INTERLABORATORY COMPARISONS OF ^{14}C MEASUREMENTS IN MILK AND VEGETATION

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ABSTRACT. The need for increased quality assurance for radiocarbon measurements performed by the monitoring laboratories at nuclear stations has spurred the introduction of a number of interlaboratory comparisons. We organized two such intercomparisons: the first set, circulated in 1994, consisted of two milk samples, one containing current global levels of ^{14}C, the other containing an added spike of ^{14}C-methylated casein. The second set, circulated in 1995, consisted of two samples of natural vegetation growing on the site of the Chalk River Laboratories (CRL), containing two different levels of ^{14}C, both well above global background. The response to our invitation to participate in these studies was very encouraging; six laboratories took part in the first intercomparison, eleven in the second. The list included both monitoring laboratories and those whose main function is ^{14}C dating. Understandably, some of the latter preferred not to analyze the higher-activity samples. The results in 3 of the 4 data sets were consistent with a statistical distribution based on the reported errors. This report provides details of two intercomparisons, including the preparation of the samples, which may now be considered potential secondary reference materials, the range of analytical techniques in use at the participating laboratories, and a statistical analysis of the results returned to us.

INTRODUCTION

Historical Review

Although the need to maintain a precise definition of the conventional radiocarbon time scale has always concerned the international ^{14}C dating community, the need for formal interlaboratory calibration programs was not recognized as early as it was in related fields (*e.g.*, natural tritium measurement). The use of oxalic acid distributed by the National Bureau of Standards as a primary standard ("present"= 1950 = 0.95 × NBS-HOxI), plus a number of *ad hoc* sample exchanges among small groups of laboratories, was considered adequate to maintain internal and outside user confidence in measurements.

One of the earliest comparisons of results was introduced by Polach (1972) in an evaluation of replicate oxalic acid measurements. Clark (1975) similarly analyzed data for bristlecone pine. By 1978 the stocks of HOxI were practically gone. Consequently, a new batch was prepared and sent out to 16 laboratories for intercomparative mass spectrometry (^{13}C) and activity-concentration (^{14}C) measurements. Close to that time, another cross-calibration exercise (Polach 1979) was organized (with 15 laboratories) to derive consensus values for two relatively homogeneous materials; Australian National University (ANU) prepared sucrose and 1850 wood. However, it was not until 1980 that the first large-scale interlaboratory comparison was organized jointly by Harwell and the British Museum Laboratories (Otlet *et al.* 1980), to include all the working ^{14}C laboratories in the United Kingdom. The experiment was run along the lines of that organized by the International Atomic Energy Agency (IAEA) for tritium, and explored the problems associated with preparation of samples for intercomparison, verification of equivalent levels and presentation of results. Samples of benzene representing five age equivalent levels between twice modern, and *ca.* 20 ka BP, were prepared and distributed. The results showed close agreement, both between laboratories and in comparison with the known relative activities of the prepared solutions.

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In 1982–1983 an International Study Group (1982) representing 20 laboratories in 12 countries organized an interlaboratory comparison of ^{14}C measurements for replicate samples from one tree. By the time of the 12th International ^{14}C Conference in 1985, a strong consensus had emerged for a new and more comprehensive intercalibration study. Consequently, a much more ambitious study was mounted the following year by a Scottish consortium, representing the Natural Environment Research Council (NERC) Radiocarbon Laboratory, Scottish Universities Research and Reactor Centre (SURRC), and Glasgow University, in which 60 laboratories took part. Details of the design and sample preparation, as well as preliminary results from stages 1 and 2, are described in Harkness *et al.* (1989) and Scott *et al.* (1989). More complete information was published in the Proceedings of the International Workshop on Intercomparison of ^{14}C Laboratories (Aitchison *et al.*; Cook *et al.*; Scott *et al.* 1990). The goal of stage 1 was a direct assessment of the inter- and intralaboratory variance as determined by ^{14}C counting procedures. Samples distributed were benzene and calcium carbonate. Stage 2 offered the opportunity to assess the contribution from routine preparation and/or synthesis methods in determining overall confidence. The sample options were algal carbonate, peat and Irish bog oak.

The final suite of samples was selected as being representative of the raw materials used in routine dating: wood from four growth sections, bivalve mollusks, and a humic extract from peat. Only relatively young ages were covered in this study (<2 half-lives in all instances).

