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RESEARCH ARTICLE

Warm season precipitation signal in δ^2H values of wood lignin methoxyl groups from high elevation larch trees in Switzerland

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Rationale: In this study, we tested stable hydrogen isotope ratios of wood lignin methoxyl groups ($\delta^2H_{methoxyl}$ values) as a palaeoclimate proxy in dendrochronology. This is a quite new method in the field of dendrochronology and the sample preparation is much simpler than the methods used before to measure δ^2H values from wood.

Methods: We measured $\delta^2H_{methoxyl}$ values in high elevation larch trees (*Larix decidua* Mill.) from Simplon Valley (southern Switzerland). Thirty-seven larch trees were sampled and five individuals analysed for their $\delta^2H_{methoxyl}$ values at annual (1971–2009) and pentadal resolution (1746–2009). The $\delta^2H_{methoxyl}$ values were measured as CH_3I released upon treatment of the dried wood samples with hydroiodic acid. 10–90 µL from the head-space were injected into the gas chromatography/high-temperature conversion/isotope ratio mass spectrometry (GC/HTC-IRMS) system.

Results: Testing the climate response of the $\delta^2H_{methoxyl}$ values, the annually resolved series show a positive correlation of r = 0.60 with June/July precipitation. The pentadally resolved $\delta^2H_{methoxyl}$ series do not show any significant correlation to climate parameters.

Conclusions: Increased precipitation during June and July, which are on average warm and relatively dry months, results in higher δ^2H values of the xylem water and, therefore, higher δ^2H values in the lignin methoxyl groups. Therefore, we suggest that $\delta^2H_{methoxyl}$ values of high elevation larch trees might serve as a summer precipitation proxy.

1 | INTRODUCTION

In the last decades the number of studies using stable carbon and oxygen isotope ratios from tree-rings has increased (see, e.g.,[1-3] and references cited therein). Stable hydrogen isotope ratios from tree-rings were used rarely as a proxy for climatic or environmental changes (e.g.,[4,5] and references cited therein). All these studies used cellulose nitrate, which was nitrated from α-cellulose, to determine δ^2H values from the wood samples.[6] This nitrification replaced the wood hydroxyl hydrogens with nitro groups.[6-8] Another method is the equilibration with water of known isotopic composition to prevent interferences with the exchangeable hydrogen atoms.[9-11] This rather complex sample preparation is necessary to determine the non-exchangeable hydrogen from cellulose, which does not exchange with xylem water after cellulose formation. The additional preparation step for tree-ring δ^2H measurements might be a key reason for the limited number of studies that have been conducted so far.[12] Early work by Yapp and Epstein[13] shows that the δ^2H values of the cellulose nitrate reflected the temperature influence on precipitation δ^2H values. However, further studies indicated that the transfer processes of precipitation δ^2H values into tree cellulose were more complex than first expected and, therefore, the temperature signal could be masked (see[14] and references cited therein). Yet, the δ^2H values show a high correlation to $\delta^{18}O$ values of the same tree-rings,[4,15] suggesting that the same environmental processes influenced both isotope ratios. The most influencing parameters are the isotopic composition of the rain water/source water taken up by the tree,[4,12,16,17] and the enrichment of the isotopic composition of the leaf water due to evaporation effects.[18-20] This results in a positive correlation of the $\delta^{18}O$ and δ^2H values with temperature and a negative correlation with precipitation amount and air humidity.[4,21] The $\delta^{18}O$ and δ^2H values in precipitation are positively correlated with temperature in the mid-latitudes (40° to 66° latitude)[22,23] and the $\delta^{18}O$ and δ^2H values of the tree-rings represent partially the isotopic composition of the source water, which is modulated by the leaf water enrichment.[20,24] On the other hand, the evaporation effect in the leaves is influenced by temperature, air humidity, and precipitation. A high relative humidity and/or lower temperatures reduces leaf water evaporation resulting in lower tree-ring $\delta^{18}O$ and δ^2H values, and vice versa.[19,20,24]

An alternative approach that has been developed in the last decade[25,26] is the measurement of δ^2H values of lignin methoxyl groups ($\delta^2H_{methoxyl}$ values) that does not require time-consuming extraction procedures prior to analyses. Their δ^2H values can be readily measured without isotope fractionation as iodomethane (CH_3I), which is released upon treatment of the wood with hydroiodic acid.[26] A further advantage is that lignin methoxyl groups of wood are chemically stable and do not isotopically exchange after formation or in the course of biotic and abiotic degradation.[26,27] Keppler et al[25] compared $\delta^2H_{methoxyl}$ values from trees around the world with corresponding δ^2H values in meteoric water and found a uniform isotopic fractionation of −216 ± 19‰. This value was slightly modified (−213 ± 17‰) by Anhäuser et al.[28] Feakins et al[29] applied this method for different tree species in a coastal ecosysthem in Florida and reported that source water δ^2H values have the greatest influence on $\delta^2H_{methoxyl}$ values. The method was tested in several studies for evaluating large-scale spatial $\delta^2H_{methoxyl}$ value-temperature relationships[25,28] and their applicability as a climate proxy.[30-32]

Anhäuser et al[28] calculated the mean annual temperature (MAT) of tree $\delta^2H_{methoxyl}$ values from mid-latitudes and low altitudes (below 1000 m asl) using the equation MAT [°C] = ($\delta^2H_{methoxyl}$ [‰] + 293)/4.09 [‰/°C]. The study of Gori et al[30] compared δ^2H values from whole wood, cellulose, and lignin methoxyl groups of *Picea abies* from three locations (between 900 and 1900 m asl) of the Southern Alps. However, in this study, the $\delta^2H_{methoxyl}$ series did not show any significant correlation to climate parameters. In contrast, the study of Mischel et al[31] analyzed *Pinus sylvestris* trees from a low elevation site (~300 m asl) in western Germany for their $\delta^2H_{methoxyl}$ values and showed high correlations with maximum temperatures.

In this study, we measured the $\delta^2H_{methoxyl}$ values of larch trees (*Larix decidua* Mill.) grown at high elevation near the tree line in Simplon Valley in southern Switzerland and compared them with temperature, precipitation, drought, cloudiness, and δ^2H values in precipitation data collected from nearby stations. This should test the applicability of $\delta^2H_{methoxyl}$ values as a climate proxy.

