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RADIOCARBON IN TROPOSPHERIC CO_2 AND ORGANIC MATERIALS FROM SELECTED NORTHERN HEMISPHERE SITES

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ABSTRACT. Radiocarbon was measured in atmospheric CO_2 from La Jolla, California and in living organic materials from six sites in the northern hemisphere. Atmospheric CO_2 $\Delta^{14}C$ values from La Jolla agreed with those previously published records from China Lake, California (Berger *et al.* 1987) and Vermunt, Austria (Levin *et al.* 1985). $\Delta^{14}C$ values of fruit and grain samples that grew during 1980 agreed with the atmospheric CO_2 $\Delta^{14}C$ measurements. Most of the $\Delta^{14}C$ results of fruit and corn samples stored since the 1940s agreed with tree-ring $\Delta^{14}C$ values for the same time period. In general, agreement was found between the atmospheric CO_2 or tree-ring $\Delta^{14}C$ records available for the Northern Hemisphere and the $\Delta^{14}C$ signatures of rapidly exchanging organic matter pools examined in this study. Exceptions were the $\Delta^{14}C$ values of carbonate from egg shells and that of organic carbon from egg insides, which demonstrate that bicarbonate and organic carbon within the egg follow different biochemical pathways.

INTRODUCTION

Time histories of $\Delta^{14}C$ in tropospheric CO_2 are available from several sources around the world (Berger *et al.* 1987; Levin *et al.* 1985; Nydal and Lovseth 1983). These records accurately document the levels of bomb ^{14}C produced by thermonuclear weapons testing since the 1950s, in the troposphere. The data presented here provide a small addition to the large data base already available for atmospheric CO_2, in a region (La Jolla, California) previously under-documented with respect to $\Delta^{14}C$ measurements. Also provided are selected $\Delta^{14}C$ measurements of plant and other organic materials from La Jolla, Heidelberg, Germany, Martha's Vineyard, Massachusetts and Harris, Louisiana.

The original premise of this study was twofold: 1) to establish the degree to which steady state existed in ^{14}C activities of a variety of plant carbon pools and those in tropospheric CO_2; and 2) to determine if there is any anomalous fractionation of carbon isotopes between CO_2 and the organic matter produced during photosynthesis by C_3 and C_4 plants. We find that the $\Delta^{14}C$ of rapidly growing vegetation is similar (within 2 σ uncertainty) to that in the atmospheric CO_2 pool from which it had been extracted.

METHODS

Tropospheric CO_2 samples reported here were collected at the Mount Soledad ^{14}C Laboratory in La Jolla, California (32°50′N, 117°20′W, 240 m above sea level) in June and August /September 1980. They were collected using two methods, the tray method and the bubble method. For the tray collections, a basic solution of $BaCl_2$ and concentrated ammonium hydroxide was placed in a shallow, plastic tray (50 cm × 50 cm) with a fan blowing air across its surface. In this way, airborne CO_2 was collected for a period of 24 h to 5 d. For the bubble method, air was pumped through three bottles in sequence containing $BaCl_2$ and concentrated ammonium hydroxide solution (with solution volumes 700, 400 and 250 ml). After CO_2 collection, the basic solutions were placed in 1-liter glass bottles, sealed, and left for 10 d to allow for $BaCO_3$ to precipitate. The solution was decanted off, and the $BaCO_3$ precipitate was dried on a hot plate to remove residual ammonium hydroxide. The dried samples were acidified with 2 N HCl and the evolved CO_2 was collected cryogenically (Linick 1980).