Reference Materials Presently Available

More recently, at a meeting held during the 13th International ^{14}C Conference in 1988, it was recognized that a number of reference materials were needed, spanning a time scale of >40 ka BP to >"modern," and in large enough supply to satisfy requirements for the foreseeable future. The IAEA undertook preparation and calibration of suitable materials. Six samples, in a wide variety of matrices (including the previously mentioned ANU sucrose), and spanning the full range of ages from "infinite" to 1.5 times modern, were prepared and sent out for intercomparison to 137 laboratories around the world. A report on the results received was presented at the 14th International ^{14}C Conference (Rozanski *et al.* 1992), and these materials are available from the IAEA on request (Table 1).

Addressing the Needs of Monitoring Laboratories

The reference materials listed in Table 1 are extremely useful to all scientists working in the field of ^{14}C. However, they do not address the specific needs of many monitoring laboratories, which routinely measure ^{14}C at levels between one and ten times modern.

Early in 1992, a four-laboratory intercomparison of the current levels of ^{14}C in milk was organized by B. C. J. Neil, at that time the senior scientist, environmental safety, of the Health and Safety Division of Ontario Hydro. A sample was made from supermarket-purchased skim milk powder, reconstituted at 100 g L^{-1}, and containing added tritium to *ca.* 100 Bq L^{-1}. The purpose of the tritium was to check on the ability of the analytical method to separate the two radioisotopes satisfactorily. Since no preservative had been added to the samples, the entire sample received in our laboratory was taken to near dryness under infrared heat lamps in lined polyethylene trays. By using this method, we avoided the excessive foaming and potential fractionation likely to occur using vacuum evaporation. The uncertainty (2 σ) of the ^{14}C results reported by the four laboratories, mean value 240 Bq L^{-1}, was *ca.* 30 Bq L^{-1} (Neil 1993).

Subsequent to this initial work, we submitted a proposal to a workshop on ^{14}C held in November 1992 (Milton 1993), to prepare samples containing ^{14}C specific activities between one and ten times

TABLE 1. ^{14}C Quality Assurance Materials Available from IAEA*

IAEA code	Material	Prepared by	^{14}C consensus value (pMC)	$\delta^{13}C$ consensus value (‰)
C-1	*Carbonate* Slab of freshly cut Carrara marble supplied by IMEG, Vareggio, Italy, and milled down to a dust-free fraction of 1.6 to 5.0 mm by the IAEA.	IAEA	0.00(0.02)	2.42
C-2	*Carbonate* Fresh-water travertine deposit collected near Munich, Germany, supplied by GSF, Institute of Hydrology, Neuherberg, and homogenized by the IAEA	IAEA	41.14	–8.25
C-3	*Cellulose* Batch of cellulose produced in 1989 from one season's harvest of about 40-year-old trees, supplied by a paper factory in Bergum, the Netherlands.	W. G. Mook J. van der Plicht	129.41	–24.91
C-4	*Subfossil Wood* Subfossil wood excavated from peat bogs in the north island of New Zealand, near Waikato.	A. G. Hogg H. A. Polach	0.20-0.44	–23.96
C-5	*Subfossil Wood* Subfossil wood originating from buried bed forest in Eastern Wisconsin, U.S.A., near the western shore of Lake Michigan.	R. M. Kalin A. Long IAEA	23.05	–25.49
C-6	*Sucrose*	H. A. Polach, ANU	150.1	–10.80

*From a report of the IAEA Consultants Group Meeting (1991)

modern. The samples comprised *ca.* 10 kg of each of the following, at two or more specific activities: 1) tree leaves; 2) milk powder; and 3) meat (beef).

To date, we have prepared and circulated samples of two of these matrices, at two different levels of specific activity. We are storing a third material for a subsequent round. This report lists the analytical laboratories that participated in the exercises and the techniques in use therein (Appendix I), lists sample preparation and homogeneity testing (Appendix II), and presents a statistical analysis of the results. It is intended that this publication will provide documentation for the quality assurance of ^{14}C measurements routinely reported by the laboratories involved, and that the materials prepared for the intercomparisons will continue to be of use as secondary reference materials during routine operations.

