Response to Reviews of Petrenko et al., "An improved method for atmospheric ^{14}CO measurements"

We would first like to thank the reviewers 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.

Reviewer 1

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 has been added to the revised manuscript (p. 6, line 171).

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" have been 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; this information has been added to the revised manuscript (p. 6, line 200).

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. This detail has been included in the revised manuscript (p. 6, line 201).

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, this detail has been added to the revised manuscript (p.7, line 222).

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 added the pressure to which canisters were evacuated in between samples (p. 5, line 164). We also added a brief statement (p.11, line 338) that clarifies that the ^{14}CO blank is not arising from outgassing or analytical artifacts and points to a more detailed discussion in the Supplement. Finally, we have added a section in the Supplement that discusses possible effects of outgassing and "memory" from sample canisters on blank ^{14}CO. In

support of this discussion, CO mole fractions measured in the blanks were also added 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 has been 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?

We agree that this correlation is puzzling (see Figure S1 in the revised Supplement), 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 S1 suggests that ≈12% 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 S2 in the revised Supplement).

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 have mentioned the ^{14}CO correlation in the blank-sample pairs in the Figure 3 caption and referred to the detailed discussion in the revised Supplement. In the revised Supplement, we have added a detailed discussion of this correlation and Figures S1 and S2. We have also added CO mole fractions for samples and blanks into Tables S1 and S2, respectively.

Dr. Martin Manning

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 have added the Poluianov et al (2016) reference (p.3, line 88). 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 have been added in the revised manuscript (p.3, lines 87 – 88).

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 has been be added to the revised manuscript (p.3, line 96).

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 have added the Jockel and Brenninkmeijer reference and give a 93 – 95% range for the ^{14}CO yield (p.3, lines 97 – 98).

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 need to 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 have clarified 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 (p.11, line 346).

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.

Further revisions / changes not related to reviewer comments

We have combined two sentences into one on page 4, line 108 to make the text more concise.

For completeness, in the Figure 2 caption we have included the published uncertainties for the true values of the ^{14}C standards, as well as references for these values.

One missing reference was added to the references section (Brasseur et al., 1999).

A few small typos were corrected.

An improved method for atmospheric ^{14}CO measurements

Vasilii V. Petrenko[1], Andrew M. Smith[2], Edward M. Crosier[1], Roxana Kazemi[1], Philip Place[1], Aidan Colton[3], Bin Yang[2], Quan Hua[2] and Lee T. Murray[1]

[1]Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627, USA
[2]Australian Nuclear Science and Technology Organisation (ANSTO), Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.
[3]NOAA Earth System Research Laboratory, Global Monitoring Division, Boulder, Colorado, USA.

Correspondence to: Vasilii V. Petrenko (vasilii.petrenko@rochester.edu)

Abstract

Important uncertainties remain in our understanding of the spatial and temporal variability of atmospheric hydroxyl radical concentration ([OH]). Carbon-14-containing carbon monoxide (^{14}CO) is a useful tracer that can help in the characterization of [OH] variability. Prior measurements of atmospheric ^{14}CO concentration ([^{14}CO] are limited in both their spatial and temporal extent, partly due to the very large air sample volumes that have been required for measurements (500 – 1000 liters at standard temperature and pressure, L STP) and the difficulty and expense associated with the collection, shipment and processing of such samples. Here we present a new method that reduces the air sample volume requirement to ≈90 L STP while allowing for [^{14}CO] measurement uncertainties that are on par with or better than prior work (≈3 % or better, 1 σ). The method also for the first time includes accurate characterization of the overall procedural [^{14}CO] blank associated with individual samples, a key improvement over prior atmospheric ^{14}CO work. The method was used to make measurements of [^{14}CO] at the NOAA Mauna Loa Observatory, Hawaii, USA, between November 2017 and November 2018. The measurements show the expected [^{14}CO] seasonal cycle (lowest in summer) and are in good agreement with prior [^{14}CO] results from another low-latitude site in the Northern Hemisphere. The lowest overall [^{14}CO] uncertainties (2.1 %, 1 σ) are achieved for samples that are directly accompanied by procedural blanks and whose mass is increased to ≈ 50 micrograms of carbon (μgC) prior to the ^{14}C measurement via dilution with a high-CO, ^{14}C-depleted gas.

1 Introduction

1.1 The importance of improving the understanding of OH variability

Atmospheric hydroxyl radical concentration ([OH]) is arguably the single most important parameter in characterizing the overall chemical state of the atmosphere because OH serves as the main atmospheric oxidant. Reaction with OH removes a large number of atmospheric trace species, including reactive greenhouse gases like methane as well as most anthropogenic pollutants (e.g., Brasseur et al., 1999). Changes in [OH] in space and time impact both global air quality and the rate of climate change. While our understanding of and ability to predict global OH abundance and variability continues to improve, large uncertainties remain. This was highlighted, for example, by the Atmospheric Chemistry and Climate Modeling Intercomparison Project (ACCMIP), where individual models disagreed by ± 50 % in their calculations of global mean [OH] (Naik et al., 2013; Voulgarakis et al., 2013).

OH is very short-lived (lifetimes of 1 s or less are typical) and heterogeneously distributed (e.g., Spivakovsky et al., 2000), making measurements inherently challenging. Therefore, characterizing global mean [OH] via direct measurements is not feasible. Instead, a number of tracers have been used for this purpose, including ^{14}CO (e.g., Brenninkmeijer et al., 1992), methane (CH_4; Montzka et al., 2011), methyl chloroform (MCF; CH_3CCl_3; e.g., Montzka, et al., 2011; Prinn et al., 2001), as well as a combination of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) (Liang et al., 2017). The approach involves selecting a trace gas with a well-characterized source and with OH as the dominant sink.

Over the last ≈2 decades, the most reliable characterization of global mean [OH] has been derived from MCF (e.g., Montzka, et al., 2011; Prinn, et al., 2001). However, MCF atmospheric mixing ratios have been declining rapidly as a result of phase-out of its production. This makes the continued use of MCF for studies of [OH] challenging, as

MCF mixing ratios approach analytical detection limits and as estimates of [OH] become increasingly sensitive to poorly-characterized residual MCF emissions (e.g., Rigby et al., 2017). Furthermore, while the moderately long lifetime of MCF (≈5 years; Rigby et al., 2013) has allowed for constraints on global and hemispheric mean [OH], less is known about [OH] temporal and spatial variability, which is critical for understanding the evolution, transport and fate of air pollutants.

