Model evaluation for reconstructing the oxygen isotopic composition in precipitation from tree ring cellulose over the last century

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Abstract

The oxygen isotope composition of tree rings is controlled by many factors, including temperature, amount of precipitation, and changes in relative humidity. In this study we present a modified leaf-water model (from Dongmann et al. [Radiation and Environmental Biophysics 11 (1974) 41]) that can be used to calculate the isotopic composition of the source-water (and thus of precipitation) that a tree used during the growing season. The calibration of the model was accomplished by comparing a previously measured oxygen isotope tree ring chronology from Central Switzerland with the Swiss Network for Isotopes in the Hydrologic Cycle station at Bern from 1971 to 1995 and integrating temperature, relative humidity data, and ring-width. In particular, our efforts focused on understanding the significance of the dampening factor \( f \), which we relate to changes in humidity, and its variability over both the calibration period (1971 to 1995) and the study period (1913 to 1995). Our results indicate that \( f \) ranging between 0.27 to 0.49 is variable, based on correlation with relative humidity, average daily temperature and ring width index. Using this model, we have constructed a record of the oxygen isotope composition of precipitation during the growing season (May through September) for the last century in central western Europe. This approach can be potentially used in other locations where isotopic and meteorological data are available to extend records of the isotopic composition of precipitation back in time beyond observational records. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oxygen isotope composition; Precipitation; Tree ring cellulose

1. Introduction

The stable isotopic ratios of past and present precipitation are important indicators of global cli-
land and Antarctica, as well as from mountain glaciers and ice caps throughout the world’s alpine regions (Johnsen et al., 1992; Mayewski et al., 1996; Schotterer et al., 1997; Thompson et al., 1995, 1997). However important ice core records may be for the reconstruction of the isotopic hydrological cycle, they are not evenly distributed throughout the globe and are typically located in remote areas. Additional terrestrial archives, such as peat bogs, speleothems, lakes, and especially tree rings, have a potential to supplement ice core records in reconstructing isotope patterns of paleo-precipitation, and thus climate history. In particular, annually laminated lake sediments and tree ring records are ideally suited for high resolution due to their yearly resolution (McKenzie and Hollander, 1993; Saurer et al., 1997b).

The Global Network of Isotopes in Precipitation (GNIP), sponsored by the International Atomic Energy Agency and the World Meteorological Organization, has been actively recording the isotopic composition of monthly precipitation since 1961. Variability observed in this global data base has been attributed to many factors including air temperature, amount of precipitation, distance from source area, and elevation (Dansgaard, 1964; Rozanski et al., 1993). The GNIP records can be used to calibrate modern high-resolution terrestrial archives in order to reconstruct the isotopic composition of monthly precipitation since 1961. This information can be used to validate scenarios generated by atmospheric global circulation models (AGCM) equipped with water isotope diagnostics, leading to enhanced forward modeling. In order to improve our understanding of global paleoclimatic change, it is important to have methods that allow for investigations in all regions, permitting better correlation of significant events among different locations. Trees, having a global distribution ranging from the tropics to the subarctic, and especially in the temperate and boreal zones, are potentially an ideal medium to develop isotopic records equivalent to those from ice cores. In this study, we present a new approach for calculating the isotopic composition of precipitation utilized by trees during their growing season using a modified leaf-water model from Dongmann et al. (1974), based on Craig and Gordon’s (1965) evaporative enrichment model, which considers a variable dampening of the signal dependent on relative humidity. This variable dampening factor is a combination of effects within the tree as in the original model, but also includes a dampening due to soil water processes and/or moisture recycling. The application of the original model in previous studies measuring both leaf cellulose and tree ring cellulose has demonstrated that it overpredicts isotopic enrichment due to transpiration and/or other biochemical effects (Anderson et al., 1998; Flanagan, 1993; Flanagan et al., 1991; Saurer et al., 1997b). We propose that our approach, based on an empirical calibration incorporating both annual meteorological data (temperature and relative humidity) and $\delta^{18}O$ of precipitation from the station at Bern (1971–1995) can be used to correct this problem. This approach is then applied to an $\alpha$-cellulose record, derived from spruce trees located in central Switzerland (Anderson et al., 1998). With this record, the average oxygen isotopic composition of precipitation during the growing season (May–September) from 1913–1995 is reconstructed.

