

## ENVIRONMENTAL MONITORING OF $^{14}\text{C}$ IN MILK AND AGRICULTURAL SAMPLES

JAMES B. MOORE

U. S. Environmental Protection Agency, National Air and Radiation Environmental Laboratory  
Montgomery, Alabama 36115-2601 USA

JOHN E. NOAKES and JAMES D. SPAULDING

Center for Applied Isotope Studies, University of Georgia, Athens, Georgia 30605 USA

**ABSTRACT.** Environmental samples can be analyzed for  $^{14}\text{C}$  using a benzene synthesis procedure, which is particularly useful for milk and agricultural samples. We document here analytical results obtained with the benzene synthesis procedure on environmental samples collected from various sites across the United States. With the exception of several pasteurized milk samples collected in 1976 from locations in the western United States, levels of  $^{14}\text{C}$  in milk and other environmental samples were within the ranges expected for the time periods examined. No significant  $^{14}\text{C}$  elevation was detected in grass samples collected around a nuclear power facility. Pasteurized milk samples collected in the United States by the U. S. Environmental Protection Agency's Environmental Radiation Ambient Monitoring System before and after the Chernobyl incident showed slight but not significant increases in  $^{14}\text{C}$  levels.

### INTRODUCTION

Monitoring  $^{14}\text{C}$  in food and agricultural products is of vital interest, as this radionuclide may be released from certain nuclear power plants, nuclear-fuel reprocessing facilities or low-level radioactive waste burial sites. One must measure background levels of  $^{14}\text{C}$  on a routine basis to detect environmental increases from a particular source. The specific activity of contemporary carbon has been determined to be about 15 dpm  $\text{g}^{-1}$  of carbon, referenced to levels found in natural samples (grapes) grown during the years 1982 and 1987 in Athens, Georgia. This value had increased to  $>20$  dpm  $\text{g}^{-1}$  of carbon during the 1960s and 1970s, primarily due to atmospheric nuclear testing. We document here  $^{14}\text{C}$  levels in various environmental samples, as determined by the benzene synthesis method of sample preparation and liquid scintillation counting (LSC).

### SAMPLING SITES AND SAMPLE TREATMENT

Grass samples (rye and bahia varieties) were collected from 1975 to 1976 from designated sampling sites near Farley Nuclear Power Facility in Dothan, Alabama, and represent a one-month growth period. The grass samples were oven-dried at a temperature of 45 °C for 24 h, and 10-g aliquots were pelletized for combustion using the benzene synthesis method for analysis.

Milk samples were collected from 1974 to 1976 through a cooperative program conducted by the Environmental Protection Agency (EPA) Office of Radiation Programs and the Milk Sanitation Section of the Food and Drug Administration. The milk sample collection program is continued through the Environmental Radiation Ambient Monitoring System (ERAMS) operated by the EPA National Air and Radiation Environmental Laboratory in Montgomery, Alabama. The samples were collected (prior to processing) from dairies at 65 locations, including at least one site in each of the 50 states, Puerto Rico and the Canal Zone (Fig. 1). Milk samples from nine of these locations, representing a wide geographical distribution, were selected and analyzed for  $^{14}\text{C}$  (Fig. 2). Samples from years both before and after the 1986 Chernobyl nuclear accident were examined. The pasteurized milk samples were composites based on the volume of milk sold by various milk processors in the sampling stations, and represent  $>80\%$  of the milk consumed in those areas. Two