1.2 ^{14}CO as a tracer for atmospheric OH

Evidence from measurements of carbon-14 of atmospheric carbon monoxide (^{14}CO) provided the first indication that carbon monoxide had a relatively short atmospheric lifetime, leading to the suggestion that tropospheric OH may be important in the removal of CO (Weinstock, 1969). Since then, measurements of ^{14}CO concentration ([^{14}CO]) have been used by several research groups to improve understanding of tropospheric [OH] (e.g., Brenninkmeijer, et al., 1992; Jöckel and Brenninkmeijer, 2002; Manning et al., 2005; Quay et al., 2000; Volz et al., 1981).

^{14}CO has a strong, reliable and well-characterized primary source (Kovaltsov et al., 2012; Poluianov et al., 2016). This is an advantage over CO, CH_4, or halocarbon tracers for OH, which typically have variable emissions that are associated with relatively large uncertainties. ^{14}C is produced from ^{14}N via interactions with neutrons (^{14}N(n,p)^{14}C) resulting from bombardment of the atmosphere by galactic cosmic rays. Production rates are highest in the upper troposphere and lower stratosphere (UT/LS), with about half of ^{14}C produced in each region. The geomagnetic field provides the strongest cosmic ray shielding in the low latitudes, resulting in higher ^{14}C production rates in the mid- and high latitudes (e.g., Masarik and Beer, 1999). Variations in the ^{14}C production rate are well-characterized from neutron monitor observations (e.g., Kovaltsov et al., 2012; Usoskin et al., 2011). Once produced, ^{14}C quickly reacts to form ^{14}CO, with ≈ 93 - 95% yield (Mak et al., 1994; Jockel and Brenninkmeijer, 2002).

The dominant ^{14}CO removal mechanism is via reaction with OH; ^{14}CO can therefore in principle serve as a tracer for OH abundance and variability. There are several aspects of

atmospheric cycling of ^{14}CO that offer either challenges or advantages in its use as a tracer for [OH], depending on the question being posed. First, ^{14}CO (and CO) has a relatively short average tropospheric lifetime of ≈2 months, which varies by latitude (shortest in the tropics) and by season (shortest in season of maximum insolation), following variations in [OH] (e.g., Spivakovsky, et al., 2000). This is much shorter than the interhemispheric mixing time of ≈1 year, and means that [^{14}CO] measurements at a given station are sensitive to regional rather than global [OH] (Krol et al., 2008), presenting a challenge for using [^{14}CO] to constrain global mean [OH] abundance and variability. To ensure robust characterization of global mean [OH] from [^{14}CO] alone, records for multiple sampling stations are necessary.

Deleted: . The fact that [^{14}CO] measurements at a given station are mainly sensitive to [OH] in a spatially limited region …

Deleted: s

The limited spatial footprint of [^{14}CO] sensitivity to [OH] can instead be an advantage if the question is one of OH spatial and seasonal variability. Driven by strong seasonality and meridional gradients in [OH], cosmogenic production rates, and stratosphere-to-troposphere (STT) transport, as well as a relatively short chemical lifetime, [^{14}CO] near the surface shows strong seasonal and meridional variability (e.g., Jöckel and Brenninkmeijer, 2002).

1.3 Atmospheric [^{14}CO] measurement techniques and associated challenges

^{14}CO is an ultra-trace constituent of the atmosphere, with surface concentrations ranging between ≈ 4 – 25 molecules / cm^3 STP. This has necessitated very large sample volumes of 500 – 1000 L STP for the analyses (e.g., Brenninkmeijer, 1993; Mak, et al., 1994). Air samples are typically collected into high-pressure aluminum cylinders with the use of modified 3-stage oil-free compressors (e.g., Mak and Brenninkmeijer, 1994). The collected air is processed by first removing condensable gases using high-efficiency cryogenic traps (Brenninkmeijer, 1991), followed by oxidation of CO to CO_2 using the Schutze reagent and subsequent cryogenic trapping of the CO-derived CO_2 using liquid nitrogen (Brenninkmeijer, 1993). The produced CO_2 is then graphitized and analyzed for ^{14}C using accelerator mass spectrometry (AMS) (Brenninkmeijer, 1993).

There are two main challenges associated with atmospheric ^{14}CO measurements. First, the very large air sample volumes and the need for high-pressure gas cylinders result in

relatively complex and expensive logistics and sample processing. These challenges have limited the extent of ^{14}CO atmospheric measurements collected to date. Second, ^{14}CO production by cosmic rays via the $^{14}N(n,p)^{14}C$ mechanism continues in air sample containers after the samples have been collected (the "*in situ* component"; e.g., Lowe et al., 2002; Mak et al., 1999). This effect is particularly large for samples stored at high altitudes / latitudes, as well as for samples transported by air, and has contributed significantly to uncertainties in interpretation of [^{14}CO] measurements (e.g., Jöckel and Brenninkmeijer, 2002).

In this paper, we describe a new method for atmospheric [^{14}CO] measurements that addresses both of the above challenges, demonstrate the use of this method, and discuss how measurement uncertainties can be minimized in this approach.

2 New method for smaller-sample atmospheric ^{14}CO measurements

2.1 Atmospheric sample collection system and procedure

The new atmospheric sampling system (Figure 1) was developed and installed at the NOAA Mauna Loa observatory (MLO; 19.5°N, 155.6°W, 3397 m above sea level) in November 2017. A 3/8" OD inlet line (Synflex 1300) was mounted near the top of a ≈36 m tower. A small diaphragm pump (Air Cadet EW-07532-40) continuously flushes the inlet line at a flow rate of ≈5 LPM when not sampling. The main part of the sampling system consists of a drying trap (45 g of anhydrous $Mg(ClO_4)_2$ in a 1" OD steel tube), a CO removal trap (25 g of Sofnocat 423 from Molecular Products in a ½" OD steel tube), a diaphragm compressor (KNF N145 with neoprene diaphragms) and a pre-evacuated (to 0.25 torr) lightweight electropolished stainless steel canister (Essex Cryogenics, 35 L internal volume).

Prior to collecting an air sample, the diaphragm compressor is leak-checked using the pressure gauge. The air flow is then started into the main part of the system and bypasses the Sofnocat CO scrubber; the flow is adjusted to ≈ 5 LPM using the metering valve. The system is flushed for 4 min; then the connection to the sample canister is pressure-flushed

(to ≈25 psig) 3 times. The sample canister is initially opened slowly, keeping the pressure upstream of the canister slightly above ambient (to minimize the impact of any leaks and help maintain a relatively constant flow rate); then opened fully once pressure in the canister reaches ambient.