2 | EXPERIMENTAL

2.1 | Study area

The study site is located in the Simplon Valley in southern Switzerland, near to Simplon Village (Figure 1), which is located south of the highest point of the Simplon Pass, dividing the inner alpine dry climate of the Rhône valley and the Mediterranean-influenced climate in the south.[33] The meteorological station in Simplon Village (1495 m asl) provides a mean annual temperature of 5.3°C (1971–1996) and a mean precipitation sum of 1310 mm (1971–1996).[34] The precipitation pattern shows a bimodal distribution reaching highest values in May and October and lowest values in January–February and July[33] (Figure 2); for further details, see Riechelmann et al.[35]

2.2 | Sampling and TRW measurements

In September 2010, 37 larch trees (*Larix decidua* Mill.) were sampled near the tree line at 2150 m asl (46°13'N, 8°04'E) on a south-west facing slope (Figure 1). In total, 78 cores (two to three cores per tree) were sampled at breast height (approximately 1.30 m height) from trees of all age classes.[36,37] The cores were cut perpendicular to the wood fibre using a microtome[38] to generate a plane surface for a better visibility of the tree-rings. The tree-ring width (TRW) was measured using a LINTAB™ measuring table equipped with TSAP-Win™ software (both RINNTECH®, Heidelberg, Germany) providing a measuring accuracy of ±0.01 mm. Cross-dating of the

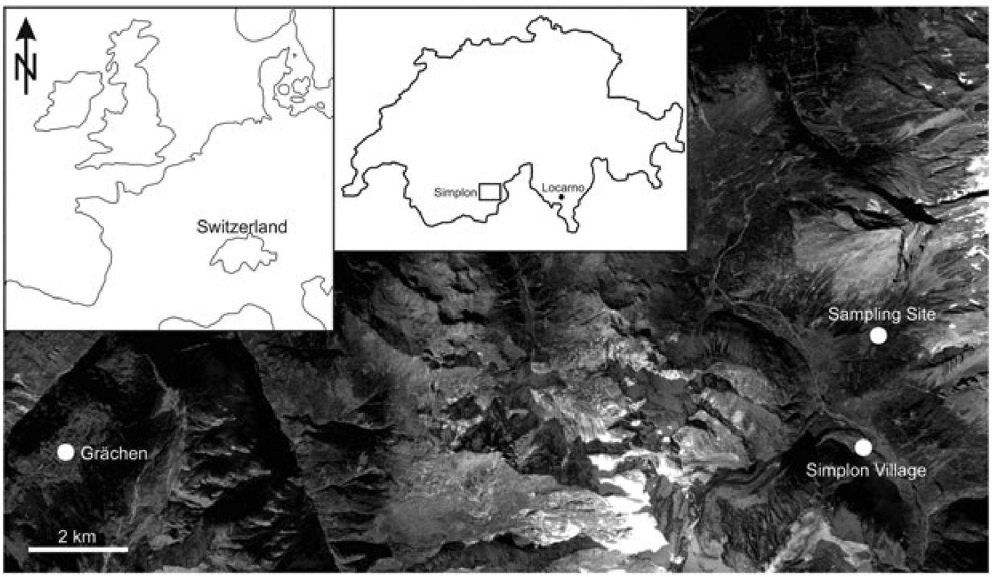

FIGURE 1 Location of the Simplon region and nearby meteorological and Global Network of Isotopes in Precipitation (GNIP) stations in southern Switzerland (modified after Riechelmann et al[35] and Google Earth)

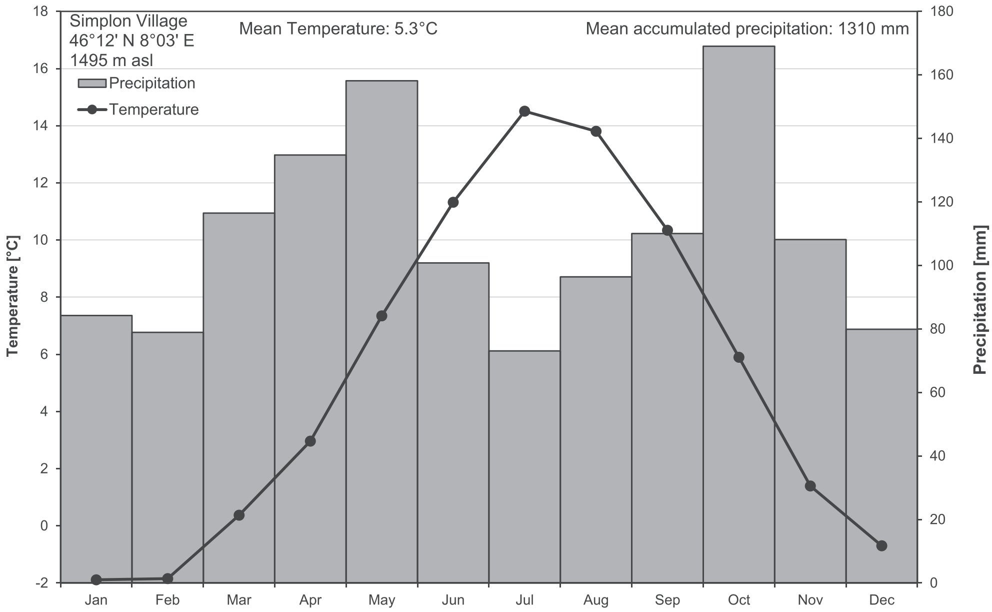

FIGURE 2 Climate diagram of the meteorological station Simplon Dorf.[34] Mean monthly temperatures and the monthly precipitation sums were calculated over the period 1971–1996

TRW series was performed visually and using COFECHA software.[39] The age-related growth trends of the TRW series were removed by calculating residuals from individually fitted negative exponential functions after power transformation[40] and variance stabilisation using 300-year splines[41] calculated with the software ARSTAN.[42]

2.3 | δ^2H values of wood lignin methoxyl groups

Five trees (one core per tree) were selected from all 37 trees for δ^2H measurements of wood lignin methoxyl groups. The period from 1971 to 2009 was measured at annual resolution, and the years before 1971 were analysed in blocks of 5 years. For the measurements of 5-year blocks, thin sections were cut from the cores using a microtome[38] and blocks of five consecutive rings of these thin sections were used for isotopic measurements. The pentadal blocks were measured to test the long-term variability in $\delta^2H_{methoxyl}$ values.