2. Oxygen isotopes in plants

In general, the focus of most terrestrial stable isotope research has been conducted on the $\alpha$-cellulose fraction of plant material. The cellulose composition of bulk plant material can range between 50% for woody plants to less than 15% for mosses and liverworts. The oxygen isotopic composition of tree ring cellulose has been related to climatic variables, such as temperature, relative humidity, and the amount of precipitation (Anderson et al., 1998; Burk and Stuiver, 1981; Lipp et al., 1996; Ramesh et al., 1986; Saurer et al., 1997b; Switsur et al., 1996). Presently, four important factors are considered to control the $\delta^{18}O$ signal contained in tree ring cellulose including: (1) the isotopic composition of the water utilized in cellulose production; (2) the biologic fractionation between cellulose and water (DeNiro and Epstein, 1979; Sternberg et al., 1986); (3) evaporative enrichment of leaf-water due to stomatal transpiration (Dongmann et al., 1974); and (4) isotopic exchange of oxygen atoms during the transfer of sucrose produced in the leaves to sites of cellulose production (DeNiro and Cooper, 1989; Farquhar et al., 1998; Sternberg et al., 1986).
Soil water represents an integrated signal of local precipitation. The residence time of the water in the soil produces a dampening of the seasonal variations observed in precipitation (Hesterberg and Siegenthaler, 1991; Buhay and Edwards, 1995), with the extent of the dampening increasing with increasing water residence time and mixing. The effect of this dampening can be minimized by carefully choosing the location of trees for isotope studies. Trees with shallow root systems that do not reach the groundwater will generally show a relatively small dampening of the seasonal $\delta^{18}O$ signal observed in precipitation. No isotopic fractionation of soil water occurs during either the uptake by the roots or the transfer to the leaves via the xylem (Förstel and Hützen, 1983; White et al., 1985). A large fractionation does occur, however, in the leaf of a plant due to transpiration. The original model of Dongmann et al. (1974), modified by Aucour et al. (1996), can be used to calculate the oxygen isotopic composition of leaf water and cellulose, as shown in Eqs. (1) and (2).

\[
\delta^{18}O_{\text{leaf water}} = (1 - f) [e_c + e_k (1 - h) + h \delta_{\text{atm}} + (1 - h) \delta_{\text{sw}}] + f \delta_{\text{sw}} 
\]

\[
\delta^{18}O_{\text{cellulose}} = \delta^{18}O_{\text{leaf water}} + e_{\text{biochem}}. 
\]

\( f \) is the fraction of leaf water not subject to evaporation (Allison et al., 1985) and accounts for the alteration of the isotopic composition of photosynthate due to exchange with stem water prior to cellulose formation, (Saurer et al., 1997b), \( e_c \) is the liquid–vapor equilibrium fractionation for water (Majoube, 1971), \( e_k \) is the water liquid–vapor kinetic fractionation, dependent on airflow dynamics at the leaf boundary layer (Buhay et al., 1996), \( h \) relative humidity, \( \delta_{\text{sw}} \) isotopic composition of source water, e.g., soil water originating from precipitation, \( \delta_{\text{atm}} \) isotopic composition of water vapor, \( e_{\text{biochem}} \) biologic fractionation factor [27 ± 3‰(DeNiro and Epstein, 1979, 1981; Sternberg, 1989)].

Combining Eqs. (1) and (2) gives a third relationship in terms of \( \delta^{18}O_{\text{cellulose}} \):

\[
\delta^{18}O_{\text{cellulose}} = (1 - f) [e_c + e_k (1 - h) + h \delta_{\text{atm}} + (1 - h) \delta_{\text{sw}}] + f \delta_{\text{sw}} + e_{\text{biochem}}. 
\]

Yakir et al. (1994) demonstrated in a laboratory study that leaf water is compartmentalized, and, therefore, not all of it may be subject to evaporation. The source of water used by the chloroplast for photosynthesis, and thus cellulose synthesis, is less enriched isotopically than water at the evaporating sites. Bulk leaf water is composed of an inhomogeneous mixture of three isotopically different waters including the evaporating surfaces, chloroplast, and the vein fractions (Yakir et al., 1994). Additionally, there is theoretical and experimental evidence that up to 45% of the leaf water’s isotopic signal transferred to the sucrose created in the chloroplasts is exchangeable with stem water prior to cellulose synthesis (DeNiro and Cooper, 1989; Farquhar et al., 1998; Sternberg et al., 1986). This exchange results in a reduction of the leaf water’s isotopic signal transferred to the cellulose.