Two samples of fig fruit and one sample of fig leaves were harvested from a tree in Hans and Ruth Suess' backyard in La Jolla in July 1980. Samples of corn (kernels) and wheat were collected from fields on the outskirts of Heidelberg, Germany (49°25′N, 08°40′E) on 15 June 1980. Samples of

corn kernels and husks were collected from Shoe Peg-Harris, Louisiana (32°N, 92°W), and Gray Summit. They were harvested in 1947 and stored dry until we analyzed them in 1980. Two locally harvested samples, one of raspberries and one of apples, were obtained from a resident of Martha's Vineyard, Massachusetts (41°30′N, 70°40′W). The samples were canned in 1942 and were not degraded by microbial activity. Two dozen eggs were obtained from Miller's Ranch in San Diego (~10 km inland of the coast) on 29 November 1979. The shells were acidified separately with 4 N HCl under vacuum and the carbon dioxide collected cryogenically. The egg insides (yolk and white combined) and each of the above described organic matter samples were dried and combusted in a flow of medical-grade oxygen, and the resultant CO_2 gas was bubbled through chromic acid and trapped cryogenically. One of the corn kernels samples from Gray Summit (LJ-5074) was extracted with hot acetone in a soxhlet extractor for 2 h and then subjected to hot base (1 N NaOH) and acid (1 N HCl), and the extracted kernels oxidized as above.

Carbon dioxide from each sample was converted to acetylene gas via a lithium carbide intermediate and purified through charcoal at 0°C. Each sample was counted for 2–5, 2-day periods in 2.2-liter quartz and 0.4- and 1.0-liter steel gas proportional beta counters according to standard procedures (Druffel and Linick 1978).

Radiocarbon results are reported as $\Delta^{14}C$ in ‰. Uncertainties given are one-sigma deviation based on statistics of sample, standard and background activities. The $\delta^{13}C$ values were measured on the reburned acetylene gas and used to correct the $\Delta^{14}C$ results according to standard methods (Stuiver and Polach 1977). All $\delta^{13}C$ measurements had uncertainties of ±0.15‰.

Results

The $\Delta^{14}C$ results of atmospheric CO_2 and plant materials are reported in Table 1 and shown in Figure 1. Atmospheric CO_2 $\Delta^{14}C$ values for the samples collected in June 1980 using two different methods are 252 and 253‰. The $\Delta^{14}C$ value for the sample collected in August/September 1980 was significantly higher (276‰).

The $\Delta^{14}C$ results from two La Jolla fig samples collected in July 1980 were 273 and 263‰. The fig leaves sample had a $\Delta^{14}C$ value of 272‰. The Heidelberg corn and wheat samples collected in June 1980 had $\Delta^{14}C$ values of 257 and 260‰, respectively. Values for the egg shells and insides were significantly different from each other (256‰ and 315‰, respectively).

$\Delta^{14}C$ measurements of raspberries and apples archived in 1942 had prebomb values of –27‰ and –20‰, respectively, and are plotted with annual tree ring $\Delta^{14}C$ values for 1935–1950 (Fig. 2). The $\Delta^{14}C$ values of corn samples from Shoe Peg-Harris were –21‰ (husk) and –13‰ (kernels), and those from Gray Summit were lower, –26‰ and –27‰ (kernels) and –27‰ (husk) (Fig. 2).

The $\delta^{13}C$ values for atmospheric CO_2 are –26.6‰ and –25.4‰ for samples collected using the tray method, and –20.5‰ for that using the bubble method. Significant fractionation is reflected in these values, compared to atmospheric CO_2 $\delta^{13}C$ values of –7.5‰ in 1978 (Keeling, Mook and Tans 1979). The $\delta^{13}C$ values for the fig, raspberries, apples and wheat samples range from –20 to –28‰, typical of C-3 plants. The corn $\delta^{13}C$ values are higher (–11.4 to –12.1‰), reflective of C-4 plants. The $\delta^{13}C$ values for the calcitic egg shells (1.2‰) are much higher than those for the organic insides (–16.6‰).

