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Using tree ring cellulose as a tool to estimate past tritium inputs to the ocean

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Abstract

Tritium (^{3}H) concentrations in tree rings should reflect ambient precipitation. Thus, to improve knowledge of the ^{3}H input to the oceans, we developed a new technique to measure ^{3}H concentrations in annual tree rings. Measurements of ^{3}H were made on cellulose, the primary constituent of wood, as the isotopic signal of its carbon bound hydrogen atoms should be unchanged since biosynthesis. Traditional cellulose extraction techniques from softwoods are slow and were found to not yield reproducibly pure cellulose. Therefore, a new microwave method was developed which reduces extraction times from 3–5 days to approximately 3 h. Potential ^{3}H contamination from the hydroxyl groups of the cellulose molecule was subsequently removed by exchange with ^{3}H-free NaOH, thus avoiding the dangers of working with large amounts of cellulose nitrate. The validity of the technique was tested by presenting a ^{3}H time series from a cedar tree which grew in Tollymore Forest Park, Northern Ireland, for comparison with ^{3}H data from the Valentia weather station. We find that the ^{3}H in the cellulose clearly reflects the ^{3}H in precipitation with no significant smearing of the bomb signal. A simple box model illustrates that the maximum reservoir residence time of source water for the tree is less than 1 yr, suggesting that groundwater is not a major source of water for this tree. In general, however, the groundwater input needs to be quantified for accurate ^{3}H reconstructions to be made. This work demonstrates the potential of using ^{3}H in wood cellulose as a proxy for ^{3}H in precipitation and, thus, opens the door to reconstruction of past ^{3}H inputs to the ocean.

Keywords: tritium; tree rings; cellulose; precipitation; dendrochronology

1. Introduction

The onset of atmospheric thermonuclear weapons testing in the 1950s produced large quantities of tritium (^{3}H), the heaviest isotope of hydrogen. The mechanisms for the production of this bomb ^{3}H, its passage through the atmosphere and subsequent de-

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livery to the earth's surface are reasonably well understood [1,2]. As ^{3}H exists as part of water molecules, it is an ideal ocean tracer, its conservative nature, other than through radioactive loss to helium-3 (^{3}He), resulting in its behaviour being solely the result of the mixing and movement of water masses. The bomb 'spike' of ^{3}H in 1963 provides a clear time marker that can be seen propagating into the ocean [3], and the timescale of ^{3}H decay to ^{3}He (12.32 yr) is particularly well suited to the study of ocean ventilation over decadal timescales, for example, to study thermocline ventilation or the renewal of Antarctic Intermediate Water. Observations of the evolving distribution of ^{3}H in the ocean have provided over the last 30 yr an improved understanding of the pathways by which tracers enter the ocean interior and better knowledge of the timescales of key oceanic processes [4].

Unfortunately the usefulness of ^{3}H to both circulation and modelling studies is limited by uncertainties in the source function of the isotope. Records of ^{3}H in precipitation provide us with important information on the time and space evolution of the delivery of ^{3}H to the Earth's surface but such records are extremely sparse over the ocean, and this lack of information leads to significant uncertainties in our knowledge of the deposition history of this isotope [39,5]. The purpose of the work reported here is to illustrate the potential of annual resolution time series of the ^{3}H concentration in the cellulose of tree rings at oceanic islands as a mechanism for improving our knowledge of the input of ^{3}H to the oceans.

The usefulness of isotopic reconstructions from tree ring cellulose is already well documented [6–8], with the cellulose deuterium signal being correlated to the deuterium concentration in precipitation [9], humidity [10] and the amount of precipitation [10]. Previous work on the ^{3}H signal recorded in tree rings has focused on areas where groundwater has been contaminated [43] and as a technique to investigate high-concentration ^{3}H releases from industrial sources. A time series was presented [11] from trees that grew in an area where tritiated compounds have been routinely produced and released since 1965, leading to elevated tritiated water (HTO) levels in local atmospheric moisture. Tritium concentrations as high as 18,700 TU (1 TU = 10^{18}.^{3}H/^{1}H) were measured in the cellulose using liquid scintillation counting. However, the uncertainties in these measurements were between 200 TU and 1000 TU, far larger than the precipitation signal that would be expected in trees away from the industrial source. Later work [12] demonstrated that the time variation of ^{3}H in spruce trees in northern Hungary was in general agreement with changes in ambient precipitation, illustrating the utility of the technique in sites not subject to ^{3}H pollution though the uncertainties in the measurements still ranged from 41 TU to 177 TU. A more recent study [44] used accelerator mass spectrometry (AMS) to reconstruct source water ^{3}H levels from milligram tree ring samples from the Nevada test site. Despite the small sample size and rapid analysis time, the instrument and sample detection limits of 70 TU and 5000 TU, respectively, although suitable for samples from such a contaminated site remain prohibitively large for the accurate reconstructions necessary for improving the ^{3}H input function on a global basis. The method presented in this paper presents a significant advance on previous work, allowing ^{3}H concentrations of less than 1 TU to be precisely measured routinely, and the potential of the technique is demonstrated by a comparison of a ^{3}H time series from an Irish cedar tree to ^{3}H in precipitation as recorded by the weather station at Valentia, Ireland.

2. Method

The individual structural components of plant matter have been shown to have very different isotopic signatures [13] so ^{3}H measurements are made on α-cellulose, the predominantly cellulosic fraction that can be extracted from whole wood. α-Cellulose is both chemically stable and physiologically reflective of environmental changes [14]. It is also relatively immobile and remains confined to the growth ring in which it was formed [15]. All of the stages involved in extracting the α-cellulose needed for the reconstruction of ^{3}H time series from tree rings are shown in Fig. 1 and described in this paper.

