Effects of Initial Age Structure of Managed Norway Spruce Forest Area on Net Climate Impact of Using Forest Biomass for Energy

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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 1σ 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. ^{14}C activity, is essential and reassuring in itself.
2. The Heidelberg global $^{14}CO_2$ 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 $^{14}CO_2$ 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 $^{14}CO_2$ activities.

FIRST PURE CO_2 INTERCOMPARISON EXERCISE

The ICOS CRL initiated a pure CO_2 ICP exercise where 12 international AMS laboratories agreed to participate (see Table 1). We used five pure CO_2 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 CO_2 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 CO_2 samples were selected to have recent atmospheric ^{14}C activities and to span a considerable δ^{13}C 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 1 Participating laboratories in alphabetical order, which is not identical to the lab number used in this study.

Laboratory/Institution	Affiliation
^{14}CHRONO Centre	Queen's University, Belfast, UK
Center for Applied Isotope Studies	University of Georgia, USA
Center for Atmospheric and Oceanic Studies & Center for Chronological Research	Tohoku University, Sendai, Japan & Nagoya University, Nagoya, Japan
Centre for Isotope Research (CIO)	University of Groningen, the Netherlands
Centre for Accelerator Science	ANSTO, Lucas Heights, Australia
Curt-Engelhorn-Center for Archaeometrie (CEZA)	Mannheim, Germany
ICOS CRL (AMS sample preparation, with AMS analysis at CEZA)	University of Heidelberg, Germany
ICOS CRL LLC	University of Heidelberg, Germany
INSTAAR & UCI	University of Colorado, Boulder, CO, USA & University of California, Irvine, CA, USA
LARA AMS Laboratory	University of Bern, Switzerland
NIES-TERRA AMS facility	Ibaraki, Japan
Rafter Radiocarbon Laboratory	GNS Science, Lower Hutt, New Zealand
University of Helsinki AMS facility	University of Helsinki, Finland

Table 2 Summary of the ICP samples.

Sample origin	Sample code	Consensus value $\Delta^{14}C$ (‰)	$\delta^{13}C$ VPDB (‰)	Collection date (DD.MM.YYYY)
CO_2 from biomass burning	30864	25.2 ± 0.7	−22.25	01.01.2010
NIST Oxalic Acid I (SRM 4990B)	30874	40.4 ± 0.7	−19.2	01.01.1950
Atmospheric sample (Cabauw 39)	30993	9.6 ± 0.7	−10.67	05.12.2012
Atmospheric sample (Heidelberg 1138)	30996	10.9 ± 0.7	−9.65	26.08.2013
Atmospheric sample (Cabauw 32)	31061	22.7 ± 0.7	−8.38	22.08.2012

$\Delta^{14}C$ according to Equation 1, along with $\delta^{13}C$ from the AMS and/or isotope ratio mass spectrometry (IRMS), together with the respective uncertainties:

$$\Delta^{14}C(‰) = \left\{ \left[\left(\frac{R_{sam}}{R_{ref}} \right) \left(\frac{1 + \frac{-25}{1000}}{1 + \frac{\delta^{13}C_{sam}}{1000}} \right)^2 e^{\lambda(1950-t)} \right] - 1 \right\} \cdot 1000 \qquad (1)$$

where R denotes the ratio of ^{14}C to C in the sample or the reference, t is the date of sample collection, and $\delta^{13}C_{sam}$ 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 Δ 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‰ 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 χ^2_{red} (see Table 4) was calculated for each laboratory according to Equation 2:

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

where x_i and σ_i denote the individual measurement and its reported 1σ 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 χ^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.

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

Lab code	Problems/Remarks
1	None
2	None
3	Break seals too large, new cracker built. Broad gas chromatographic peaks in elemental analyzer combustion for the standards. δ^{13}C could not be measured with AMS at this point.
4	Split aliquot amount into two halves and prepared two targets each. The two sets of targets were analyzed 1 month apart.
5	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.
6	Sample 30874 was apparently insufficiently graphitized and the entire AMS was under repair after a large earthquake.
7 to 12	None

Table 4 Measurement bias (i.e. mean difference of measured Δ^{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 χ^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.