Methods of preparation of materials for intercomparison and their subsequent testing for homogeneity

The following brief description of methods of preparation and homogeneity testing has been abstracted from the journal publications indicated in the text; see those documents for details. The analytical techniques used during the tests are described in Milton and Brown (1993). All samples were combusted in oxygen under 20 atmospheres pressure using a Parr bomb. The ^{14}C concentrations were determined by liquid scintillation counting of the CO_2 evolved, using a Carbo-Sorb/Permafluor E+ cocktail.

The basic requirements in each case were preparation of sufficient amounts, homogeneity of material, and sample packing for long-term storage. (Suggested test for homogeneity: if ^{14}C concentrations measured in five out of six samples differed by <5% of the average, then inhomogeneity was said to be <5%.)

Milk (Used in the First Round of Intercomparison)[1]

Two materials, MK-B at the natural level of ^{14}C, and MK-C4 at an elevated level, were prepared from pasteurized 2% dairy milk. The MK-C4 was spiked with an appropriate amount of ^{14}C-methylated casein tracer to achieve the elevated level, taking precautions to avoid spoilage during the mixing stage. Aliquots of both spiked and unspiked material were poured into cans that were hermetically sealed with a canning machine and steam autoclaved. Several cans chosen at random from both sets were opened, and the entire contents were freeze-dried and rehomogenized by grinding to a fine powder.

The samples treated in this manner were subsequently analyzed to test the homogeneity of these materials for the distribution of ^{14}C. The results indicate that the materials are homogeneous with respect to ^{14}C concentration even in subsample sizes of 0.25 g of the freeze-dried material. Table A2-1, Appendix II, from Rao *et al.* (1995), provides the supporting data.

Vegetation (Used in the Second Round of Intercomparison)[2]

Vegetation was picked at two sites on the Chalk River Laboratories (CRL) property; the first (labeled Veg A) was collected midway between the Public Information Centre and the Custodia Chimney, and the second (Veg B) was collected outside the fence at Waste Management Area C. Gloves were worn while picking the leaves; stems were separated from the leaves at that time. The leaves were subsequently rinsed in double distilled water, placed in glass beakers, which were covered with watch glasses, and oven-dried (Fisher Isotemp Oven Series 200, Model 230F) overnight at *ca.* 65°C. Following hand crushing, the dried leaves were ground in a Waring Commercial Blender, and the resulting powder was put through a 300-mm sieve. The collected fines were bottled in 30-mL Nalgene bottles (~20 g in each), with a heat-shrink sealant placed around the neck of each bottle.

Samples were set aside after filling every fifth bottle to assess the homogeneity within a sample set. One bottle of each label was subsampled repeatedly in order to evaluate variability between subsamples as a function of sample size. The data listed in Table A2-2, Appendix II, indicate that these materials are homogeneous in samples of 0.5 g or greater.

[1]Abstracted from Rao *et al.* (1995).
[2]Abstracted from a Chalk River Laboratories internal report, manuscript in preparation.

Bovine Muscle (Prepared and Stored for a Subsequent Intercomparison)[3]

Ca. 1 kg of beef muscle tissue, well trimmed of fat and connective tissue, was ground to a thin paste in a domestic meat grinder, as well as in domestic and commercial blenders. Following subsampling to determine the uniformity of water content and the natural ^{14}C specific activity, the remaining homogenized tissue was spiked with ^{14}C-methylated bovine hemoglobin. Immediately after this addition, the material was rehomogenized in the blender. Subsamples were taken at this stage to evaluate the partitioning of ^{14}C between the solid matrix and the juices before and after sterilization, and to demonstrate the uniformity of mixing of the labeled compound in the bulk sample. The remaining paste was apportioned into eight cans of ~100 g sample size; six were sealed under nitrogen, and two under ambient atmosphere. The cans were then sterilized in a steam autoclave. All subsamples taken, including the contents of two sealed cans, were mixed thoroughly, freeze-dried in their entirety, and ground to a fine powder. Table A2-3, Appendix II, summarizes the measurements made on these samples. These observations indicate that the ^{14}C-labeled compound is homogeneously distributed in the freeze-dried material. Furthermore, the results for the raw material and the two cans confirm that the whole batch of muscle is homogeneous with respect to ^{14}C concentration, with no measurable subsampling uncertainty for sample sizes of ≥2 g.

