

DETERMINATION OF ENVIRONMENTAL TRITIUM IN TREE RINGS

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ABSTRACT. Measurement of organically bound tritium in wood has yielded a useful record of environmental ^3H levels. Although it is the preferred method, cellulose extraction from wood makes the sample preparation tedious and time-consuming. I compared the ^3H contents of cellulose, wood and wood after extraction of resin, and found no significant differences among these materials. Blank values, determined on old wood and cellulose, are insignificant for modern samples. Correction for OH^- exchange in cellulose is not necessary.

INTRODUCTION

Historical environmental ^3H levels (particularly in rain and soil moisture) can be determined by measuring organically bound ^3H in tree rings. Such a record can verify data from monitoring around nuclear facilities and may be useful for sites where no other ^3H data are available.

Until now, cellulose has been used for analyzing ^3H bound organically in tree rings (Brown 1979; Kozák 1982; Kozák, Obelić & Hortavinčić 1989; Rank *et al.* 1986; Yamada *et al.* 1989). Cellulose is chemically well defined, whereas wood is a mixture of many components, each of varying ^3H content. Thus, an inconstant cellulose/lignin ratio will affect measurement results. Further, other components, such as resins, may be deposited in the wood structure years after ring formation. On the other hand, fluctuations of the cellulose/lignin ratio should not be pronounced in normal wood, contrary to reaction wood¹, and the resin content is only a few percent. Thus, it is important to compare the ^3H -content of whole wood, of wood after resin extraction and of cellulose. I report on the analysis of a sequence of 35 annual rings, and evaluate the necessity for tedious and time-consuming cellulose separation.

I studied a 70-yr-old pine from the Neustadtler Hügelland, Lower Austria, south of Grein *ca.* 500 m above sea level. This tree was felled in spring 1990, so that the outermost fully developed ring was that of 1989. Wood was sampled near the base of the trunk. The 1984–1989 rings of three 20-yr-old pines from Steinakirchen am Forst and Puchenstuben (Lower Austria) were also examined, but only by measuring ^3H in whole wood.

METHODS

Sections 2 cm thick were cut, and the rings were separated manually with a chisel. For whole wood, the chips were dried in an oven (105°C) for 48 h before combustion. Resin and lignin removal followed a modified Cross and Bevan method (Wise 1946; Fengel & Wegener 1989). For resin extraction, the chips were ground to 0.5 mm; 40 g of wood dust were treated with an ethanol-toluene mixture (1:2) in a Soxhlet apparatus for 24 h. After washing free of solvent with ethanol and hot water, either the cellulose was separated or the samples were dried for combustion.

For cellulose separation, the sample was boiled in a Na_2SO_3 solution (~50 g Na_2SO_3 per liter H_2O) for 20 min. Then, 4M H_2SO_4 was added to facilitate the filtration process. Treatment with a chlorine-water solution (5 min at room temperature) followed. These two steps were repeated al-

¹Reaction wood = eccentricity in width and structure of a tree ring, usually associated with cell anatomical characteristics

ternately until the material failed to show color upon addition of the Na_2SO_3 solution. Eight to 10 chlorine treatments were necessary for pine wood. The pulp was then boiled in water for at least 1 h to eliminate contamination with Na_2SO_3 . The yield generally was 18–20 g cellulose from a 40-g dry sample.

According to Brown (1979), Kozák (1982), Kozák *et al.* (1989) and Rank *et al.* (1986), the OH^- -bound hydrogen of cellulose (30%) is exchangeable. Hydroxyl groups are protected in the intact wood structure by molecular orientation (Brown 1979), but the original ^3H content of cellulose changes during pretreatment. Thus, samples were equilibrated by boiling for 1 h in 0.4 M HCl solution prepared from ^3H -free water (from Grafendorf, Styria), and then washed free of acid with ^3H -free water. To avoid exchange with atmospheric HTO, the wet sample was sealed immediately in the combustion apparatus and dried overnight (or at least for 7 h) *in vacuo* at $\sim 150^\circ\text{C}$. However, comparing a sample treated in this way and an equivalent, but not equilibrated, sample showed no differences in ^3H content. Two possible explanations for this are: the OH^- exchange occurred during preparation with tap water, or the portion of exchangeable hydrogen groups is very low ($\sim 10\%$) as reported by Yamada *et al.* (1992), and thus, cannot alter the result significantly.

