Identification of Age Anomalous Components of Food Commodities by Radiocarbon (^{14}C) Analyses

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"Post-maximum-bomb" ^{14}C activities (1964 to the present) provide a natural isotopic signature to obtain information on biomass source age in contemporary food preparations. An analysis of the ^{14}C content in frozen orange juice-containing products purchased in 1996 suggested, in one case, an inferred growth period between 1992 and 1994 for oranges used in the preparation of this commodity. In another case, the ^{14}C analysis indicated an inferred average growth period of 1988−90 for the organics in a "frozen concentrated enriched citrus beverage". The presence of significant amounts of chemical additives obtained or synthesized from fossil carbon sources can also be documented by measuring ^{14}C content.

INTRODUCTION

The use of radiocarbon (^{14}C) as a method of determining the chronometric age of archaeologically and historically related carbon containing (e.g., wood, charcoal, bone) materials is the most widely known use of this isotope (Taylor, 1987, 1996). Although the radiocarbon dating method has made its major impact in archaeological studies, it has been used in a wide range of scientific fields including biochemistry, environmental science, forensic studies, geochemistry, geology, geophysics, hydrology, and oceanography (Taylor et al., 1989, 1992). This paper discusses how the "bomb" ^{14}C content can be used as a tracer to make inferences concerning the age of sources of contemporary food raw materials processed by various commodity industries. Previous studies (Martin et al., 1983, 1985) have employed ^{14}C content to identify fossil fuel-based additives to alcoholic beverages.

The natural production of radiocarbon (^{14}C) is a continuous process, traceable to the production of neutrons from the interaction of high energy cosmic rays with the nuclei of gas molecules in the upper levels of the earth's atmosphere and subsequent reactions of the resultant "thermalized" neutrons, i.e., neutrons of reduced energies, with ^{14}N. Radiocarbon is then rapidly oxidized in the atmosphere to form ^{14}CO$_2$. Because of relatively rapid mixing in the stratosphere, atmospheric ^{14}C concentrations are approximately uniform by the time a ^{14}C-tagged CO$_2$ molecule reaches the planetary surface. Most ^{14}C—about 85%—is absorbed in the oceans by several mechanisms, while about 2% becomes part of the terrestrial biosphere, primarily by means of photosynthetic processes and the distribution of ^{14}C-tagged carbon compounds through the chemically complex pathways of the carbon cycle.

Metabolic processes in most terrestrial living organisms maintain their ^{14}C content in approximate equilibrium with atmospheric ^{14}C concentrations, i.e., while ^{14}C decays in living tissue, it is replaced through the ingestion of plant or animal tissue. However, once metabolic processes cease, as at the death of an animal or plant, the amount of ^{14}C begins to decrease by radioactive decay—in the case of ^{14}C, by β decay to ^{14}N—at a rate measured by the ^{14}C half-life of about 5700 years. The *radiocarbon age* of a sample is based on measurement of its residual ^{14}C content (Taylor, 1987).

To derive ^{14}C ages for chronological purposes over about the last 5×10^4 years, a wide range of geochemical and geophysical issues and constraints must be considered. However, for modern or contemporary ^{14}C tracer applications, other issues and problems need to be considered. Modern tracer uses of ^{14}C take advantage of the fact that, in the period from 1945 to 1964, the detonation of nuclear ("atomic bombs") and thermonuclear ("hydrogen bombs") devices in the atmosphere created another source of ^{14}C. This is known as "bomb ^{14}C" which is created by the very intense production of neutrons that occurs when a nuclear or thermonuclear device is detonated.

EXPERIMENTAL PROCEDURES

Figure 1 is a plot of the measured ^{14}C activity in living organisms (biospheric carbon) from 1940 to 1995 based on samples collected at many locations around the world. In Figure 1, ^{14}C activity has been plotted by using the expression "Δ^{14}C". By convention, Δ^{14}C is expressed in *per mill* (‰) units rather than in *percent* (%), i.e., 10 ‰ = 1%. The "0" level in Figure 1 represents the "zero ^{14}C" level, i.e., the presumed natural equilibrium ^{14}C content of living organics in the biosphere assuming a stable isotope (δ^{13}C) value of −25‰ (Stuiver and Polach, 1977). The presence of bomb ^{14}C can be observed beginning about 1955 and, by 1964, biospheric ^{14}C levels had almost doubled. In late 1963, an international treaty halted atmospheric testing by most of the nuclear powers and the production of "bomb ^{14}C" reaching the atmo-