2.1. Microwave cleaning of cellulose in soft woods

The first step required in order to measure ^{3}H in tree rings is to extract cellulose from each wood sample. Prior to lignin removal, which typically com-

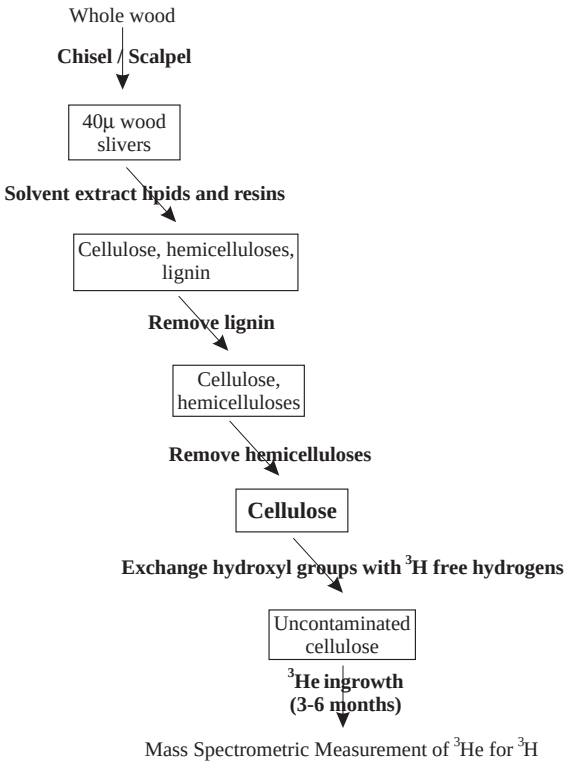

Fig. 1. Flowchart of the stages involved in the preparation of tree ring samples for ^{3}H analysis.

prises 20–30% of most woods and is isotopically depleted in deuterium relative to cellulose [13], the extraction of cellulose from soft woods requires the removal of lipids, oils and resins. This has traditionally been done by Soxhlet extraction [9,20]. However, the long extraction times and difficulty in obtaining an uncontaminated α-cellulose product (indicated by a pure white colour), despite trying a variety of solvent systems, provided the motivation to develop an alternative method.

Microwave energy has been used to enhance chemical digestions since 1975 [16], and the first use of microwave technology for the extraction of organic compounds from soils and plants is reported in [17]. The use of sealed sample vessels allows higher pressures and temperatures to be reached resulting in greatly reduced reaction times. Comparisons between microwave and traditional techniques have been made [18,19], which show that microwave methods give an improved yield and better protection of the compounds to be analysed. The main disadvantages of Soxhlet extraction (variable extraction efficiency, time consuming, large solvent volume) are mainly eliminated by microwave extraction techniques. The ability to precisely control temperature makes the technique more reproducible and running costs tend to be lower due to the smaller volumes of solvent required. The new method below replaces the multi-day Soxhlet stage in the cleaning of α-cellulose in whole wood with a microwave procedure that takes only 3 hours (Table 2). In this work, the method was developed using cedar wood, which provides a rigorous test of the technique as it contains large quantities of resinous and other natural compounds that must be removed prior to delignification.

The extractions were performed in a 650 W MDS-2000 microwave system (CEM) that allowed both pressure and temperature to be monitored continuously with the microwave power being cut if a pre-set maximum in either was exceeded. The risk of over-pressurisation of the sample vessels leading to vessel failure and the leakage of fumes into the microwave cavity makes this an important safety feature. All samples were extracted in fluorinated ethylene propylene (FEP) vessels with laboratory-manufactured locking rings made of Teflon PTFE, since the conventional polyetherimide rings were attacked by the solvents used and quickly damaged.

Initial optimisation experiments focused on extraction time, vessel pressure and solvent choice. High microwave powers for short time periods, ranging from 2 to 10 min, led to excessive pressures developing within the vessels that on occasion led to leakage of solvent fumes. An improvement was found when microwave energy was applied in a cyclical manner. Once the solvent is boiling, the addition of extra microwave energy will not improve extraction but will increase the pressure inside the vessel. The use of two solvent mixtures in sequence (2:1 chloroform–ethanol followed by an azeotropic mixture of benzene and methanol) was found to yield cleaner α-cellulose products than either solvent mixture alone. This probably reflects the very different chemistries of the two solvent mixtures, with benzene being more successful at removing phenolic compounds from the wood. In an attempt to optimise the technique further, the two solvents were combined but the yellow colour of the product indicated that the

extraction was incomplete. Longer microwave extraction times of up to 90 min did not improve product purity, yield or reproducibility. Smaller volumes of wood and solvent can be used in each vessel but the microwave power should be changed accordingly. It should be noted, however, that the power changes are unlikely to be linear as it was found that tripling the number of sample vessels required only a doubling in microwave power.

