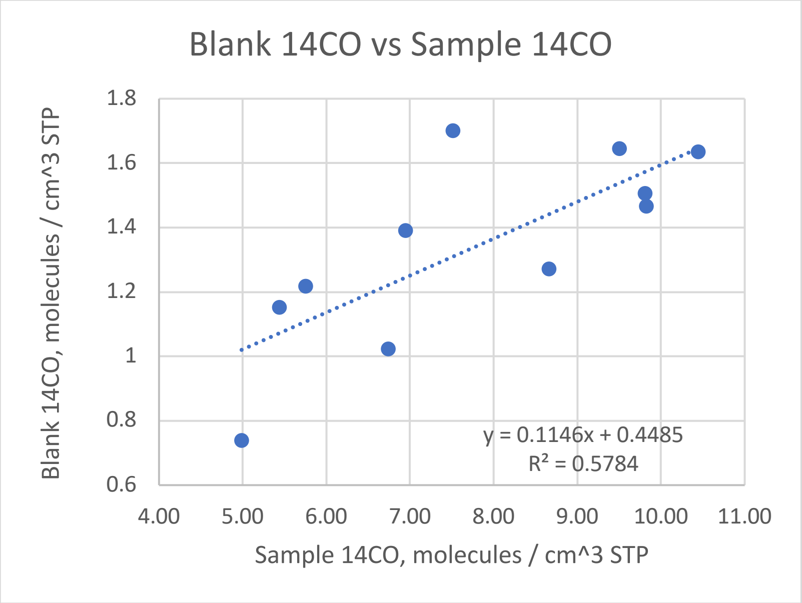

Figure R1. Observed ^{14}CO correlation for blank-sample pairs collected and analyzed as part of the Mauna Loa ^{14}CO campaign. This correlation appears to be significant, with a p value of 0.007.

We agree that this correlation is puzzling (see figure R1 above), but it cannot be due to analytical artifacts, for the following reasons. One analytical problem that could in principle result in such a correlation would be a failure of the Sofnocat 423 reagent (see Figure 1 in manuscript) to fully oxidize all CO (and ^{14}CO) in the sampled air when sampling is performed in blank mode. In this case, the blank-sample ^{14}CO relationship in Figure R1 suggests that ≈11% of sample CO (and ^{14}CO) breaks through the Sofnocat CO scrubber. However, this is ruled out by the consistently low CO mole fraction in the blanks (see response to point 6 above) that is not positively correlated to the CO mole fraction in the samples collected on the same days (see Figure R2 below).

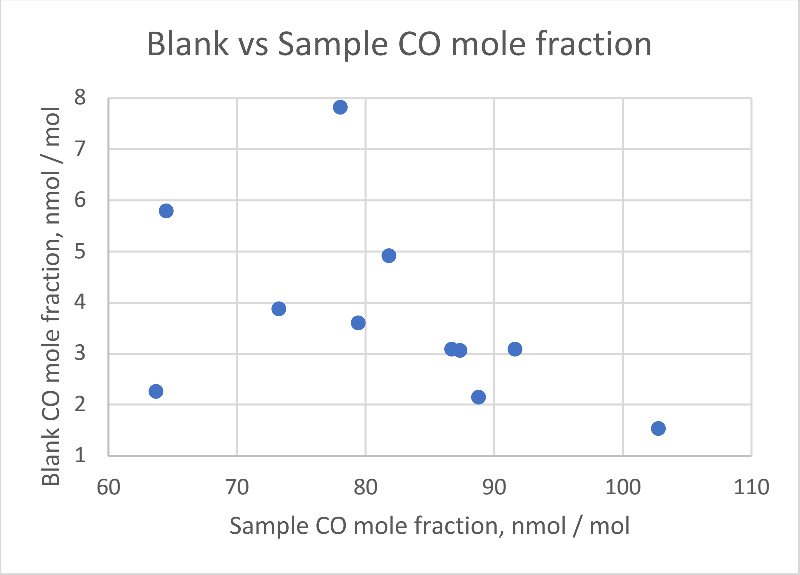

Figure R2. Comparison of measured CO mole fraction for blank-sample pairs collected and analyzed as part of the Mauna Loa ^{14}CO campaign. While the data suggest a negative slope for the dependence of blank CO mole fraction on sample CO mole fraction, in this case the correlation does not appear to be significant, with a p value of 0.17.

The possibility of ^{14}CO in the blanks being significantly affected by “memory” in the sampling canisters was already discussed and ruled out in the response to reviewer’s point 6 above. We also considered the possibility that the correlation could be due to carbon memory in the air processing system at the U Rochester laboratory. A very similar system at the National Institute for Water and Atmospheric Research (NIWA) in Wellington, New Zealand utilizing similar components (including the same type of platinized quartz wool) has been previously demonstrated to be free of memory artifacts when operated in CH_4 mode (Petrenko et al., 2008). To examine whether any carbon memory might exist in the U Rochester system operated in CO mode, we compared measured ^{14}CO for sample-sample pairs collected on the same days (values for all samples were already shown in Table S1). There are six such pairs where one of the samples was processed on the system following a sample, and another following a blank. If the system does indeed have a memory, we would expect lower ^{14}CO for samples that were processed following a blank. The average ^{14}CO offset between such pairs is 0.03 molecules / cm^3 STP, while the standard deviation of the offsets is 0.35 molecules / cm^3 STP. We thus conclude that there is no evidence for a significant memory effect in the U Rochester air processing system.

We can also rule out memory effects in the micro-conventional furnaces used to graphitize the sample-derived CO_2 at ANSTO based on tests conducted on these furnaces (Yang and Smith, 2017).

Based on all of the above, we can rule out the possibility that the ^{14}CO correlation observed for blank-sample pairs is due to analytical artifacts. We further note that ^{14}CO concentrations observed in blanks 9 and 10 (1.15 and 0.74 molecules / cm^3 STP) are similar to prior estimates of in situ ^{14}CO production from a jet aircraft flight (0.9 molecules / cm^3 STP, with a ≈30% uncertainty; Lowe et al., 2002). Blanks 9 and 10 were filled in a single day, transported to sea level within hours and shipped to U Rochester the following day; thus ^{14}CO in these blanks likely represents only the in situ ^{14}CO from aircraft transport.

Unfortunately, we do not at this point have a clear explanation for the correlation. It may be possible that this effect is related to airplane trajectories being influenced by atmospheric conditions. Lower atmospheric ^{14}CO at Mauna Loa is generally associated with warmer low-latitude air masses. It may be possible that in such conditions, the airplanes that transport our samples and blanks from Hawaii to Rochester fly at cruising altitudes corresponding to somewhat higher pressures (to maintain constant air density in warmer air). This would result in lower in situ ^{14}CO production rates in the tanks during airplane transport. Unfortunately, FedEx (the carrier for all our samples) does not provide routing information for past shipments, so we are unable to verify this hypothesis.

In the revised manuscript, we will mention the ^{14}CO correlation in the blank-sample pairs and include the detailed above discussion in the supplement.

References:

Yang, B. and Smith, A.M., 2017. Conventionally heated microfurnace for the graphitization of microgram-sized carbon samples. *Radiocarbon*, 59, 859 – 873.