Wood pieces of 0.41 to 13.93 mg were weighed using a model R200D microbalance (±0.01 mg; Satorius Research, Göttingen, Germany) and filled into glass vials. The stable hydrogen isotope ratios of lignin methoxyl groups were measured as CH_3I released upon treatment of the dried wood samples with hydroiodic acid (HI).[26] The acid (0.25 mL, 55–58%) was added to the sample in the glass vials. The vials were sealed with crimp caps containing PTFE-lined butyl rubber septa (thickness 0.9 mm) and incubated for 30 min at 130 °C. After heating, the vials were left for equilibration at room temperature (22 ± 0.5 °C, air-conditioned room) for at least 30 min before 10–90 μL from the head-space were directly injected into the gas chromatography/high-temperature conversion isotope ratio mass spectrometry (GC/HTC-IRMS) system. Measurements were performed with an HP 6890 gas chromatograph (Agilent, Santa Clara, CA, USA) equipped with an A200S autosampler (CTC Analytics, Zwingen, Switzerland), coupled to a Delta^{PLUS}XL isotope ratio mass spectrometer (ThermoQuest Finnigan, Bremen, Germany) via a thermo conversion reactor (ceramic tube (Al_2O_3), length 320 mm, 0.5 mm i.d., reactor temperature 1450 °C) and a GC Combustion III interface (ThermoQuest Finnigan). For further details of the GC/IRMS measurements, refer to Greule et al.[26]

The isotope signatures were measured relative to a high purity H_2 reference working gas (Air Liquide, Düsseldorf, Germany). All measured sample δ^2H values were monitored for their relative trueness by analysing an in-house working standard of known δ^2H_{VSMOW} value side-by-side. The δ^2H value of CH_3I was calibrated against international reference substances VSMOW2 [δ^2H_{VSMOW} = 0.0 ± 0.3 ‰] and SLAP2 [δ^2H_{VSMOW} = −427.5 ± 0.3 ‰] using TC/EA-IRMS (elemental analyser-isotopic ratio mass spectrometer, IsoLab, Max Planck Institute for Biogeochemistry, Jena, Germany). The calibrated δ^2H value vs VSMOW for CH_3I was −173 ± 1.5‰ (n = 9, 1σ). Every wood sample was measured in triplicate followed by consecutive injections of the working standard. Standard deviations (n = 3, 1σ) were in the range of 0.1 to 9.5‰.

As this procedure represents solely a one-point calibration, it has to be pointed out that the δ^2H values might be affected by an additional error ('scale compression'). The authors are aware that international comparability of stable isotope abundance measurements ideally requires a two-scale anchor calibration with accepted isotope abundance values as recommended by the IUPAC guidelines.[43] However, in order to test our hypothesis we decided on the method described above since the annually as well as pentadally resolved sample $\delta^2H_{methoxyl}$ values thus obtained could be compared on a like-for-like basis because scale normalisation or not, differences in $\delta^2H_{methoxyl}$ values from one time point to another as well as longitudinal trends would still tell the same story. Please note that in the meantime two-point linear calibration has become available in our laboratory (e.g. [28,32]).

To test whether a long-term signal influences the correlation between the annually and pentadally resolved $\delta^2H_{methoxyl}$ series, as well as the corresponding TRW chronologies, all series were high-pass filtered using a 10-year and 10-point FFT-filter (fast Fourier transformation filter) using the software Origin® (OriginLab Corporation, Northampton, MA, USA), respectively.

2.4 | Meteorological data

The climate response of the $\delta^2H_{methoxyl}$ records was tested by comparison with monthly resolved temperature (1866–2009), precipitation (1866–2009), and cloudiness (1966–2009) data from the meteorological station Grächen (46°12'N, 7°50'E, 1605 m asl). Grächen is located 15 km west of Simplon Village (Figure 1) and is the nearest station to the sampling site, providing continuous monthly temperature and precipitation data from 1866 to 2009. Additional precipitation data were used from the meteorological station Simplon Village (46°12'N, 8°03'E, 1495 m asl) over the 1971–2009 period covered by the annually resolved $\delta^2H_{methoxyl}$ values.

To test combined effects of temperature and precipitation on the $\delta^2H_{methoxyl}$ values, the drought index (DRI) of Bigler et al,[44] i.e. DRI = P − PET, was considered, with P being the monthly precipitation sum and PET the potential evapotranspiration, according to Thornthwait,[45] derived from data from the Grächen station. Furthermore, the δ^2H data from the Global Network of Isotopes in Precipitation (GNIP) station in Locarno were used for comparison with the $\delta^2H_{methoxyl}$ values from the trees. Unfortunately, these data were not continuously measured between 1983 and 2008 (data available[46] in the intervals: 1983–1984, 1990–1992, 2002–2008). Therefore, the mean annual and monthly δ^2H values for precipitation were calculated for the sampling site using the Online Isotopes in Precipitation Calculator (OPIC),[47] to calculate the overall fractionation between precipitation and $\delta^2H_{methoxyl}$ values of the trees.

3 | RESULTS

3.1 | Tree-ring width

The TRW chronology of all 78 samples consists of 18,538 rings and has an inter-series correlation of r = 0.74 using the COFECHA software.[35,39] The five cores used for $\delta^2H_{methoxyl}$ measurements contain 1173 rings and have an inter-series correlation of r = 0.67. The TRW chronology spans 445 years with a minimum replication of five cores, whereas the five cores used for $\delta^2H_{methoxyl}$ analyses span 229 years with a minimum replication of four series. The correlation of the TRW chronology integrating all 78 series with the mean of the five TRW series used for $\delta^2H_{methoxyl}$ measurements is r = 0.88 ($p < 0.001$). This indicates that the five subsamples for $\delta^2H_{methoxyl}$ analyses closely represent the common TRW signal of the site chronology (Figure 3).

