Supplement of Atmos. Meas. Tech., 14, 2055–2063, 2021
https://doi.org/10.5194/amt-14-2055-2021-supplement

Atmospheric Measurement Techniques
Open Access
EGU

Supplement of

An improved method for atmospheric ^{14}CO measurements

Vasilii V. Petrenko et al.

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

This Supplement contains:

Discussion of possible effects of outgassing and "memory" from sample canisters on blank ^{14}CO
Discussion of the observed correlation of ^{14}CO values for sample-blank pairs
Figures S1 and S2
Tables S1 and S2
References

Discussion of possible effects of outgassing and "memory" from sample canisters on blank ^{14}CO

The CO mole fraction measured in the blanks is consistently low at 3.7 ± 1.8 (1σ) nmol mol^{-1} (Table S2, Figure S2). This CO could in principle arise from outgassing from the sampling pump, the canisters or from canister "memory". In the case that this CO is due to outgassing, even if this CO is fully "modern" with a ^{14}C activity of ≈100 pMC, this would translate to 0.12 ^{14}CO molecules / cm^3 STP – an order of magnitude lower than the observed blank ^{14}CO values and more than 2 times lower than the standard deviation observed for blank ^{14}CO values (Table S2). CO from outgassing therefore cannot explain either the blank ^{14}CO values or their variability.

We also considered whether canister memory from the previous sample could potentially affect the measured blank ^{14}CO values. Following 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. The ^{14}C activity of CO in diluted 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. This is again much smaller than the observed blank ^{14}CO values and variability (Table S2). Further, the CO mole fractions observed in the blanks are consistent with values expected from combined CO outgassing by the KNF N145 pump and the sample canisters. Canister memory therefore does not significantly affect the blank ^{14}CO values.

Discussion of the observed correlation of ^{14}CO values for sample-blank pairs

A correlation is observed between blank-corrected ^{14}CO values in the samples and ^{14}CO values in the blanks collected on the same days (Figures 3 and S1). One analytical problem that could in principle result in such a correlation would be a failure of the Sofnocat 423 reagent (see Figure 1) 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 that is not positively correlated to the CO mole fraction in the samples collected on the same days (see Figure S2 and Table S2).

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 (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 (sample processed after another sample – sample processed after a blank) 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 previous 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. Unfortunately, we do not at this point have a clear explanation for the correlation. We speculate that that this may be 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 test this hypothesis.

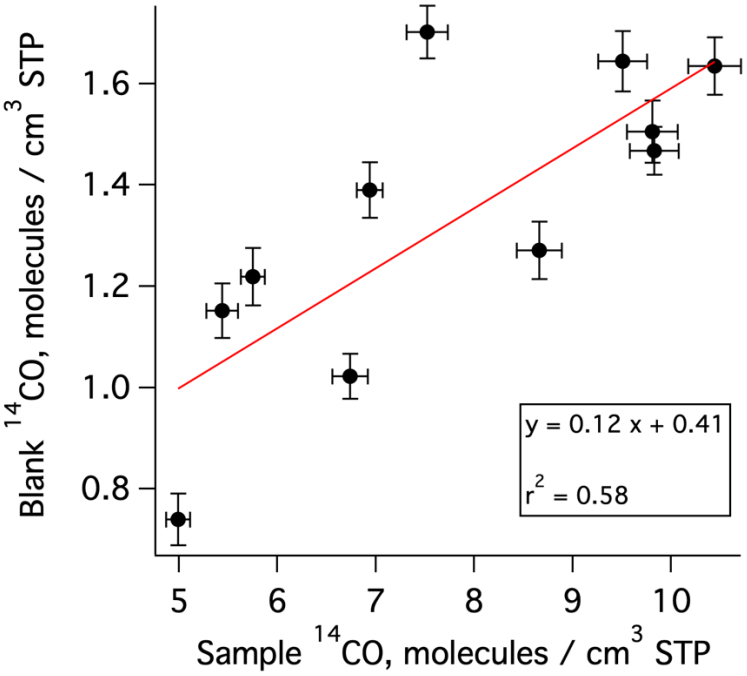

Figure S1. Observed ^{14}CO correlation for blank-sample pairs collected on the same days and analyzed as part of the Mauna Loa ^{14}CO campaign. This correlation appears to be significant, with a p value of 0.007.

