COMPATIBILITY OF ATMOSPHERIC (CO2)-C-14 MEASUREMENTS

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Published in:
Proceedings of the 22nd International Radiocarbon Conference

DOI:
10.1017/RDC.2016.62

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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COMPATIBILITY OF ATMOSPHERIC $^{14}$CO$_2$ MEASUREMENTS: COMPARING THE HEIDELBERG LOW-LEVEL COUNTING FACILITY TO INTERNATIONAL ACCELERATOR MASS SPECTROMETRY (AMS) LABORATORIES

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10Earth System Science Department, University of California, Irvine, California 92612, USA.
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13National Institute for Environmental Studies, Tsukuba, Japan.

ABSTRACT. Combining atmospheric $\Delta^{14}$CO$_2$ data sets from different networks or laboratories requires secure knowledge on their compatibility. In the present study, we compare $\Delta^{14}$CO$_2$ results from the Heidelberg low-level counting (LLC) laboratory to 12 international accelerator mass spectrometry (AMS) laboratories using distributed aliquots of five pure CO$_2$ samples. The averaged result of the LLC laboratory has a measurement bias of $–0.3 \pm 0.5$‰ with respect to the consensus value of the AMS laboratories for the investigated atmospheric $\Delta^{14}$C range of 9.6 to 40.4‰. Thus, the LLC measurements on average are not significantly different from the AMS laboratories, and the most likely measurement bias is smaller than the World Meteorological Organization (WMO) interlaboratory compatibility goal for $\Delta^{14}$CO$_2$ of 0.5‰. The number of intercomparison samples was, however, too small to determine whether the measurement biases of the individual AMS laboratories fulfilled the WMO goal.

KEYWORDS: atmospheric radiocarbon, LLC, AMS, intercomparison.

INTRODUCTION

The Heidelberg global atmospheric $^{14}$CO$_2$ sampling network (Levin et al. 2010) is unique in terms of its spatial and temporal coverage. The tropospheric measurements cover the bomb peak in the Northern Hemisphere and have thus, among other reasons, become of major importance after other laboratories largely discontinued their global observations (e.g. Nydal and Lövseth 1983). Current $^{14}$CO$_2$ observations are not only used for global carbon cycle research (e.g. Levin and Kromer 2004; Naegler et al. 2006; Turnbull et al. 2009; Levin et al. 2010, 2013; Francey et al. 2013), but they are also applied in various other research disciplines. These range from firn core studies (e.g. Buizert et al. 2012), aerosol source attribution (e.g. Gelencsér et al. 2007), soil carbon turnover (e.g. Trumbore 1993; Lindahl et al. 2007), to neuroscience (e.g. Spalding et al. 2013) and forensics (e.g. Santos et al. 2015), just to name a few of the many applications.

The sampling strategy in the Heidelberg $^{14}$CO$_2$ network (i.e. weekly or biweekly integrated absorption of atmospheric CO$_2$ in NaOH solution) is similar for all stations and has remained...

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essentially unchanged since the inception of the network in 1959. A detailed description of the sampling procedures is available in Levin et al. (1980). All of the samples have been analyzed using gas proportional counting in the Heidelberg low-level laboratory. The counting facilities are described in depth by Kromer and Münnich (1992). These two constant features have been fundamental to achieving and maintaining highest intranetwork compatibility.

Over the last 2 decades, other global $^{14}$CO$_2$ networks and single stations (Turnbull et al. 2007; Graven et al. 2012) have become operational. All of these new data sets make use of accelerator mass spectrometry (AMS) analyses of whole air samples. Combining $^{14}$C data sets from different groups comprising different measurement techniques immediately raises the question of intertechnique and interlaboratory compatibility. This is especially crucial for atmospheric studies since the $^{14}$CO$_2$ gradients in background air are very small (Levin et al. 2010). The World Meteorological Organization–Global Atmosphere Watch (WMO-GAW) guidelines have therefore set a desired level of interlaboratory compatibility (ILC) of only 0.5‰ (WMO-GAW 2013). It should be noted that the compatibility goal refers to the averaged deviation between laboratories and not the uncertainty of individual samples.

