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Stable hydrogen isotope values of lignin methoxyl groups of four tree species across Germany and their implication for temperature reconstruction

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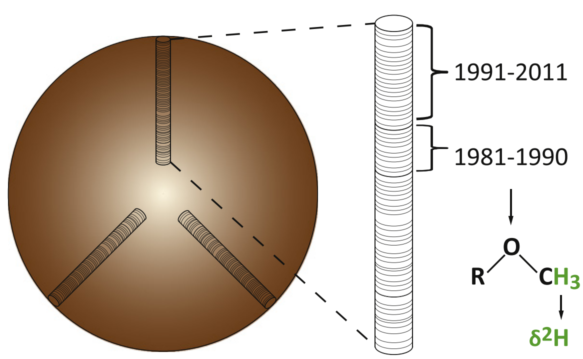
HIGHLIGHTS

- The δ^2H values of lignin methoxyl of 660 tree-ring cores were analyzed.
- δ^2H values differ within and between trees by ≤10 and ≤28 mUr or ‰, respectively.
- Species-specific differences in the apparent isotope fractionation were found.
- The potential use of δ^2H of lignin methoxyl as a paleotemperature proxy was tested.
- For this approach European beech trees showed most potential.

GRAPHICAL ABSTRACT



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ABSTRACT

Stable hydrogen isotope ratios of lignin methoxyl groups (δ^2H_{LM} values) in wood have been shown to mirror the δ^2H signatures of precipitation (δ^2H_{precip} values). Thus, δ^2H_{LM} values were suggested to serve as a potential paleotemperature proxy since δ^2H_{precip} values are dominantly controlled by air temperature in the mid-latitudes. A recent study where a significant δ^2H_{LM}-temperature relationship was found for a European transect with mean annual temperatures ranging from −4 to 17 °C strengthened this assumption. However, using δ^2H_{LM} values as a paleotemperature proxy requires quantification of noise from site-, species- and biosynthetic-specific influences to determine the significance of recording smaller temperature changes. Here, we measured δ^2H_{LM} values of tree-ring sections covering 1981–1990 and 1991–2011 of four different tree species (European beech, English oak, Scots pine, Norway spruce) at 15 sampling sites across Germany. The maximum difference in mean annual temperature between sample sites was 5 °C and all sites showed small temperature increases from 1981 to 1990 to 1991–2011 (mean $\Delta = 0.7$ °C). For all species investigated, the maximum difference of δ^2H_{LM} within the tree was <10 mUr or ‰ (median values) and between trees at a single site was ≤28 mUr (median values). The general pattern of the spatial δ^2H_{LM}-temperature relationship found for the European transect was confirmed here although a significant correlation was lacking. This can be explained by the lower spatial δ^2H_{precip}-temperature correlation ($R^2 = 0.39$) found for sampling sites in this study and the δ^2H_{LM} differences between trees. Nevertheless, the temporal changes in δ^2H_{LM} values of European beech trees correctly reflected within ±2 °C the temperature change at every sampling site. Therefore, we suggest that δ^2H_{LM} values of European beech trees have

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considerable potential for reconstructing temperature changes when applied on tree-ring chronologies and consider this approach particularly suited for Late Holocene climate studies.

1. Introduction

Tree-ring chronologies are valuable climate archives for the reconstruction of late Holocene temperature variability as they provide continuous records at annual resolution (Büntgen et al., 2016; Esper et al., 2012; McCarroll and Loader, 2004; Wilson et al., 2016). Temperature reconstructions can be inferred from plant physiological parameters such as tree-ring width or maximum latewood density from trees growing at altitudinal or latitudinal treeline (Briffa et al., 2002; Esper, 2000; Esper et al., 2003, 2002a, 2002b; Jacoby and D'Arrigo, 1989; Wilson et al., 2016). However, for non-treeline regions additional temperature proxies are necessary to increase spatial coverage and to improve our understanding of past climate evolution/change globally. In this context, stable hydrogen isotope ratios (δ^2H values) of tree-rings seem suitable since they are derived from the δ^2H values of precipitation (δ^2H_{precip}), which are dominantly controlled by temperature in the mid-latitudes (Dansgaard, 1964; Gat, 1996). Hence, δ^2H values complement and even broaden the potential of tree-rings as a climate archive (Esper et al., 2015; Hartl-Meier et al., 2014; Liu et al., 2015; McCarroll and Loader, 2004).

Recently it was suggested that the δ^2H values of lignin methoxyl groups (expressed here as δ^2H_{LM} values) of tree-ring wood could be used as a paleotemperature proxy (Anhäuser et al., 2016, 2015, 2014; Keppler et al., 2007; Mischel et al., 2015). Methoxyl groups in tree wood are predominantly ether bonded in lignin. Their δ^2H value can be readily measured without isotope fractionation as iodomethane (CH_3I) which is released upon treatment of the wood with hydroiodic acid (Greule et al., 2008). The δ^2H value of CH_3I is measurable by gas chromatography-high temperature conversion-isotope ratio mass spectrometry (GC-HTC-IRMS). The speed and simplicity of the procedure enables the collection of large isotope data sets.