3.2 | δ^2H values

The annually resolved raw $\delta^2H_{methoxyl}$ series shows a mean value of −251.1‰. The range of the five series spans from −288.4‰ to −220.5‰ and show the same pattern in all five series during the period 1971–2009 (Figure 4a). This is reflected by the significant inter-series correlation of r = 0.53 ($p < 0.001$; Table 1). The annually resolved $\delta^2H_{methoxyl}$ series were averaged in 5-year blocks for comparison and combination with the pentadally resolved $\delta^2H_{methoxyl}$ values reaching back to 1746. These five pentadally resolved $\delta^2H_{methoxyl}$ series show a mean value of −249.9‰. The range of these five series spans from −283.0‰ to −221.6‰ and they do not cohere well (Figure 4b) reaching only r = 0.11 ($p > 0.05$; Table 1).

The correlation of the mean annually resolved $\delta^2H_{methoxyl}$ series with the TRW chronology is r = −0.54 ($p < 0.001$; Table 1). In contrast, the pentadally resolved $\delta^2H_{methoxyl}$ series correlates at only r = −0.14 ($p > 0.05$) with the corresponding TRW chronology, which is insignificant. The inter-series correlation of the high-pass filtered $\delta^2H_{methoxyl}$ series increased slightly, compared with the original data, but still reaches r = 0.57 ($p < 0.001$) for the annually resolved data (Table 1). The pentadally resolved $\delta^2H_{methoxyl}$ series only reaches r = 0.15 ($p > 0.05$; Table 1), which is also insignificant. The correlation of the high-pass filtered $\delta^2H_{methoxyl}$ series with the corresponding TRW chronologies decreases slightly to r = −0.51 ($p < 0.001$) and r = −0.05 ($p > 0.05$) for the annually and pentadally resolved data series, respectively (Table 1).

3.3 | Climate signal in TRW and $\delta^2H_{methoxyl}$ series

The annually resolved TRW record shows the highest correlation with mean temperature of May–July (MJJ) (r = 0.68, $p < 0.001$), as well as a negative correlation of r = −0.61 ($p < 0.01$) with MJJ

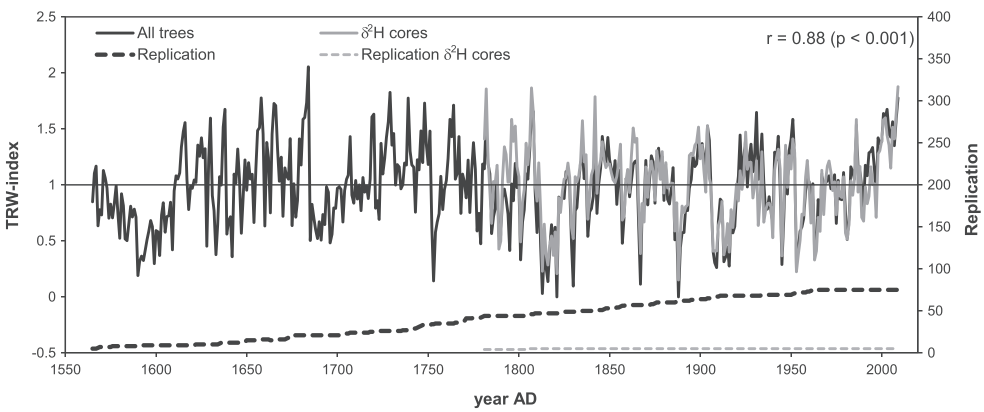

FIGURE 3 TRW chronology of all trees, and the TRW of the five selected cores for $\delta^2H_{methoxyl}$ measurements. Individual records were detrended using negative exponential functions. The records were truncated at a minimum replication of five series for TRW of all trees and four series for TRW of the five cores used for $\delta^2H_{methoxyl}$ measurements

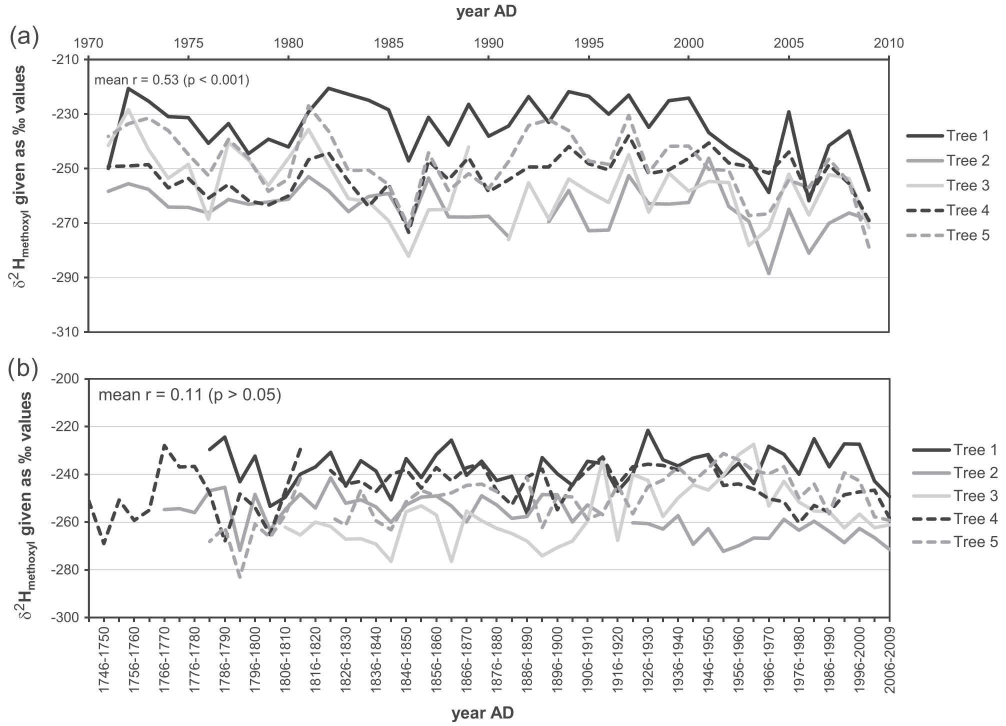

FIGURE 4 Individual $\delta^2H_{methoxyl}$ records (a) the annually resolved period 1971–2009 and (b) the pentadally resolved period 1746–2009