Participating Laboratories

We sent a letter, inviting participation in our first intercomparison exercise, to a wide range of analytical laboratories thought to be active in the measurement of ^{14}C, either for monitoring purposes or ^{14}C dating. We recognized that many of the dating laboratories would not wish to handle the higher-activity samples we planned to send out. However, we considered it important to have some of these laboratories involved, at least in the measurement of the lower-activity samples, to take advantage of the high credibility given to their measurements by the international scientific community.

In January 1993, we mailed out nine pairs of cans (*ca.* 150 g in each) of our two milk samples. The results were reported by six laboratories for the contemporary or "background" sample, and by five laboratories for the sample containing *ca.* 60 times contemporary ^{14}C. These results, their mean and standard deviation, were reported to the participating laboratories in a letter dated 3 June 1994.

Later that year, we sent a second set of letters, soliciting participation in a planned second round, which would use two samples of vegetation growing naturally on the CRL site. The response was considerably higher than in the first round. Starting in December 1994, we mailed out 13 parcels, containing 2–20 g each of the two different specific activity samples. At the time of the specified cut-off date for reporting results, 10 analyses of the low-level sample, and 10 analyses of the higher-level sample, had been received. A preliminary report was mailed to all participants on 30 October 1995. Since that date, one more result has been reported, and will be included in this final document. The full addresses, contact persons, and analytical methods for each participating laboratory are listed in Appendix I.

Results and Discussion

Interim Reports

We derived consensus values from the results reported to us for these two intercomparisons. We sent interim reports to all participants, accompanied by displays of the data in bar graph format (Figs. 1

[3]Abstracted from Cooper and Rao (1995)

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and 2). The agreement among measurements reported for MK-B was extremely good (Fig. 1). The larger variability in the results for the higher specific activity sample was unexpected, but suggested that some fractionation may have occurred whenever our recommended method of freeze drying and homogenization of the entire sample was not followed prior to subsampling. The agreement in the measurements reported for the vegetation samples was also good (Fig. 2).