The δ^2H_{LM} values of tree wood are, at a first order of control, derived from the δ^2H_{precip} values and are modulated by a large uniform apparent fractionation (ε_{app}) (Anhäuser et al., 2016; Feakins et al., 2013; Keppler et al., 2007). For trees located in the mid-latitudes it was shown that they primarily reflect the mean annual δ^2H_{precip} value since tree source water integrates multiple precipitation events potentially involving water from the previous year (Anhäuser et al., 2016). In the Anhäuser et al. study it was also shown that the mid-latitudinal temperature signal of δ^2H_{precip} is reflected by δ^2H_{LM} values of tree wood since a significant correlation between δ^2H_{LM} values and mean annual temperatures (MAT) ranging from -4 to 17 °C was found for various tree species across a European north-south transect. However, in order to determine the significance of δ^2H_{LM} when temperature ranges are lower (<2 °C) further assessment of the noise emerging from site-specific (prior to methoxyl formation) such as secondary δ^2H_{precip} alterations at climatically homogenous sites, species-specific differences in ε_{app} also termed as "plant taxonomy effect" (Liu et al., 2016) as well as biosynthetic-specific due to isotope fractionation. Further insight regarding these issues may also help to improve tree-ring sampling strategies.

Here, we collected tree-ring sections of four different species including European beech, English oak, Scots pine and Norway spruce at 15 sampling sites across Germany with MATs in the range of 6.5 to 11.5 °C. At every sampling site three core samples per tree and up to five trees per species were collected. Besides the spatial (geographic) temperature variations, at every sample site a small temperature increase from 1981 to 1990 to 1991–2011 (0.7 °C on average) was also reported. Each core was dissected for both time periods and subsequently homogenized prior to δ^2H_{LM} measurements. Hence, the sampling design allowed for four tree species a detailed assessment of the following aspects:

(i) the 'within tree' variability as assessed circumferentially and temporally
(ii) the 'between tree' variability of the δ^2H_{LM} values at climatically homogeneous sampling areas
(iii) ε_{app}—species-specific differences and within species variability
(iv) the effect of pooling sample material on δ^2H_{LM} values. Instead of measuring δ^2H_{LM} of every core separately, it may be suitable to 'pool' material from multiple trees from each species at each site into one sample. This would considerably reduce the analytical workload and hence save time and resources
(v) the relationship between δ^2H_{LM} values and both the spatial and temporal temperature variations

2. Materials and methods

2.1. Study sites and tree-ring sampling strategy

The 15 study sites were located across Germany (Fig. 1a) with typically flat terrains in closed forests. At every study site, if available, four tree species, European beech (*Fagus sylvatica*), English oak (*Quercus robur*), Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), were sampled within a few kilometers (Fig. 1b). When possible, samples from five trees of each species were taken within a radius of 200 m of each other (Fig. 1b). All trees sampled had a minimum circumference of 120 cm thus ensuring a tree age of approximately ≥60 years. From each tree, three core samples were taken (Fig. 1c) using a 5-mm diameter borer equidistant at approximately 1.2 m above ground with a minimum core length of 150 mm. In total, this led to 660 tree-ring cores of 220 trees.

After collection the samples were dried in a drying cabinet (48 h at 30 °C). The annual growth rings were counted visually under a magnifier in order to separate the time sections 1981–1990 and 1991–2011. For some sections it was necessary to enhance the visibility of the ring structure using white chalk powder. Each tree-ring section was homogenized with a micro-mill (mesh size 1 mm).

To generate 'pooled samples', sub-samples of the homogenized material were mixed (in equal amounts) so as to provide one representative sample of each investigated tree species at every site. For this we used the time section 1991–2011. Depending on the number of trees sampled at each site, a 'pooled sample' included material from 9 to 15 tree-ring cores.

2.2. Temperature and stable isotope data of precipitation

Except for the site at Annweiler, weather stations of the *Deutsche Wetterdienst* (DWD) were located within 1 to 15 km of all other sampling sites which allowed comparison of the δ^2H_{LM} values with measured temperature data (Table 1). For the sampling site at Annweiler interpolated temperature data were used (Harris et al., 2014). For the δ^2H_{precip} values we used measured data from stations of the Global Network of Isotopes in Precipitation (GNIP)[1] that were available for the majority of the sampling sites. The δ^2H_{precip} and temperature data were averaged to match those of the prepared tree-ring time sections of 1981–1990 and 1991–2011. Both parameters showed an increase in

[1] Data available at http://isohis.iaea.org.