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INTERCOMPARISON OF HIGH-PRECISION ^{14}C MEASUREMENTS AT THE UNIVERSITY OF ARIZONA AND THE QUEEN'S UNIVERSITY OF BELFAST RADIOCARBON LABORATORIES

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ABSTRACT. High-precision measurements were completed concurrently at the University of Arizona and the Queen's University of Belfast on blind samples of Irish oak originally measured for the 1986 radiocarbon calibration curve. Subsequent single-year *Sequoiadendron* results were decadally averaged and compared with published results on decadal Douglas-fir samples. The results of these intercomparisons show that the Arizona high-precision results compare favorably with published values from the University of Washington, but show a systematic offset with published Belfast data.

INTRODUCTION

During the last four years, considerable discussion has focused on quality assurance/quality control (QA/QC) and intercomparison between radiocarbon laboratories (Long and Kalin 1990; Rozanski *et al.* 1992; Stuiver, Long and Kra 1993). The results of international intercomparison studies (Scott *et al.* 1992) allow laboratories to identify bias in their ^{14}C results, as compared with the geometric mean of all the participating laboratories. Few laboratories produce high-precision ^{14}C analyses due to the time, expense and effort required to determine natural ^{14}C activity to ±0.2% precision.

Two publications dedicated to the calibration of the ^{14}C time scale have resulted from high-precision ^{14}C research (Stuiver and Kra 1986; Stuiver, Long and Kra 1993). Studies of variations in the ^{14}C record (Jirikowic 1994; Stuiver 1993; Jirikowic and Kalin 1993; Damon and Jirikowic 1992; Stuiver *et al.* 1991) show that solar, geophysical, oceanographic and paleoclimate changes may account for variability in the record. Therefore, to study this variability with data that were measured at different laboratories on wood from different geographical settings, it is imperative that detailed and continuing intercomparisons between high-precision laboratories be conducted to determine any minor laboratory bias in the results.

METHODS

The University of Arizona ^{14}C laboratory began using liquid scintillation counting (LSC) in 1992 for high-precision measurement of natural ^{14}C variations. Bidecadal samples of Irish oak, originally measured by Pearson *et al.* (1986), were provided by Prof. Michael Baillie, Palaeoecology Centre, The Queen's University of Belfast to both Arizona and Queen's ^{14}C labs. The bidecade that each sample represented was not known until the results had been completed. As part of ongoing research at the University of Arizona, single-year *Sequoiadendron* samples were separated at the Laboratory of Tree-Ring Research. Due to limited sample size for single-year samples, we decided that sample size for LSC measurements at Arizona could not exceed 7 g carbon. Therefore, counting times would have to be extended to ensure that ±0.2% precision was attained.

A slightly modified treatment after Linick *et al.* (1986) was used to remove the non-cellulose matter from the wood, leaving only holocellulose. This new procedure involves the use of an ultrasonic bath to facilitate the removal of resins from the wood prior to soxhlet reflux treatment. This modifi-

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cation was needed to remove the excessive resin in *Sequoiadendron* samples. The procedure listed in the ^{14}C laboratory QA/QC manual is:

1. Weigh sample and record all relevant sample information in notebook.
2. Cut sample into matchstick pieces with hammer and chisel.
3. Pulverize sample in the Whiley mill (20 mesh). **Make sure mill is spotless,** clean mill before and after sample with Kimwipes® and 95% ethanol to ensure sample integrity.
4. Resin extraction:
   a. The sample is placed in a 1000-ml beaker and 500 ml of toluene is added. The beaker is placed in an ultrasonic bath for 30 min. The toluene is decanted off, and the process is repeated until the removal of resins ceases.
   b. Clean soxhlet apparatus.
   c. In the bottom of soxhlet, place *ca.* 2.5 cm glass wool, place the ground sample on glass wool, then cover with *ca.* 2.5 cm glass wool. Make sure the sample is below the siphon outlet. Put 400 ml of 95% 95% ethanol into the boiling flask (be sure there are sufficient boiling stones).
   d. Assemble the soxhlet apparatus and turn on cooling water to the condensing tower.
   e. Turn on the heat, check the apparatus after 1 h to ensure proper function. Record the date and action in the lab book.
   f. After 24 h, turn off the heat, let cool.
   g. Remove the 95% ethanol solution and discard in an appropriate waste bottle.
   h. Dry the sample by blowing air through it.
   i. If the sample is not clean, refill the 500-ml bulb with 400 ml of 95% ethanol and restart extraction. Record the date and action in the lab book.
   j. After 24 h, turn off the heat, let cool.
   k. Remove the sample, place it in a 1000-ml beaker, and dry in the oven at low heat. Record the date and action in the lab book.
   l. Discard the 95% ethanol in an appropriate waste bottle.
   m. Clean soxhlet apparatus fully, rinsing with 95% ethanol.
5. Place the beaker on a hot plate, add *ca.* 500 ml of distilled water, cover with a watch glass and bring the sample to a boil for 6 h. Add distilled water as needed. Record the date and action in the lab book.
6. Remove from heat and decant distilled water from the sample. If unable to continue the treatment at this time, dry the sample in the oven and store. Record the date and action in the lab book.
7. In a 1000-ml beaker, add 500 ml of distilled water. To this add several drops of phosphoric acid, and at the same time, add *ca.* 0.5 g of sodium chlorite. Cover and place on a hot plate on low heat.
8. Repeat every 2 h for 8 h and leave on low heat overnight.
9. Remove from heat and uncover the beaker. If the sample is not paper white, repeat steps 7 and 8. Decant the liquid and rinse the sample 6 times with 1000 ml of distilled water. Dry the sample, record the date, weight and action and store the sample for combustion.

The samples were synthesized to benzene following the procedures outlined in Witkin *et al.* (1993) and Long and Kalin (1992), in which specific steps were determined to ensure the purity and reproducibility of synthesized benzene. Two Wallac Quantulus LS counters were used to measure the ^{14}C activity of the synthesized benzene. The vial selection, counting windows and manual high-voltage settings on these two counters were determined based on the results published by Pearson (1979,

1983) and McCormac (1992). The counters were modified at the Arizona laboratory to allow for manual adjustment of the high voltage applied to each photomultiplier tube. State-of-the-art equipment and the underground lab reduced our need to apply corrections originally used by Pearson (1983) with older LSC equipment (*e.g.*, atmospheric pressure, diurnal effect and sample evaporation), and corrections for benzene purity (after McCormac 1992) are very small due to steps taken during benzene synthesis to ensure purity (Witkin 1992). The LS counters are housed in a stable underground counting laboratory (Kalin and Long 1989). Samples of Oxalic Acid I, background benzene and sample benzene are counted sufficiently long to attain better than ±0.2% precision (10 k min minimum for samples).

Results and Discussion

The results of this intercomparison exercise are listed in Table 1 (Irish oak) and in Table 2 (*Sequoiadendron*). Long (1990) presented the consensus QA protocol for ^{14}C dating laboratories in which total analytical precision (TAP) was defined to be the total uncertainty applied to each laboratory result. Stuiver and Pearson (1986) showed that, for high-precision data, a laboratory multiplier (K) should be applied to results. The value of K represents uncertainty in the precision of results above that predicted by normal statistics. Therefore, the TAP presented by Long (1990) is the product of the laboratory error multiplier K and the counting statistics.

TABLE 1. Intercomparison of the First University of Arizona High-Precision ^{14}C LSC Analyses on Bidecadal Samples of Irish Oak

		Pearson and Qua (1993)		Pearson *et al.* (1986)		Belfast University (this study)		Arizona (this study)	
Sample site	Bidecadal center year	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)
Blackwater	3450 BC	73.2 ± 2.3	N.A.*	75.0 ± 2.1	N.A.	77.6 ± 2.1	−25.7	77.3 ± 1.8	−24.4
Blackwater	3470 BC	75.5 ± 2.5	N.A.	78.0 ± 2.5	N.A.	77.2 ± 1.8	N.A.	81.5 ± 1.6	−24.5
Motorway	2490 BC	42.4 ± 1.7	N.A.	43.0 ± 1.7	N.A.	44.2 ± 2.1	−26.2	42.5 ± 1.4	−26.1
Garry Bog	390 BC	−2.6 ± 1.9	N.A.	−0.8 ± 1.9	N.A.	N.A.	N.A.	−0.5 ± 1.5	−25.3
Garry Bog	370 BC	1.8 ± 1.4	N.A.	3.9 ± 1.4	N.A.	1.2 ± 2.0	−26.1	6.5 ± 1.1	−24.8