In an attempt to provide some temporal averaging for ^{14}CO samples at MLO, most sample canisters were filled in 2 separate sessions ≈1 week apart, with half the air volume collected each time. A few of the canisters (Table S1) were filled in a single session, when atmospheric conditions at MLO did not allow for sampling during one of the targeted weeks (e.g., during volcanic plumes). The final air volumes in the canisters were ≈ 90 L STP, allowing for non-hazardous shipping. The system also allows for air collection in blank mode, where the flow is directed through the Sofnocat CO scrubber. This removes all ^{14}CO (and CO), allowing to assess the cumulative procedural addition of extraneous ^{14}CO to the samples, including *in situ* ^{14}CO production by cosmic rays inside the canisters during transport and storage. Samples were collected between November 2017 and November 2018. Every 2 weeks, 2 canisters were filled: either 2 samples, or a sample and a blank (Tables S1 and S2). Once complete, sample and blank canisters were moved down to sea level on the same day to minimize *in situ* ^{14}CO production (which increases approximately exponentially with altitude in the troposphere) and shipped via air to the University of Rochester within 1 – 2 days.

Formatted: Font: Italic

Formatted: Font: Italic

2.2 Sample air processing and measurements

Sample air processing and measurement approaches at U Rochester are based on methods developed earlier for ^{14}CO analyses in samples of air extracted from glacial firn and ice (Dyonisius et al., 2020; Hmiel et al., 2020; Petrenko et al., 2016; Petrenko et al., 2017). Here we provide a brief description, including changes and details specific to the MLO ^{14}CO samples. The air samples are first measured for CO mole fraction ([CO]) against NOAA-calibrated standards using a Picarro G2401 cavity ring-down spectroscopic analyzer; this measurement consumes ≈800 cm^3 STP. A high-[CO] gas (10.02 ± 0.06 µmol mol^{-1}; from Praxair, Inc.) containing ^{14}C-depleted CO is then added to the sample canisters; this step will henceforth be referred to as the "dilution". The dilution simultaneously serves

to increase the carbon mass in the sample to a level that is necessary for robust measurement by AMS and reduce the ^{14}C activity of the samples to values that are within the range of common ^{14}C measurement standards.

The relative proportions of sample air and the high-[CO] dilutant gas are determined using a Paroscientific 745-100A pressure transducer (0.01% absolute accuracy) while monitoring the canister temperatures. For the first ≈ 2/3 of the samples, the dilutions were designed to produce a final sample size of ≈22 micrograms of carbon (µgC). For the final ≈1/3 of the samples, the amount of the dilutant gas was increased to produce final sample sizes of ≈ 50 µgC, to investigate whether the somewhat larger sample sizes would yield smaller overall uncertainties.

The diluted air samples were processed using a system previously developed at U Rochester (Dyonisius, et al., 2020; Hmiel, et al., 2020). Briefly, the sample air stream (at 1 LPM STP) first passes through a coaxial Pyrex trap held at -75˚C, followed by four Pyrex traps containing nested fiberglass thimbles ("Russian Doll" traps; Brenninkmeijer, 1991) held at -196˚C with liquid nitrogen. These traps serve to remove H_2O, CO_2 and other condensable gases. The Russian Doll traps are also very effective at removing hydrocarbons, including C2 hydrocarbons (Brenninkmeijer, 1991; Petrenko et al., 2008; Pupek et al., 2005). Following cryogenic purification, the air stream passes through a furnace containing 2 g of platinized quartz wool (Schimadzu part no. 630-00996-00) held at 175˚C; this oxidizes CO to CO_2 while allowing CH_4 to pass through unaffected. The CO-derived CO_2 is then cryogenically trapped and further purified to remove trace amounts of H_2O and air. The amount of collected CO_2 is then quantified in a calibrated volume, and the CO_2 is flame-sealed into 6 mm OD Pyrex tubes for storage and shipment to the AMS facility. This CO_2 is converted to graphite (Yang and Smith, 2017) and subsequently measured for ^{14}C using the 10 MV ANTARES accelerator facility at ANSTO (Smith et al., 2010). The MLO samples and blanks were processed at ANSTO in four separate sets, and each of these sets was accompanied by commensurately-sized ^{14}C standards and blanks prepared at ANSTO, including the international ^{14}C standards HOxII, IAEA-C7, IAEA-C8, and aliquots from a previously well-characterized cylinder of ^{14}C-depleted CO_2.

$\delta^{13}C$ of CO in the high-[CO] ^{14}C-depleted dilution gas (needed for ^{14}C normalization; e.g., Stuiver and Polach, 1977) was measured as described in Dyonisius et al. (2020). $\delta^{13}C$ of CO in the air samples was measured using a new system at the University of Rochester, following the design and procedure described in Vimont et al. (2017).

2.3 Data processing and corrections

The data processing and corrections approach largely follows prior work (e.g., Dyonisius et al., 2020; Petrenko et al., 2016). Here we provide a brief summary as well as highlight differences from prior work. First, in a departure from prior work, measured ^{14}C values (in pMC units; Stuiver and Polach, 1977) are empirically corrected for any effects of processing at ANSTO (handling of sample-derived CO_2, conversion to graphite and the AMS measurement). This is accomplished by plotting the measured ^{14}C values of commensurately-sized standards against the accepted ^{14}C values for these standards, and using the Igor Pro software to determine linear fit coefficients and associated uncertainties (Fig. 2). This correction was determined separately for each measured set of MLO samples and blanks, and is small (<2% in all cases).

[CO] in the diluted samples and blanks was calculated based on [CO] in the samples and in the high-[CO] dilution gas and the pre- and post-dilution pressures, corrected for any temperature change in the canisters in between the two pressure measurements. $\delta^{13}C$ of CO in the diluted samples was calculated using an equivalent approach. ^{14}CO content in the diluted samples and blanks is then calculated using:

$$^{14}C = \frac{pMC}{100} \times e^{-\lambda(y-1950)} \times \frac{\left(1+\frac{\delta^{13}C}{1000}\right)^2}{0.975^2} \times 1.1694 \times 10^{-12} \times [CO] \times \frac{1}{22400} \times N_A \quad (1)$$

where ^{14}C is the number of ^{14}CO molecules per cm^3 STP, pMC is the measured sample or blank ^{14}C activity in pMC units after the empirical correction for ANSTO processing, λ is the ^{14}C decay constant (1.210 x 10^{-4} yr^{-1}), y is the year of measurement, $\delta^{13}C$ is the calculated $\delta^{13}C$ of CO in the diluted sample or blank, 0.975 is a factor arising from ^{14}C activity normalization to $\delta^{13}C$ of -25 ‰ associated with pMC units, 1.1694×10^{-12} is the ^{14}C / (^{13}C + ^{12}C) ratio corresponding to the absolute international ^{14}C standard activity

(Hippe and Lifton, 2014), 22400 is the number of cm^3 STP of gas per mole, and N_A is the Avogadro constant.