Keeping the above points in mind, it is reasonable to use a dampening factor, as proposed by Saurer et al. (1997a), when trying to model the cellulose isotopic composition in plants. This dampening is represented by the \( f \) factor in Eq. (1), which reduces the overestimation of evaporation from the leaf water, the probable exchange with the stem water, and the dampening of the isotopic signal by groundwater homogenization. Allison et al. (1985) estimated \( f \) to be 0.2, that is 20% of the leaf water is not subject to evaporation. However, Saurer et al. (1997a) concluded that a dampening factor equivalent to \( f = 0.5 \) to 0.7 is appropriate based on a field study of four different tree species growing in different soil moisture conditions (Fagus sylvatica, Picea abies, Pinus sylvestris, and Fraxinus excelsior).

In order to back-calculate the oxygen isotopic composition of the source water used by the plant from the oxygen isotopic value of cellulose, it is necessary to solve Eq. (3) for the \( \delta_{\text{sw}} \) term. \( \delta_{\text{atm}} \) is assumed to be in equilibrium with the soil water, which is typically the case for the growing season in Europe (Förstel and Hützen, 1983). This assumption must be made because no direct measurements of \( \delta_{\text{atm}} \) are available (and are typically not available for most areas). Eq. (3) can be stated in terms of \( \delta_{\text{sw}} \) by including the equilibrium fractionation factor \( \alpha \):

\[
\alpha = (\delta_{\text{sw}} + 1000) / (\delta_{\text{atm}} + 1000). 
\]
Using Eq. (4), $\delta_{atm}$ can be expressed as:
\[
\delta_{atm} = \left[\left(\delta_{sw} + 1000\right)/\alpha\right] - 1000.
\]
Finally, by substituting Eq. (5) for $\delta_{atm}$ in Eq. (3), $\delta_{sw}$ is solved as follows:
\[
\delta_{sw} = \frac{\alpha (1 - f) \left(\varepsilon_{e} + \varepsilon_{k}(1 - h) + h \left(\frac{1000}{\alpha}\right) - 1000(h)\right) + \varepsilon_{biochem} - \delta^{18}O_{cellulose}}{(1 - f)\left[\alpha(h) - h - \alpha\right] - \alpha(f)}.
\]

With Eq. (6), it is possible to back-calculate the oxygen isotopic composition of the source water for a plant from the isotopic composition of cellulose synthesized during a designated period, such as the growing season, if relative humidity measurements and/or proxies of humidity are available.

As an approximation of Eq. (5), we can set $\delta_{atm} = \delta_{sw} - \varepsilon_{e}$. Then, Eq. (6) simplifies to:
\[
\delta_{sw} = \delta^{18}O_{cellulose} - (1 - f)(1 - h)(\varepsilon_{e} + \varepsilon_{k}) - \varepsilon_{biochem},
\]
which is similar to expressions proposed by Yapp and Epstein (1982) and Saurer et al. (1997b).

3. Setting and analytical methods

Eigentobel is situated on the Swiss plateau (47°10′47″N, 8°15′26″E), 600 m above sea level, with the Jura Mountains to the northwest and the Alps to the south (Fig. 1). Here we present only a brief description of the site setting and methodology; for a more complete explanation, please refer to Anderson et al. (1998). Spruce trees ($P. abies$) selected for this study are from a mixed stand of trees located at a semi-dry site on a southerly facing slope of 10–20°. The site is located near two Schweizerische Meteorologische Anstalt (SMA) weather stations, Buch–Suhr to the north (25 km) and a rain station named Beromuenster to the west (<5 km). Data combined from these stations provide a continuous record of climatic parameters (precipitation, relative humidity, temperature, etc.) over the last century. The study site receives over 1 m of precipitation annually on average, with 0.6 m occurring during the growing season, defined as May to September. Precipitation originating in the Atlantic...
Ocean is carried into the region by westerly to southwesterly winds or northwesterly winds (Fliri, 1984; Lamb, 1985). The GNIP station at Bern (60 km to the southwest of the site) is operated in association with the Swiss Network for Isotopes in the Hydrological Cycle (SNIHC) and has produced a monthly record of the oxygen isotopic composition of precipitation since 1971 (IAEA/WMO, 1998). Oxygen isotope ratios of precipitation from the Bern GNIP/SNIHC station, which is run by the Swiss National Hydrological and Geological Survey, were measured at the Stable Isotope Laboratory of the Physics Institute, University of Bern.