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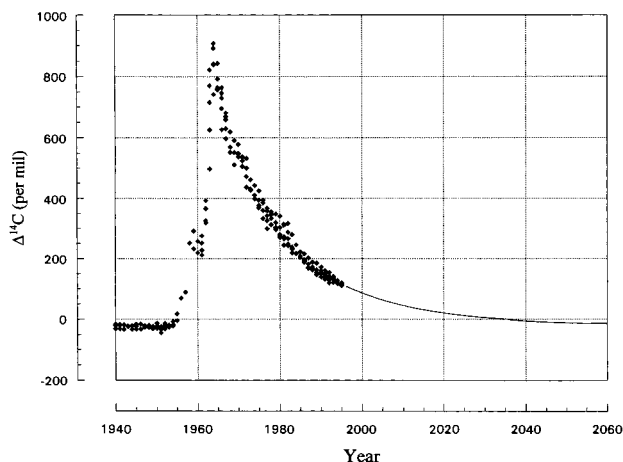‡ Lawrence Livermore National Laboratory.

Figure 1. Clean air atmospheric ^{14}C concentrations from CO_2 and tree rings. Sources of data for period from 1940 to 1995: Berger et al., 1987; Burchuladze et al., 1980, 1989; Dai and Fan, 1986; Damon et al., 1989; Kaimei et al., 1992; Levin et al., 1985, 1989, 1992; Rozanski et al., 1995; Stuiver and Quay, 1981; and unpublished data measured at the Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory. Solid line after 1995 represents estimate of future atmospheric ^{14}C concentrations (Stuiver, 1997).

Table 1. Radiocarbon Content of Frozen Orange Juice-Containing Products Purchased in 1996

laboratory no.	product	$\delta^{13}C$,[a] ‰	^{14}C content ($\Delta^{14}C$, ‰)[b]	inferred growing period[c]
Frozen Orange Juice				
UCR-2862	A	−26.62	+100.7 ± 3.1	1995−1996
UCR-2863	B	−25.94	+117.4 ± 4.1	1994−1995
UCR-2864	C	−27.20	+125.0 ± 5.4	1992−1994
Frozen Orange Juice with Non-Orange Juice Component Added				
UCR-2865	D	−12.63[d]	+161.5 ± 3.8[d]	1988−1990[d]

[a] Expressed with reference to PDB (Pee Dee Belemnite, Chicago) standard. Error on value ±0.02‰. [b] Normalized to a $\delta^{13}C$ value of −25‰. [c] Inferred growing period determined by comparing $\Delta^{14}C$ values measured in samples with that previously measured in known age materials. [d] $\delta^{13}C$, $\Delta^{14}C$ value, and inferred growing period reflect the high concentration of the non-orange juice component (high fructose corn syrup).

sphere was dramatically reduced. Since 1964, "post-maximum-bomb" ^{14}C activity has been decreasing as the massive amounts of artificial ^{14}C injected into the atmosphere have been mixed into other carbon reservoirs—most importantly, into the oceans where, as noted above, most natural ^{14}C resides.

The solid line in Figure 1 extending past 1995 is an estimate of future biospheric ^{14}C activity to the year 2060 assuming that no additional "bomb" ^{14}C is added to the atmosphere and that there is no change in the current production rate of CO_2 derived from the combustion of fossil carbon sources such as coal, oil, and natural gas (Stuiver, 1997). Because of its great geological age, fossil fuel-derived CO_2 should contain no measurable amounts of ^{14}C. Reductions up to about 3% in atmospheric and biospheric ^{14}C levels were observed in samples growing in the 19th and 20th centuries due to fossil fuel CO_2 production (Suess, 1955). Because of rapid atmospheric mixing, ^{14}C activity in most carbon-containing terrestrial compounds is very similar in materials growing at the same time and does not vary as a function of geographic location except under very unusual conditions in atypical environments.

Maximum $\Delta^{14}C$ values of 920‰ or 92% above 1950 levels were measured in materials growing in 1964. It should be noted that these values have been derived from samples collected at "clean air sites". These sites are those areas far removed from regions where localized variations in ^{14}C concentrations caused by the combustion of large amounts of fossil fuels, e.g., from coal in power plants or gasoline in automobile engines in large urban areas, have been measured. Measurement of contemporary atmospheric ^{14}C activity from these sites is continuing on an annual and subannual basis by several investigators (e.g., Levin et al., 1992; Rozanski et al., 1995).

The data in Figure 1 provide a baseline against which comparisons of ^{14}C activity in organics from other samples growing during the period from 1964 (the bomb ^{14}C maximum) to, at present, 1995 can be made. Two types of inferences concerning significant deviations from these baseline values can be offered. Significantly higher values indicate an extended age for some or all of the components of the commodity. For example, the $\Delta^{14}C$ value of a fresh food product being offered for sale in 1996 should be in the range 100−110‰. If the product exhibits a $\Delta^{14}C$ value more characteristic of carbon-containing materials living in 1985 (e.g., about 200‰), some question could be raised concerning the age of the ingredients of the foodstuffs. It should be noted that a $\Delta^{14}C$ value exhibited by a sample would reflect a "net" or "mass averaged"

signal in that it would be a composite of all carbon-containing ingredients contained in the sample.