Traditionally, $^{14}$C labs perform internal quality-control (QC) checks by measuring secondary standard reference materials, such as those provided by the IAEA (Rozanski et al. 1992). However, only a few laboratories make those QC results publicly available. In addition to the laboratory internal QC, the $^{14}$C community has a long tradition of performing intercomparison exercises. The most recent intercomparison was carried out from 2004 to 2008, called VIRI (Scott et al. 2007), with 70 participating labs. The $^{14}$C activities of the distributed materials ranged from 0 to 110 pMC. One aim of VIRI was to examine the effects of sample preparation for a range of materials to determine the amount of total variability that may be associated with pretreatment. For the samples with recent activity, an overall $1\sigma$ standard deviation of 25‰ was found (including all outliers). Comparing only the AMS laboratories resulted in much better compatibility of 5 to 6‰. This is due to the typical practice, when using AMS, of measurement and normalization to primary reference materials (typically OxI or OxII), in the same measurement sequence as the unknown samples. Counting techniques do not permit such within-run calibration and are instead dependent on careful periodic calibration (compare Kromer and Münnich 1992), which is subsequently interpolated to the point in time when the measurement of the unknown sample took place.

The atmospheric $^{14}$CO$_2$ community identified a need for an additional intercomparison program, which is more tailored towards ambient atmospheric activities and sample handling procedures. So far, two dedicated atmospheric intercomparisons have been published. Graven et al. (2013) made use of co-located sampling of two different sampling programs at Point Barrow, Alaska, testing thereby the entire data genesis from sampling through sample preparation and analysis. Graven et al. (2013) report on 22 samples (analyzed and pretreated in two independent AMS laboratories) with an overall agreement of the two data sets of 0.2 ± 0.7‰. This result is certainly remarkable and proves that the WMO-GAW interlaboratory compatibility goal is achievable. Since not all laboratories involved in atmospheric $^{14}$C measurement have access to co-located sampling, Miller et al. (2013) initiated a flask intercomparison program (ICP) for $^{14}$CO$_2$. In this program, the flasks of the participating laboratories are filled with atmospheric air from high-pressure cylinders. Miller et al. (2013) have so far accomplished three intercomparison rounds with eight participating laboratories. Three of the labs showed compatibility within 1‰ and four of them within 2‰. The Heidelberg LLC laboratory cannot participate in such flask ICP exercises since samples for low-level counting require around 20 m$^3$ of atmospheric air, greatly exceeding the available sample size of
those ICPs. Therefore, we were encouraged by the WMO-GAW community to undertake a focused ICP program that would link the Heidelberg LLC to state-of-the-art AMS laboratories. The results of this ICP are reported in the present paper; they are important for three reasons:

1. Comparing two independent and fundamentally different measurement techniques, which determine the same physical quantity, i.e. 14C activity, is essential and reassuring in itself.

2. The Heidelberg global 14CO2 network, for the sake of continuity, will carry on applying the same sampling and analysis techniques for the coming years. Therefore, secure constraints on possible interlaboratory deviations, at least for the analytical part, is vital when combining data sets from different networks in global 14CO2 assimilation models.

3. The Heidelberg radiocarbon laboratory was recently transferred into the ICOS Central Radiocarbon Laboratory (CRL) (www.icos-ri.eu), and plans to use both analytical techniques, LLC and AMS, to provide coherent information on European 14CO2 activities.

FIRST PURE CO2 INTERCOMPARISON EXERCISE

The ICOS CRL initiated a pure CO2 ICP exercise where 12 international AMS laboratories agreed to participate (see Table 1). We used five pure CO2 samples, which were analyzed by low-level counting, split volumetrically into 1-mg C aliquots and stored in break seals. In total, 20 aliquots of each pure CO2 sample were prepared and distributed among the participating AMS labs in a blind test (1 aliquot of each sample per lab). Some labs (e.g. lab 12) indicated interest in participating in the ICP only after the first results have been presented at conferences.