In the optimised microwave technique, extractions were carried out by placing 1 g of wood, cut into slivers approximately 40 μm thick, in each of six microwave digestion vessels to which 20 ml of 2:1 chloroform–ethanol was then added. Care was taken to ensure that all of the solid material was submerged in the liquid. The samples were then extracted for 45 min with 3 cycles of 5-min heating at 380 W followed by 10 min at 65 W. The vessels were then cooled for 30 min in a water bath before opening. The supernatant was decanted and the wood slivers were washed with a small volume of benzene–methanol azeotrope, before 20 ml of fresh azeotrope was added to each vessel. The samples were then extracted for a further 45 min as 3 cycles of 5 min at 325 W followed by 10 min at 65 W, before cooling and removing the supernatant. All traces of the benzene were then removed by washing each sample with a small volume of acetone before 20 ml of fresh acetone was added to each vessel. The samples were then heated for 5 min at 325 W followed by 10 min at 65 W, cooled and the supernatant removed. Finally the samples were allowed to dry overnight in a fume cupboard prior to subsequent lignin removal. The final microwave conditions used to routinely extract α-cellulose from cedar wood are outlined in Table 1. In all cases, cellulose was then retrieved following the procedure of [20] which is a modified version of the sodium chlorite delignification procedure of [21]. Using this method, lignin is dissolved and removed from the wood slivers by repeated chlorine bleaching treatments using a combination of sodium chlorite and glacial acetic acid. Hemicelluloses, which are non-glucan polysaccharides [34], are then removed from the white residue by sequential treatment with 10% and 17% NaOH. The chemical heterogeneity between different softwood species may require some modifications of the method described here and shorter or longer extraction times may be required, depending on the range of natural products present in the raw wood sample.

Table 1
The final microwave parameters used to routinely extract α-cellulose from Irish cedar wood

Parameter	Value
Rated power of the microwave	650 W
Calculated microwave APO	542.0 ± 24.2 W
Mass of wood per vessel	1 g
Solvent volume per vessel	20 ml
Maximum extraction temperature	120 °C[a]
Maximum extraction pressure	110 psi[a]
Stage 1 (chloroform–ethanol)	3 × (5 min at 350 W followed by 10 min at 65 W)
Stage 2 (benzene–methanol)	3 × (5 min at 325 W followed by 10 min at 65 W)
Stage 3 (acetone)	5 min at 325 W followed by 10 min at 65 W

[a] These levels were chosen on the advice of CEM based on their experience of working with petroleum hydrocarbons.

2.2. Removal of hydroxyl group contamination

Before a ^{3}H measurement can be made that reflects atmospheric water present at the time of formation of the wood, ^{3}H contamination from the readily exchangeable hydroxyl groups must be removed. Most dendroclimatological studies [9,22,23] have achieved this through nitration and measuring the isotopic ratio of the resultant cellulose nitrate. For ^{3}H analysis, large cellulose samples of up to 5 g were routinely flame sealed in glass bulbs for helium ingrowth. These large sample sizes and the highly explosive nature of cellulose nitrate make nitration of cellulose a dangerous proposition. An alternative approach is to control the isotopic composition of the cellulose hydroxyl groups by equilibration of the cellulose with water or vapour of a known isotopic composition [24,25]. However, infrared spectroscopy has shown that only 40–42% of hydroxyls, those on the surface of the cellulose fibrils, will react [26]. In order to exchange those in the interior, it is necessary to penetrate the more strongly bound crystalline regions of the cellulose polymer. To aid reaction and achieve a higher degree of substitution, sodium hydroxide (NaOH) has been used as this causes swelling of cellulose fibres, enhancing exchange [24]. These results showed that with no chemi-

cal pre-treatment, equilibration still had not occurred to any significant degree after 2 days whilst equilibration was rapidly achieved if the cellulose was soaked in 17% NaOH prior to water exchange.

Here the exchange technique was modified further. Rather than only initially soaking the cellulose, the actual substitution reaction was performed in NaOH so that the cellulose remained swollen during the entire procedure. Cellulose samples were routinely exchanged by submerging them in a large excess of ^{3}H-free NaOH for 24 h at room temperature to deprotonate the exchangeable hydrogens. The samples were then flushed with ^{3}H-free phosphoric acid (H_3PO_4) and copious amounts of ^{3}H-free water to reprotonate the exchangeable hydrogen sites, this time with hydrogens that contain no ^{3}H. Room temperature was chosen for the reaction to balance the competing effects of increased swelling at low temperatures and the kinetic advantages offered for substitution at high temperatures.

The NaOH and H_3PO_4 needed for the exchange were produced from ^{3}H-free groundwater, samples of which had been independently carbon dated and found to be approximately 5000 yr old. The ^{3}H content of the water was measured by helium ingrowth (see below) and found to have a mean concentration of 0.005 ± 0.003 TU. Tritium-free NaOH was synthesised from ^{3}H-free water and metallic sodium [27], using considerable care to ensure the reaction proceeded safely. Phosphoric acid was used to reprotonate the hydroxyl groups because it can be synthesised in a low ^{3}H form and has less tendency to both degrade and esterify cellulose than other acids [28]. The H_3PO_4 was produced by reacting phosphorous pentoxide (P_4O_{10}) with ^{3}H-free water in an argon-filled glove box as it was found that the strongly hydroscopic nature of P_4O_{10} leads to significant atmospheric ^{3}H contamination in the general laboratory atmosphere. Great care is needed to minimise contamination in the production of both NaOH and H_3PO_4 as both reagents were found to have significantly higher ^{3}H concentrations than the water from which they were synthesised (NaOH mean concentration = 0.40 TU, H_3PO_4 mean concentration = 0.091 TU). Contamination in the base is likely from the paraffin that coats sodium pieces during storage and was minimised by wiping the pieces of sodium before adding them to the reaction vessel. The large increase in NaOH ^{3}H content between samples 3 and 5 (see Table 3) does not coincide with any procedural change and can be explained by the use of a fresh batch of sodium. It is likely that the paraffin this batch of sodium was stored in contained more ^{3}H than the previous one. Using an argon glove box minimised contamination of the phosphoric acid and any residual contamination came from within the matrix of the P_4O_{10}.