If $\Delta^{14}C$ values are significantly depressed below the baseline values, then one possible inference is the presence of chemical additives obtained or synthesized from fossil carbon sources. The usefulness of using $\Delta^{14}C$ values to detect the addition of chemical additives, including limits of detection, is a function of the ratio of the introduced materials to the original sample mass and the amount of offset in $\Delta^{14}C$ values between the original material and introduced additive.

$\Delta^{14}C$ values on four samples of frozen orange juice-containing products purchased from a retail grocery store in Riverside, CA, in December 1996 have been obtained. In each case, the water content of the thawed product was removed, leaving only a solid residue. No other pretreatment was applied. An aliquot of the thoroughly dried solid residue was combusted to CO_2 in a stream of oxygen in an apparatus that isolates the resultant sample CO_2 from contamination from atmospheric CO_2. Since the distribution of ^{14}C in plants is isotropic at the atomic level, any portion of a sample can be measured and this will accurately represent the ^{14}C activity of the entire sample. The ^{14}C activity of each sample aliquot was measured by CO_2 gas proportional counting in the Radiocarbon Laboratory, University of California, Riverside, while the $\delta^{13}C$ values were obtained by conventional mass spectrometry (Platzner, 1997).

RESULTS AND DISCUSSION

The $\Delta^{14}C$ values of the four orange juice-containing samples are presented in Table 1. The basis on which an "inferred growing period" is derived for each sample is illustrated in Figure 2. For one sample (UCR-2864), the inferred growing period for the oranges used in the product is 1992−1994. In making this and all other inferences concerning age on the basis of $\Delta^{14}C$ values, it is assumed that all carbon contained in the analyzed samples was derived from orange juice used in the preparation of the product.

In the case of UCR-2865, product D, this assumption is not correct. The product D container indicated the product is a "frozen concentrated enriched citrus beverage", one can of which is to be diluted with three cans of water (similar to the other products studied). The following descending order of ingredients were listed: water, high fructose corn syrup, concentrated orange juice, citric acid, sucrose, and minor amounts of 15 other ingredients. In the absence of information regarding the exact composition and $\Delta^{14}C$ activity of each of the non-orange juice constituents of this product, it is not possible to estimate the growing period of the oranges from which the juice was derived unless separation of specific chemical components known to be derived from
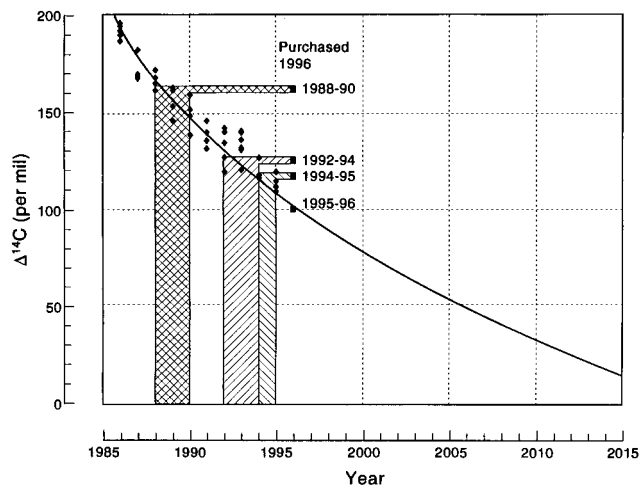
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Figure 2. Clean air atmospheric ^{14}C concentrations taken from Figure 1 compared with ^{14}C activity measured in orange juice containing samples purchased in 1996 taken from Table 1.

oranges could be isolated. In addition, we should note that UCR-2865 exhibits a $\delta^{13}C$ value of $-12.63‰$ indicating the addition of significant amounts of carbon derived from a C4 (Hatch-Slack cycle) plant. This value is fully consistent with the statement on the product label that high fructose corn syrup, a material derived from a C4 plant, had been added (Bender, 1968). All of the other samples exhibited $\delta^{13}C$ values consistent with having all or most of their carbon derived from a C3 (Calvin cycle) plant. Citrus plants utilize only C3 metabolic pathways in their photosynthesis processes (Doner and Bills, 1981; McManus, 1996).

In making "inferred growing period" determinations, we must also assume that the oranges from which the frozen orange juice samples were derived were grown in a "clean air" environment similar to that from which the reference data points in Figures 1 and 2 are derived and that no other contamination, fractionation, or other factors have influenced the ^{14}C activity of these samples.

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