The five pure CO2 samples were selected to have recent atmospheric 14C activities and to span a considerable δ13C range as listed in Table 2. We chose one sample to be oxalic acid I (SRM 4990B) in order to provide one independent reference sample of known value. All labs reported

<table>
<thead>
<tr>
<th>Laboratory/Institution</th>
<th>Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHRONO Centre</td>
<td>Queen’s University, Belfast, UK</td>
</tr>
<tr>
<td>Center for Isotope Studies</td>
<td>University of Georgia, USA</td>
</tr>
<tr>
<td>Center for Atmospheric and Oceanic Studies &amp; Center for Chronological Research</td>
<td>Tohoku University, Sendai, Japan</td>
</tr>
<tr>
<td>Centre for Isotope Research (CIO)</td>
<td>&amp; Nagoya University, Nagoya, Japan</td>
</tr>
<tr>
<td>Centre for Accelerator Science</td>
<td>University of Groningen, the Netherlands</td>
</tr>
<tr>
<td>Curt-Engelhorn-Center for Archaeometrie (CEZA)</td>
<td>ANSTO, Lucas Heights, Australia</td>
</tr>
<tr>
<td>ICOS CRL (AMS sample preparation, with AMS analysis at CEZA)</td>
<td>Mannheim, Germany</td>
</tr>
<tr>
<td>ICOS CRL LLC</td>
<td>University of Heidelberg, Germany</td>
</tr>
<tr>
<td>INSTAAR &amp; UCI</td>
<td>University of Colorado, Boulder, CO, USA &amp; University of California, Irvine, CA, USA</td>
</tr>
<tr>
<td>LARA AMS Laboratory</td>
<td>University of Bern, Switzerland</td>
</tr>
<tr>
<td>NIES-TERRA AMS facility</td>
<td>Ibaraki, Japan</td>
</tr>
<tr>
<td>Rafter Radiocarbon Laboratory</td>
<td>GNS Science, Lower Hutt, New Zealand</td>
</tr>
<tr>
<td>University of Helsinki AMS facility</td>
<td>University of Helsinki, Finland</td>
</tr>
</tbody>
</table>
\[ \Delta^{14}C(\text{%e}) = \left\{ \left( \frac{R_{\text{sam}}}{R_{\text{ref}}} \right) \left( \frac{1 + \frac{25}{1000}}{1 + \frac{\delta^{13}C_{\text{sam}}}{1000}} \right)^2 e^{\lambda(1950-t)} \right\} - 1 \} \cdot 1000 \] (1)

where \( R \) denotes the ratio of \(^{14}C \) to C in the sample or the reference, \( t \) is the date of sample collection, and \( \delta^{13}C_{\text{sam}} \) is the \(^{13}C/^{12}C \) ratio of the sample with respect to VPDB scale. Note that this \( \Delta^{14}C \) definition is equivalent to the definition of \( \Delta \) in Stuiver and Polach (1977).

### RESULTS

The main focus of this study is to determine the compatibility of the Heidelberg LLC with the international AMS laboratories performing atmospheric \(^{14}CO_2 \) measurements. Moreover, we can investigate whether such an ICP exercise is also suitable to further evaluate the 0.5\( \text{%e} \) WMO-GAW interlaboratory compatibility goal among the individual AMS labs. Some labs have reported issues with processing the pure \( CO_2 \) aliquots. A common problem was the apparently large size of the break seals, requiring modification of vacuum-sealed crackers and/or splitting of samples. Table 3 summarizes the reported problems in the different laboratories.

