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ANTHROPOGENIC ^{14}C VARIATIONS IN ATMOSPHERIC CO_2 AND WINES

A A BURCHULADZE*, MARTIN CHUDÝ**, I V ERISTAVI*
S V PAGAVA*, PAVEL POVINEC**, ALEXANDER ŠIVO**
and G I TOGONIDZE*

ABSTRACT. As an extension of the Bratislava – Tbilisi collaboration, thermonuclear bomb-produced ^{14}C variations in atmospheric CO_2 of Bratislava (1967–1987) and in annually produced Georgian wines (1950–1987) are discussed. ^{14}C produced in bomb tests performed in the atmosphere has considerably modified the natural ^{14}C levels in the atmosphere and biosphere. Measurements of ^{14}C in monthly samples of atmospheric CO_2 show typical seasonal variations with maxima in summers and deep minima in winters. There is very good agreement between ^{14}C measured in CO_2 and in wine samples. Four maxima (1959, 1964, 1970 and 1978) were identified in the wine data. Our results confirm that wines prepared from annually grown grapes without any addition of other substances are good indicators of the ^{14}C content of atmospheric CO_2.

INTRODUCTION

Thermonuclear weapon tests performed in the atmosphere have considerably modified the natural ^{14}C concentration in the environment. Large tests performed in 1961 and 1962 increased the ^{14}C concentration in the north atmosphere in 1963 to ca 100% above the natural level (Nydal & Lövseth, 1965). Radioactive clouds reached the upper troposphere and lower stratosphere, and due to the specific mixing processes in the atmosphere, seasonal variations of ^{14}C concentration in the troposphere have been observed (Münnich, 1963; Nydal & Lövseth, 1965; Chudý *et al*, 1970). After the nuclear moratorium for atmospheric tests in 1963, ^{14}C excess has been decreasing with small interruptions caused by subsequent nuclear tests (Povinec, Chudý & Šeliga, 1971; Levin, Münnich & Weiss, 1980; Povinec, Chudý & Šivo, 1986).

Bomb-produced ^{14}C has considerably influenced ^{14}C concentration in the environment. Present levels in the atmosphere are still ca 15% above natural ^{14}C concentration. The distribution of carbon in the environment has been traced using anthropogenic $^{14}CO_2$. This enables us to study exchange processes among various carbon reservoirs in the atmosphere, biosphere and ocean, and to estimate transport coefficients (Oeschger *et al*, 1975).

Investigations of this kind are important for understanding natural variations of ^{14}C in the environment. Except for long-term variations, which are difficult to study (Stuiver, 1978), these investigations are important also for short-term ^{14}C variations studies (eg, 11-yr solar ^{14}C cycle), which have very small amplitudes (Povinec, Burchuladze & Pagava, 1983).

From this point of view, studies of the correlation between ^{14}C concentration in the atmosphere and in annually dated samples (eg, tree rings, wine, etc) are very important. Wines prepared from annually grown grapes

*Tbilisi State University, Faculty of Physics, Department of Nuclear Physics, 380028 Tbilisi, USSR
**Comenius University, Faculty of Mathematics and Physics, Department of Nuclear Physics, 84215 Bratislava, Czechoslovakia

without any addition of substances should represent the average ^{14}C content of the atmosphere during the time of growth of the grapes. Annual wines represent a year-by-year record that goes back to the beginning of this century. Together with tree rings that date back several thousand years, wines enable us to study, with high precision, ^{14}C variations in the atmosphere. Careful investigation has shown 11-yr ^{14}C variations in wine over four solar cycles (Burchuladze *et al,* 1980). Another possibility is to study annually prepared whiskies (Baxter, Ergin & Walton, 1969).

This work is a continuation of the Bratislava-Tbilisi collaboration on short-term variations of ^{14}C in annual Georgian wine samples (Burchuladze *et al,* 1977; Burchuladze *et al,* 1980; Povinec, Burchuladze & Pagava, 1983) with emphasis on the response of wines to short-term fluctuations of ^{14}C concentration in the atmosphere caused by nuclear bomb tests.