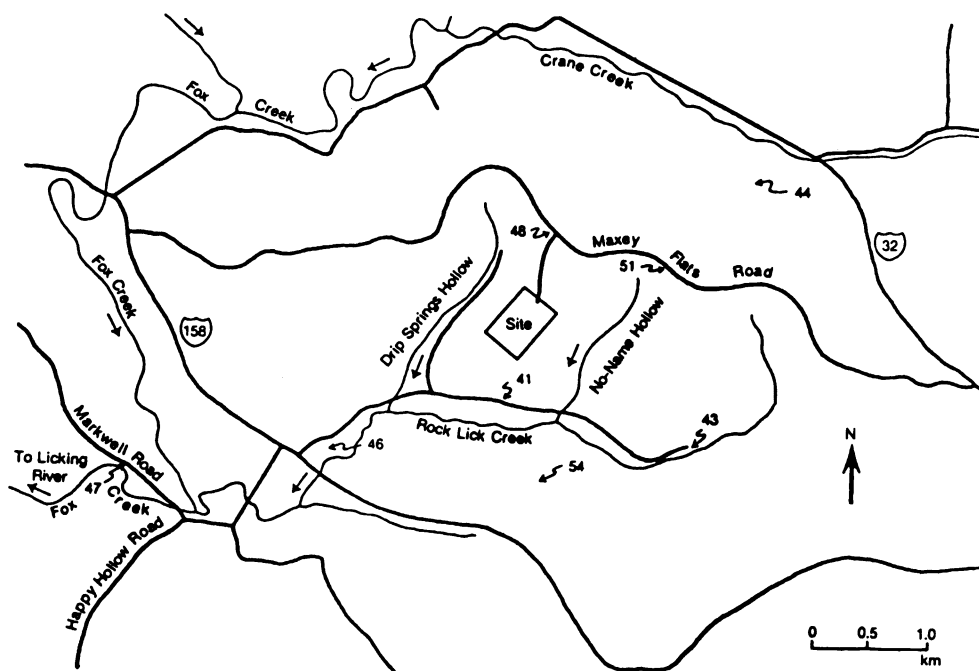


Fig. 3. Milk and vegetable sampling locations at Maxeys Flats Radioactive Waste Burial Site

milk samples were collected in 1976 near the Maxeys Flats Radioactive Waste Burial Site in northeast Kentucky (Fig. 3). Samples were freeze-dried and the powder pelletized to 2 cm × 5 cm disks prior to combustion.

Fresh tomatoes were picked from gardens at two locations near the Maxeys Flats Radioactive Waste Burial Site in northeast Kentucky on 9 August 1976 (Fig. 3). To provide background data, tomatoes were collected from Aberdeen, Ohio, about 48 km north of the site. The samples were homogenized, freeze-dried and pelletized prior to combustion. Samples of oats, rye, wheat and sugar purchased locally in Athens, Georgia in September 1974 were also analyzed.

#### PREPARATION AND MEASUREMENT OF COUNTING SAMPLE

During benzene synthesis, each sample is converted to carbon dioxide by dry combustion, water is frozen out, and the pure CO<sub>2</sub> is passed into a reaction chamber containing hot lithium metal. The Li and CO<sub>2</sub> combine to form lithium carbide (LiC<sub>2</sub>). Water is then passed into the reaction chamber, acetylene (C<sub>2</sub>H<sub>2</sub>) forms, and is passed through a purification column into storage, and subsequently, onto a vanadium alumina catalyst. The catalyst acts to trimerize the C<sub>2</sub>H<sub>2</sub> into benzene (C<sub>6</sub>H<sub>6</sub>), which is collected for LSC.

We weighed the benzene from individual combusted samples to determine the carbon content and placed it in low-K borosilicate glass 6-ml vials. Two scintillators, PPO (diphenyloxazole) and POPOP (1,4-bis(2-(5-phenyloxazolyl)benzene), were dissolved in the benzene sample in concentrations of 0.5 and 0.2% by weight, respectively, and the sample volume brought up to 5 ml with spectrograde benzene. The LS counters, a Picker 220 and a Beckman LS 100, were set

to count  $^{14}\text{C}$  with energy windows between the  $E_{\text{max}}$  energies for  $^3\text{H}$  and  $^{14}\text{C}$  to eliminate any  $^3\text{H}$  activity from the  $^{14}\text{C}$  determination.