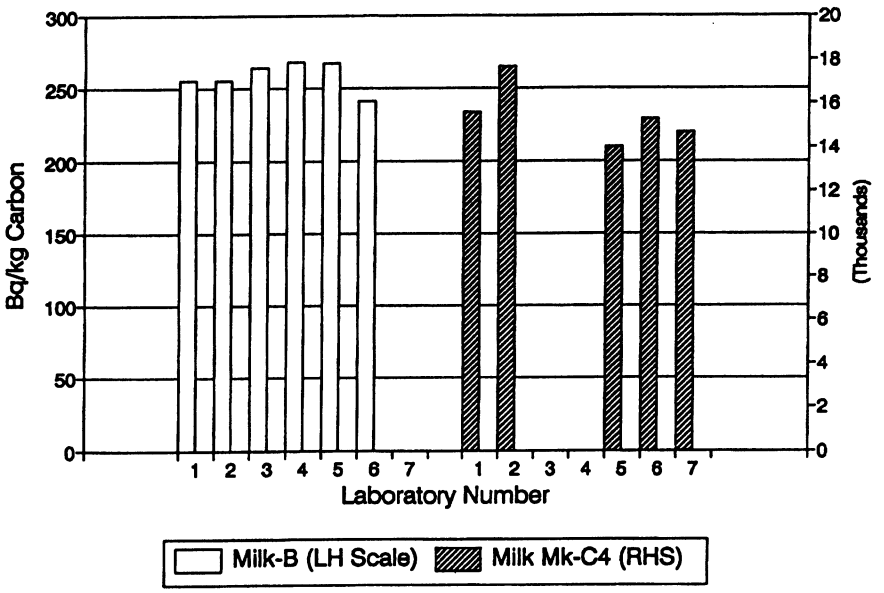

Fig. 1. ^{14}C intercomparison in milk samples

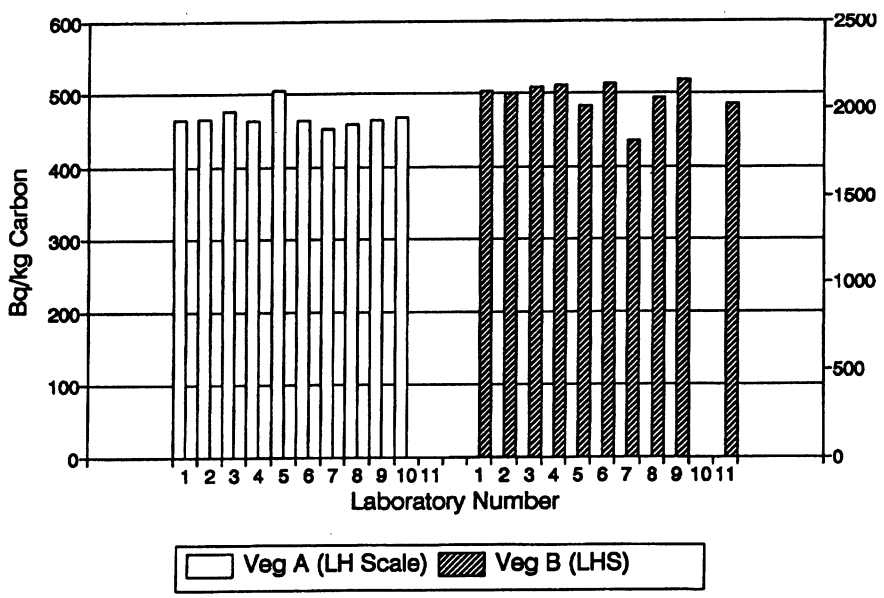

Fig. 2. ^{14}C intercomparison in vegetative samples

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TABLE 2. Results of an Interlaboratory Comparison of ^{14}C Content in Two Milk Samples

Lab	No. of determinations	Arithmetic ave. (Bq kg^{-1} C)	Weighted ave. (Bq kg^{-1} C)*	Weighted SD of mean	Assigned error in the mean†	Reduced chi‡	P (chi)
MK-C4							
Code 1	3	15,574.0	15,562.2	221.36	1.42%	28.55	2.71E-19
Code 2	3	17,650.0	17,650.0	28.87	0.65%	0.04	9.39E-01
Code 3	0						
Code 4	0						
Code 5	6	14,002.2	14,129.6	59.91	0.42%	4.07	1.80E-04
Code 6	24	15,265.5	15,149.7	82.26	0.54%	3.83	3.52E-10
Code 7	5	14,675.2	14,669.8	113.42	1.30%	0.28	8.40E-01
No. of laboratories		5	5				
Total no. of determinations		41	41				
Average		15,433.38	15,432.25				
Standard deviation		1231.62	1207.75				
Standard deviation of sample		1376.99	1350.31				
Standard deviation of mean		615.81	603.88				
Rel. Stand. deviation of mean		3.99%	3.91%				
Confidence level (95%)		1206.97	1183.58				
MK B							
Code 1	3	255.3	255.8	5.54	3.14%	0.32	6.21E-01
Code 2	3	255.0	255.0	25.98	15.85%	0.28	6.61E-01
Code 3	3	264.0	264.0	0.46	0.23%	0.40	5.50E-01
Code 4	1	268.0	268.0	3.00	1.12%	0.00	0.00E+00
Code 5	6	267.2	267.5	1.25	0.47%	3.84	3.31E-04
Code 6	27	241.3	239.9	2.53	1.06%	0.47	9.86E-01
No. of laboratories		6	6				
Total no. of determinations		43	43				
Average		258.48	258.36				
Standard deviation		9.27	9.72				
Standard deviation of sample		10.15	10.65				
Standard deviation of mean		3.78	3.97				
Rel. Stand. deviation of mean		1.46%	1.54%				
Confidence level (95%)		8.90	9.33				

*The variance, s^2, is given by $s^2 = \Sigma (x_i - x)^2 w_i / \Sigma w_i$, where i runs from 1 to n, $w_i \equiv 1$ for the arithmetic average column, and $w_i = 1/(\text{assigned error})^2$ in the weighted average column, where x is the average. The standard deviation, σ, is $s/n^{1/2}$, the standard deviation of the sample, σ_s, is $s/(n-1)^{1/2}$, and the standard deviation of the mean, σ_n, frequently called the standard error, equals $\sigma_s/n^{1/2}$.

†The error assigned to each laboratory was calculated from the larger of the variances calculated from the individual determinations (reduced χ^2 greater than one), or the variance expected on the basis of the quoted errors (reduced χ^2 less than one).

‡The column headed "reduced chi" is the square root of χ^2; that headed P(chi) is the probability of obtaining χ^2 by chance.