The sample was burned in a fused-quartz combustion tube half-filled with CuO wires maintained at 800°C for complete oxidation of the combustion gases. The sample was loaded in a fused-quartz boat and covered with CuO powder, then was heated by a large burner moving in the direction against the oxygen stream, which was held at a low flow rate. After passing over the entire sample, the direction of burner movement was reversed, the oxygen flow rate increased considerably and the sample was burned completely. The combustion product water was collected in a dry ice/methanol cold trap. The combustion of a 20 g sample lasted *ca.* 2 h.

Collected water was purified with charcoal filtration and by distillation. This is necessary to remove traces of ^{40}K , which, otherwise, would contribute to the ^3H -region of the β spectrum. Distillation also removes an unknown blue contaminant, which causes long-lived chemiluminescence. One can overcome the latter problem by using a cocktail that suppresses this spurious luminescence (*e.g.*, Optiphase HiSafe™ 3). Up to 8 ml of sample water were added to 12 ml cocktail and stored in a dark and cool place for a few hours before measurement.

I used a low-level Wallac Quantulus LS counter for ^3H measurement. Usually, 1500 counts per sample were collected. Typical counting times were 500–1000 min except for samples from years with the highest ^3H concentrations. I determined efficiency either by adding a known amount of a standard solution to the samples or *via* quench parameter and quench curve.

RESULTS AND DISCUSSION

Figure 1 and Table 1 show measurement results. ^3H contents of precipitation in Vienna were taken from IAEA and Austrian reports (IAEA 1969, 1981, 1983, 1986, 1990; Rank, Rajner & Lust 1989, 1990). Because no pre-1961 ^3H data exist for Vienna, data for Ottawa, Canada are given instead. Because the Ottawa data give monthly mean values, but not the amount of rain for each month, and because the highest ^3H concentrations are found for the months with the most rainfall, it was not possible to calculate a representative mean value. Thus, maximum values appeared to be more significant for the estimates to be made here. ^3H concentrations in whole wood and in cellulose (Fig. 1, Table 1) were adjusted for radioactive decay only ($t_{1/2} = 12.43$ yr); the concentrations in precipitation are annual weighted-mean values. Data for wood after extraction of resin are included in the evaluation of whole wood data because no significant difference was found between them. One-sigma errors are given, and result from determining up to 4 different whole wood, but only 2 cellulose samples, per tree ring. If no error is given, only one sample was measured for that ring.

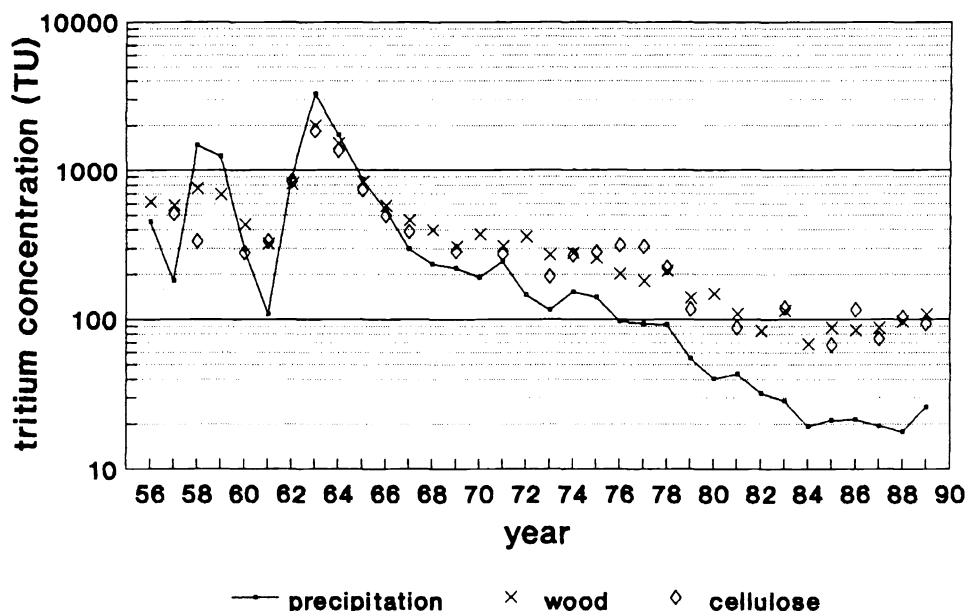


Fig. 1. ³H levels in precipitation, wood and cellulose at the year of growth. ³H concentrations are given in TU (1 TU = 0.11815 Bq kg⁻¹); see text.

