

TRITIUM AND ^{14}C IN TREE RINGS OF THE LAST THREE DECADES

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ABSTRACT. Tree rings spanning the past three decades were collected from *Picea* spp trees grown in Matra, northern Hungary. Cellulose was prepared from the wood and samples were separately combusted for tritium and ^{14}C analyses. Methane was synthesized from CO_2 obtained by sample combustion via catalytic reaction with tritium-free hydrogen. ^{14}C activity was measured by proportional counter. The exchangeable tritium was removed from cellulose samples used for tritium analysis. Water samples produced by combustion were measured by liquid scintillation counting. The distribution of tritium and ^{14}C activities in tree rings are shown for years 1956-1986. Results are compared with published data on global-scale distribution of ^{14}C and HTO. A comparison of tritium activity in precipitation and wine samples from the same region is presented.

INTRODUCTION

Nuclear weapon tests resulted in a significant discharge of tritium and ^{14}C to the atmosphere. During and after this era, the concentration of these isotopes in the air was extensively monitored. A worldwide monitoring network was established by the International Atomic Energy Agency and World Meteorological organization for tritium and stable isotopes in precipitation (IAEA, 1981). Atmospheric ^{14}C concentration was also measured by many investigators (Fairhall & Young, 1970; Nydal & Lövseth, 1970; Levin, Münnich & Weiss, 1980). The basic features of spatial and time variations of ^3H and ^{14}C , eg, meridional gradient, seasonal fluctuation, continental effect, were soon recognized (Schell, Sauzay & Payne, 1974; Levin, Münnich & Weiss, 1980).

Although tritium and ^{14}C concentration in the air is still influenced by bomb-produced activity, environmental air can be locally affected by emission from nuclear facilities and institutions that are producing and applying labeled materials. Since instant monitoring records are rare, tree-ring analysis is accepted and often used for reconstructing local history of ^{14}C excess (Hertelendi & Csongor, 1982; Obelić *et al*, 1986; Dai & Fan, 1986). This method was also adopted earlier for reconstructing tritium activity (Kigoshi & Tomikura, 1961), but there are few published papers (Brown, 1979; Kozák, 1982; Kozák *et al*, 1986).

^3H and ^{14}C activity was measured in tree rings to obtain reference values over a 30-yr period. The results are discussed and compared with data on airborne $^{14}\text{CO}_2$ and HTO published in the literature.

SAMPLING AND ANALYSIS

A spruce tree was felled at the end of the 1986 growing season at Matra Mt in northern Hungary (47°54'N, 19°55'E). The sampling site was in a forest area at 650m altitude. The tree grew at the edge of a 60-yr-old plantation. The tree-ring material was separated from sections near the base of the tree. All analyses were performed on the cellulose component of the wood, as this is regarded as the most reliable chemical constituent (Tans, De Jong & Mook, 1978). Lignin and resins were first removed by the sulphate process, *ie*, by boiling wood in alkaline solution of sodium sulphide in an autoclave at 165°C. This treatment was followed by bleaching the material in acidified sodium chlorite solution at 75°C following a method modified after Green (1963). The holocellulose was then rinsed with distilled water and dried at 105°C.

For ^{14}C measurements, 15g of cellulose were combusted and resulting CO_2 was converted into methane. After purification, methane was used to fill a proportional counter. Details on sample preparation, purification and proportional counting were discussed elsewhere (Srdoč, Breyer & Sliepčević, 1971).

^{14}C activity is expressed as a relative difference from the Absolute International Standard Activity (AISA) equal to 0.95 NBS oxalic acid, normalized for isotopic fractionation (Stuiver & Polach, 1977). $\delta^{13}\text{C}$ values were measured for the same cellulose samples and results from -19 to -21‰ vs PDB standard were obtained. Uncertainty of ^{14}C measurement was in the range of 1.5–2.4‰ (1σ). Cellulose samples were isotopically equilibrated with tritium-free water before tritium analysis in order to elucidate meaningful tritium concentration recorded in the C-H bounded hydrogen (70%). The O-H bounded hydrogen of cellulose (30%) is exchangeable (Mann, 1971), and thus has a different tritium concentration. Twenty grams of cellulose were immersed in tritium-free water in an autoclave. After treatment for four hours at 175°C, 92% of the O-H bounded hydrogen underwent an exchange (Wadehra & Manley, 1965). The cellulose was then dried in the combustion line at 105°C under vacuum and was combusted. The water produced by combustion was analyzed for tritium by liquid scintillation counting. The tritium concentration of C-H bounded hydrogen was estimated from the activity of the water obtained by combustion. First, a blank value was experimentally found from blank samples (cellulose prepared from old wood); the result was then divided by 0.7, the contribution of C-H bounded hydrogen to the total. Finally, tritium concentration was corrected for radioactive decay ($T_{1/2} = 12.43$ yr). Uncertainty of tritium measurement of combusted water was 20 TU¹ (1σ). This value was enhanced due to corrections involved in the calculation of tritium concentration of cellulose. Ultimate uncertainty was 41 TU (latest ring) to 177 TU (oldest ring).

