COMPARISON OF INDEPENDENT $\Delta^{14}CO_2$ RECORDS AT POINT BARROW, ALASKA

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ABSTRACT. Two independent programs have collected and analyzed atmospheric CO_2 samples from Point Barrow, Alaska, for radiocarbon content ($\Delta^{14}C$) over the period 2003–2007. In one program, flask collection, stable isotope analysis, and CO_2 extraction are performed by the Scripps Institution of Oceanography's CO_2 Program and CO_2 is graphitized and measured by accelerator mass spectrometry (AMS) at Lawrence Livermore National Laboratory. In the other program, the University of California, Irvine, performs flask collection, sample preparation, and AMS. Over 22 common sample dates spanning 5 yr, differences in measured $\Delta^{14}C$ are consistent with the reported uncertainties and there is no significant bias between the programs.

INTRODUCTION

A standard method to assess the comparability of radiocarbon laboratories is to distribute common materials for independent processing and analysis at each laboratory (Polach 1989; Scott 2003), including CO_2 in dry air (Miller et al. 2011, 2013). For laboratories analyzing ^{14}C content ($\Delta^{14}C$) in atmospheric CO_2, a more complete intercomparison is possible using duplicate atmospheric samples collected at the same location and time. This allows for comparing all factors influencing the measurements, including sampling, storage, processing, and analysis. Such co-located sampling programs have been utilized for assessing comparability of laboratories measuring the concentration of atmospheric CO_2 and other atmospheric compounds (Hudec and Trivett 1997; Masarie et al. 2001), but they have not yet been employed for $\Delta^{14}C$ in CO_2 measured by accelerator mass spectrometry (AMS).

Here, we compare 2 independent measurement programs for $\Delta^{14}C$ in CO_2 at Point Barrow, Alaska. One program is run by a collaboration between the Scripps Institution of Oceanography and Lawrence Livermore National Laboratory (SIO/LLNL) and the other program is run by the University of California, Irvine (UCI). The programs employ whole air flask sampling, CO_2 extraction and graphitization, and AMS using slightly different techniques described below.

Our analysis focuses on a statistical comparison of $\Delta^{14}C$ measurements on groups of samples that were collected on the same date by both programs. We determine whether the differences in $\Delta^{14}C$ are commensurate with the reported measurement uncertainties and evaluate the data for any consistent bias in $\Delta^{14}C$ between the 2 programs.

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Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 1541–1545

https://doi.org/10.1017/S0033822200048463 Published online by Cambridge University Press

METHODS

SIO/LLNL Measurements

The Scripps CO_2 Program collects whole air samples at Point Barrow using 5-L glass flasks that have been pre-evacuated at SIO (Keeling et al. 2001). Flasks are filled to atmospheric pressure by opening a single glass stopcock sealed with Apiezon® grease. CO_2 concentration is measured in the flask at SIO and then CO_2 is extracted cryogenically from a portion of the remaining air and sealed in Pyrex® tubes. Each sample is approximately 0.5 mg C in size.

At LLNL, CO_2 samples are converted to graphite by reducing with H_2 gas over an iron catalyst and then measured by AMS (Graven et al. 2007; Graven 2008). Measurements are reported as $\Delta^{14}C$ (equivalent to Δ in the work by Stuiver and Polach [1977]), where $\delta^{13}C$ measurements from concurrent samples (Keeling et al. 2001) are used to correct for mass dependent fractionation. Total measurement uncertainty for $\Delta^{14}C$ in CO_2 is ±1.7–2.8‰ (Graven et al. 2007, 2012; Graven 2008).

UCI Measurements

The UCI program collects whole air samples at Point Barrow using 6-L, 1-valve stainless steel canisters (Silco Can, Restek Co.) that have been pre-evacuated at UCI (Xu et al. 2007a). The canisters are pressurized to ~2 atm using an oil-free pump (Tyler et al. 2007). For the period from 17 June 2005 to 17 March 2006, 6 air samples that are included in this study were collected using 32-L, 1-valve stainless steel canisters (Tyler et al. 2007). Subsamples were then taken from these samples for ^{14}C analysis. CO_2 is extracted cryogenically at UCI then converted to graphite by the sealed tube zinc reduction method (Xu et al. 2007b). Each sample is ~2.7 mg C in size. Analysis of $\Delta^{14}C$ is performed at the W M Keck AMS facility at UCI with total measurement uncertainty of ±1.3–2.4‰ (X Xu, unpublished data). Mass dependent fractionation is corrected for using "on-line" $\delta^{13}C$ measurements during AMS analysis, which accounts for fractionation that occurred during graphitization and inside the AMS.