Lab code	Measurement bias (‰ Δ^{14}C)	Error of the measurement bias (‰ Δ^{14}C)	Reduced χ^2 based on consensus value	Reduced χ^2 based on median
LLC	−0.3	0.5	0.4	—
1	0.1	0.7	0.4	0.6
2	1.8	0.1	0.8	0.6
3*	−2.9	2.4	11.6	13.3
4a	1.0	0.6	0.6	0.8
4b	1.4	1.2	2.2	1.6
5	−1.4	1.1	1.9	2.8
6*	−12.0	9.0	45.4	44.8
7	1.6	0.5	0.4	0.3
8	−2.9	1.6	4.7	5.9
9	0.7	2.3	1.6	1.3
10	1.6	0.6	1.0	0.8
11*	7.3	1.6	15.4	13.6
12	−1.8	0.7	1.3	1.7

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:

$$\bar{x} = \frac{\sum_{i=1}^{n}\left(x_i \sigma_i^{-2}\right)}{\sum_{i=1}^{n} \sigma_i^{-2}} \tag{3}$$

$$\sigma_{\bar{x}}^2 = \frac{1}{\sum_{i=1}^{n} \sigma_i^{-2}} \tag{4}$$

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 ± 0.7‰ (normalized to $\delta^{13}C = -25‰$). 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‰ (normalized to $\delta^{13}C = -25‰$) (red dashed line in Figure 1), shows that it is accurate within its 1σ 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 ± 0.5‰ and is thus not significant. The measurement biases for the individual laboratories along with their uncertainties and the reduced χ^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‰ interlaboratory compatibility (ILC) goal is met by each AMS laboratory. Assuming a 2‰ measurement uncertainty, approximately 50 samples would be needed for reducing the

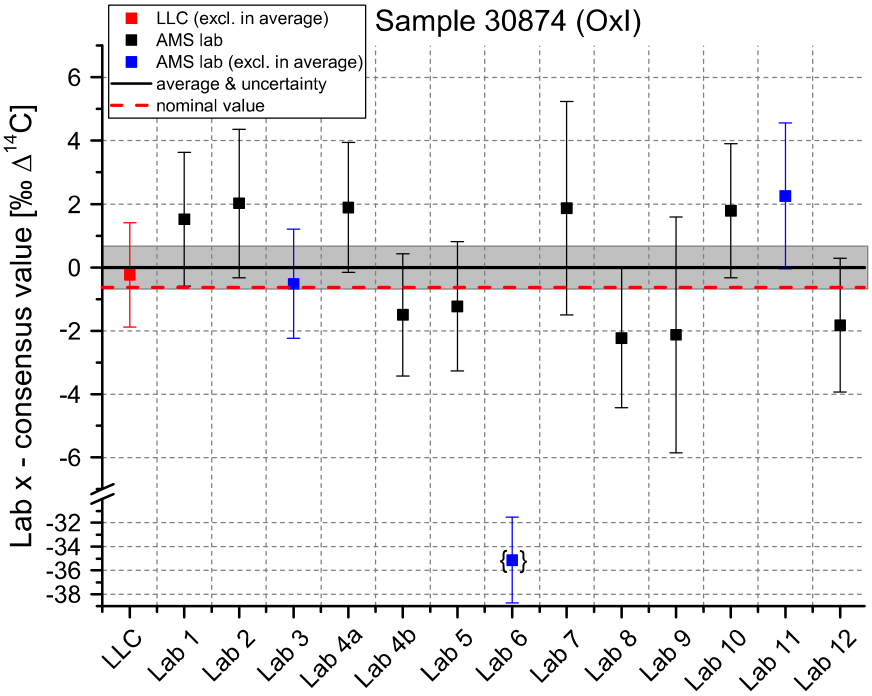

Figure 1 Differences of the individual labs to the consensus value of sample 30874 (OxI). The gray shaded area indicates the uncertainty of the consensus value. The difference between the consensus value and the nominal value of the NIST oxalic acid I (SRM 4990B) is shown as red dashed line. Lab 6 reported insufficient graphitization for this sample 30874.