METHODS AND SAMPLES

Atmospheric CO_2 Samples

Monthly and short-term samples of atmospheric CO_2 have been collected at various sites in Slovakia (Bratislava, Jaslovské Bohunice and Modra) since 1967 using the method of static and dynamic absorption of CO_2 in NaOH solution (Povinec *et al,* 1968) and in molecular sieve Calsit 5A (Povinec, 1975). Up to 1975, Bratislava samples were taken from the center of the town. Later, they were collected on the roof of a new department store on Mlynská dolina, which is in the outskirts. Thus, all samples represent surface air samples.

The CO_2 absorbed in NaOH was precipitated as $BaCO_3$, converted to CO_2 by adding H_3PO_4 and the CO_2 purified to remove electronegative impurities; the sample was counted as CO_2 or as CH_4 after reduction. Low-level proportional counters were used for ^{14}C activity measurements. The methods of ^{14}C sample collection and measurement have been described previously (Povinec *et al,* 1968; Povinec, 1972; Povinec *et al,* 1973) and will not be outlined here.

Wine Samples

Georgian wine samples were collected by the Tbilisi Wine Museum and the Research Institute of Grape-Growing in Tbilisi. The samples were stored separately in bottles for each year. They were well preserved, which was already documented by dating wine samples from the beginning of this century (Burchuladze *et al,* 1980). No admixtures (eg, sugar, artificial ingredients) were added to the samples.

The samples were distilled, and the condensed ethyl alcohol was burned in a high-pressure combustion bomb to form CO_2 that was used for preparation of benzene. Intertechnique SL-20 and SL-30 liquid scintillation spectrometers were used for ^{14}C counting. This technique was described previously (Povinec *et al,* 1980; Burchuladze *et al,* 1980). Several cross-check measurements between the Bratislava and Tbilisi laboratories have shown results within statistical errors.

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RESULTS AND DISCUSSION

Figure 1 shows a comparison of the ^{14}C concentration in Georgian wine samples with the ^{14}C concentration of monthly sampled Bratislava CO_2. Wine samples from different Georgian villages (~38° N, ~45° E) from 1950–1987 are listed in Table 1. The wine samples were collected in non-industrial areas; thus, they can be expected to produce "clean-air" data. However, some local influences from nearby villages cannot be excluded. The ^{14}C record in Bratislava (~48° N, ~17° E) CO_2 is given from 1967–1987 (Povinec *et al,* 1986).

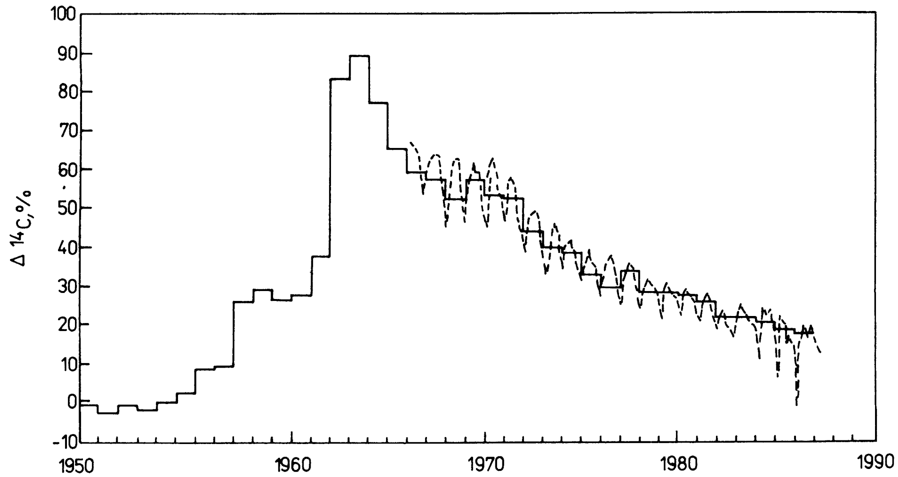

Fig 1. Thermonuclear bomb-produced ^{14}C variations in samples of annually produced Georgian wines (~38° N, ~45° E) and in monthly samples of atmospheric CO_2 in Bratislava (~48° N, ~17° E)
—— = wines; - - - = CO_2

We have obtained very good agreement between ^{14}C measured in wine samples and in atmospheric CO_2. Although Bratislava atmospheric results cannot be accepted as clean-air data, they predict well, until 1980, ^{14}C concentration in wines. After 1980, the influence on atmospheric data of the annual Suess effect, especially during winter, is remarkable. The wine data are systematically higher than the mean annual atmospheric data; this is due not only to the Suess effect, but also to the fact that the growth period of grapes is only ca 10–15 weeks during the year at a time when the ^{14}C concentration in atmospheric CO_2 is around its maximum.