We calculated the counting efficiency of the Picker 220 at these energy windows at 55%, using the NIST (formerly NBS)  $^{14}\text{C}$  oxalic acid standard (14.27 dpm  $\text{g}^{-1}\text{C}$ ) that was first converted to benzene. We then determined the efficiency of the Beckman counter at 77% by using a  $^{14}\text{C}$  standard especially prepared in benzene with an overall error of  $\pm 3\%$ . Each benzene sample was counted for  $^{14}\text{C}$  for 28 100-min intervals to achieve good counting statistics. Any values that were outside two standard deviations ( $2\sigma$ ) were discarded. We calculated the values listed as dpm  $\text{g}^{-1}\text{C}$  by correcting the sample count for background, counting efficiency and total carbon content.

## RESULTS AND DISCUSSION

Table 1 lists  $^{14}\text{C}$  concentrations in grass samples collected near Farley Nuclear Power Facility in Dothan, Alabama during the growing seasons of 1975 and 1976. The concentrations in these samples show increases of  $\sim 24\%$  above natural (18-21 dpm  $\text{g}^{-1}\text{C}$ ), which may be attributed to atmospheric nuclear testing by the People's Republic of China in 1973 and 1974. The Farley Nuclear Power Facility did not reach initial criticality until 9 August 1977, and did not become commercial until 11 December 1977.

The milk and tomato samples (Table 2) collected from a garden near the Maxey Flats Radioactive Waste Burial Site are all in the normal range of 18–19 dpm  $\text{g}^{-1}\text{C}$ .

TABLE 1.  $^{14}\text{C}$  Activity in Grass Samples Collected Near Farley Nuclear Power Plant

Sample no.	Collection date	dpm $\text{g}^{-1}\text{C}^*$	% Natural
1	8/11/76	23.7 $\pm$ 0.3	124 $\pm$ 0.79
2	6/15/76	23.8 $\pm$ 0.3	125 $\pm$ 0.84
3	7/15/76	24.1 $\pm$ 0.5	126 $\pm$ 1.26
4	8/11/76	23.3 $\pm$ 0.4	122 $\pm$ 0.94
5	6/11/75	24.1 $\pm$ 0.3	126 $\pm$ 0.84
6	11/11/75	23.3 $\pm$ 0.2	120 $\pm$ 0.57
7	9/22/76	22.3 $\pm$ 0.2	117 $\pm$ 0.52
8	10/12/76	23.2 $\pm$ 0.2	121 $\pm$ 0.63

TABLE 2.  $^{14}\text{C}$  Concentration in Tomatoes and Milk (Maxey Flats)

Sample no.	Type	Collection date	dpm $\text{g}^{-1}\text{C}^*$	% Natural
48	Tomatoes	8/9/76	18.2 $\pm$ 0.6	95
51	Tomatoes	8/9/76	19.5 $\pm$ 0.8	102
AB	Tomatoes	8/9/76	19.0 $\pm$ 0.8	100
41	Milk	9/1/76	18.0 $\pm$ 0.6	94
46	Milk	9/2/76	19.8 $\pm$ 0.6	104

\* 2- $\sigma$  counting error

TABLE 3. Miscellaneous Samples Analyzed

Analysis date	Sample type	dpm g <sup>-1</sup> C*	% Natural
9/2/74	Oats	21.26 ± 0.2	107
9/3/74	Rye	20.58 ± 0.2	103
9/4/75	Wheat	19.56 ± 0.1	100
9/6/74	Sugar	19.45 ± 0.1	98