TABLE 1. $\Delta^{14}C$ and $\delta^{13}C$ Values for Tropospheric CO_2 (Tray and Bubble Methods of Collection) and a Variety of Plants from 6 Northern Hemisphere Sites

Sample type	La Jolla no.	Date collected	Collection site	Δ14C ‰	± ‰	δ13C ‰
Air CO_2 (tray)	5210	19-20 June1980	Mt. Soledad, La Jolla, CA	252	11	-26.6
Air CO_2 (bubble)	5209	19-20 June1980	Mt. Soledad, La Jolla, CA	253	11	-20.5
Air CO_2 (tray)	5213	28 Aug-2 Sept 1980	Mt. Soledad, La Jolla, CA	276	4	-25.4
Fig fruit	5193	Jul-80	Suess yard, La Jolla, CA	273	7	-25.4
Fig fruit	5194	Jul-80	Suess yard, La Jolla, CA	263	5	-25.1
Fig leaves	5195	Jul-80	Suess yard, La Jolla, CA	272	4	-28.0
Corn	5197	15-Jun-80	Heidelberg, GER	257	5	-12.4
Wheat	5196	15-Jun-80	Heidelberg, GER	260	5	-27.0
Raspberries	5517	1942	Martha's Vineyard, MA	-27	3	-25.2
Apples	5518	1942	Martha's Vineyard, MA	-20	3	-20.2
Egg Shells	4963	29-Nov-79	Miller's Ranch, San Diego, CA	256	3	1.2
Egg (inside)	4976	3-Dec-79	Miller's Ranch, San Diego, CA	315	3	-16.6
Corn husk	5076	1947	Shoe Peg-Harris, Louisiana	-21	4	-12.1
Corn kernels	5077	1947	Shoe Peg-Harris, Louisiana	-13	4	-11.8
Corn kernels	5073	1947	Gray Summit	-26	4	-11.5
Corn kernels(extr.)	5074	1947	Gray Summit	-27	4	-12.0
Corn husk	5075	1947	Gray Summit	-27	4	-11.4

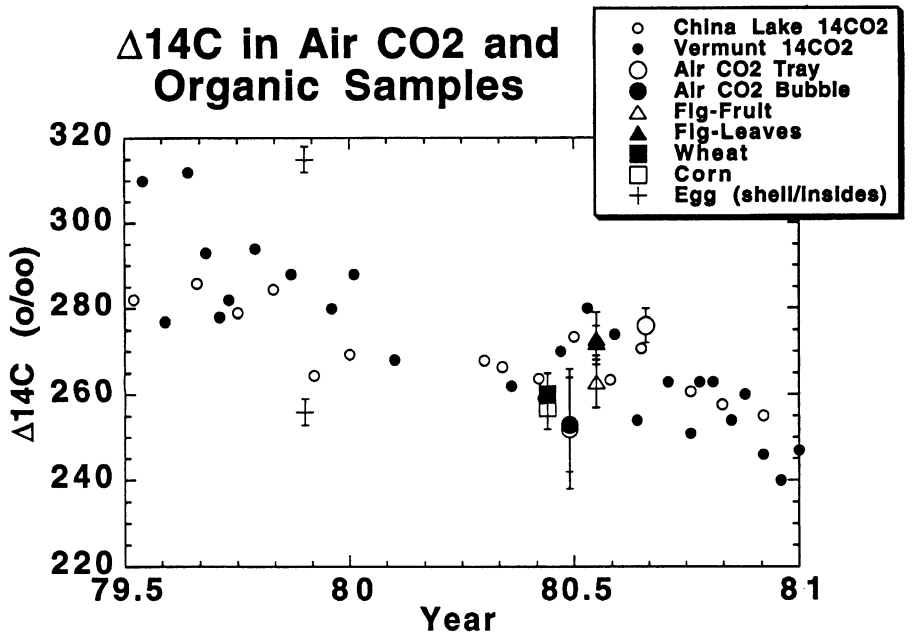

Fig. 1. $\Delta^{14}C$ measurements for tropospheric CO_2 (tray and bubble method of collection) and fig (fruit and leaves) samples from La Jolla, California, and for corn and wheat samples from Heidelberg, Germany. All samples were collected in the summer of 1980. Also plotted for comparison are the $\Delta^{14}C$ results for atmospheric CO_2 collected from Vermunt, Austria (Levin *et al.* 1985) and China Lake, California (Berger *et al.* 1987).