*Not available

TABLE 2. Intercomparison of averaged single-year* high-precision ^{14}C LSC analyses with decadal samples (Stuiver and Becker 1993). Arizona samples are *Sequoiadendron*, California. Stuiver and Becker (1986, 1993) samples are Douglas fir, Vancouver Island, British Columbia. Pearson *et al.* (1986) and Pearson and Qua (1993) samples are *Quercus* spp. from the British Isles.

	Arizona (this study)		Pearson *et al.* (1986)	Stuiver and Becker (1986)	Stuiver and Becker (1993)	Pearson and Qua (1993)
Decadal center year	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\Delta^{14}C$ (‰)	$\Delta^{14}C$ (‰)	$\Delta^{14}C$ (‰)
AD 1085	−10.5 ± 2.3	−20.5 ± 0.3		−8.6 ± 1.4	−10.8 ± 1.5	
AD 1095	−15.9 ± 2.8	−19.9 ± 0.3	−10.0 ± 1.4	−12.3 ± 2.0	−15.5 ± 2.1	−11.6 ± 1.4
AD 1105	−17.2 ± 1.4	−20.0 ± 0.4		−14.6 ± 1.8	−17.0 ± 1.9	
AD 1115	−17.8 ± 2.7	−19.8 ± 0.2	−13.3 ± 1.5	−15.7 ± 2.0	−17.9 ± 2.1	−14.8 ± 1.5
Avg. value	−15.35		−11.65	−12.80	−15.30	−13.20

*Arizona dates are the average of separate analyses on individual rings with standard deviation (σ). We did not divide σ by √n to obtain the standard deviation of the mean due to small but real variation between annual rings.

The data in Table 1 show that the initial high-precision results obtained by Arizona vary more than counting statistics alone would suggest. The calculated bias among these initial values (Table 1) and the results of Pearson *et al.* (1986) is 1.6‰. The offset of these data with Pearson and Qua (1993) is 3.4‰. The calculated bias between the new Belfast data (Table 1) and the results of Pearson *et al.* (1986) is 0.08‰. The offset of these data with Pearson and Qua (1993) is 1.8‰. It is interesting to note that, when compared to the mean of all three results, the mean bias of the published results of Pearson and Qua (1993) is −1.7‰, the mean bias of the new Belfast data is +1.5‰ and the mean bias of the Arizona data is +1.7‰ (Table 3). The nature of this bias changes substantially when the data published by Pearson *et al.* (1986) is used in the intercomparison. Here the mean bias of the published results of Pearson *et al.* (1986) is −0.4‰, the mean bias of the new Belfast data is −0.7‰ and the mean bias of the Arizona data is +1.0‰ (Table 3). This intercomparison would suggest that new analyses at the Belfast ^{14}C lab are nearly identical to the results obtained in the same laboratory a decade ago, and that there may be a +1.8‰ offset between the Arizona and Belfast ^{14}C laboratories. The data presented in Table 1 represent the first five high-precision LSC ^{14}C analyses performed at the Arizona laboratory. Therefore, given the sparse data set, no exhaustive statistical treatment of the data in Table 1 is possible.

TABLE 3. Laboratory Bias (Offset) from Mean of Three High-Precision Results

	Bias (‰) 1993 average	Bias(‰) 1986 average
Pearson and Qua (1993)	−1.7	--
Arizona	+1.7	+1.1
Belfast	+1.5	−0.7*
Pearson *et al.* (1986)	--	−0.4

*Intercomparison of the new Arizona and Belfast data show little offset with the results of Pearson *et al.* (1986). Intercomparison of the new Arizona and Belfast data show significant offset with the revised ^{14}C calibration data of Pearson and Qua (1993).