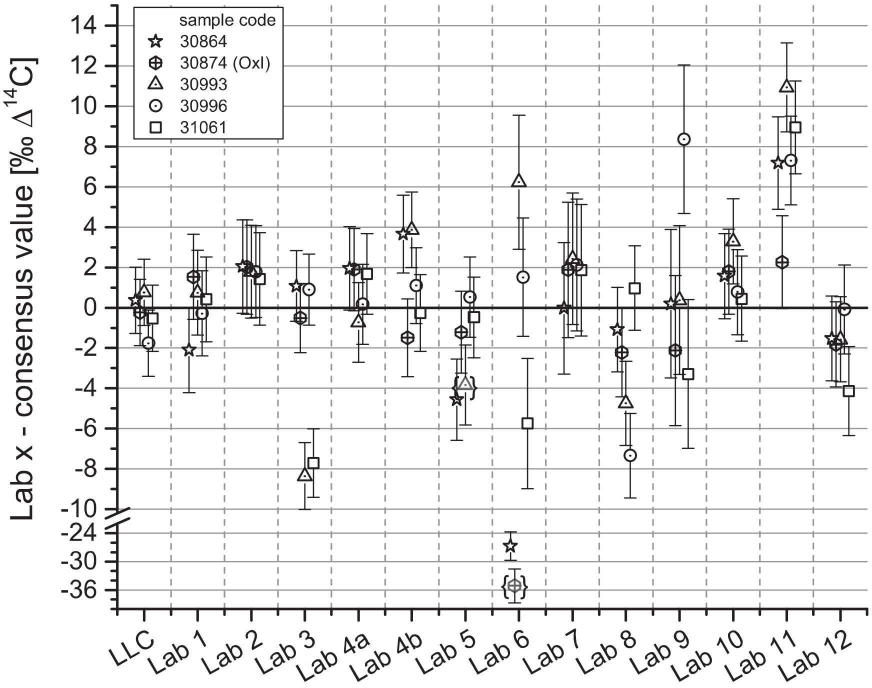

Figure 2 Summary of all ICP results. The difference for each sample to the consensus value based on 9 labs is shown. Labs 3, 6, and 11 have been excluded from calculation of the consensus value (compare also reduced χ^2 vs. the median in Table 4 for those labs). The measurements in brackets from labs 5 and 6 are subject to sample handling problems (compare Table 3).

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 CO_2 samples, which have been analyzed for ^{14}C 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 ^{14}C 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 $\Delta^{14}CO_2$ compatibility goal. We plan to address this shortcoming in a second pure CO_2 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.

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REFERENCES

Buizert C, Martinerie P, Petrenko VV, Severinghaus JP, Trudinger CM, Witrant E, Rosen JL, Orsi AJ, Rubino M, Etheridge DM, Steele LP, Hogan C, Laube JC, Sturges WT, Levchenko VA, Smith AM, Levin I, Conway TJ, Dlugokencky EJ, Lang PM, Kawamura K, Jenk TM, White JWC, Sowers T, Schwander J, Blunier T. 2012. Gas transport in firn: multiple-tracer characterisation and model intercomparison for NEEM, Northern Greenland. *Atmospheric Chemistry and Physics* 12:4259–77.

Francey RJ, Trudinger CM, van der Schoot M, Law RM, Krummel PB, Langenfelds RL, Steele LP, Allison C, Stavert A, Andres R, Rodenbeck C. 2013. Atmospheric verification of anthropogenic CO_2 emission trends. *Nature Climate Change* 3(5): 520–4.

Gelencsér A, May B, Simpson D, Sánchez-Ochoa A, Kasper-Giebl A, Puxbaum H, Caseiro A, Pio C, Legrand M. 2007. Source apportionment of PM2.5 organic aerosol over Europe: primary/secondary, natural/anthropogenic, and fossil/biogenic origin. *Journal of Geophysical Research* 112:D23S04.

Graven HD, Guilderson TP, Keeling RF. 2012. Observations of radiocarbon in CO_2 at seven global sampling sites in the Scripps flask network: analysis of spatial gradients and seasonal cycles. *Journal of Geophysical Research* 117:D02303.

Graven H, Xu X, Guilderson TP, Keeling RF, Trumbore SE, Tyler S. 2013. Comparison of independent delta $^{14}CO_2$ records at Point Barrow, Alaska. *Radiocarbon* 55(2–3):1541–5.