TABLE 1 Inter-series correlation (mean of the correlations of each series with each series) of annually and pentadally resolved $\delta^2H_{methoxyl}$ records. The annually and pentadally resolved $\delta^2H_{methoxyl}$ records were high-pass filtered with a 10-year (annually resolved) and 10-point (pentadally resolved) FFT filter. Correlation with the TRW is shown for all $\delta^2H_{methoxyl}$ records. Correlation with JJ precipitation is only shown for the annually resolved $\delta^2H_{methoxyl}$ records. Correlation coefficients with p <0.001 are shown in bold. The degrees of freedom were reduced, due to lag-1 autocorrelation in the $\delta^2H_{methoxyl}$, TRW records as well as the JJ precipitation series, before calculation of the correlation coefficients between the different time series

Annual resolution (1971–2009)	Raw $\delta^2H_{methoxyl}$ values	$\delta^2H_{methoxyl\ high\ frequency}$ values	Pentadal resolution	Raw $\delta^2H_{methoxyl}$ values	$\delta^2H_{methoxyl\ high\ frequency}$ values
Inter-series correlation n = 39	**0.53**	**0.57**	Inter-series correlation n = 41–48 (1806–2009)-(1766–2009)	0.11	0.16
Correlation with TRW chronology n = 39	**−0.54**	**-0.51**	Correlation with TRW chronology n = 46 (1781–2009)	-0.14	−0.05
Correlation with JJ precipitation n = 39	**0.60**	**0.61**			

cloudiness (Figures 5a and 5d). The $\delta^2H_{methoxyl}$ series show the highest correlation of r = 0.60 (p <0.001) with June–July (JJ) precipitation (Figure 5b). Furthermore, the $\delta^2H_{methoxyl}$ series correlates just below the 99% significance level with JJ temperatures (negative) and the JJ drought index (DRI) (positive) (Figures 5a and 5c). A higher correlation of r = 0.48 (p <0.01) occurs with JJ cloudiness (Figure 5d), and a significantly negative correlation is observed between the $\delta^2H_{methoxyl}$ series and the δ^2H values in precipitation of the GNIP station in Locarno with r = −0.82 (p <0.01) (Figure 5e). However, the data from the GNIP station are very patchy.

The pentadally resolved TRW record shows positive correlations with JJA temperature, AM precipitation and DRI (Figure 6). The correlation with JJA temperature is highest at r = 0.73 (p <0.001). The pentadally resolved $\delta^2H_{methoxyl}$ series does not show any significant correlations with temperature, precipitation, or DRI (Figure 6). To conclude, the highest correlations for the $\delta^2H_{methoxyl}$ values were found between JJ precipitation and the annually resolved $\delta^2H_{methoxyl}$ series (Figure 7).

4 | DISCUSSION

4.1 | δ^2H values of lignin methoxyl groups

The high inter-series correlation of the annually resolved $\delta^2H_{methoxyl}$ series fits well to the observations of other stable isotope studies (e.g.[1,21,48]). The correlation of the annually resolved $\delta^2H_{methoxyl}$ series and precipitation amount supports the hypothesis of a stronger year-to-year variability than long-term trends, as JJ precipitation varies strongly from year-to-year (~150 mm, Figure 7) but shows no long-term variance (~30 mm over the last 140 years).