Four maxima can be identified in the wine data. The first, in 1959, is due to nuclear bomb tests during the 1950s. The second, the sharp 1964 maximum, is due to the largest tests in 1961 and 1962, and it corresponds to the maximum observed in atmospheric CO_2 in 1963 (Nydal & Lövseth, 1965). The one-year shift between the atmospheric ^{14}C level and ^{14}C concentration in wine is typical, and it is observed also when two much smaller maxima, due to more recent nuclear bomb tests, are found at 1970 and 1978. After the atmospheric nuclear test moratorium in 1963, the ^{14}C con-

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TABLE 1

^{14}C content of Georgian wine samples

Growth yr	Sample	$\Delta^{14}C$ (%)
1950	Georgian no. 20	−1.42±0.20
1951	Tsolikauri	−4.37±0.24
1952	Tsinandali	−1.37±0.36
1953	Khvanchkara	−2.53±0.26
1954	Tibaani	−0.67±0.36
1955	Mukuzani	1.66±0.29
1956	Gurdzhaani	6.95±0.42
1957	Tsolikauri	8.87±0.42
1958	Teliani	25.21±0.43
1959	Tsolikauri	29.12±0.42
1960	Tsinandali	25.71±0.38
1961	Gurdzhaani	27.52±0.34
1962	Tsinandali	36.52±0.29
1963	Tsinandali	82.31±0.43
1964	Kardanakhi	89.16±0.42
1965	Sviri	76.48±0.39
1966	Gurdzhaani	62.68±0.46
1967	Mukuzani	59.71±0.53
1968	Kardanakhi	55.15±0.47
1969	Tibaani	51.03±0.31
1970	Gurdzhaani	57.77±0.32
1971	Tsinandali	53.40±0.34
1972	Tibaani	53.28±0.32
1973	Tibaani	42.63±0.24
1974	Saero	39.77±0.28
1975	Tsinandali	36.80±0.25
1976	Tsitska	33.20±0.29
1977	Telavi	29.77±0.26
1978	Rkatsiteli	34.49±0.28
1979	Tsinandali	29.45±0.24
1980	Tsinandali	27.93±0.26
1981	Lechkhumi	27.15±0.26
1982	Rkatsiteli	26.57±0.24
1983	Telavi	22.98±0.25
1984	Tsolikauri	21.59±0.25
1985	Lechkumi	20.87±0.25
1986	Racha	18.98±0.23
1987	Rkatsiteli	16.79±0.23

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centration in wines, with these two interruptions, has been decreasing with approximate time constants 6.3% per year during the 1960s, 3.1% per year during the 1970s and 1.5% per year during the 1980s.

Atmospheric ^{14}C data show typical seasonal variations with maxima in summer months which are due to stratospheric injection of fresh air to the troposphere during the spring in the Northern Hemisphere. Deep minima during the winter are due to dilution of ^{14}C concentration by addition of fossil-fuel CO_2 (Segl *et al,* 1983).

CONCLUSION

^{14}C produced during thermonuclear bomb tests in the atmosphere has considerably modified the natural ^{14}C levels in the atmosphere. The present ^{14}C concentration is still ca 15% above the natural level, as documented by ^{14}C measurements in atmospheric CO_2 and in recent wines. Monthly sampled atmospheric CO_2 shows typical seasonal ^{14}C variations with maxima in summer and deep minima in winter.

The present study has confirmed that wines prepared from annually grown grapes without any addition of other substances are good indicators of the ^{14}C content of atmospheric CO_2. They represent a year-by-year record that dates back to the beginning of this century. Together with tree rings that date back several thousand years, wine samples enable us to investigate, with high precision, ^{14}C variations in the atmosphere.

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