Next, the ^{14}CO content in the diluted samples and blanks that is attributable to the high-[CO] ^{14}C-depleted dilution gas is calculated, again using Equation 1. Triplicate aliquots of dilution gas (all ≈50 µgC) were processed and measured for ^{14}C near the start and again at the end of the 1-year sampling campaign. The ^{14}C activity of CO in the dilution gas is expected to increase slowly with time due to *in situ* production in the gas cylinder. For the analysis of the first MLO sample set, the mean value obtained from the initial set of ^{14}C measurements of the dilution gas was used (0.19 ± 0.04 pMC, 1σ, after corrections for ANSTO processing). For the analysis of the final MLO sample set, the mean value obtained from the second set of ^{14}C measurements of the dilution gas was used (0.46 ± 0.10 pMC). For the analysis of the second and third MLO sample sets, the average of the two sets of ^{14}C measurements on the dilution gas was used. For the ^{14}CO content calculation in this case, [CO] is the CO mole fraction in the diluted samples and blanks that is attributable to the dilution gas only.

Formatted: Font: Italic

The ^{14}CO content that is attributable to the high-[CO] ^{14}C-depleted dilution gas is then subtracted from the total ^{14}CO content. The ^{14}CO content is then further corrected for the volumetric effect of the dilution, which reduces the number of ^{14}CO molecules per cm^3 STP of gas. This yields the ^{14}CO content in undiluted samples and blanks. The final step of the data processing involves the procedural blank correction. For samples that were directly accompanied by a blank, the ^{14}CO content of that blank is subtracted. This accounts for all extraneous ^{14}CO affecting that particular sample. For samples that were not directly accompanied by a blank, the average ^{14}CO content determined from all blanks collected in a similar mode (tanks filled on 2 separate days ≈1 week apart versus tanks filled in a single session) was subtracted.

All uncertainties were propagated through the data reduction / correction calculations using standard error propagation techniques. For one of the sample sets, the errors were also

propagated using a Monte Carlo approach to confirm that this yields equivalent uncertainties.

3 Results and Discussion

The MLO sample and blank [^{14}CO] results are shown in Figure 3 and listed in Tables S1 and S2. [^{14}CO] at MLO during the year of sampling ranged from 5 – 13 molecules per cm^3 STP. There is a clear seasonal cycle, with lowest values during the summer and highest values during the winter, as observed in prior work (e.g., Manning et al., 2005). The relatively high temporal variability in [^{14}CO], which is particularly prominent in the winter season, is likely driven by the competing influences of low-latitude versus mid-latitude air masses at MLO ([^{14}CO] shows a very strong meridional gradient, particularly in the winter season, with much higher values at higher latitudes; e.g. Jöckel and Brenninkmeijer, 2002). For a first-order comparison with prior [^{14}CO] measurements we consider Ragged Point, Barbados (13.2˚N), which is the station with available finalized and previously published [^{14}CO] measurements that is closest in latitude to MLO (19.5˚N). The prior Barbados [^{14}CO] measurements (July 1996 - July 1997; Mak and Southon, 1998) showed seasonal [^{14}CO] variability in a similar range (5 – 12 molecules per cm^3 STP) as our new MLO data, although the Barbados measurements were not corrected for *in situ* ^{14}CO production in the sample tanks and atmospheric ^{14}C production may have been somewhat different during 1996 -1997 as compared to 2017 - 2018.

The average 1 σ overall uncertainty of the measured MLO [^{14}CO] values after corrections (obtained via uncertainty propagation) is 0.27 molecules per cm^3 STP, or 3.3% of the average [^{14}CO] value. Pooled standard deviation computed from 12 replicate sample pairs provides an estimate of repeatability and is 0.18 molecules per cm^3 STP, corresponding to 2.2% of the average ^{14}CO value for all the replicate samples. MLO is a low-latitude site, with lower [^{14}CO] as compared to most previously-monitored sites; this means that the same absolute [^{14}CO] uncertainty would translate into a larger relative uncertainty for MLO than for most other sites. Despite this, our results compare well with overall 1 σ uncertainties reported in prior work that used much larger samples at sites with higher

Deleted: ,

Formatted: Font: Italic

[^{14}CO] (4% for Quay et al., 2000 and 4 – 5% for Manning et al., 2005). Brenninkmeijer (1993) and Röckmann et al. (2002) report [^{14}CO] uncertainties of ≈2%, but those estimates did not take into account the uncertainty associated with the correction for *in situ* ^{14}CO production in sample tanks during storage and transport.

The overall procedural blank for the MLO ^{14}CO samples (Fig. 3; Table S2) is relatively large (average blank [^{14}CO] amounts to 16% of the average corrected sample [^{14}CO]) and variable (relative standard deviation of 21%), highlighting the need for accurate blank characterization. This blank is not due to outgassing from system components or other analytical artifacts (see Supplement for detailed discussion) but arises almost entirely from in situ ^{14}CO production by cosmic rays. *In situ* ^{14}CO production in the sample canisters during storage at the high altitude MLO site in between the two days on which the canisters are filled and during aircraft transport from Hawaii to Rochester both appear to be important. Two of the blank canisters were filled in a single day, rather than half-filled on two separate days a week apart (Table S2). For these two blanks, average [^{14}CO] is 0.95 molecules per cm^3 STP, as compared to average [^{14}CO] of 1.42 molecules per cm^3 STP for the ten blanks half-filled on two separate days. In situ production in the canisters during aircraft shipment between Hawaii and Rochester thus appears to be larger than production during canister storage at MLO.

One of the main objectives with the MLO sample set was method optimization to reduce uncertainties. We used a two-sample t-test to investigate the effects of sample carbon mass and whether or not a sample was directly accompanied by a procedural blank on the overall sample [^{14}CO] uncertainties after corrections (Table 1). A procedural blank that directly accompanies a sample should in principle be affected by the same amount of *in situ* ^{14}CO production, allowing for the blank ^{14}CO content to be directly subtracted from the ^{14}CO content of the accompanying sample. For samples that are not directly accompanied by a blank, the variability in the blanks must be considered, adding to uncertainty. As expected, the overall uncertainties are significantly lower for samples that are accompanied by blanks (Table 1). This finding is true if all samples are considered, as well as for the ≈22 µgC and ≈50 µgC sample subsets.