In the optimised method, cellulose samples were dried overnight in a 70 °C nitrogen-filled oven and each sample was then added to ~17% w/v ^{3}H-free NaOH solution (45 ml/g of cellulose) in a conical flask, with stirring. To minimise contamination, all glassware had also been dried overnight in a 70 °C nitrogen oven and then flushed with argon prior to use. The headspace in each flask was flushed with Argon for 1 h before the flasks were stoppered and tightly taped to prevent contamination from ambient

Table 2
A direct comparison of the speed and efficiency of microwave and soxhlet extraction for the extraction of α-cellulose from Irish cedar wood

Variable	Soxhlet	Microwave
Solvent volume	250–350 ml	20 ml
Solvent temperature	Condensed from atmospheric boiling point (58.3 °C benzene–methanol, 59.4 °C chloroform–ethanol)	Average of 89.2 °C for benzene–methanol and 96.8 °C for chloroform–methanol
Time in chloroform–ethanol	24 h	45 min + 30 min cooling
Time in benzene–methanol	24 h	45 min + 30 min cooling
Time in acetone	24 h	15 min + 30 min cooling
Total time	6 g wood in 72 h	6 g wood in 3.25 h
Ease of control	Hard to control—often a high degree of variability in the extraction	Microwave power, maximum temperature and pressure can all be controlled
End-product colour	Variable from cream to yellow—significant levels of impurities remain	White—excellent reproducibility

Table 3
A comparison of the ^{3}H ratios of the pre-bomb samples used to test the exchange technique with that of the reagents used for the exchange

Sample	NaOH (TU)	H_3PO_4 (TU)	Detection limit (TU)	Tritium ratio (TU)
1	–	–	0.09	0.6 ± 0.2
2	0.042 ± 0.022	0.086 ± 0.009	0.04	0.5 ± 0.2
3	0.042 ± 0.022	0.086 ± 0.009	0.13	$<0.13 \pm 0.3$
4	–	0.096 ± 0.008	0.15	$<0.15 \pm 0.9$
5	0.57 ± 0.10	$<0.029 \pm 0.053$	0.15	$<0.15 \pm 0.78$
6	0.51 ± 0.10	$<0.0096 \pm 0.015$	0.14	0.37 ± 0.43

Where a sample is given a ratio preceded by a less than symbol, then the concentration in the sample is lower than the detection limit, the number quoted. The detection limit, which is determined by the mass spectrometer detection limit, sample size and storage time is the smallest ^{3}H signal that could be measured in that sample.

air. The contents were stirred for a further 23 h. Each sample solution was then neutralised with ^{3}H-free H_3PO_4 and then stirred for 30 min to allow all of the hydroxyl sites to reprotonate. The samples were then centrifuged and the supernatant was decanted in an argon glove box. Each sample was then washed with ^{3}H-free water, centrifuged and decanted a further four times in succession before being carefully transferred in an argon atmosphere to a pre-weighed 250-ml round aluminosilicate bulb for degassing, sealing and helium ingrowth.

2.3. Tritium determination by ^{3}He ingrowth and mass spectrometry

Once the exchanged cellulose samples had been transferred to pre-weighed alumino-silicate glass bulbs, they were degassed and partially dried prior to flame-sealing under vacuum. The bulbs containing the wet cellulose samples were quickly transferred from the argon glove box to a dedicated vacuum system where they were vacuum pumped through a liquid nitrogen cooled trap. When the pressure behind the liquid nitrogen cooled trap fell below 1×10^{-7} torr each sample bulb was flame-sealed by melting the neck of the flask whilst the sample was still open to the vacuum pump, thus minimising any atmospheric helium contamination introduced by the heating of the glass. The dry weight of the sample was then obtained by reweighing the sealed bulb and remaining glass. Samples were subsequently stored in a freezer to minimise helium permeation through the glass, which has a strong temperature dependence [29], for at least 4 months before analysis of the ^{3}He produced by ^{3}H decay. The concentrations of ^{3}He and, hence, ^{3}H in each sample were determined using a coupled statically operated, dual collector, magnetic sector and quadrupole mass spectrometer system [29]. Sample gases were cryogenically separated [30] with ^{3}H being measured by the helium ingrowth technique [29]. A more detailed discussion of the sample preparation and the mass spectrometry system used for low-level ^{3}H measurements is given in [31].

3. Validation of the method

To test the efficiency of the optimised exchange technique outlined above, cellulose samples from an oak tree collected in Killarney, Ireland, that were formed before the bomb testing and thus should contain no appreciable bomb ^{3}H were exchanged and analysed. Wood from rings formed between 1839 and 1875 was combined and used in bulk. Although ambient water from these years should contain no appreciable ^{3}H, having subsequently decayed to infinitesimal levels, the wood will have been subjected to both water and vapour with much higher concentrations of ^{3}H during and after the weapons tests. If the exchange is successfully removing all of the hydroxyl group ^{3}H contamination, only the background near-zero concentration will be present. Estimates of the natural, pre-anthropogenic ^{3}H concentration of precipitation vary from less than 1 TU at equatorial latitudes to 6 TU for Chicago precipitation [32]. Assuming pre-bomb precipitation has a ^{3}H concentration of 5 TU for Ireland, the maximum signal that would be expected from 1875 is 0.004 TU for samples analysed in 2002.