The intercomparison of routine high-precision results (Table 2) with published results of Stuiver and Becker (1986, 1993), Pearson *et al.* (1986) and Pearson and Qua (1993) may also be used to investigate routine laboratory bias at Arizona. Table 2 presents the decadal average of single-year samples analyzed at Arizona to study solar variability during the Medieval Warm period (provided by P. E. Damon, personal communication). These data compare favorably with the published data of Stuiver and Becker (1993) showing an average bias of only 0.05‰. Although the samples are not identical, they are from the same geographical region, thus spatial differences in atmospheric ^{14}C (Jirikowic and Kalin 1993) probably do not affect the comparison of these two data sets. However, the data show a bias of 2.55‰ with the uncorrected data of Stuiver and Becker (1986). This weakens the case for a favorable comparison between the Seattle data and the Arizona data unless we endorse the corrected data of Stuiver and Becker (1993).

Comparison of the *Sequoiadendron* ^{14}C results with published results on bidecadal oak from the British Isles for the same time period show a bias of 3.70‰ with the data of Pearson *et al.* (1986) and a bias of 2.15‰ with the data of Pearson and Qua (1993). The intercomparison of the new Arizona and Belfast data (Table 1) suggest a possible bias of +1.8‰. The nature of the divergence of the *Sequoiadendron* results and the oak results could represent evidence for a geographical effect or may represent a true bias between results of the two laboratories. There is clear evidence for a sys-

tematic offset between the data presented in Table 2, but it is difficult to endorse one data set (1986 or 1993) as offering the best intercomparison of results.

Conclusion

The results of intercomparison between published data (Pearson and Qua 1993) and new high-precision ^{14}C measurements from the University of Arizona and the Queen's University of Belfast ^{14}C laboratories show the data as originally published by Pearson *et al.* (1986) compare more favorably than the "revised" 1993 data. Statistically, no offset can be determined between new results at Belfast and those produced a decade before. Routine high-precision analyses at the University of Arizona on single-year *Sequoiadendron* samples have resulted in decadal averages that compare remarkably well with the published decadal results of Stuiver and Becker (1993), but do show bias with the uncorrected results of Stuiver and Becker (1986) supporting the use of the 1993 data. There is a systematic offset between the new Arizona and Belfast oak results and between the Arizona *Sequoiadendron* and published Belfast oak data (Pearson *et al.* 1986; Pearson and Qua 1993).

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References

Damon, P. E. and Jirikowic, J. L. 1992 The sun as a low-frequency harmonic oscillator. *Radiocarbon* 34(2): 199–205.

Jirikowic, J. L. (ms.) 1994 Solar and Geomagnetic Forcing of the Terrestrial Radiocarbon Cycle. Ph.D. dissertation, Department of Geosciences, The University of Arizona: 126 p.

Jirikowic, J. L. and Kalin, R. M. 1993 A possible ENSO indicator in the spatial variation of tree-ring radiocarbon. *Geophysical Research Letters* 20(6): 439–442.

Kalin, R. M. and Long, A. 1989 Radiocarbon dating with the Quantulus in an underground counting laboratory: Performance and background source. *Radiocarbon* 31(3): 368–373.

Linick, T. W., Long, A., Damon, P. E. and Ferguson, C. W. 1986 High-precision radiocarbon dating of bristlecone pine from 6554 to 5350 BC. *Radiocarbon* 28(2B): 943–953.

Long, A. 1990 A quality assurance protocol for radiocarbon dating laboratories. *In* Scott, E. M., Long, A. and Kra, R. S., eds. Proceedings of the International Workshop on Intercomparison of Radiocarbon Laboratories. *Radiocarbon* 32(3): 393–396.

Long, A. and Kalin, R. M. 1990 A suggested quality assurance protocol for radiocarbon dating laboratories. *In* Scott, E. M., Long, A. and Kra, R. S., eds. Proceedings of the International Workshop on Intercomparison of Radiocarbon Laboratories. *Radiocarbon* 32(3): 329–334.