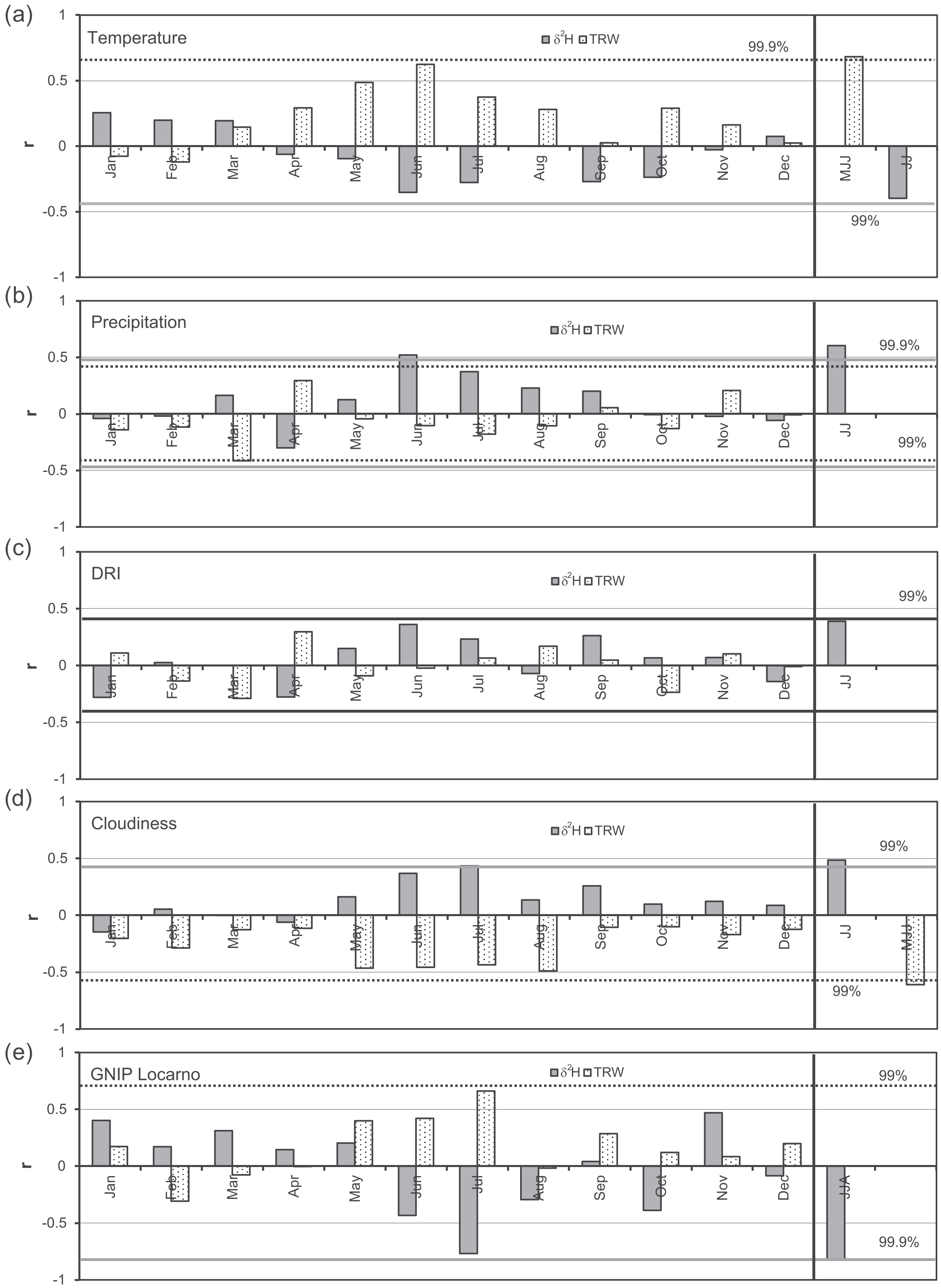

FIGURE 5 Monthly correlation coefficients between the annually resolved $\delta^2H_{methoxyl}$ record, the TRW record for comparison and temperature (a), precipitation (b), DRI (c), cloudiness (d), and GNIP data from Locarno (e) for the current year together with the highest correlations for a combination of months for the period 1971–2009. Significance levels are given in each panel. Where correlation coefficients for specific seasons are calculated, these are given after the reduction of the degrees of freedom due to lag-1 autocorrelation of the data series. Bold grey lines (a, b, d, e) indicate significant level for the correlation of $\delta^2H_{methoxyl}$ records. Dotted black lines (a, b, d, e) indicate significant level for the correlation of the TRW record. Solid black line (c) indicates significance level for $\delta^2H_{methoxyl}$ and TRW records

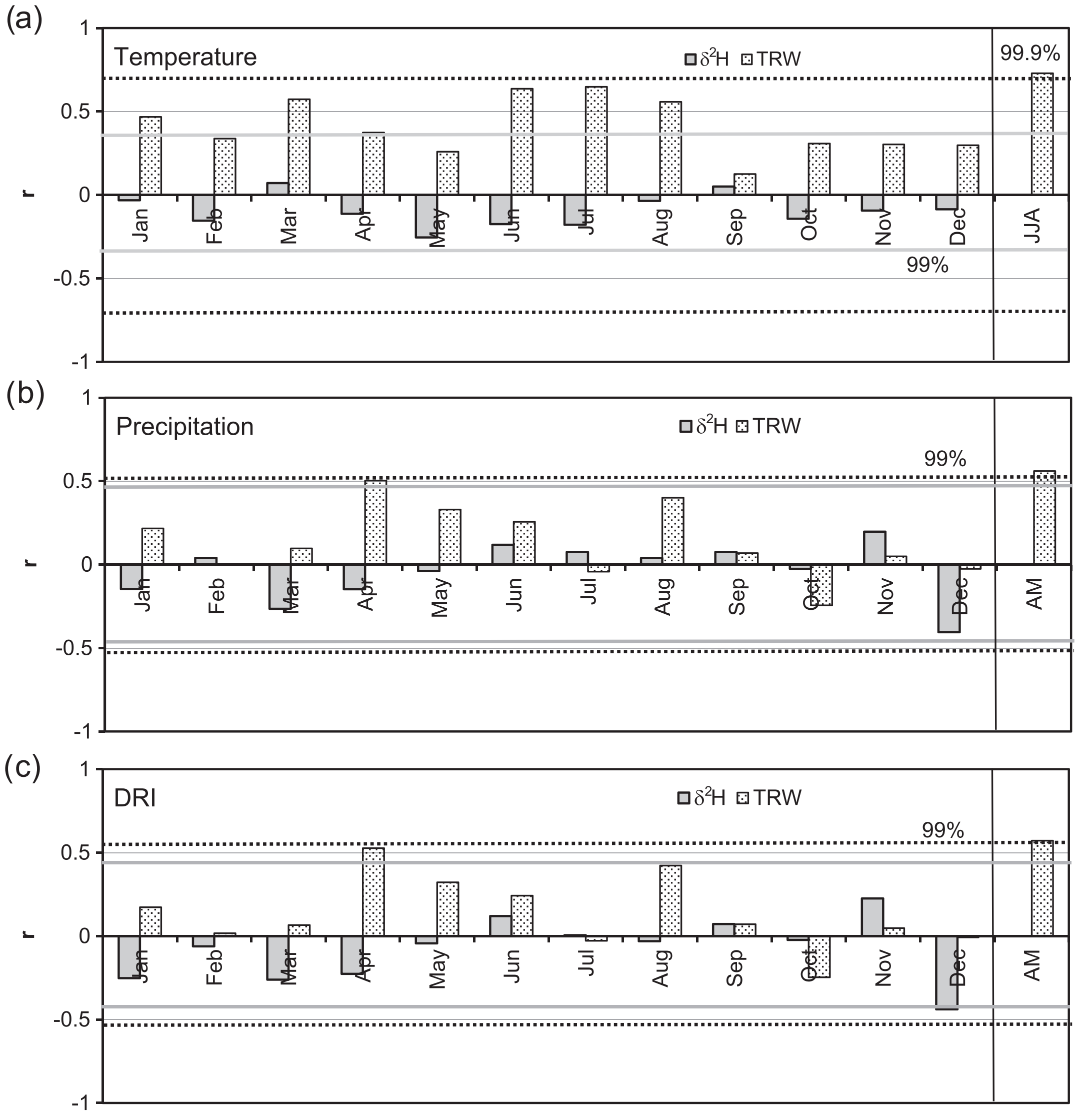

FIGURE 6 Monthly correlation coefficients between the pentadally resolved $\delta^2H_{methoxyl}$ record, TRW record and temperature (a), precipitation (b), and DRI (c) for the current pentade together with the highest correlations for a combination of month for the period 1866–2009. Significance levels are given in each panel. Where correlation coefficients for specific seasons are calculated (a, b, c), these are given after the reduction of the degrees of freedom due to lag-1 autocorrelation of the data series. Bold grey lines (a, b, c) indicate significance level for the correlation of the $\delta^2H_{methoxyl}$ record. Dotted black lines (a, b, c) indicate significance level for the TRW record