The results of these tests (Table 3) show that all of the samples have ^{3}H concentrations of less than 1 TU. However, values are greater than both the instrument detection limits and the expected 1875 signal of 0.004 TU. Possible sources of ^{3}H contamination include exchange with ambient laboratory air during sample handling and from the reagents used in the exchange. Additionally, it has been assumed that the rigorous washing of the NaOH-soaked cellulose was adequate to remove extraneous ^{3}H, as has been suggested in the

literature for deuterium [24]. This assumption is validated in part by the results in Table 3, which illustrates that there is no 1:1 relationship between reagent and cellulose sample ^{3}H contents. A further potential source of contamination is the inefficient removal of exchangeable ^{3}H from hydroxyl groups on the cellulose, which would be a reflection of the partially crystalline nature of the polymer. To rigorously test this, either a direct comparison with nitrated samples or analysis of a series of exchanges with solutions of differing ^{3}H concentrations is required. The latter approach was used for deuterium [24] and the degree of exchange, $x_{e,}$ was calculated. Additionally the results were compared with nitration of exchangeable hydroxyl groups (the extent of which was determined using C/N ratios) and the exchange process led to 25.5% of the total hydrogens present (85% of the exchangeable hydrogen) in the cellulose being removed. This value of the degree of exchange (x_e) was considered to be robust enough to be assumed in future exchange work [24]. Here this value is used when results are presented in Tritium Units, as it is necessary to know the amount of hydrogen in each sample, and thus, x_e must be known or assumed.

The large relative errors in Table 3 reflect the extremely small signals being measured and are primarily due to Poisson counting statistics associated with the integrated ^{3}He ion beam during mass spectrometric analysis and have two implications. Firstly, a larger ^{3}H signal will have a larger absolute error but a smaller relative error. Secondly, when a sample has been significantly contaminated with atmospheric helium, the error will be inflated by these counts. The latter occurs due to the fact that atmospheric helium contamination contains ^{3}He that can be accounted for in the analysis, but which inflates the uncertainty in the ^{3}He component by increasing the absolute Poisson statistical error. Whilst some small residual ^{3}H contamination is evident from a variety of sources (reagents, incomplete exchange, and handling), the validation tests show that the exchange technique is removing most of the potential hydroxyl group contamination from the cellulose molecules as these samples have ^{3}H concentrations of 0.6 TU or less, a much lower level than to which the tree will have been exposed. Thus, whilst this validation serves to highlight the difficulty of obtaining good precision for small low level samples, and the importance of minimising contamination, it is also evident that compared to the low background measured, ^{3}H signals from major bomb spikes should be very clear. All future measurements discussed below should be less contaminated than the validation samples as improved protocols for reagent production and sample handling, developed during the validation tests, particularly during sample transfer and analysis, were followed.

4. A time series of tree ring ^{3}H measurements from Valentia, Ireland

The potential for ^{3}H in precipitation reconstructions was explored by comparing a time series of ^{3}H measurements from tree ring cellulose to historical records from the Valentia weather station. The availability of one of the few long duration ^{3}H in precipitation records at the Valentia observatory made the location an ideal choice. However, as no suitable tree was found in close proximity to the observatory site a tree from Tollymore Forest Park, Northern Ireland, about 450 km from Valentia was used (see Fig. 2).

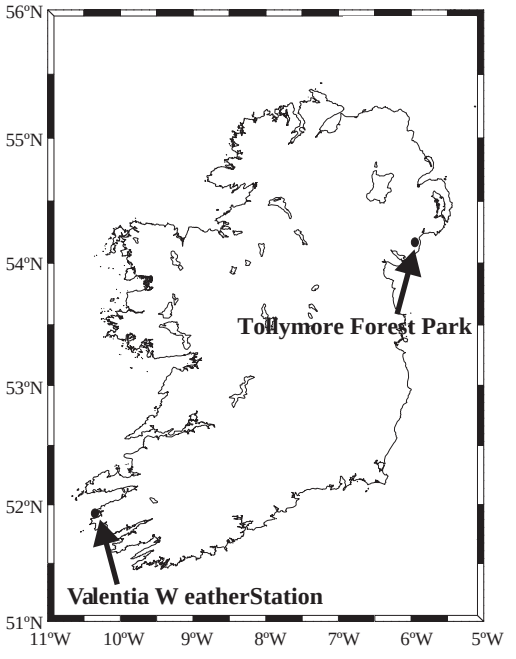

Fig. 2. Map of Ireland showing the location of the Valentia weather station (51.9°N, 10.25°W) and Tollymore Forest Park (54.21°N, 5.93°W) from where the cedar tree sample was collected.

Despite the relatively remote location of the tree, the predominantly zonal nature of Irish climate allows corrections for the large-scale trends of isotopes in precipitation and a meaningful comparison with data from the Valentia weather station to be made. In many ways, Ireland is an ideal location for an initial test of whether cellulose ^{3}H reflects ambient precipitation as its location in the northern hemisphere ensures there is a large and relatively easy ^{3}H signal to detect and the area's wet climate makes it more likely that precipitation will be the dominant source of water for a tree.

For the time series study, 1–2 g of cellulose samples were prepared as described above from approximately 5 g of wood from each annul ring. To provide enough material, it was necessary to use the entire ring width, as has been done previously [9], and it has been assumed that this will reflect the average conditions during the growth year and allow interannual trends to be seen [9].