Four trees with similar growth histories were selected for this study. Previous carbon isotope investigations have shown that composite isotope chronologies from four trees generate a representative record (Leavitt and Long, 1984; Robertson et al., 1997; Saurer et al., 1995). Samples were cored using a 5 mm borer. Ring widths were measured on all cores, using the computer aided system at the Swiss Federal Institute of Forestry, Snow, and Land-

![Graph showing the raw data for δ¹⁸O values, mid-day relative humidity (RH), average daytime temperature, tree ring index (TRX), a relative index constructed from all trees, and the f values calculated using the other parameters in the graph (see text). All data are from Anderson et al. (1998).]
scape Research in Birmensdorf, and cross-dated (Fig. 2). Pooled annual whole wood samples were milled and processed to extract α-cellulose, following the Jayme and Wise method outlined by Green (1963).

For oxygen isotope analysis, $^{18}\text{O}/^{16}\text{O}$ ratios were measured on-line with CO gas produced by pyrolysis of annual tree ring cellulose samples in an elemental analyzer coupled to a stable isotope ratio mass spectrometer (EA-IRMS), following the method of Werner et al. (1996) and Saurer et al. (1998). Isotopic measurements are normalized to the VSMOW-VSLAP scale using internal cellulose standards, which have been measured off-line as CO$_2$ using the standard nickel pyrolysis method in operation at the University of Bern (Saurer et al., 1997b). Analytical reproducibility for $\delta^{18}$O values using the on-line method, based on 44 measurements of an internal cellulose standard at the ETH Stable Isotope Laboratory, is $\pm 0.32\%$ (1σ).

4. Approach

4.1. Calibration

In order to test whether it is possible to back-calculate the annual isotopic composition of water used by a tree, a well-defined record must be used, accompanied by the necessary climate data and oxygen isotopic data from precipitation. Our approach comprises three different objectives: (1) to evaluate the sensitivity of the $\delta^{18}$O$_{\text{cellulose}}$ in Eqs. (3) and (6) to changes in the dampening factor ($f$) and relative humidity ($h$); (2) to establish a relationship between $f$ and other parameters, including $h$, temperature, and tree-ring width index (Fig. 2); and (3) to apply the modified and calibrated model to the entire record from Eigentobel. Therefore, we used the record of Anderson et al. (1998) to test and calibrate the source-water model and its $f$ parameter (Eq. (6)) with the available climatic data (Table 1) and the Bern oxygen isotope data from 1971 to 1995, which is the calibration period. Anderson et al. (1998) have previously shown that the months of May through September have the highest correlation between the average monthly oxygen isotopic composition of the Bern station and the spruce isotopic record (Fig. 3), and thus are defined as the growing season. Saurer et al.’s (1997b) oxygen isotopic study of beech trees near Bern also had a similar relationship with the months of May to September, which is the typical growing season of trees in Switzerland growing at low elevations. By combining the calibrated source-water model and the existing data sets, it is the aim of this work to model the oxygen isotopic composition of precipitation over the last century in central Europe, or any geographic location where similar data would be available. This strategy requires an independent measurement or a proxy of relative humidity and temperature in order to be applied. For older paleo-studies it is possible that a pollen transfer function could be used to estimate climate parameters from nearby pollen chronologies.