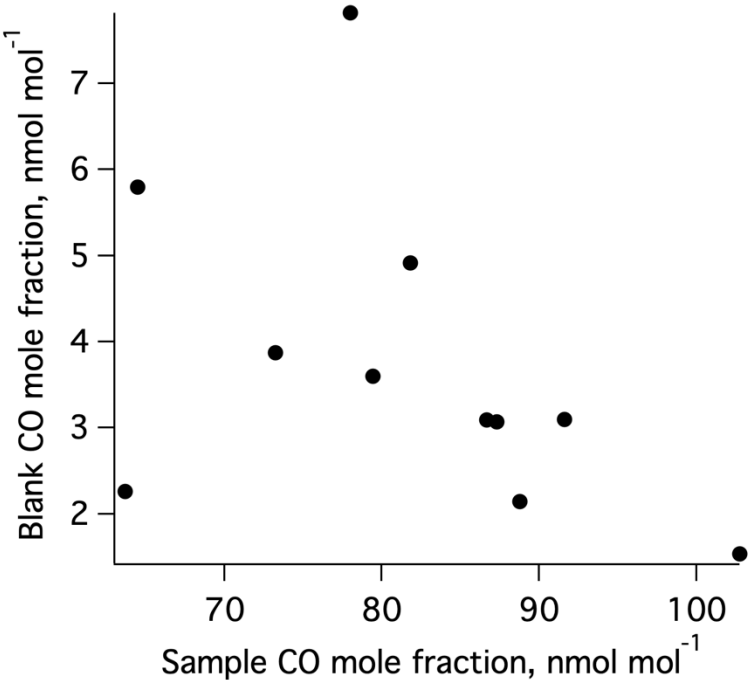

Figure S2. Comparison of measured CO mole fraction for blank-sample pairs collected on the same days and analyzed as part of the Mauna Loa ^{14}CO campaign. In this case the correlation does not appear to be significant, with a p value of 0.17.