\* 2-σ counting error

Table 3 presents <sup>14</sup>C results for oats, rye, wheat and sugar purchased in Athens, Georgia, in September 1974. The <sup>14</sup>C concentrations of these miscellaneous samples are in the normal range of 19 to 21 dpm g<sup>-1</sup> C for that year. Table 4 shows <sup>14</sup>C concentrations in freeze-dried pasteurized milk samples collected through ERAMS and earlier collection programs. Samples collected in April 1974 and 1975 show no significant increases in <sup>14</sup>C levels. We selected April because this is when grass turns green and domestic cows begin grazing. Of particular interest are milk samples collected in April 1976 from stations in Los Angeles, Portland, Chicago, Idaho Falls and Honolulu, all of which have <sup>14</sup>C levels from 1.5 to 2.7 times the natural (18–19 dpm g<sup>-1</sup> C) <sup>14</sup>C levels. Chinese nuclear atmospheric testing did not take place until 26 September 1976, and no explanation is apparent for the increased levels of <sup>14</sup>C for these particular western stations. The original milk samples were re-analyzed and sent to an independent laboratory for cross-check analysis. The results from re-analysis and the independent laboratory were the same as those achieved in the original analyses. The pasteurized milk samples for the years 1982 to 1986 that were collected prior to the May 1986 Chernobyl nuclear accident show no increases in <sup>14</sup>C levels. The milk samples collected following the Chernobyl accident show insignificant increases in <sup>14</sup>C levels.

TABLE 4. Freeze-Dried Pasteurized Milk Samples

Collection date	City	dpm g <sup>-1</sup> C*	% Natural	
4/74	Charleston, SC	18.7 ± 0.2	95	
	Boston, MA	18.9 ± 0.2	95	
	Los Angeles, CA	18.6 ± 0.2	94	
	Portland, OR	17.8 ± 0.2	90	
	New Orleans, LA	18.8 ± 0.2	95	
	Honolulu, HI	18.7 ± 0.2	94	
	Idaho Falls, ID	18.6 ± 0.2	94	
	4/75	Charleston, SC	17.6 ± 0.5	91
		Boston, MA	18.0 ± 0.5	93
Los Angeles, CA		17.6 ± 0.6	91	
Portland, OR		18.0 ± 0.5	92	
New Orleans, LA		17.6 ± 0.6	91	
Honolulu, HI		21.2 ± 0.7	109	
Idaho Falls, ID		19.3 ± 0.6	99	
Chicago, IL		21.2 ± 0.7	109	
4/76–5/76		Charleston, SC	18.2 ± 0.6	95
	Boston, MA	19.9 ± 0.6	104	
	Los Angeles, CA	47.6 ± 1.8	249	
	Portland, OR	48.5 ± 1.9	254	
	New Orleans, LA	18.3 ± 0.6	96	
	Honolulu, HI	50.5 ± 1.7	265	
	Idaho Falls, ID	30.9 ± 1.1	159	
	Chicago, IL	51.0 ± 1.8	267	

TABLE 4. (Continued)