Discussion

Comparison between the atmospheric CO_2 results reported here and those previously reported for Vermunt, Austria (47°N, 10°E) (Levin *et al.* 1985) and China Lake, California (35°32'N, 117°41'W) (Berger *et al.* 1987) is shown in Figure 1. The atmospheric CO_2 $\Delta^{14}C$ result from La Jolla (276 ± 4‰) in August/September 1980 agrees with the China Lake $\Delta^{14}C$ (271 ± 4‰) result taken at the same time. The two La Jolla atmospheric CO_2 $\Delta^{14}C$ results from June 1980 (252 ± 11‰ and 253 ± 11‰) are 1–2 σ lower than the Vermunt, Austria atmospheric CO_2 sample (270 ± 4‰) taken at the same time, and 1–2 σ lower than the China Lake CO_2 samples (264 ± 4‰, 273 ± 4‰) taken 15 d before and 7 d after ours, respectively. Hourly records of wind-direction in La Jolla during the 24-h June collections show an offshore, northwestward flow (Lott 1980) that may have included continental air that had been exposed to fossil fuel sources from the inland San Diego area. Similarly, the August/September 1980 atmospheric CO_2 sample was collected during a period of westward wind flow, also bringing continental air to the La Jolla area. However, $\Delta^{14}C$ values for atmospheric CO_2 in La Jolla during August/September are similar to the China Lake and Vermunt, Austria values; this indicates that all three locations may have a small amount of fossil fuel carbon from anthropogenic sources.

The fig fruit and leaf samples and the Heidelberg corn and wheat samples had $\Delta^{14}C$ values that agree (within 10‰) with the atmospheric CO_2 $\Delta^{14}C$ values from this study (Fig. 1) and the Vermunt and China Lake atmospheric CO_2 $\Delta^{14}C$ records during the summer of 1980. The annual decline of tropospheric $\Delta^{14}C$ during 1976–1983 was 18‰ yr^{-1} at China Lake (Berger *et al.* 1987). From the agreement between $\Delta^{14}C$ values from the post-bomb plant materials and precursor atmospheric

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CO_2, it appears that there is a maximum time lag of 0.5–1 yr in the transfer of CO_2 from the troposphere to plants.