¹1 TU (tritium unit) = $\frac{1 \text{ tritium atom}}{10^{18} \text{ hydrogen atoms}}$

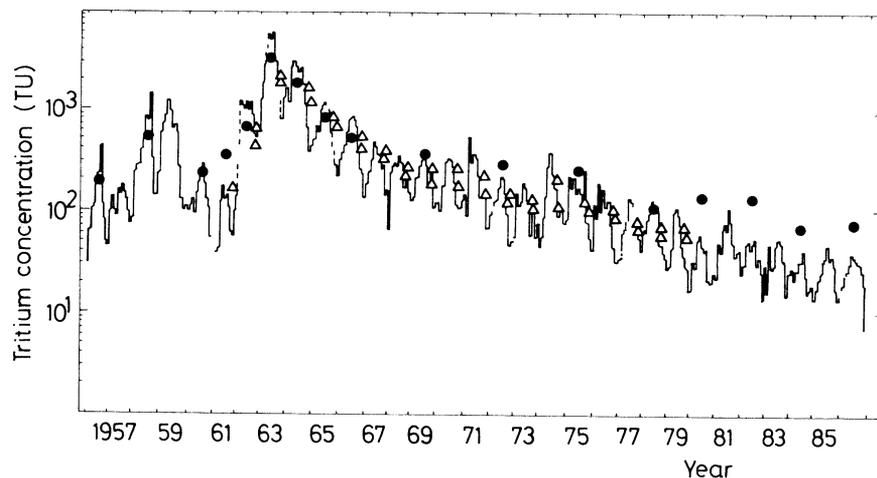


Fig 1. Comparison of tritium activity in tree rings (●), in wine samples (Δ) and in precipitation (-) since 1956; see text.

RESULTS AND DISCUSSION

Tritium data for tree rings are illustrated in Figure 1 together with tritium concentration in precipitation and wine samples. Tritium in precipitation of Ottawa (1956–1960) and Vienna (1961–1976) were taken from IAEA reports (IAEA, 1981, 1983, 1986). Precipitation of Budapest (1977–1986) was measured by the Institute of Isotopes of the Hungarian Academy of Sciences. The tritium concentration in wine samples from Hungary were previously published (Kozák & Biró, 1984). The tritium concentration in precipitation changed by two orders of magnitude during the investigation

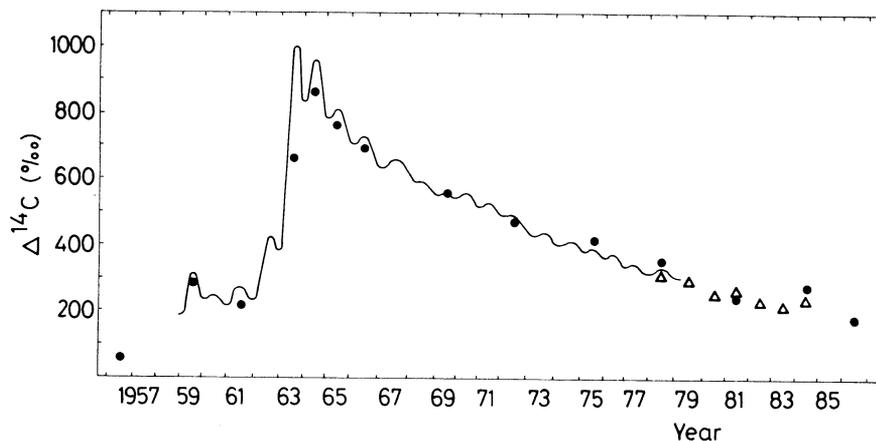


Fig 2. Comparison of ^{14}C concentration in tree rings: spruce from Hungary (●), linden from Yugoslavia (Δ), atmospheric CO_2 (-) since 1956; see text.

period. The time variation of tritium concentration in tree rings and precipitation are in general agreement. The differences are, in most cases, within the experimental uncertainty. ^{14}C activities of tree rings are presented in Figure 2 together with ^{14}C data in tropospheric CO_2 in the Northern Hemisphere according to Levin, Münnich and Weiss (1980). Results agree with the ^{14}C activity in rings of a linden tree, felled near Zagreb to measure the influence of the first Yugoslav nuclear power plant on the environment (Obelić *et al*, 1986).

CONCLUSIONS

Tritium, as well as ^{14}C activity in tree rings in the last three decades, follow the general trend of the activity in the Northern Hemisphere. Some deviations are visible only for tritium activity in tree rings in recent years when it is significantly higher from activity in precipitation and wine. This fact could be explained when considering that soil water available for a tree still contains some "old" water (10–20 yr old) that contributes to higher activity in recent rings. Such deviations are not significant for ^{14}C .

Our results, based on measurements of only one series of tree rings, have a rather qualitative character. Measurements of tritium and ^{14}C activity in tree rings of a spruce tree felled in a sparsely populated area in Yugoslavia, which are in progress, will fill the gap in the environmental data for this part of Europe.

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