Collection date	City	dpm g <sup>-1</sup> C*	% Natural
4/5/82	Los Angeles, CA	16.9 ± 0.4	99
4/6/82**	Honolulu, HI	16.8 ± 0.3	98
4/6/82**	Honolulu, HI	16.6 ± 0.4	97
4/7/82	Idaho Falls, ID	15.3 ± 1.5	90
4/8/82	Montgomery, AL	17.2 ± 0.4	101
4/9/82	New Orleans, LA	17.0 ± 0.5	100
4/22/82	Palmer, AK	16.8 ± 0.4	99
4/27/82	Charleston, SC	17.1 ± 0.3	100
5/3/82	Manchester, NH	17.5 ± 0.6	103
5/3/82	Chicago, IL	17.3 ± 0.4	102
5/4/82	Honolulu, HI	16.8 ± 0.2	99
4/4/83	Honolulu, HI	16.8 ± 0.1	101
4/4/83	Chicago, IL	16.8 ± 0.1	101
4/11/83	Los Angeles, CA	16.3 ± 0.1	98
4/18/83	Idaho Falls, ID	16.9 ± 0.1	101
4/25/83	Charleston, SC	17.1 ± 0.1	101
4/26/83	New Orleans, LA	16.8 ± 0.1	101
5/2/83	Portland, OR	16.9 ± 0.1	101
4/2/84	New Orleans, LA	16.8 ± 0.1	103
4/2/84	Chicago, IL	17.5 ± 0.1	107
4/2/84	Chicago, IL	17.5 ± 0.1	107
4/3/84	Honolulu, HI	16.3 ± 0.1	99
4/3/84	Portland, OR	16.7 ± 0.1	102
4/9/84	Los Angeles, CA	17.2 ± 0.1	105
4/16/84	Idaho Falls, ID	16.7 ± 0.1	102
5/3/84	Palmer, AK	16.3 ± 0.1	99
3/4/85**	Manchester, NH	16.6 ± 0.1	103
3/4/85**	Manchester, NH	16.9 ± 0.1	105
4/2/85	Honolulu, HI	17.2 ± 0.1	107
5/6/85	Idaho Falls, ID	16.6 ± 0.1	103
5/6/85**	Idaho Falls, ID	15.9 ± 0.1	99
2/2/86	Los Angeles, CA	16.1 ± 0.1	102
4/1/86	Honolulu, HI	16.4 ± 0.1	104
4/11/86**	Montgomery, AL	16.5 ± 0.1	104
4/11/86**	Montgomery, AL	16.2 ± 0.1	103
8/21/86	Los Angeles, CA	16.7 ± 0.1	106
3/4/87	Anchorage, AK	16.0 ± 0.5	103
4/1/87	New Orleans, LA	16.1 ± 0.3	104
4/2/87**	Los Angeles, CA	15.9 ± 0.4	103
4/2/87**	Los Angeles, CA	15.8 ± 0.3	102
4/6/87	Portland, OR	16.2 ± 0.3	104
4/6/87**	Chicago, IL	16.1 ± 0.2	104
4/6/87**	Chicago, IL	16.1 ± 0.3	104
4/6/87**	Honolulu, HI	16.0 ± 0.3	103
4/6/87**	Honolulu, HI	16.1 ± 0.3	104
4/10/87	Montgomery, AL	15.9 ± 0.2	102
4/13/87	Idaho Falls, ID	16.0 ± 0.3	104
5/11/87	Charleston, SC	15.7 ± 0.3	102

\*2-σ counting error

\*\*Split samples

## CONCLUSIONS

We have shown that sample preparation using benzene synthesis followed by LSC is effective in evaluating <sup>14</sup>C in various types of environmental samples. The method has particular significance for the evaluation of samples of consumable goods, such as milk. With the exception of several pasteurized milk samples collected in 1976 from locations in the western United States, levels of <sup>14</sup>C in milk and other environmental samples were within the ranges expected for the time periods examined. Analysis of <sup>14</sup>C in milk samples taken from 1982–1987 showed no significant increases in <sup>14</sup>C levels from expected natural levels near 15 dpm g<sup>-1</sup> C following the Chernobyl nuclear accident in May 1986.

## REFERENCES

- Montgomery, D.M., Kolde, H.E. and Blanchard, R.L. 1975 Radiological measurements at the Maxey Flats Waste Burial site: 1974-1975. Eastern Environmental Radiation Facility, Montgomery, Alabama, USA. *EPA Report No. 520/5-76/020*.
- Noakes, J.E., Kim, S.M. and Stipp, J.J. 1965 Chemical and counting advances in liquid scintillation counting. In Chatters, R.M., and Olson, E.A., eds., *Proceedings of the Sixth International Conference on Radiocarbon and Tritium*. Clearinghouse for Federal Scientific and Technical Information, NBS, Washington, DC: 68–92.
- Smith, J.M., Norwood, D.L., Strong, A.B. and Broadway, J.A. 1982 Assessment of fallout in the United States from atmospheric nuclear testing by the People's Republic of China on September 17, 1977. *EPA Report No. 520/5-82-008*.
- U.S. Environmental Protection Agency 1988 Environmental Radiation Data: Report 54. National Air and Radiation Environmental Laboratory: Montgomery, Alabama, USA. *EPA Report No. 520/5-88-058*.