Kromer B, Münnich KO. 1992. CO_2 gas proportional counting in radiocarbon dating—review and perspective. In: Taylor RE, Long A, Kra S, editors. *Radiocarbon after Four Decades*. New York: Springer. p 184–97.

Levin I, Naegler T, Kromer B, Diehl M, Francey RJ, Gomez-Pelaez AJ, Steel LP, Wagenbach D, Weller R, Worthy DE. 2010. Observations and modelling of the global distribution and long-term trend of atmospheric $^{14}CO_2$. *Tellus B* 62:26–46.

Levin I, Kromer B. 2004. The tropospheric $^{14}CO_2$ level in mid-latitudes of the Northern Hemisphere (1959–2003). *Radiocarbon* 46(3): 1261–72.

Levin I, Münnich KO, Weiss W. 1980. The effect of anthropogenic CO_2 and ^{14}C sources on the distribution of $^{14}CO_2$ in the atmosphere. *Radiocarbon* 22(2):379–91.

Levin I, Kromer B, Hammer S. 2013. Atmospheric $\Delta^{14}CO_2$ trend in Western European background air from 2000 to 2012. *Tellus B* 65:20092.

Lindahl BD, Ihrmark K, Boberg J, Trumbore SE, Högberg P, Stenlid J, Finlay RD. 2007. Spatial separation of litter decomposition and mycorrhizal nitrogen uptake in a boreal forest. *New Phytologist* 173(3):611–20.

Miller J, Lehman S, Wolak C, Turnbull J, Dunn G, Graven H, Keeling R, Meijer H, Aerts-Bijma A, Palstra S, Smith A, Allison C, Southon J, Xu X, Nakazawa T, Aoki S, Nakamura T, Guilderson T, LaFranchi B, Mukai H, Terao Y, Uchida M, Kondo M. 2013. Initial results of an intercomparison of AMS-based atmospheric $^{14}CO_2$ measurements. *Radiocarbon* 55(2–3):1475–83.

Naegler T, Ciais P, Rodgers KB, Levin I. 2006. Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO_2 by the oceans. *Geophysical Research Letters* 33:L11802.

Nydal R, Lövseth K. 1983. Tracing bomb ^{14}C in the atmosphere 1962–1980. *Journal of Geophysical Research* 88(C6):3621–42.

Rozanski K, Stichler W, Gonfiantini R, Scott EM, Beukens RP, Kromer B, van der Plicht J. 1992. The IAEA ^{14}C Intercomparison Exercise 1990. *Radiocarbon* 34(3):506–19.

Santos GM, De La Torre HAM, Boudin M, Bonafini M, Saverwyns S. 2015. Improved radiocarbon analyses of modern human hair to determine the year-of-death by cross-flow nanofiltered amino acids: common contaminants, implications for isotopic analysis, and recommendations. *Rapid Communications in Mass Spectrometry* 29(19): 1765–73.

Scott E, Cook G, Naysmith P, Bryant C, O'Donnell D. 2007. A report on Phase 1 of the 5th International

Radiocarbon Intercomparison (VIRI). *Radiocarbon* 49(2):409–26.

Spalding KL, Bergmann O, Alkass K, Bernard S, Salehpour M, Huttner HB, Possnert G. 2013. Dynamics of hippocampal neurogenesis in adult humans. *Cell* 153(6):1219–27.

Stuiver M, Polach H. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Trumbore SE. 1993. Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements. *Global Biogeochemical Cycles* 7(2):275–90.

Turnbull JC, Lehman SJ, Miller JB, Sparks RJ, Southon JR, Tans PP. 2007. A new high precision $^{14}CO_2$ time series for North American continental air. *Journal of Geophysical Research* 112:D11310.

Turnbull J, Rayner P, Miller J, Naegler T, Ciais P, Cozic A. 2009. On the use of $^{14}CO_2$ as a tracer for fossil fuel CO_2: quantifying uncertainties using an atmospheric transport model. *Journal of Geophysical Research* 114:D22302.

WMO-GAW (World Meteorological Organization–Global Atmosphere Watch). 2013. *17th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques*. Volume 213, Global Atmosphere Watch. Beijing, China, 10–14 June 2013.