We followed a two-stage data evaluation approach. First, the medians for all samples were calculated using data from all AMS laboratories. According to those median values, the reduced \( \chi^2_{\text{red}} \) (see Table 4) was calculated for each laboratory according to Equation 2:

\[ \chi^2_{\text{red}} = \frac{\chi^2}{N-1} = \frac{1}{N-1} \cdot \sum_{i=1}^{n} \frac{(x_i - \bar{x}_i)^2}{\sigma_i^2} \] (2)

where \( x_i \) and \( \sigma_i \) denote the individual measurement and its reported 1\( \sigma \) uncertainty, \( \bar{x}_i \) is the median of all laboratories for sample \( i \), and \( N \) is the total number of analyzed aliquots per sample. Based on this preliminary evaluation, three laboratories (labs 3, 6, and 11) showed very large reduced \( \chi^2 \) values (>6), indicating that the spread in their results is not compatible with the provided measurement uncertainties (likelihood <1\%). Therefore, the results of those labs have been excluded in the calculation of the consensus values for the five samples.
In the second step, we calculated the consensus values (i.e. weighted means, compare Equation 3) for each of the five CO$_2$ samples based on the results of the remaining AMS laboratories excluding lab 3, 6, and 11. The weight of each measurement was chosen as inverse of its squared uncertainty. The uncertainty of the consensus value was calculated according to Equation 4:

\[
\bar{x} = \frac{\sum_{i=1}^{n} (x_i \sigma_i^{-2})}{\sum_{i=1}^{n} \sigma_i^{-2}} \\
\sigma_{\bar{x}}^2 = \frac{1}{\sum_{i=1}^{n} \sigma_i^{-2}}
\] (3) (4)

Table 3 Remarks and problems with the ICP samples as reported by the laboratories.

<table>
<thead>
<tr>
<th>Lab code</th>
<th>Problems/Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>Break seals too large, new cracker built. Broad gas chromatographic peaks in elemental analyzer combustion for the standards. $\delta^{13}C$ could not be measured with AMS at this point.</td>
</tr>
<tr>
<td>4</td>
<td>Split aliquot amount into two halves and prepared two targets each. The two sets of targets were analyzed 1 month apart.</td>
</tr>
<tr>
<td>5</td>
<td>Aliquot size was too big; thus, the target of sample 30993 might have overheated in the AMS source. Remaining aliquots where split in half prior to graphitization.</td>
</tr>
<tr>
<td>6</td>
<td>Sample 30874 was apparently insufficiently graphitized and the entire AMS was under repair after a large earthquake.</td>
</tr>
<tr>
<td>7 to 12</td>
<td>None</td>
</tr>
</tbody>
</table>

Table 4 Measurement bias (i.e. mean difference of measured $\Delta^{14}C$ minus consensus value for all five CO$_2$ samples) and respective uncertainties given as standard error of the mean. In addition, the reduced $\chi^2$ values are listed, based on the consensus value and the median (see text for explanation). Results from laboratories marked by an asterisk have not been included in the calculation of the consensus value.

<table>
<thead>
<tr>
<th>Lab code</th>
<th>Measurement bias (%(\Delta^{14}C))</th>
<th>Error of the measurement bias (%(\Delta^{14}C))</th>
<th>Reduced $\chi^2$ based on consensus value</th>
<th>Reduced $\chi^2$ based on median</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLC</td>
<td>-0.3</td>
<td>0.5</td>
<td>0.4</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.7</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>0.1</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>3*</td>
<td>-2.9</td>
<td>2.4</td>
<td>11.6</td>
<td>13.3</td>
</tr>
<tr>
<td>4a</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>4b</td>
<td>1.4</td>
<td>1.2</td>
<td>2.2</td>
<td>1.6</td>
</tr>
<tr>
<td>5</td>
<td>-1.4</td>
<td>1.1</td>
<td>1.9</td>
<td>2.8</td>
</tr>
<tr>
<td>6*</td>
<td>-12.0</td>
<td>9.0</td>
<td>45.4</td>
<td>44.8</td>
</tr>
<tr>
<td>7</td>
<td>1.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>8</td>
<td>-2.9</td>
<td>1.6</td>
<td>4.7</td>
<td>5.9</td>
</tr>
<tr>
<td>9</td>
<td>0.7</td>
<td>2.3</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>10</td>
<td>1.6</td>
<td>0.6</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>11*</td>
<td>7.3</td>
<td>1.6</td>
<td>15.4</td>
<td>13.6</td>
</tr>
<tr>
<td>12</td>
<td>-1.8</td>
<td>0.7</td>
<td>1.3</td>
<td>1.7</td>
</tr>
</tbody>
</table>
The differences between the individual aliquot measurements and the respective consensus values were calculated for all labs, including the LLC laboratory. The uncertainty of the difference is the propagation of the uncertainty of the consensus value and the measurement error in quadrature. Figure 1 shows the deviations of all laboratories to the consensus value (of this study) for the OxI sample, which is $40.4 \pm 0.7\%e$ (normalized to $\delta^{13}C = -25\%e$). The uncertainty of the consensus value is represented as the gray shaded area in Figure 1. Comparing our consensus value to the nominal value of OxI, which is $39.8\%e$ (normalized to $\delta^{13}C = -25\%e$) (red dashed line in Figure 1), shows that it is accurate within its $1\sigma$ uncertainty.