Sample number	First sampling date, mo/day/yr	Second sampling date, mo/day/yr	CO mole fraction, nmol mol^{-1}	Sample mass, µg C	^{14}CO, molecules / cc STP	Error
Sample 1	11/14/17	11/21/17	88.8	21.8	9.83	0.25
Sample 2	11/28/17	12/4/17	96.9	22.6	11.48	0.36
Sample 3	11/28/17	12/5/17	95.1	22.0	11.08	0.34
Sample 4	12/12/17	12/19/17	81.8	21.6	7.52	0.21
Sample 5	12/26/17	1/2/18	83.4	21.6	8.60	0.30
Sample 6	12/26/17	1/2/18	85.9	21.8	8.39	0.30
Sample 7	1/11/18	1/18/18	102.8	22.2	10.44	0.27
Sample 8	1/25/18	2/1/18	83.4	22.1	8.45	0.31
Sample 9	1/25/18	2/1/18	83.5	21.7	8.39	0.32
Sample 10	2/8/18	2/15/18	99.0	23.1	12.94	0.38
Sample 11	2/8/18	2/15/18	99.9	21.8	13.04	0.38
Sample 12	2/22/18	3/1/18	91.6	22.1	9.51	0.25
Sample 14	3/6/18	3/15/18	94.1	21.4	9.76	0.32
Sample 16	4/5/18	4/12/18	78.0	21.9	6.74	0.18
Sample 17	4/17/18	4/26/18	96.7	22.4	9.92	0.32
Sample 18	4/17/18	4/26/18	96.1	21.4	9.68	0.32
Sample 19	5/3/18	5/8/18	87.3	21.9	8.66	0.23
Sample 20	5/18/18	5/24/18	86.5	21.7	8.25	0.30
Sample 21	5/18/18	5/24/18	89.5	21.4	8.72	0.31
Sample 22	5/31/18	6/7/18	86.7	22.1	9.81	0.26
Sample 23	6/19/18	N/A	73.3	21.5	5.44	0.16
Sample 24	6/26/18	7/3/18	75.5	20.9	6.99	0.29
Sample 25	6/26/18	7/3/18	73.2	20.8	6.77	0.28
Sample 26	7/12/18	7/17/18	71.3	21.2	5.92	0.27
Sample 27	7/12/18	7/17/18	70.7	20.6	6.21	0.28
Sample 28	8/2/18	N/A	64.5	50.4	4.99	0.12
Sample 29	8/14/18	N/A	80.3	50.6	6.11	0.32
Sample 30	8/14/18	N/A	81.9	50.4	6.41	0.31
Sample 31	8/21/18	8/28/18	63.7	49.3	5.75	0.12
Sample 32	9/4/18	9/11/18	66.5	48.3	6.35	0.24
Sample 33	9/4/18	9/11/18	66.6	49.7	6.55	0.24
Sample 35	10/4/18	10/11/18	85.1	52.0	6.89	0.25
Sample 36	10/4/18	10/11/18	85.7	49.7	6.98	0.25
Sample 37	10/18/18	10/25/18	79.4	49.8	6.94	0.13
Sample 38	11/1/18	11/6/18	78.2	50.0	8.22	0.25
Sample 39	11/1/18	11/6/18	78.5	48.2	8.02	0.25

Table S1. Summary of all successfully measured MLO ^{14}CO samples. Samples with "N/A" indicated for second sampling date were collected in a single session. Uncertainty estimated for the CO mole fraction measurements (as a combination of calibration uncertainty and measurement reproducibility) is 2 nmol mol^{-1}. Sample carbon mass is as determined at ANSTO. Blank-corrected ^{14}CO values are shown. Errors shown for ^{14}CO are 1 σ. Based on ^{14}CO and CO mole fraction values, we suspect that Samples 13 and 15 were accidentally switched during processing; these samples are therefore not included. Sample 34 was lost due to a procedural error.

Blank Number	First sampling date, mo/day/yr	Second sampling date, mo/day/yr	CO mole fraction, nmol mol^{-1}	Sample mass, µg C	^{14}CO, molecules / cc STP	Error
Blank 1	11/14/17	11/21/17	2.1	18.4	1.47	0.05
Blank 2	12/12/17	12/19/17	4.9	18.3	1.70	0.05
Blank 3	1/11/18	1/18/18	1.5	20.0	1.64	0.06
Blank 4	2/22/18	3/1/18	3.1	20.2	1.64	0.06
Blank 5	3/22/18	3/29/18	5.0	18.5	1.38	0.05
Blank 6	4/5/18	4/12/18	7.8	18.8	1.02	0.04
Blank 7	5/3/18	5/8/18	3.1	18.9	1.27	0.06
Blank 8	5/31/18	6/7/18	3.1	18.0	1.51	0.06
Blank 9	6/19/18	N/A	3.9	18.3	1.15	0.05
Blank 10	8/2/18	N/A	5.8	49.4	0.74	0.05
Blank 11	8/21/18	8/28/18	2.3	50.0	1.22	0.06
Blank 13	10/18/18	10/25/18	3.6	49.2	1.39	0.06

Table S2. Summary of all successfully measured MLO ^{14}CO blanks. Blanks with "N/A" indicated for second sampling date were collected in a single session. Uncertainty estimated for the CO mole fraction measurements (as a combination of calibration uncertainty and measurement reproducibility) is 2 nmol mol^{-1}. Sample carbon mass is as determined at ANSTO. Errors shown for ^{14}CO are 1 σ. Blank 12 was lost due to a procedural error.

References

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.

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