___1992 High-sensitivity radiocarbon dating in the 50,000 to 75,000 BP range without isotopic enrichment. *Radiocarbon* 34(3): 351–359.

McCormac, F. G. 1992 Liquid scintillation counter characterization, optimization and benzene purity correction. *Radiocarbon* 34(1): 37–45.

Pearson, G. W. 1979 Precise ^{14}C measurement by liquid scintillation counting. *Radiocarbon* 21(1): 1–21.

Pearson, G. W. (ms.) 1983 The Development of High Precision ^{14}C Measurement and Its Application to Archaeological Time-Scale Problems. Ph.D. dissertation, The Queen's University of Belfast.

Pearson, G. W., Pilcher, J. R., Baillie, M. G. L., Corbett, D. M. and Qua, F. 1986 High-precision ^{14}C measurement of Irish oaks to show the natural ^{14}C variation from AD 1840 to 5210 BC. *In* Stuiver, M. and Kra, R., eds., Proceedings of the 12th International ^{14}C Conference. *Radiocarbon* 28(2B): 911–934.

Pearson, G. W. and Qua, F. 1993 High-precision ^{14}C measurement of Irish oaks to show the natural ^{14}C variation from AD 1840 to 5210 BC: A correction. *In* Stuiver, M., Long, A. and Kra, R. S., eds., Calibration 1993. *Radiocarbon* 35(1): 105–124.

Rozanski, K., Stichler, W., Gonfiantini, R., Scott, E. M., Beukens, R. P., Kromer, B., and van der Plicht, J. 1992 The IAEA ^{14}C intercomparison exercise 1990. *In* Long, A. and Kra, R. S., eds., Proceedings of the 14th International ^{14}C Conference. *Radiocarbon* 34(3): 506–519.

Scott, E. M., Cook, G. T., Harkness, D. D., Miller, B. F. and Baxter, M. S. 1992 Further analysis of the Inter-

national Intercomparison Study (ICS). *In* Long, A. and Kra, R. S., eds., Proceedings of the 14th International ^{14}C Conference. *Radiocarbon* 34(3): 520–527.

Stuiver, M. 1993 A note on single-year calibration of the radiocarbon time scale, AD 1510–1954. *Radiocarbon* 35(1): 67–72.

Stuiver, M. and Becker, B. 1986 High-precision decadal calibration of the radiocarbon time scale, AD 1950–2500 BC. *In* Stuiver, S. and Kra, R. Calibration Issue. *Radiocarbon* 28(2B): 863–910.

____1993 High-precision decadal calibration of the radiocarbon time scale, AD 1950–6000 BC. *Radiocarbon* 35(1): 35–66.

Stuiver, M., Braziunas, T. F., Becker, B. and Kromer, B. 1991 Climatic, solar, oceanic and geomagnetic influences on late-glacial and Holocene atmospheric $^{14}C/^{12}C$ change. *Quaternary Research* 35(1): 1–24.

Stuiver, M. and Kra, R., eds. 1986 Calibration Issue. *Radiocarbon* 28(2B): 805–1030.

Stuiver, M., Long, A., and Kra, R. S., eds. 1993 Calibration 1993. *Radiocarbon* 35(1): 1–244.

Stuiver, M. and Pearson, G. 1986 High-precision calibration of the radiocarbon time scale, AD 1950–500 BC. *In* Stuiver, S. and Kra, R. Calibration Issue. *Radiocarbon* 28(2B): 805–838.

Witkin, D. (ms.) 1992 Production of Impurities in Benzene Synthesis for Liquid Scintillation Counting and Its Effect on High-Precision Radiocarbon Measurements. M.S. thesis, Department of Geosciences, The University of Arizona: 18 p.

Witkin, D., Kalin, R. M., Long, A., Rigali, M. J. and Nagy, B. 1993 Production of impurities in benzene synthesis for liquid scintillation counting and its effect on high-precision radiocarbon measurements. *In* Noakes, J. E., Schönhofer, F. and Polach, H. A., eds., *Liquid Scintillation Spectrometry 1992.* Tucson, Arizona, Radiocarbon: 115–124.