4.1. Comparison of wood ^{3}H to ^{3}H in annual precipitation

To allow the cellulose tritium ($^3H_{CELL}$) values to be compared to annual precipitation records from the Valentia weather station, it was necessary to apply a continental correction to account for the distant location of the tree sample relative to the observations. Atmospheric circulation over the European continent has an essentially zonal character and the isotopic composition of precipitation can be considered as a flux across the western boundary. Consequently, precipitation at the location of the tree (Fig. 2) will be depleted in ^{3}H relative to that at Valentia. International Atomic Energy Agency (IAEA) data from 10 stations across Europe was used [40] to show, assuming that the meridional component of water vapour transport is minimal, that the deuterium composition of precipitation depleted with distance from the coast by −3.3‰ per 100 km in winter and −1.3‰ per 100 km in summer. Here, a depletion of −2.3‰ per 100 km, the average of the summer and winter values, was assumed to be representative of annual climatic conditions. To relate these gradients to ^{3}H, it was assumed that the fractionation of ^{3}H relative to deuterium is purely mass dependent and that the two can be related using Eq. (1). This form of equation was developed for sulphur isotopes and has been shown to hold for the three isotopes of oxygen [33].

$$\delta T/\delta D = \frac{1 - m_H/m_T}{1 - m_H/m_D} \quad (1)$$

Using Eq. (1), where the subscripts H, D and T refer to the three isotopes of hydrogen, m is mass and a zonal distance of 295 km between Valentia and Tollymore Forest Park, a ^{3}H correction of −9.1‰ was applied to all of the IAEA Valentia precipitation values to allow direct comparisons with $^3H_{CELL}$ to be made. It should be noted that this correction, along with any possible ^{3}H enrichment due to re-evaporation over Ireland, is an order of magnitude smaller than the uncertainty in the cellulose ^{3}H measurements, the contribution to the sample error being minimal from all terms apart from the analytical error due to Poisson counting statistics.

The ^{3}H in precipitation concentrations are compared with $^3H_{CELL}$ in Fig. 3, which shows that the cellulose is reflecting ambient precipitation with a clear bomb spike in 1963. It appears that the cellulose is depleted in ^{3}H with respect to ambient precipitation, as has been seen with deuterium [34,9,35], though the lack of IAEA data before 1960 makes a complete comparison impossible. As there is no smearing of

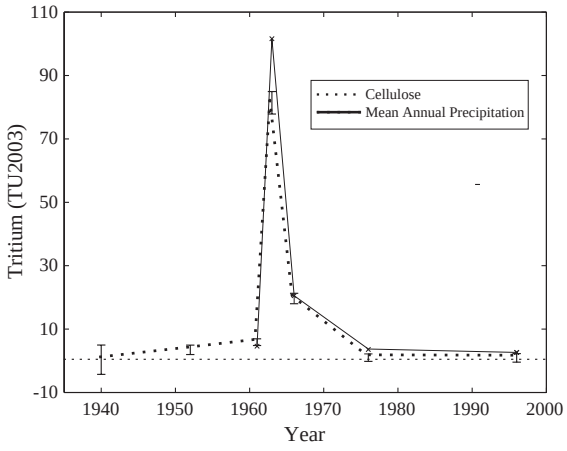

Fig. 3. Comparison of $^3H_{CELL}$ from a Northern Ireland cedar tree with annual mean ^{3}H in precipitation from the Valentia weather station. All precipitation values have been corrected for the continental effect and all ^{3}H concentrations have been decay corrected to January 1, 2003 (TU2003). For the cellulose measurements which were sub-detection limit (1976 and 1996), the number plotted is the detection limit for the sample at the time of analysis.

the precipitation signal evident in the $^3H_{CELL}$ values, we may conclude that the cellulose is reflecting conditions in the year the material was synthesised, with stored starch being of secondary importance. The ^3H signal in precipitation may be reflected so clearly in the annual tree rings because of two factors. Firstly, the tree grew in shallow soil with no obvious major groundwater supply, and secondly, there is a consistently wet climate in Ireland (the weather station records in excess of 70 mm of precipitation in July, the driest month of the year). Thus, the major supply of water to the tree is probably directly or indirectly from rain.

5. Discussion

The cellulose ^3H time series shows that the cedar tree from Tollymore Forest Park does reflect growth year ^3H in precipitation. However, the relationship between $^3H_{CELL}$ and ^3H in precipitation is not 1:1 as illustrated by Fig. 4, so other factors, although more minor, are important. Quantifying these other factors is hampered by the lack of available data so the importance of different water sources for the tree or the magnitude of the individual fractionations involved in cellulose synthesis are hard to discern. The visible offset of the magnitude of the ^3H signal between $^3H_{CELL}$ and the precipitation signal is likely a reflection of several factors.

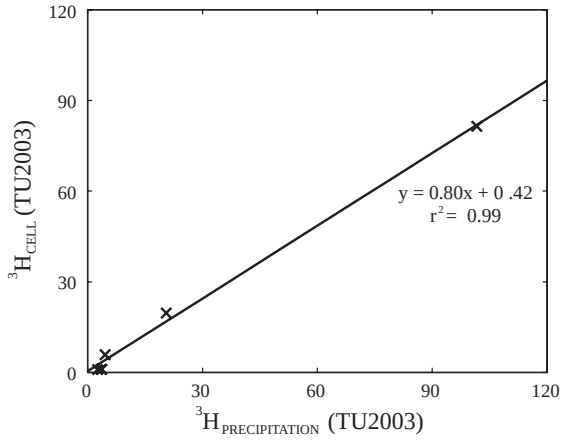

Fig. 4. Correlation of the cellulose ^3H concentrations with annual precipitation records at the Valentia weather station. All the values have been decay corrected to January 1, 2003 (TU2003) and the precipitation values have been corrected for the continental effect as described in the text.