A similar evaluation for all five samples is shown in Figure 2, summarizing all results of the pure CO$_2$ ICP samples. The averaged differences of all five samples from the consensus values is defined as measurement bias of the individual laboratory. The uncertainty of the measurement bias is calculated as the standard error of the mean difference. The LLC measurement bias is $-0.3 \pm 0.5\%e$ and is thus not significant. The measurement biases for the individual laboratories along with their uncertainties and the reduced $\chi^2$ values based on the consensus value (calculated according to Equation 2, replacing the median with the consensus value) are also given in Table 4. Considering the uncertainty of the measurement bias of each AMS lab, which describes how well the measurement bias can be known from five samples, it is evident that the number of samples used in this exercise is too low to determine whether the 0.5\%e interlaboratory compatibility (ILC) goal is met by each AMS laboratory. Assuming a 2\%e measurement uncertainty, approximately 50 samples would be needed for reducing the
error of the measurement bias to better than 0.3‰ (assuming Gaussian distributions). As highlighted by the results of lab 4, which had prepared duplicate sets of AMS targets, measured 1 month apart, the temporal variability within a laboratory needs also to be considered. Although our study has too little statistical significance to judge regarding the 0.5‰ ILC goal, we can still conclude that the measurement bias of three AMS labs is within 1‰ and for six labs within 2‰.

**CONCLUSIONS**

In this study, we prepared aliquots of five pure CO₂ samples, which have been analyzed for ¹⁴C activity by low-level counting and by 12 labs by AMS. The averaged LLC result agrees well with the overall averaged AMS results to within −0.3 ± 0.5‰. Thus, the most likely LLC measurement bias accomplishes the WMO-GAW interlaboratory compatibility goal. However, taking into account the uncertainty of the individual ¹⁴C analyses, and thus the resulting uncertainty of the measurement bias, the number of samples was too small to determine whether the LLC nor the individual AMS laboratories met the Δ¹⁴CO₂ compatibility goal. We plan to address this shortcoming in a second pure CO₂ ICP round in the near future, in which 10 aliquots for each of the five samples will be distributed to each laboratory. This should provide the statistics needed to address whether the 0.5‰ ILC goal is satisfied by the individual AMS labs. However, since a significant amount of work is associated to prepare this large quantity of aliquots, the number of participating labs will be reduced to those performing
atmospheric background $^{14}$CO$_2$ observations. Note that the ultimate aim of this exercise is to merge individual data sets from different labs, thus providing optimum benefit for global carbon cycle research.

**ACKNOWLEDGMENTS**

We are deeply indebted to Ingeborg Levin who initiated, pushed forward and greatly supported this study. This work would also not have been possible without the help of Sabine Kühr and Eva Gier, technicians at the ICOS CRL lab, who prepared the aliquots for the ICP exercise with utmost care. This work has been funded by the German Ministry of Education and Research (Project No. 01LK1225A).

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