Final Report

We have subsequently applied more rigorous statistical analyses to the results (Barington 1969). Tables 2 and 3 list the arithmetic and weighted averages (average of replicates submitted by the analysts, weighted by their stated errors) for all values reported, and the standard deviation of the replicates so weighted in each case. When a first calculation of the overall mean for the vegetative samples showed that the results reported by one laboratory in each group met the specifications for an outlier (>3 standard deviations (SD) from the mean), those values were omitted from the final analyses reported here.

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TABLE 3. Results of an Interlaboratory Comparison of ^{14}C in Two Vegetation Samples

Lab	No. of determinations	Arithmetic ave. (Bq kg^{-1} C)	Weighted ave. (Bq kg^{-1} C)	Weighted SD of mean	Assigned error in the mean	Reduced chi	P (chi)
Veg A							
Code 1	3	464.3	460.0	21.60	8.68%	0.54	7.42E-01
Code 2	2	465.5	464.6	11.47	3.95%	0.63	5.31E-01
Code 3	2	475.5	474.8	9.47	3.86%	0.52	6.05E-01
Code 4	6	463.3	463.6	0.43	0.14%	0.64	8.26E-01
Code 5	5	504.2	504.1	8.82	2.62%	0.67	7.75E-01
Code 6	1	462.9	462.9	2.30	0.50%		
Code 7	5	451.9	452.2	2.93	0.65%	2.08	1.61E-03
Code 8	14	457.4	456.6	5.79	1.27%	2.01	1.08E-06
Code 9	2	463.5	464.0	1.77	0.38%	1.11	2.51E-01
Code 10	1	467.0	467.0	3.00	0.64%		
Code 11	5	712.7	715.8	69.22	14.82%	0.65	7.90E-01
Total no. of determinations		46	46				
Average of 11 labs		489.85	489.60				
Average (W.O. #11)		467.56	466.98				
Standard deviation		71.65	72.71				
Standard (W.O. #11)		13.50	13.62				
Standard deviation of sample		75.15	76.26				
Standards (W.O. #11)		14.23	14.35				
Standard deviation of mean		22.66	22.99				
Standard deviation of mean (W.O. #11)		4.50	4.54				
Rel. Stand. deviation of mean		4.63%	4.70%				
Rel. Stand. deviation of mean (W.O. #11)		0.96%	0.97%				
Confidence Level (95%)		44.41	45.07				
Confidence (95%) W.O. #11		8.41	8.48				
Veg B							
Code 1	3	2095.00	2093.13	30.51	8.68%	0.54	9.72E-01
Code 2	2	2081.50	2081.42	3.50	3.95%	0.63	9.09E-01
Code 3	3	2116.67	2125.03	28.96	3.86%	0.52	3.65E-03
Code 4	4	2125.25	2125.92	2.58	0.14%	0.64	5.48E-01
Code 5	4	2006.93	2006.82	19.60	2.62%	0.67	2.82E-01
Code 6	1	2138.20	2138.20	9.80	0.50%		
Code 7	5	1815.24	1815.24	15.78	0.38%	1.11	3.59E-01
Code 8	16	2056.88	2042.48	6.90	0.65%	2.08	2.57E-10
Code 9	2	2155.24	2153.92	8.38	1.27%	2.01	5.80E-03
Code 11	5	2021.60	1987.41	9.80	0.50%	1.00	1.85E-01
Total no. of determinations		45	45				
Average of 10 labs		2061.25	2056.96				
Average (W.O. #7)		2088.58	2083.81				
Standard deviation		94.09	96.59				
Standard (W.O. #7)		48.64	56.14				
Standard deviation of sample		99.18	101.81				
Standards (W.O. #7)		51.59	59.55				
Standard deviation of mean		31.36	32.20				
Standard dev. of mean (W.O. #7)		17.20	19.85				
Rel. Stand. deviation of mean		1.52%	1.57%				
Rel. Stand. deviation of mean (W.O. #7)		0.82%	0.95%				
Confidence level (95%)		58.61	60.16				
Confidence level (95%) W.O. #7		30.49	35.19				

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The assigned relative error in the mean is the larger of the error calculated from the observed variance and that from the variance expected on the basis of the quoted errors.