Deleted: ,
Deleted: ,
Formatted: Font: Italic
Deleted: due almost entirely to ^{14}CO production in sample canisters during storage and transport. This blank is
Formatted: Superscript
Formatted: Font: Italic
Formatted: Font: Italic

Sample carbon mass (mass of graphite actually measured for ^{14}C by AMS) may matter for two reasons. First, a larger carbon mass in principle makes the sample less susceptible to problems during graphitization and AMS measurement. Second, an analysis of the relative contributions of individual uncertainties to the final overall uncertainty revealed that the uncertainty arising from the dilution with the high-[CO] ^{14}C-depleted gas was a key contributor. For the smaller ≈22 µgC final sample masses, a relatively small amount of the high-[CO] gas (≈4 L STP) was being added to a large amount of sample air (≈90 L STP). This resulted in a relative error of ≈2% for the fraction of the diluted sample carbon that originated from the high-[CO] gas. Increasing the final sample carbon mass to ≈50 µgC via increasing the amount of the high-[CO] gas added during dilution reduces this relative error to < 1%. Surprisingly, we did not observe a significant reduction in the relative [^{14}CO] uncertainty when all ≈22 µgC samples are compared to all ≈50 µgC samples (Table 1). However, there was a significant uncertainty reduction associated with larger sample mass if only the subset of samples directly accompanied by blanks was considered.

Conclusions

The described new atmospheric [^{14}CO] measurement method uses much smaller sample air volumes than prior work, simplifying sample collection, processing and field logistics and reducing costs; the new method appears to perform well. The MLO [^{14}CO] measurements made with this method show good first-order agreement with prior measurements at a different Northern Hemisphere low latitude site. The method allows for accurate characterization of the extraneous ^{14}CO component from *in situ* cosmogenic production in sample canisters, showing that this component can be relatively large and variable. In terms of sample measurement uncertainties, the new method compares favorably with prior work that utilized 5 – 10 times larger air sample volumes. A significant improvement in overall measurement uncertainties is achieved for samples that are directly accompanied by procedural blanks, highlighting the usefulness of this mode of sample collection. The lowest overall [^{14}CO] uncertainties (2.1 %, 1 σ) were achieved for samples that were directly accompanied by procedural blanks and were diluted with a relatively

Formatted: Font: Italic

larger amount of high-[CO] ^{14}C-depleted gas to increase the final sample sizes for AMS analysis to ≈ 50 µgC.

Data availability

All the new [^{14}CO] data discussed in this manuscript are available in the Supplement (Tables S1 and S2).

Author Contributions

V.V.P. and L.T.M. designed the study. V.V.P. guided all aspects of system development, sample collection and processing, analyzed the results and wrote the manuscript. A.M.S. made the ^{14}C measurements. E.M.C. built the air sampler. A.C. collected the air samples. E.M.C, R.K. and P.P. processed the air samples. B.Y. and Q.H. graphitized the samples. All authors contributed to improving the manuscript.

Competing Interests

The authors declare that they have no conflict of interest.

Acknowledgements

This work was supported by the David and Lucille Packard Fellowship for Science and Engineering (to Petrenko). We acknowledge the financial support from the Australian Government for the Centre for Accelerator Science at ANSTO through the National Collaborative Research Infrastructure Strategy. We thank Ed Dlugokencky, Brian Vasel and Darryl Kuniyuki for facilitating access to sampling at MLO, and Emily Mesiti for assistance with researching and ordering system components. This manuscript was improved as a result of reviews by Dr. Martin Manning and an anonymous reviewer.

References

Brasseur, G., Orlando, J., Tyndall, G. (Eds): Atmospheric Chemistry and Global Change, Oxford University Press, New York, 654 pp, 1999.

Deleted: W

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Normal

Formatted: Font: (Default) Times New Roman, 12 pt

Brenninkmeijer, C. A. M.: Robust, High-Efficiency, High-Capacity Cryogenic Trap, Analytical Chemistry, 63, 1182-1184, 1991.

Brenninkmeijer, C. A. M., Manning, M. R., Lowe, D., Wallace, G., Sparks, R., and Volz-Thomas, A.: Interhemispheric asymmetry in OH abundance inferred from measurements of atmospheric ^{14}CO, Nature, 356, 50-52, 1992.

Brenninkmeijer, C. A. M.: Measurement of the Abundance of (CO)-C-14 in the Atmosphere and the C-13 C-12 and O-18 O-16 Ratio of Atmospheric CO with Applications in New Zealand and Antarctica, Journal of Geophysical Research-Atmospheres, 98, 10595-10614, 1993.

Dyonisius, M. N., Petrenko, V. V., Smith, A. M., Hua, Q., Yang, B., Schmitt, J., Beck, J., Seth, B., Bock, M., Hmiel, B., Vimont, I., Menking, J. A., Shackleton, S. A., Baggenstos, D., Bauska, T. K., Rhodes, R. H., Sperlich, P., Beaudette, R., Harth, C., Kalk, M., Brook, E. J., Fischer, H., Severinghaus, J. P., and Weiss, R. F.: Old carbon reservoirs were not important in the deglacial methane budget, Science, 367, 907-910, 10.1126/science.aax0504, 2020.

Hippe, K., and Lifton, N. A.: Calculating Isotope Ratios and Nuclide Concentrations for in Situ Cosmogenic C-14 Analyses, Radiocarbon, 56, 1167-1174, 10.2458/56.17917, 2014.

Hmiel, B., Petrenko, V. V., Dyonisius, M. N., Buizert, C., Smith, A. M., Place, P. F., Harth, C., Beaudette, R., Hua, Q., Yang, B., Vimont, I., Michel, S. E., Severinghaus, J. P., Etheridge, D., Bromley, T., Schmitt, J., Fain, X., Weiss, R. F., and Dlugokencky, E.: Preindustrial (CH4)-C-14 indicates greater anthropogenic fossil CH4 emissions, Nature, 578, 409-412, 10.1038/s41586-020-1991-8, 2020.

Jöckel, P., and Brenninkmeijer, C. A. M.: The seasonal cycle of cosmogenic (14)CO at the surface level: A solar cycle adjusted, zonal-average climatology based on observations, Journal of Geophysical Research-Atmospheres, 107, Artn 4656, Doi 10.1029/2001jd001104, 2002.