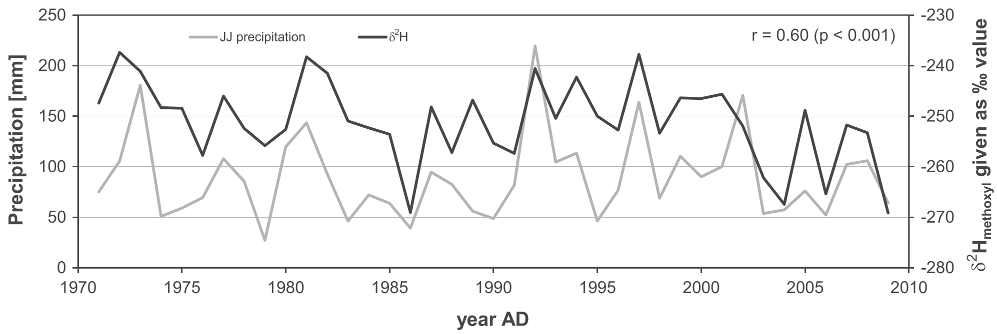

FIGURE 7 June-July (JJ) precipitation and the annually resolved $\delta^2H_{methoxyl}$ record for the period 1971–2009

The non-significant correlation of the pentadally resolved $\delta^2H_{methoxyl}$ series is probably due to this stronger year-to-year instead of long-term variations. The precipitation changes since 1866 have no pronounced influence on raw $\delta^2H_{methoxyl}$ values, which are smoothed due to the pentadal resolution. This is confirmed by the minor increase in inter-series correlations of the high frequency annually and pentadally resolved $\delta^2H_{methoxyl}$ series, which indicate no pronounced long-term trend in the $\delta^2H_{methoxyl}$ series (Table 1). Furthermore, the signal-to-noise ratio of both chronologies was calculated after Fritts and Swetnam.[49] This shows a much lower signal-to-noise ratio for the pentadally resolved chronology of 0.5:1 than for the annually resolved chronology of 5.5:1.

The maximum difference between the mean $\delta^2H_{methoxyl}$ values of the five different trees is 30‰ over the annually resolved period (1971–2009) and 20‰ for the pentadally resolved period (1746–2009). This is in good agreement with the findings of Anhäuser et al,[32] showing differences in $\delta^2H_{methoxyl}$ values between trees at a single site of ≤28‰ as well as with the 5–30‰ difference in δ^2H values from cellulose between trees reported by Leavitt,[50] and the 6–26‰ reported for $\delta^2H_{methoxyl}$ values of a single year among different trees by Mischel et al.[31] Furthermore, the δ^2H values of the lignin methoxyl groups are much lower (~ −250‰) than the δ^2H values from whole wood (−70‰) or cellulose (−40‰) as reported by Gori et al.[30] Nevertheless, all three series in the study of Gori et al[30] showed significant correlations with each other. These results indicate that the annually resolved data in this study are the most promising proxy and that pooling of several years, in this case five consecutive years, results in a substantial loss of signal, which is reflected by the very low signal-to-noise ratio of 0.5:1 for the pentadally resolved chronology.

4.2 | $\delta^2H_{methoxyl}$ values and TRW response to climate

The annually resolved $\delta^2H_{methoxyl}$ chronology shows the highest correlation with the JJ precipitation signal ($r = 0.60$, $p < 0.001$). Furthermore, a negative correlation to the JJA δ^2H values in precipitation of the nearest GNIP station (Locarno) is observed (Figure 5). A positive correlation to the δ^2H values of precipitation and source water has been reported in several other studies.[12,16,28,29,51] Furthermore, positive correlations with temperature and negative correlations with precipitation were expected, based on findings reported previously.[4,30,31] Gori et al[30] reported a positive correlation to temperature for $\delta^2H_{whole\ wood}$ and $\delta^2H_{cellulose}$ values, but no significant correlation of $\delta^2H_{methoxyl}$ values to climate parameters. In contrast, the study by Mischel et al[31] showed high correlations with maximum temperatures, and Anhäuser et al[28] showed high correlations with mean annual temperatures indicating the potential of $\delta^2H_{methoxyl}$ values as a temperature proxy for trees collected from mid-latitudes and lower altitudes. However, previously investigated sampling sites, between 900 and 1900 m asl on the southern site of the Alps,[30] and at a low altitudinal site in western Germany,[31] are not near to the limit of tree growth, which could be the reason for no or different correlations to climate parameters. In this study the larch trees were sampled close to the tree line in 2150 m asl, a site where tree growth is limited to a very short growing season during the summer months.

4.3 | $\delta^2H_{methoxyl}$ values as a climate proxy

The observed apparent, constant fractionation (ε_{app}) between δ^2H values in precipitation and the lignin methoxyl groups for most trees is around −213 ± 17‰.[28] Calculating the δ^2H values of the precipitation from the measured $\delta^2H_{methoxyl}$ values of −251‰ results in −48‰ for the precipitation. When this value is compared with the δ^2H values in precipitation at the study site (using the OIPC, see section 2.4) it can be noted that our calculation matches the mean value for June/July (−49‰) and not the annual mean (−88‰).

Anhäuser et al[28] provided an equation to calculate the mean annual temperature from the $\delta^2H_{methoxyl}$ value of low altitudinal trees that have been shown to use annually accumulated precipitation as source water (MAT [°C] = ($\delta^2H_{methoxyl}$ [‰] + 293)/4.09 [‰/°C]). Applying this equation to the mean $\delta^2H_{methoxyl}$ value (−251‰) measured in high elevation larch trees results in a temperature of 10.2°C, exceeding the observed value of the mean annual temperature of 5.3°C (Simplon, 655 m below the study site). Hence, the equation of Anhäuser et al[28] seems not 'straightforwardly' applicable at this high-altitudinal tree-site. However, the overestimation of the mean annual temperature can be explained by the findings above that the $\delta^2H_{methoxyl}$ values being considered here reflect a summer signature of the δ^2H values in precipitation. Since a constrained growing season can be expected for these high elevation larch trees, we explain this finding by a low soil water capacity at the study site leading to a strong seasonal weighted isotopic signal of the tree source water at the time of growth.