The reduced chi square (χ^2) is equal to $s^2/(n-1)$, with $s^2 = \Sigma(x_i - x)^2 w_i / \Sigma w_i$, where i runs from 1 to n, and the w_i are given by the inverse square of the quoted errors. A value near unity indicates that the observed variance is close to the value expected from the quoted errors. A value less than one means that all the replicates are close together by chance, or that the errors have been overestimated. A value much greater than unity means that the individual values differ by more than just chance (systematic errors), or that the errors have been underestimated.

Because a weighted average of the laboratories gives too much weight to a few laboratories reporting very small errors, we have chosen to compute an arithmetic average of the weighted averages of the individual laboratories.

Recommended Values (Bq kg^{-1} C)

Milk Samples

MK-C4 15,432 ± 604 (1σ), ± 1184 (95% confidence level)

MK-B 258.4 ± 4.0 (1σ), ± 9.3 (95%)

An analysis of the variance indicates that for:

Milk MK-C4: With only five laboratories reporting, three of the values are outside the ± 1 σ band about the average; two of them are well outside. The probability $P(\chi)^2$ is zero, implying that the hypothesis that the values reported by the various laboratories are statistically distributed by chance is false. Because the internal consistency of three of the laboratories was also poor, this observation probably implies that most of the laboratories have nonstatistical variations in their results. It is possible that a knowledge of the high activity of the sample caused some analysts to reduce sample size, introducing an increased risk of inhomogeneity. Of course, the errors could be underreported, but that seems unlikely in this instance.

Milk MK-B: Results for this sample, on the other hand, showed very good consistency both within and between laboratories. As the activity in this sample is low, it would indicate that the sample was homogeneous and that the background corrections were adequate.

Vegetation Samples

Veg A 467.0 ± 4.5 (1σ), ± 8.5 (95% confidence level)

Veg B 2083.8 ± 19.9 (1σ), ± 35.2 (95%)

An analysis of variance indicates that for:

Veg A: The variance of all the laboratories taken together is approximately consistent with the errors assigned to each individual laboratory. The probability $P(\chi^2) \approx 0.5$ [without #11].

Veg B: The variance of all the laboratories taken together is inconsistent with the errors assigned to each individual laboratory. The probability $P(\chi^2) \approx 0$ [without #7]. Much of the contribution to the variance comes from laboratory 7, but no good reason for rejecting it could be found.

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This means that in the case of Veg B, either:

a) There are systematic differences between laboratories, or
b) Some of the errors are underreported, or
c) Replicate measurements within a given laboratory are unusually consistent by chance, or
d) The sample homogeneity was inadequate, or
e) A combination of all four above.

We believe that (e) provides the most likely explanation.

Summary

Five materials, in three different organic matrices, have been prepared as potential ^{14}C secondary reference materials and tested in our laboratory for homogeneity. Subsamples of four of these were subsequently sent out for ^{14}C analysis by a number of laboratories that utilize a variety of analytical techniques. Statistical analyses of the measurements returned to us are contained in this report; the data presented in graphical form. The close agreement among the participating laboratories reflects very favorably on the caliber of the analyses performed, and permits the use of this report in laboratory Quality Assurance documentation.

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APPENDIX I. PARTICIPATING LABORATORIES

TABLE A1. List of Participating Laboratories

Lab	Analytical technique: Oxidation; final form; measurement*	Sample analyzed			
		Mk-B	Mk-C4	Veg A	Veg B
Berkeley Tech.	Wet oxidation; CO_2 in Carbo-sorb/ Permafluor; LSC			x	x
CRL, AECL	Parr bomb; CO_2 in Carbo-sorb/ Permafluor; LSC	x	x	x	x
Hungarian Academy of Science	Parr bomb; CO_2 in CO_2 carrier gas; GPC			x	x
Hydro-Québec	Bomb; CO_2 in Carbo-sorb/Permafluor; LSC	x	x	x	x
Lawrence Livermore National Laboratory	Bomb; graphite; AMS	x	x	x	x
Ministry of Agriculture, Fisheries and Food	Wet oxid.; $CaCO_3$; LSC			x	x
NERC	Bomb; C_6H_6; LSC			x	x
Ontario Hydro	Bomb; CO_2 in Carbo-sorb/Permafluor; LSC	x	x	x	x
Radiocarbon Dating	Bomb; C_6H_6; LSC	x		x	
U. of Bern	Tube comb.; CO_2 in CH_4; GPC			x	x
U. of Waterloo	Bomb; C_6H_6; LSC	x			
Whiteshell Laboratories, AECL	Canberra/Packard Oxid.; CO_2 in Carbo-sorb/Permafluor; LSC		x		x