TABLE 1. ³H* Levels in Precipitation, in Wood and Cellulose at the Year of Growth

Ring year	Precipitation	Whole wood	Cellulose	Ring year	Precipitation	Whole wood	Cellulose
1989	26	107±17	93	1972	145	357±54	
88	18	96±8	103	71	243	308±38	274±69
87	19	87	74±29	70	191	368±75	
86	22	84±17	115±110	69	219	305±17	286±33
85	21	87±23	68±2	68	235	394±48	
84	19	68±15		67	297	459±94	386
83	29	113±9	119	66	545	575±63	497
82	32	83±18		65	864	826±106	740±40
81	43	108±4	88	64	1738	1509±15	1357±70
80	41	147±70		63	3278	1990±20	1846±13
79	55	139±30	116±77	62	902	803±16	847±186
78	92	210±61	221±33	61	108	321±3	335±70
77	94	179±31	309±104	60	292	432±86	279±85
76	97	200±40	314	59	1246	681±58	
75	140	256±90	283±70	58	1475	754±250	335
74	153	278±47	270±122	57	181	583±236	511
73	116	270±19	193±48	56	451	611±159	

*³H concentrations are given in TU (1 TU = 0.11815 Bq kg⁻¹).

Samples from the same ring were not mixed before combustion or cellulose separation. The variation in values, as shown by the error bars, seems to be largely due to changes in the contribution of early and late wood in different parts of the investigated ring. For wood, the 1-σ error is 10–25%, except for the years around 1963, where it is only a few percent. For cellulose,

I found deviations around 25%, again with smaller scatter of the values between 1963 and 1965. A few outliers occur, for unknown reasons.

I also analyzed old cellulose and wood of years 1930–1940 from this tree. The result for whole wood was 46 TU ($\pm 10\%$), and for cellulose, it was 15 TU ($\pm 20\%$). These concentrations may have resulted from influx and exchange with highly active free water dating from the years 1963–1964. However, such “background” concentrations are not significant for evaluating modern rings, because the time for possible ^3H exchange has been much shorter, and free water of higher concentration is no longer present. Further, investigation of three 20-yr-old pines from other sites in Lower Austria also showed ^3H levels of ~ 100 TU for the years 1984–1989. This seems to be an average level for the 1980s, irrespective of the age of the tree, and thus, of possible interaction between rings of higher and lower ^3H concentration. Unlike other workers, I do not correct ^3H levels found in modern rings for “blank” levels from “pre-nuclear age” rings.

The enhanced ^3H levels in wood, compared to those of precipitation in the 1970s and 1980s, probably result from older, more active groundwater. On the other hand, groundwater of pre-1963 origin may be the cause for the ^3H depletion in biological materials formed during years of maximum precipitation (1963–1964).

The timing and extent of OH^- exchange during cellulose preparation are unknown. The measured 15 TU ($\pm 20\%$) in cellulose of 1930–1940 rings may have entered the organic matter of the tree by exchange during 1930–1989, corresponding to the 46 TU in whole wood, or they may have been introduced during pretreatment. For example, a cellulose sample containing no ^3H will show a ^3H concentration of about 12 TU after (irreversible) exchange of its OH^- groups with 40 TU water, a value typical for modern tap water. In both cases, subtraction of a “blank” value is not warranted. In the second case, subtraction of 15 TU and adjustment for OH^- exchange would enhance the calculated ^3H levels by up to 30%, but this is within statistical uncertainty.

The temporal trend of ^3H concentrations in tree-ring cellulose and precipitation are in general agreement. Data reported here also show that the difference between ^3H activities in whole wood and in cellulose is, in most cases, within the experimental uncertainty. Thus, the tedious and time-consuming cellulose preparation step is not required to get satisfactory data. Sample preparation time is much shorter for whole wood. Significant concentration variations from different samples of the same ring make it advisable to perform several whole wood measurements. Twice the number of measurements are possible using whole wood samples than using cellulose samples. This enables analyzing a greater number of samples from the same ring.

CONCLUSIONS

The integrated annual pattern of ^3H concentration in tree rings follows generally the ^3H activities in precipitation. The sharp rise in 1963 can be used for dating purposes; data for whole wood and cellulose agree well. Thus, much time and effort can be saved by analyzing whole wood for environmental ^3H studies.

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