Kovaltsov, G. A., Mishev, A., and Usoskin, I. G.: A new model of cosmogenic production of radiocarbon 14C in the atmosphere, Earth and Planetary Science Letters, 337-338, 114–120, 2012.

Deleted: -

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

Le Clercq, M., van der Plicht, J., and Gröning, M.: New ^{14}C reference materials with activities of 15 and 50 pMC, Radiocarbon, 40, 295-297, 1998.

Liang, Q., Chipperfield, M. P., Fleming, E. L., Abraham, N. L., Braesicke, P., Burkholder, J. B., Daniel, J. S., Dhomse, S., Fraser, P. J., Hardiman, S. C., Jackman, C. H., Kinnison, D. E., Krummel, P., Montzka, S. A., Morgenstern, O., McCulloch, A., Muhle, J., Newman, P., Orkin, V. L., Pitari, G., Prinn, R., Rigby, M., Rozanov, E., Stenke, A., Tummon, F., Velders, G. J. M., Visioni, D., and Weiss, R. F.: Deriving Global OH Abundance and Atmospheric Lifetimes for Long-Lived Gases: A Search for CH3CCl3 Alternatives, Journal of Geophysical Research: Atmospheres, 122, 11,914–911,933, 2017.

Lowe, D. C., Levchenko, V. A., Moss, R. C., Allan, W., Brailsford, G. W., and Smith, A. M.: Assessment of "storage correction" required for in situ (CO)-C-14 production in air sample cylinders, Geophysical Research Letters, 29, NO. 7, 1139, 10.1029/2002GL014719, 2002.

Mak, J., and Brenninkmeijer, C. A. M.: Compressed Air Sample Technology for Isotopic Analysis of Atmospheric Carbon Monoxide, Journal of Atmospheric and Oceanic Technology, 11, 425-431, 1994.

Mak, J., Brenninkmeijer, C. A. M., and Tamaresis, J.: Atmospheric 14CO observations and their use for estimating carbon monoxide removal rates, Journal of Geophysical Research, 99, 22915-22922, 1994.

Mak, J., Brenninkmeijer, C. A. M., and Southon, J.: Direct measurement of the production rate of 14C near the Earth's surface, Geophysical Research Letters, 26, 3381-3384, 1999.

Mak, J. E., and Southon, J. R.: Assessment of tropical OH seasonality using atmospheric (CO)-C-14 measurements from Barbados, Geophysical Research Letters, 25, 2801-2804, Doi 10.1029/98gl02180, 1998.

Manning, M. R., Lowe, D. C., Moss, R. C., Bodeker, G. E., and Allan, W.: Short-term variations in the oxidizing power of the atmosphere, Nature, 436, 1001-1004, 2005.

Masarik, J., and Beer, J.: Simulation of particle fluxes and cosmogenic nuclide production in the Earth's atmosphere, Journal of Geophysical Research-Atmospheres, 104, 12099-12111, 1999.

Montzka, S. A., Krol, M., Dlugokencky, E., Hall, B., Jockel, P., and Lelieveld, J.: Small Interannual Variability of Global Atmospheric Hydroxyl, Science, 331, 67-69, Doi 10.1126/Science.1197640, 2011.

Naik, V., Voulgarakis, A., Fiore, A. M., Horowitz, L. W., Lamarque, J. F., Lin, M., Prather, M. J., Young, P. J., Bergmann, D., Cameron-Smith, P. J., Cionni, I., Collins, W. J., Dalsoren, S. B., Doherty, R., Eyring, V., Faluvegi, G., Folberth, G. A., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., van Noije, T. P. C., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R., Shindell, D. T., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., and Zeng, G.: Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmospheric Chemistry and Physics, 13, 5277-5298, Doi 10.5194/Acp-13-5277-2013, 2013.

Petrenko, V. V., Smith, A. M., Brailsford, G., Riedel, K., Hua, Q., Lowe, D., Severinghaus, J. P., Levchenko, V., Bromley, T., Moss, R., Muhle, J., and Brook, E. J.: A new method for analyzing C-14 of methane in ancient air extracted from glacial ice, Radiocarbon, 50, 53-73, 2008.

Petrenko, V. V., Severinghaus, J. P., Schaefer, H., Smith, A. M., Kuhl, T., Baggenstos, D., Hua, Q., Brook, E. J., Rose, P., Kulin, R., Bauska, T., Harth, C., Buizert, C., Orsi, A., Emanuele, G., Lee, J. E., Brailsford, G., Keeling, R., and Weiss, R. F.: Measurements of C-14 in ancient ice from Taylor Glacier, Antarctica constrain in situ cosmogenic (CH4)-C-14 and (CO)-C-14 production rates, Geochimica Et Cosmochimica Acta, 177, 62-77, 10.1016/j.gca.2016.01.004, 2016.

Petrenko, V. V., Smith, A. M. S., Schaefer, H. S., Riedel, K., Brook, E., Baggenstos, D., Harth, C., Hua, Q., Buizert, C., Schilt, A., Fain, X., Mitchell, L., Bauska, T., Orsi,

A., Weiss, R. F., and Everinghaus, J. P. S.: Minimal geological methane emissions during the Younger Dryas-Preboreal abrupt warming event, Nature, 548, 443-446, 10.1038/nature23316, 2017.

Poluianov, S.V., Kovaltsov, G.A., Mishev, A.L., and Usoskin, I.G.: 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, 121, 8125-8136, 2016.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R. H. J., Porter, L., and Miller, B. R.: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, Science, 292, 1882-1888, 2001.

Pupek, M., Assonov, S. S., Muhle, J., Rhee, T. S., Oram, D., Koeppel, C., Slemr, F., and Brenninkmeijer, C. A. M.: Isotope analysis of hydrocarbons: trapping, recovering and archiving hydrocarbons and halocarbons separated from ambient air, Rapid Communications in Mass Spectrometry, 19, 455-460, 2005.

Quay, P., King, S., White, D., Brockington, M., Plotkin, B., Gammon, R., Gerst, S., and Stutsman, J.: Atmospheric 14CO: A tracer of OH concentration and mixing rates, Journal of Geophysical Research, 105, 15147-15166, 2000.