*GPC=gas proportioned counting; LSC=liquid scintillation counting

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APPENDIX II. HOMOGENEITY TESTING

TABLE A2-1. Homogeneity Tests for ^{14}C Distribution in Milk Candidate Reference Materials*

Sample code	No. of samples analyzed	Mean ± SD (Bq g^{-1} of carbon)	RSD (%)	RSE (%)
I. Candidate reference material: MK-B				
Test of homogeneity between samples at natural levels of ^{14}C in 2% dairy milk				
MK-B-5 to MK-B-39	6	0.26 ± 0.01	3.8	1.6
II. Candidate reference material: MK-C4				
(a) Test of homogeneity between randomly selected samples at elevated levels of ^{14}C				
MK-C4-2 to MK-C4-29	6	15.4 ± 0.3	1.9	0.8
(b) Test of homogeneity within a sample				
MK-C4-19a to MK-C4-19f	6	15.1 ± 0.3	2.0	0.8
(c) Test of homogeneity as a function of sub-sample mass (varying between 2 g and 0.25 g)				
MK-C4-7a to MK-C4-7h	8	15.3 ± 0.4	2.6	0.9
Mean ± SD of the three population means between sample groups (a),(b) and (c)				
	3	15.3 ± 0.2	1.3	0.8
Grand mean ± SD of all 20 individual values within sample groups (a), (b) and (c)				
	20	15.3 ± 0.4	2.6	0.6

*Taken from Rao *et al.* (1995)

TABLE A2-2. Homogeneity Tests for ^{14}C Distribution in Vegetative Candidate Reference Materials*

Sample code	No. of samples analyzed	Mean ± SD (Bq g^{-1} of carbon)	S.E.
I. Candidate Reference Material: Veg A (vegetation containing slightly elevated levels of ^{14}C)			
(a) Test of homogeneity between randomly selected samples all >2 g			
Veg A #1–32	9	0.456 ± 0.033	0.011
(b) Test of homogeneity within a sample, all >2 g			
Veg A #18(a–e)	5	0.456 ± 0.040	0.018
	4	0.457 ± 0.026	0.013
(c) Test of homogeneity as a function of sub-sample mass (varying between 1.5 g and 0.5 g)			
Veg A #18 (f–j)	5	0.439 ± 0.032	0.015
II. Candidate reference material: Veg B (vegetation containing elevated levels of ^{14}C)			
(a) Test of homogeneity between randomly selected samples, all >2 g			
Veg B #5–6 to #25–26	11	2.076 ± 0.017	0.81
(b) Test of homogeneity within a sample, all >2 g			
Veg B #13 (a–f)	6	2.035 ± 0.027	0.011
	5	2.075 ± 0.018	0.008
(c) Test of homogeneity as a function of subsample mass (varying between 2.6 g and 0.5 g)			
Veg B #13 (g–k)	5	2.065 ± 0.052	0.023

*In each set of tests there were three values outside 1 σ, and none outside 2 σ; consequently, the materials can be considered homogeneous down to sample sizes of 0.5 g.

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TABLE A2-3. Natural Levels of ^{14}C in Bovine Muscle Tissue

Sample and code	Individual values: Bq kg^{-1} of carbon	Individual values: RSD of count rates from three cycles (%)	Mean ± SD (Bq kg^{-1} of carbon)	RSD (%)	RSE (%)
BF-B-1	266	2.8			
BF-B-2	253	3.1	260 ± 7	2.6	1.5
BF-B-3	262	2.6			
I. Samples taken from different parts of the blender before canning					
BF-H-1	7880	4.3			
BF-H-2	8320	4.7	8250 ± 340	4.2	2.4
BF-H-3	8550	3.7			
II. Samples from the can sealed under ambient atmosphere					
BF-A-1	8070	1.7			
BF-A-2	8420	2.9	8210 ± 190	2.3	1.3
BF-A-3	8140	4.5			
III. Samples from the can sealed after purging with nitrogen					
BF-N-1	7910	3.3			
BF-N-2	8230	3.5	8110 ± 180	2.2	1.3
BF-N-3	8200	3.6			
IV. Mean ± SD of all nine results			8190 ± 220	2.7	0.9

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