Comparison of the Two Programs

The observations from SIO/LLNL and UCI overlap for the period 2003–2007, with 22 individual sample dates common to both programs (Figure 1). For 13 of the 22 sample dates, replicate samples were collected and analyzed for $\Delta^{14}C$ by the UCI program. No replicate observations were made by the SIO/LLNL program.

We compare the observations by first averaging any replicate measurements from UCI, then averaging the mean $\Delta^{14}C$ from UCI with the $\Delta^{14}C$ measured by SIO/LLNL. We calculate the residual by subtracting this overall mean from the $\Delta^{14}C$ measured by each program. The bias is given by the difference in the average residual for UCI and SIO/LLNL (μ_{UCI} and $\mu_{SIO/LLNL}$), which is compared to the standard error to assess significance.

Flasks from both programs are filled by NOAA personnel at the Point Barrow station, who check for clean air conditions prior to filling flasks for trace gas and isotope analyses. Most of the SIO and UCI flasks were collected within an hour of each other on each sample date, with sampling times between 8:00 and 15:30 local time. However, for 8 sample dates, indicated by empty symbols in Figure 1, the SIO flask was collected 4–6 hr later than the UCI flask(s). We also perform separate calculations of the bias for samples collected with larger time differences, in case the measurements are affected by natural daily variations.

https://doi.org/10.1017/S0033822200048463 Published online by Cambridge University Press

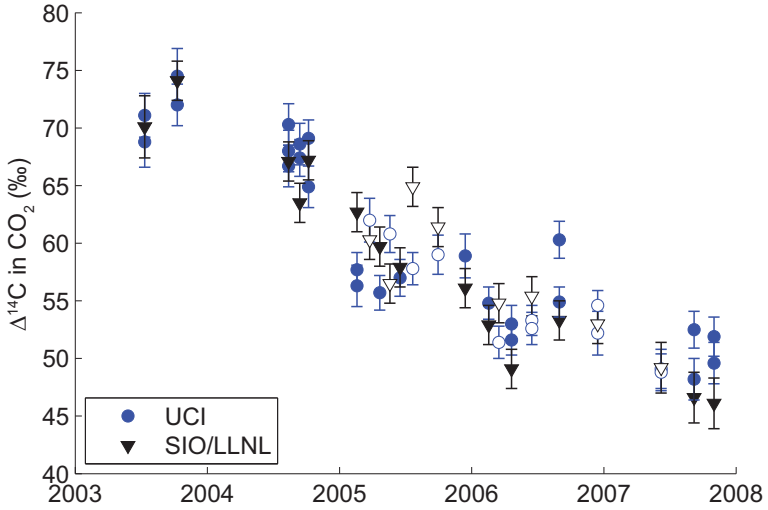


Figure 1 Observations of $\Delta^{14}CO_2$ at Point Barrow, Alaska, for sample dates in common from the SIO/LLNL and UCI measurement programs. Filled symbols indicate the UCI and SIO flasks were collected within 1 hr of each other, while empty symbols indicate the SIO flask was collected 4–6 hr later than the UCI flask on that date.

RESULTS

There is very good agreement between the $\Delta^{14}CO_2$ measurements from the SIO/LLNL and UCI programs at Point Barrow. The residual $\Delta^{14}C$ is within $\pm1\sigma$ for 60% of the sample dates, and within $\pm2\sigma$ for all but 1 sample date (Figure 2). For 5 of the 13 sample dates with replicate samples from UCI, the SIO/LLNL measurement was bracketed by the UCI measurements (Figure 1). Correspondence between the 2 laboratories is consistent with their average reported uncertainties of ±1.7‰.