The hydrogen isotope composition of the carbon-bound fraction of cellulose relative to that of its source water is related to three main factors: isotopic enrichment of leaf water because of evapotranspiration, fractionations associated with photosynthesis and post-photosynthetic metabolism. The relative importance of these three factors for a particular tree that grew under a specific set of environmental conditions determines whether the cellulose hydrogen reflects source water. For example, numerous studies [36,35,8,37] have illustrated that humidity affects the isotopic signal recorded in tree ring cellulose, as it determines the amount of evapotranspiration that occurs by varying the water vapour gradient between the leaf and the atmosphere. The other major factor that determines the extent to which a cellulose sample from a particular tree will reflect precipitation is the magnitude of the groundwater contribution. As Ireland has a temperate climate, it seems likely that an intermediate water source case where groundwater is available to deep roots and summer rain to roots near the soil surface will apply [41]. Before the onset of thermonuclear weapons testing in 1952, groundwater will have been essentially ^3H-free. Therefore, in the early bomb years, the groundwater signal will have diluted the increasingly tritiated precipitation signal. Over time, as groundwater ^3H levels increased, the relative importance of this ^3H will also have increased, particularly in later years as the precipitation signal relaxed to its pre-bomb state. If groundwater was an important water source for our tree, we would expect to see a larger offset between $^3H_{CELL}$ and the precipitation records in the early years of bomb testing compared with later in the record. Annual $^3H_{CELL}$ data, which was beyond the scope of this exploratory study would be needed to accurately determine the importance of groundwater to this tree.

The effect of soil water residence time on the ^3H signal of the water used by the cedar tree to synthesise cellulose was explored using a simple reservoir renewal model for Valentia precipitation. The model assumes that the tree forms cellulose in the presence of trunk water, with isotopic enrichment due to evapotranspiration in the leaves being ignored. Evapotranspiration typically enriches leaf water in deuterium by 40–50‰ [42], so using Eq. (1), this is equivalent to a

^{3}H enrichment of ~53–60‰. This is less than the uncertainty in the tree ring ^{3}H measurements which justifies neglecting evapotranspiration in the model. The calculation was based on the water used by the tree having a characteristic residence time (τ in years) in the soil–tree system before being used to synthesise carbohydrates in the trunk. The reservoir size was defined as

$$\text{Reservoir Size} = \tau \times \text{Annual Average Precipitation Rate} \quad (2)$$

Monthly precipitation ^{3}H concentrations and precipitation rates were taken from the Valentia weather station data set, having been corrected for the distance between Valentia and the trees location as before, and steady state and a pre-bomb precipitation ^{3}H concentration of 5 TU were assumed. Twelve integrations of the model were done with residence times ranging from 2 months to 2 yr. The model does not include groundwater from deep aquifers, which is reasonable for this particular tree as it grew on granitic bedrock and was therefore unlikely to have access to deep water sources. The results of the model, which predicts the ^{3}H concentration of water used by the tree, for six different residence times are shown in Fig. 5.

The graphs in Fig. 5 indicate that the cellulose data diverge from the model for residence times in excess of 10 months, and that for timescales longer than 1 yr, there is significant smearing of the ^{3}H signal. Therefore, it can be inferred that the tree is assimilating ^{3}H from precipitation that is less than 1 yr old. This is to be expected given the good correlation between $^3H_{CELL}$ and annual precipitation (Figs. 3 and 4) but it also presents the possibility that during the summer growing season, a fraction of the water used may reflect conditions at the end of the previous year. Although other factors mentioned above, such as humidity and isotopic fractionation, may account for the offset between the model and cellulose concentrations, the reservoir model emphasises that a large part of the cellulose ^{3}H signal can be explained by precipitation alone. The model also highlights the importance of careful site selection for doing ^{3}H reconstructions. For values of τ in excess of 1 yr, there is significant smearing of the model water ^{3}H signal, and the values deviate significantly from the measured $^3H_{CELL}$ values. If the model is run with a much longer residence time, from 10 to 100 yr, radioactive decay is the dominant factor determining the model reservoir water ^{3}H concentration and it is seen to diverge further from the data with time, becoming a flat line after 50 yr. This illustrates that if a tree did have access to a deep aquifer whose water was essentially ^{3}H-free then this could have a significant impact on its hydrogen isotopic composition, making the tree less suitable for time series work. Despite the idealised nature of the model, it sets a quantitative limit on the magnitude of groundwater influence, confirming further that accurate ^{3}H in precipitation reconstructions can be generated from tree ring cellulose.

Although the ^{3}H measurements presented here are too few to quantify the mechanism of fractionation and water uptake, they do confirm that the cellulose ^{3}H signal is accurately recording precipitation. Fig. 3 is extremely encouraging as it shows that the shape of the $^3H_{CELL}$ curve mirrors that of annual precipitation, though a perfect correlation has not been found (Fig. 4). The bomb spike ^{3}H signal, which is important for ventilation and modelling studies, is clearly detectable in this cellulose time series. This confirms the potential of the technique to improve knowledge of the ^{3}H input to the oceans, the magnitude of which is strongly dominated by deposition in the early 1960s. However, to be convinced that precipitation is a major source of ^{3}H for a particular tree, a comprehensive study comparable to that by [38] for deuterium and oxygen needs to be done. In such a study, measurements of the ^{3}H composition of groundwater, sap, leaf water, humidity, atmospheric vapour, precipitation and temperature would be made in parallel to measurements of $^3H_{CELL}$. This would allow the relative importance of different water sources and other climatic parameters to be quantified and would allow estimates of net biochemical fractionation to be made. Such a study would be particularly important for precipitation time histories from tree rings at oceanic islands.