The strong positive correlation of the annual $\delta^2H_{methoxyl}$ series with JJ precipitation is clearly significant but was not observed in any of the previous studies. A possible explanation could be found in two opposite trends: while the rainout effect would result in progressively decreasing δ^2H values of the precipitation in the course of strong precipitation events,[22] the turnover rates of source water through the plant will dramatically decrease as the ambient humidity increases. With a decreased air-to-leaf VPD (vapour pressure deficit) the transpirative demand will decrease to nearly zero (RH close to 100%) and as a consequence the water flow from roots to leaves is nearly zero. As the δ^2H values of precipitation show a positive correlation with both monthly temperatures[22] (data from the GNIP station in Locarno and calculated monthly values from the OPIC[47]), this residual ^2H-enriched water from the previous warmer periods remains in the plant tissue and is incorporated during growth. Consequently, the potential local amount effect with a characteristic negative correlation between precipitation and $\delta^2H_{methoxyl}$ values was probably masked by the halt of a water flow in the plant tissue. Based on the available knowledge the significant positive correlation between $\delta^2H_{methoxyl}$ values and JJ precipitation appears difficult to explain. However, we provide the following explanation: lignin in trees is directly formed in xylem tissue[29] whereas cellulose is formed from sugars produced by photosynthesis in the leaves.[12] Therefore, studies using δ^2H values from cellulose do see the evaporative enrichment effect in ^2H of leaf water in the isotopic composition, which is related to temperature and humidity.[12] Summer precipitation has considerably higher δ^2H values and contributes a higher fraction to the source water that is involved in generating the δ^2H value of the lignin methoxyl group at this high elevation site, due to strongest growth of the tree-rings being in MJJ (Figure 5a). In the case of a higher amount of precipitation in June and July, which are on average quite dry months compared with May, which is on average the wettest month in this region (Figure 2), the water taken up by the tree would contain a higher portion of rainwater with higher δ^2H values, than for earlier times in the growing season (MJJ). Therefore, the relative fraction of methoxyl groups formed in spring (with lower δ^2H values) is decreasing. Thus, the fraction of $\delta^2H_{methoxyl}$ values formed during summer becomes higher, due to increasing amounts of summer precipitation and the $\delta^2H_{methoxyl}$ values will be higher. Further, the summer months (MJJ) are the growing season of these high elevation trees and thus the precipitation during this season might be considered at this site as the main source water for the formation of the tree methoxyl groups. The trees also do not have access to stored soil or ground water, due to high alpine shallow soils and the steep slope. There is one other study by Lawrence and White[17] who postulated that trees using summer rainfall could record the amount of precipitation although they measured δ^2H values from cellulose and saw a negative correlation to precipitation.

However, the expected positive correlation of the $\delta^2H_{methoxyl}$ values with the δ^2H values in precipitation is not observed. The δ^2H value in precipitation is strongly influenced by temperature. These increasing $\delta^2H_{precipitation}$ values, due to temperature, are reflected in the $\delta^2H_{methoxyl}$ values in the tree, in the case of a higher amount of precipitation during June and July, which increases the proportion of water with higher δ^2H values taken up by the tree. However, this does not result in a positive correlation of the $\delta^2H_{methoxyl}$ values with temperature but in a positive correlation to JJ precipitation, because this overwhelms the temperature effect in the δ^2H values of the water taken up by the tree. All other studies[12,16,28,29,51] reporting a positive correlation of the δ^2H values of trees to the δ^2H values of precipitation either measured wood components other than lignin methoxyl groups or measured the $\delta^2H_{methoxyl}$ values from trees which were not growing at such an extreme site with these aforementioned specific conditions.

Hence the $\delta^2H_{methoxyl}$ values at the Simplon site seem to reflect a summer (JJ) δ^2H_{precip} signature based on (i) steep slopes and thin soil columns preventing the source water from accumulating and (ii) a constraint growth period prevailing at this high altitudinal site. In contrast, Anhäuser et al[28] showed for low altitude/mid-latitude sites with an expanded growth period and flat terrains that the $\delta^2H_{methoxyl}$ values reflect the mean annual δ^2H_{precip} signature. Thus, these studies highlight that the site-specific hydrology and ecological conditions control the δ^2H_{precip}– $\delta^2H_{methoxyl}$ relationship and consequently the palaeoclimate significance of $\delta^2H_{methoxyl}$ values.

Taking the information provided by Riechelmann et al[35] into account, showing that $\delta^{13}C_{methoxyl}$ values are a summer temperature proxy and from the results of this study, it could be envisaged that a multiproxy approach including also other stable isotope proxies shows the potential of a multi-parameter climate reconstruction of summer temperature and precipitation. However, this needs to be proven by further studies from different tree species and locations at similar altitudes and climate zones.

5 | CONCLUSIONS

The strongest correlation of the annually resolved $\delta^2H_{methoxyl}$ series is that to JJ precipitation. The pentadally resolved $\delta^2H_{methoxyl}$ series do not provide any significant correlation to climate. However, this strong summer precipitation signal is probably related to the higher fraction of June and July precipitation taken up by the tree and used as source water for the formation of the lignin methoxyl groups. More rain during these months will increase the δ^2H values of the source water, due to the temperature-related higher δ^2H values in precipitation. Due to the highest tree growth being during MJJ the trees have to use this rainwater, and on average June and July are quite dry months. Therefore, we suggest that the $\delta^2H_{methoxyl}$ values of high elevation larch trees might serve as a summer precipitation proxy. The measured $\delta^2H_{methoxyl}$ and $\delta^{13}C_{methoxyl}$ values and the TRW[35] might be combined when aiming for multi-parameter reconstruction, which could also include isotope analyses from cellulose and whole wood. This would significantly strengthen the validity of such climate reconstructions.

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