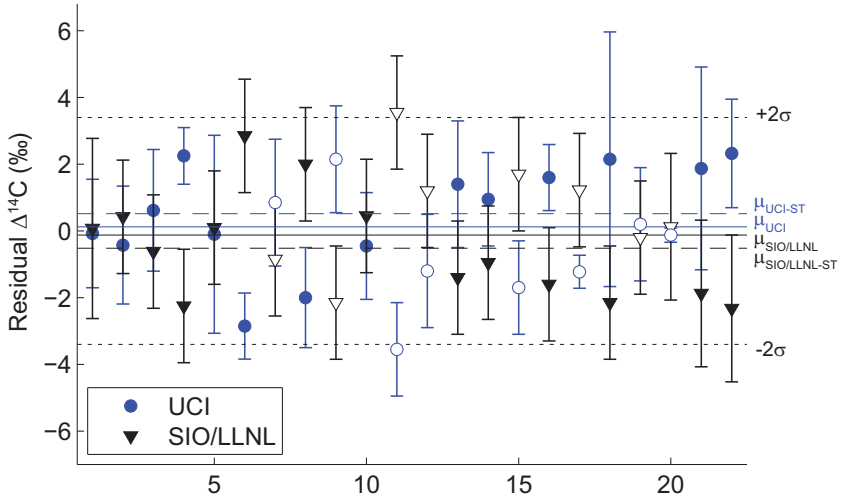


Figure 2 Residual $\Delta^{14}C$ for 22 individual sample dates. Replicate samples from UCI have been averaged. Error bars show the reported measurement uncertainty or, for UCI, the standard deviation in replicate measurements. The average residuals, μ_{UCI} and $\mu_{SIO/LLNL}$, are shown by solid lines. The average residuals for samples collected within 1 hr of each other only, $\mu_{UCI\text{-}ST}$ and $\mu_{SIO/LLNL\text{-}ST}$, are shown by dashed lines. Dotted lines show a $\pm2\sigma$ envelope around the average reported uncertainty of ±1.7‰.

https://doi.org/10.1017/S0033822200048463 Published online by Cambridge University Press

There is no significant bias between the 2 programs. The difference in the average residuals is 0.2 ± 0.7‰ for UCI compared to SIO/LLNL (Figure 2, Table 1). Including only the samples collected with 1 hr of each other increases the mean bias to 1.0‰, but it remains similar to the standard error of ±0.9‰. Likewise, the mean bias in the samples collected more than 4 hr apart is not significantly different from zero (–1.2 ± 1.3‰, Table 1).

Diurnal variations of $\Delta^{14}C$ have not been characterized at Point Barrow, but observations of CO_2 concentration vary by only ±0.4 ppm between the morning and afternoon (Thoning et al. 2012). Making the extreme assumption that this variation was due to ^{14}C-free CO_2, this would cause $\Delta^{14}C$ to vary by only ±1‰, which we can take as an upper bound to the corresponding $\Delta^{14}C$ variability. Our observations also indicate that diurnal cycles in $\Delta^{14}C$ at Point Barrow are small, and that samples collected at different times of day are likely to have consistent $\Delta^{14}C$ values. A lack of diurnal variation reflects the remoteness of Point Barrow, differing from sampling stations located near local fossil fuel emission sources where $\Delta^{14}C$ is typically higher in the afternoon because of enhanced ventilation of emissions (Graven et al. 2009; Newman et al. 2012).

Table 1 Bias (UCI-SIO/LLNL) and standard error in all samples, in samples collected within 1 hr of each other and in samples collected more than 4 hr apart.

Group	Bias and standard error
All samples	0.2 ± 0.7‰
Collected within 1 hr	1.0 ± 0.9‰
Collected more than 4 hr apart	–1.2 ± 1.3‰

CONCLUSIONS

Our comparison shows there is no significant bias between measurements of $\Delta^{14}C$ in atmospheric CO_2 conducted by SIO/LLNL and UCI at Point Barrow. The 2 programs meet the ±1‰ criteria for comparability recommended by the World Meteorological Organization (WMO 2011). As SIO/LLNL and UCI both perform $\Delta^{14}C$ measurements at several other sites, this result suggests that observations from the 2 programs at other sites can be compiled and compared without adjustment of the reported data.

ACKNOWLEDGMENTS

We are grateful to NOAA and the Point Barrow field station personnel for collecting flask samples. Alane Bollenbacher performed stable isotopic analyses at SIO. A portion of this work was performed under the auspices of the US Department of Energy under contract DE-AC52-07NA27344.

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