As a first study of low-level ^{3}H measurements in tree ring cellulose, this work is a significant step forward from the earlier studies [11,12]. Here the use of ^{3}He ingrowth allows much lower ^{3}H signals to be measured with much improved accuracy and the results presented in this study would not have been

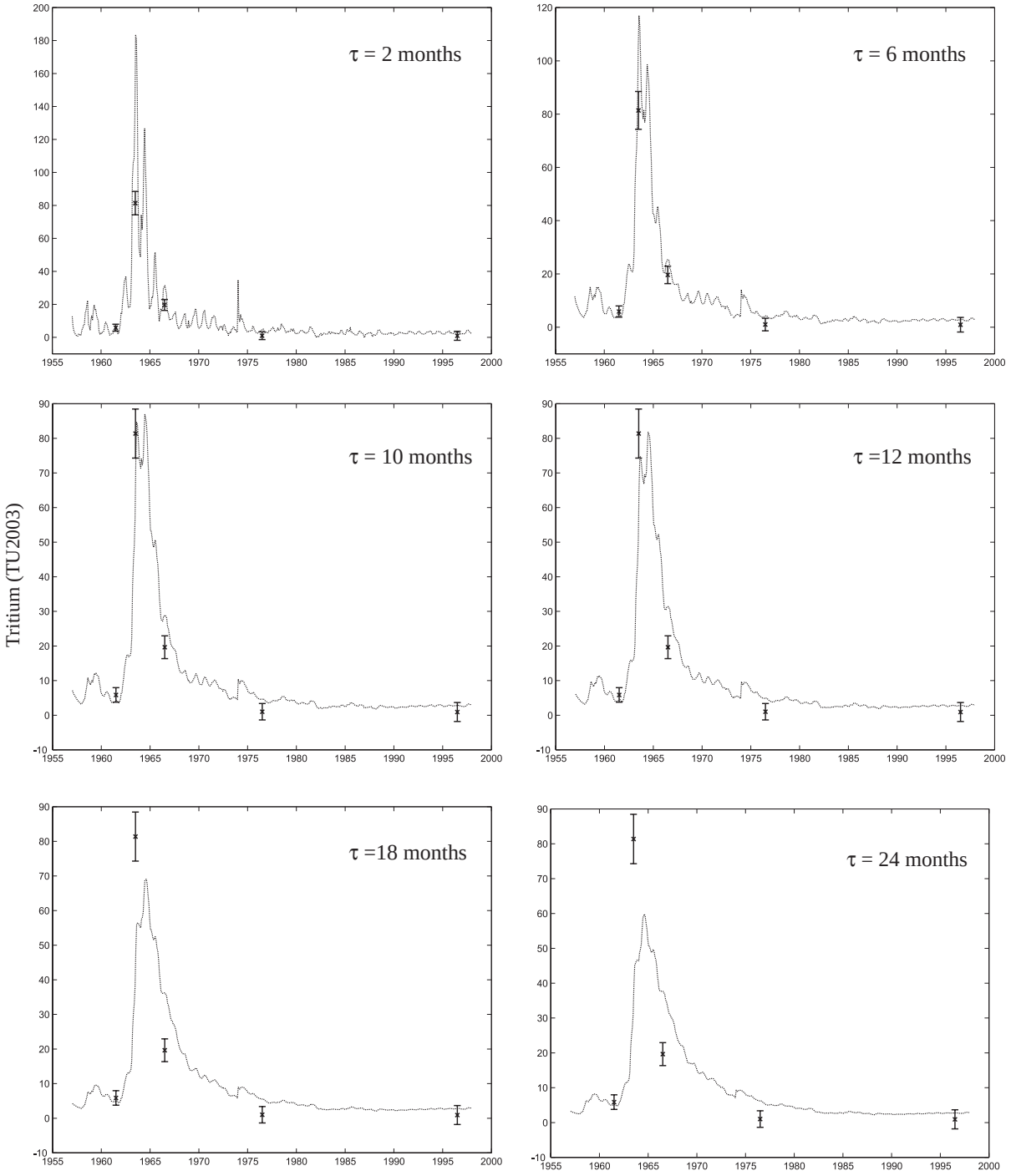

Fig. 5. Comparison of the source water ^{3}H concentrations used by the cedar tree predicted by the reservoir renewal model (line) with the measured cellulose concentrations (points). For clarity, note the different vertical scales used on the 2-month and 6-month residence time plots. All the results have been decay corrected to January 1, 2003.

detected using the techniques presented in the earlier papers. Improved cellulose sampling with a more complete exchange technique and a reduction in the large errors in sample ^{3}H measurement will further improve the utility of this technique. Sealing larger cellulose samples for longer time periods and improving mass spectrometer precision will both allow smaller ^{3}H signals to be measured and reduce the error in each sample measurement. This will become extremely important if ^{3}H reconstructions are to be made at oceanic locales or in the southern hemisphere where ^{3}H levels are significantly lower than in the continental northern hemisphere. To confirm the validity of the technique at a less optimal location, it would be useful to measure ^{3}H at an ocean island. Bermuda would be a good choice for such an experiment as there is some precipitation ^{3}H data available there.

6. Conclusion

Despite recent advances (e.g., [3]) the utility of ^{3}H as a tracer in circulation and modelling efforts is fundamentally limited by uncertainties in its input function, particularly over the oceans where the available data set is extremely sparse [39]. The extraction and exchange technique described here combined with high sensitivity ^{3}H measurement by helium ingrowth demonstrates the potential for precipitation ^{3}H signals to be measured in tree ring cellulose and thus provides an approach to filling the gaps in the global ^{3}H input function. The application of the method described here to a Valentia time series highlights this potential as the bomb spike inputs of ^{3}H can be clearly seen. Further work will be required to fully exploit this potential, particularly with regards to the refinement of contamination control procedures, exchange protocols and understanding of environmental factors that can influence ^{3}H uptake and incorporation into cellulose. In addition to offering a route to reconstruct ^{3}H input time series, the microwave extraction procedure described here offers workers in all areas of dendrochronology a rapid alternative to Soxhlet extraction for obtaining a reliably clean cellulose product. Not only are extraction times reduced by an order of magnitude, but the simultaneous extraction of numerous samples is straightforward.

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