Rigby, M., Prinn, R., O'Doherty, S., Montzka, S. A., McCulloch, A., Harth, C., Muhle, J., Salameh, P., Weiss, R., Young, D., Simmonds, P., Hall, B., Dutton, G. S., Nance, D., Mondeel, D. J., Elkins, J. W., Krummel, P., Steele, L. P., and Fraser, P. J.: Re-evaluation of the lifetimes of the major CFCs and CH3CCl3 using atmospheric trends, Atmospheric Chemistry and Physics, 13, 2691–2702, 2013.

Rigby, M., Montzka, S. A., Prinn, R., White, J. W. C., Young, D., O'Doherty, S., Lunt, M. F., Ganesan, A. L., Manning, A. J., Simmonds, P., Salameh, P., Harth, C., Muhle, J., Weiss, R., Fraser, P., Steele, L. P., Krummel, P., McCulloch, A., and Park, S.: Role of atmospheric oxidation in recent methane growth, Proceedings of the National Academy of Sciences of the United States of America, 114, 5373–5377, 2017.

Röckmann, T., Jöckel, P., Gros, V., Braunlich, M., Possnert, G., and Brenninkmeijer, C. A. M.: Using C-14, C-13, O-18 and O-17 isotopic variations to provide insights

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, Font color: Text 1

Formatted: Font color: Text 1

into the high northern latitude surface CO inventory, Atmospheric Chemistry and Physics, 2, 147-159, 2002.

Smith, A. M., Hua, Q., Williams, A., Levchenko, V., and Yang, B.: Developments in micro-sample C-14 AMS at the ANTARES AMS facility, Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 268, 919-923, 10.1016/j.nimb.2009.10.064, 2010.

Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., Foreman-Fowler, M., Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, Journal of Geophysical Research, 105, 8931-8980, 2000.

Stuiver, M., and Polach, H. A.: Reporting of C-14 Data - Discussion, Radiocarbon, 19, 355-363, 1977.

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

Vimont, I. J., Turnbull, J. C., Petrenko, V. V., Place, P. F., Karion, A., Miles, N. L., Richardson, S. J., Gurney, K., Patarasuk, R., Sweeney, C., Vaughn, B., and White, J. W. C.: Carbon monoxide isotopic measurements in Indianapolis constrain urban source isotopic signatures and support mobile fossil fuel emissions as the dominant wintertime CO source, Elementa – Science of the Anthropocene, 5, ARTN 63, 10.1525/elementa.136, 2017.

Volz, A., Ehhalt, D. H., and Derwent, R. G.: Seasonal and Latitudinal Variation of 14CO and the Tropospheric Concentration of OH Radicals, Journal of Geophysical Research, 86, 5163-5171, 1981.

Voulgarakis, A., Naik, V., Lamarque, J. F., Shindell, D. T., Young, P. J., Prather, M. J., Wild, O., Field, R. D., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsoren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Folberth, G. A., Horowitz, L. W., Josse, B., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Stevenson, D. S., Strode, S. A., Sudo, K., Szopa, S.,

Deleted: ¶

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, Font color: Auto

Formatted: Font: (Default) Times New Roman

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, Font color: Auto

Formatted: Font: (Default) Times New Roman

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, Font color: Auto

Formatted: Font: (Default) Times New Roman

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, Font color: Auto

Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, Font color: Auto

Formatted: Check spelling and grammar

Deleted: -

and Zeng, G.: Analysis of present day and future OH and methane lifetime in the ACCMIP simulations, Atmospheric Chemistry and Physics, 13, 2563-2587, Doi 10.5194/Acp-13-2563-2013, 2013.

Wacker, L., Bollhalder, S. Sookdeo, A., and Synal, H.A.: Re-valuation of the new oxalic acid standard with AMS, Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 455, 178-180, 10.1016/j.nimb.2018.12.035, 2019.

Weinstock, B.: Carbon Monoxide - Residence Time in Atmosphere, Science, 166, 224-225, DOI 10.1126/science.166.3902.224, 1969.

Yang, B., and Smith, A. M.: Conventionally Heated Microfurnace for the Graphitization of Microgram-Sized Carbon Samples, Radiocarbon, 59, 859-873, 10.1017/Rdc.2016.89, 2017.

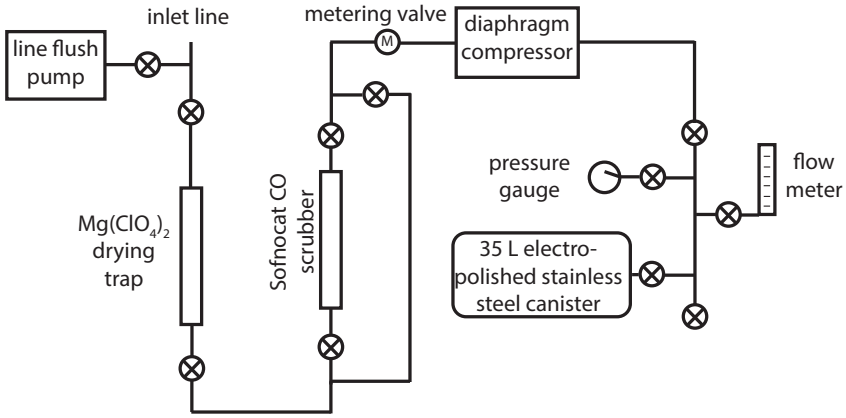


Figure 1. Schematic of the new atmospheric ^{14}CO sampling system deployed at the Mauna Loa Observatory. An "X" within a circle denotes a valve (Swagelok, 4H bellows-sealed).

