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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-