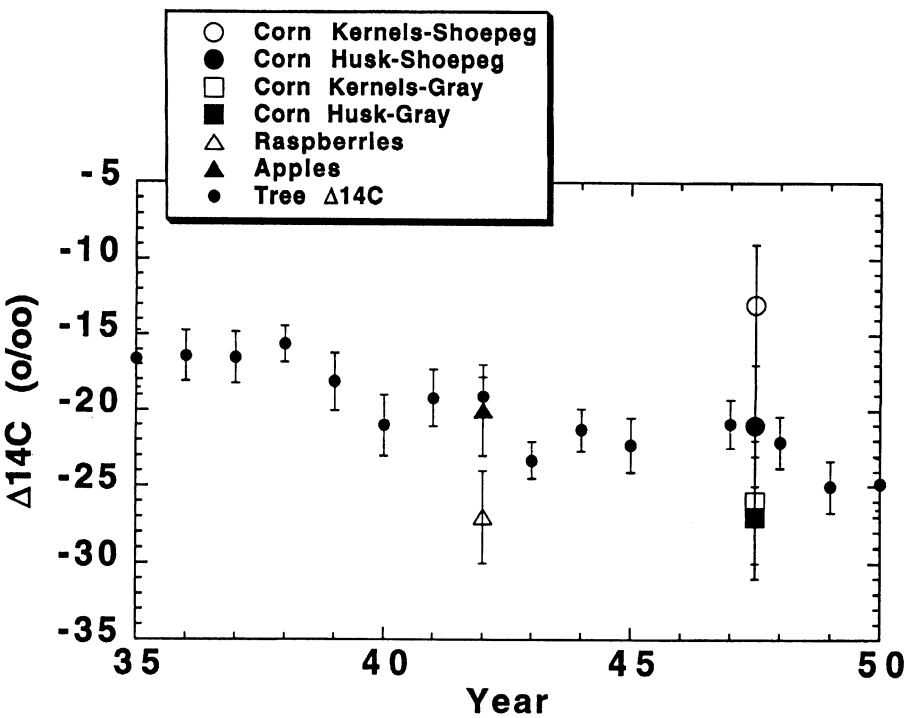

Fig. 2. $\Delta^{14}C$ measurements for corn (kernels and husks) from Shoe Peg-Harris, Louisiana and Gray Summit, and for canned raspberries and apples from Martha's Vineyard, Massachusetts. The corn samples were collected in 1947 and the fruit samples in 1942. Also plotted for comparison are the $\Delta^{14}C$ results for tree rings from the northwestern U.S. (Stuiver and Quay 1981).

The egg results reveal a different story. The egg shells have a slightly lower $\Delta^{14}C$ value (256 ± 3‰) than atmospheric CO_2 (264 ± 3‰) taken at the same time at China Lake 200 miles away; this is probably due to a small amount of "dead" calcium carbonate that is included in the chickens' feed. In contrast, the egg insides had a $\Delta^{14}C$ (315 ± 3‰) that was much higher than atmospheric CO_2 $\Delta^{14}C$, likely owing to several years that could have elapsed between harvesting of the feed and the ingestion by the chickens. These results reveal that bicarbonate and organic carbon within the egg do not equilibrate, but follow completely different biochemical pathways.

In 1942, fossil fuels and other effects (Suess 1953) had caused atmospheric CO_2 $\Delta^{14}C$ to decrease (the Suess effect) in the northern hemisphere to –20‰ (Stuiver and Quay 1981). This is reflected in the $\Delta^{14}C$ values reported for the fruit from Martha's Vineyard, Massachusetts (Fig. 2). The prebomb $\Delta^{14}C$ value for apples (–20‰) that grew in 1942 was equal to tree ring $\Delta^{14}C$ results for the early 1940s (Stuiver and Quay 1981), whereas the raspberries $\Delta^{14}C$ value (–27 ± 3‰) was significantly lower (>2 σ).

The corn husk and kernel samples showed $\Delta^{14}C$ signatures that agreed with the tree ring results. One exception was the $\Delta^{14}C$ value of corn kernels (–13 ± 4‰) from Shoe-Peg-Harris that was higher than the corn results from Gray Summit (–27‰, –26‰) or the husk from Shoe Peg-Harris

(−21‰). The reason for this high value is not known, though this example demonstrates the variability of $\Delta^{14}C$ that may be typical within certain plant types. Nonetheless, there appears to be no evidence of anomalous fractionation between atmospheric CO_2 and the organic matter fixed by C_3 and C_4 plants, given the limited results presented here.

Conclusion

The atmospheric CO_2 $\Delta^{14}C$ measurements from June and August/September 1980 agreed within the reported uncertainty with those published from China Lake, California (Berger *et al.* 1987). This offers a calibration of $\Delta^{14}C$ values for this coastal California site during the summer of 1980. Post-bomb fruit and grain $\Delta^{14}C$ measurements showed general agreement with atmospheric CO_2 $\Delta^{14}C$ values available from California and central Europe. The shells and insides of eggs had $\Delta^{14}C$ values that were significantly different from the atmospheric CO_2 $\Delta^{14}C$ values, owing to separate sources of stored carbon whose $\Delta^{14}C$ signatures are different. Agreement between $\Delta^{14}C$ values in fruit and corn and those from tree rings, both from the 1940s, was demonstrated. These data are a small addition to the large body of ^{14}C data already available documenting the 20th century distribution of ^{14}C in the rapidly exchanging carbon pools on Earth.

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