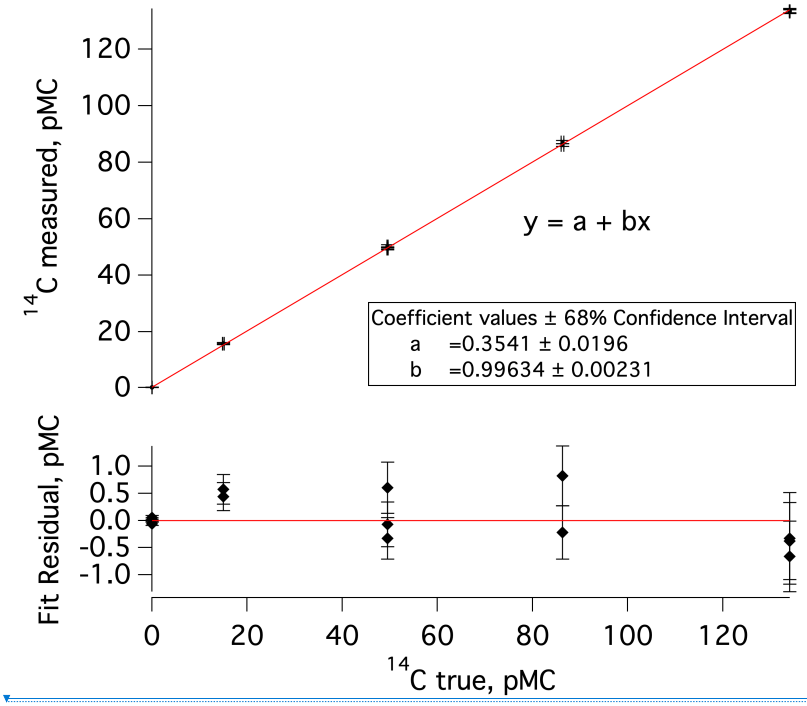
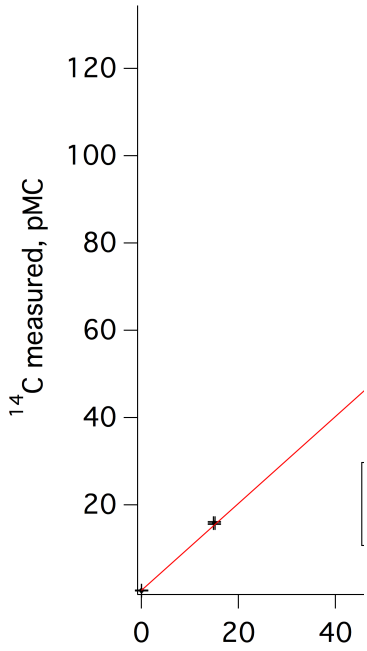


Figure 2. Top: a plot of measured versus true (accepted) ^{14}C values for commensurately-sized ^{14}C standards and blanks that were processed at ANSTO concurrently with the second set of MLO ^{14}CO samples and blanks (Samples 7 – 18 in Table S1 and Blanks 3 – 6 in Table S2). The data point clusters, going from left to right, represent a previously-characterized cylinder of ^{14}C-depleted CO_2 (^{14}C true = 0.03 pMC), IAEA-C8 (^{14}C true = 15.03 ± 0.17 pMC; Le Clercq et al., 1998), IAEA-C7 (^{14}C true = 49.53 ± 0.12 pMC; Le Clercq et al., 1998), a second previously-characterized cylinder of CO_2 (^{14}C true = 86.27 pMC) and HOxII (^{14}C true = 134.06 ± 0.04 pMC; Wacker et al., 2019 and references therein). Bottom: residuals from the linear fit in the upper plot; error bars represent uncertainty in ^{14}C measured.

Deleted:



Deleted: A

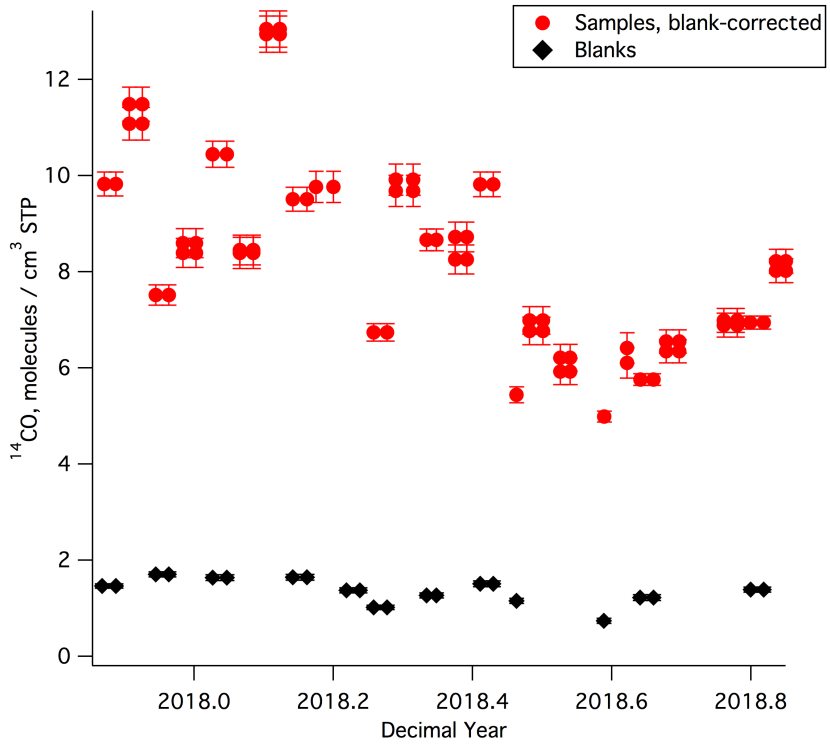


Figure 3. [^{14}CO] results for all MLO samples and blanks. Most samples and blanks were collected by half-filling the canisters on 2 separate days. To illustrate this, [^{14}CO] values for these samples and blanks are plotted for each of these dates, appearing twice as adjacent data points. All shown [^{14}CO] uncertainties are 1 σ. We observed a correlation for sample – blank pairs collected on the same days. This correlation is not due to analytical artifacts and is discussed in detail in the Supplement.

Sample subset 1	N	Mean 1 σ uncertainty, as % of value	Sample subset 2	N	Mean 1 σ uncertainty, as % of value	Can null hypothesis be rejected at 5% significance level?	p
All ≈22 µgC	25	3.3	All ≈50 µgC	11	3.4	NO	0.72
All accompanied by blanks	11	2.5	All not accompanied by blanks	25	3.7	YES	1.2×10^{-6}
≈22 µgC not accompanied by blanks	17	3.6	≈50 µgC not accompanied by blanks	8	3.9	NO	0.29
≈22 µgC accompanied by blanks	8	2.7	≈50 µgC accompanied by blanks	3	2.1	YES	8.4×10^{-4}
≈22 µgC not accompanied by blanks	17	3.6	≈22 µgC accompanied by blanks	8	2.7	YES	7.4×10^{-5}
≈50 µgC not accompanied by blanks	8	3.9	≈50 µgC accompanied by blanks	3	2.1	YES	4.9×10^{-3}

Table 1. Results of a two-sample t-test investigating the effects of measured sample mass, whether the sample was accompanied by a blank, or both on the final relative uncertainty in the determined sample [^{14}CO] value. N is the number of samples in a particular subset. The null hypothesis is that the two subsets being compared are drawn from populations with equal means. The null hypothesis is rejected (i.e., the t-test indicates that the means of the subsets are significantly different) if the probability (p) of the observed subsets occurring when the underlying populations have equal means is less than 0.05 (< 5%).