### Table 1

<table>
<thead>
<tr>
<th>Year</th>
<th>$f$</th>
<th>Avg. temp.</th>
<th>Rel. humidity</th>
<th>TRX</th>
</tr>
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<tr>
<td>1995</td>
<td>0.44</td>
<td>16.1</td>
<td>0.59</td>
<td>0.934</td>
</tr>
<tr>
<td>1994</td>
<td>0.44</td>
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<td>0.60</td>
<td>1.478</td>
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<td>1993</td>
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<td>15.9</td>
<td>0.62</td>
<td>1.107</td>
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<td>17.0</td>
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<td>0.729</td>
</tr>
<tr>
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<td>16.2</td>
<td>0.56</td>
<td>0.901</td>
</tr>
<tr>
<td>1990</td>
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<td>16.3</td>
<td>0.56</td>
<td>1.163</td>
</tr>
<tr>
<td>1989</td>
<td>0.49</td>
<td>16.2</td>
<td>0.55</td>
<td>1.359</td>
</tr>
<tr>
<td>1988</td>
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<td>16.2</td>
<td>0.60</td>
<td>1.133</td>
</tr>
<tr>
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<td>15.6</td>
<td>0.60</td>
<td>0.911</td>
</tr>
<tr>
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<td>16.1</td>
<td>0.57</td>
<td>0.861</td>
</tr>
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<td>16.0</td>
<td>0.58</td>
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<td>17.3</td>
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<tr>
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<td>0.57</td>
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</tr>
<tr>
<td>1971</td>
<td>0.43</td>
<td>15.7</td>
<td>0.55</td>
<td>1.049</td>
</tr>
</tbody>
</table>

*Midday relative humidity.*
and $e_s$ for the models, come from the SMA weather station at Buchs–Suhr (Table 1). Both $\alpha$ and $e_s$ are calculated using the temperature-dependent relationship of the liquid–vapor fractionation for $H_2O$ after Majoube (1971). This gives values of $e_s$ ranging from 9.97% to 10.33% in our set-up, which is based on changes in average air temperature during the growing season for our study area, ranging between 14°C and 18°C (with an average of 15.8°C from 1913 to 1995). All climate parameters used in the models are averaged daytime values collected during the growing season of May to September. For temperature, two values are used, average daily and average monthly maximum. Relative humidity ($h$) is measured as a daytime average and at mid-day (13:00 h). $e_b$ is dependent on leaf morphology and leaf boundary-layer vapor transport conditions (Buhay et al., 1996). Spruce trees have fine needles and the boundary layer conditions are nearly stagnant (molecular); thus, it can be assumed that $e_b = 28\%$ (Allison et al., 1985; Buhay et al., 1996). The source water ($\delta_{sw}$) is defined as soil water used by the tree. We used the monthly filtered-data set of the Bern station from Anderson et al. (1998), which was weighted for the precipitation used by the trees from our study area (Saurer et al., 1997b). The relationship between the raw Egentobel $\delta^{18}O$ cellulose data and the $\delta^{18}O$ value of precipitation during the calibration period has been calculated with $r = 0.64$ and a slope of 0.34‰/$\%e$ (Fig. 3). This relationship serves as a baseline to compare other modeled results. During the calibration years of the Bern station, $\delta_{sw}$ is calculated from $\delta_{sv}$ assuming equilibrium conditions using Majoube’s (1971) liquid–vapor fractionation for $^{18}O$ in water. The biologic fractionation factor, $\varepsilon$, has been previously determined to be $27\%e \pm 3\%e$, which is true for a variety of plants (DeNiro and Epstein, 1979, 1981; Sternberg, 1989). We adopted a value of exactly $27\%e$ for calculation purposes (although another biogeochemical fractionation factor could be selected within the accepted range for plants).

5. Results

5.1. Testing the models

Using average climate parameters from the calibration period (1971 to 1995) as fixed values (Table 1) and keeping $\delta_{sw}$, $e_s$, $e_b$, and $\delta_{sw}$ constant, we tested the sensitivity of $\delta^{18}O$ cellulose to changes in the dampening factor ($f$) and relative humidity ($h$) in both the leaf-water–cellulose model (Eq. (3)), and the source-water model (Eq. (6)). Fig. 4a shows the $\delta^{18}O$ value of cellulose relative to $f$ for the leaf-water–cellulose model, based on average daytime relative humidity of 74% and average mid-day relative humidity of 57%. The $f$ values have a negative correlation with both humidity parameters (Fig. 4a).
Fig. 4. Plots showing the relationships of the modeled cellulose $\delta^{18}O$ values with the cellulose model $f$ and relative humidity (RH) values, Eq. (3), using averaged climate parameters from the calibration period (1971–1995) for $f$ and RH. In (a), two relationships are plotted from the leaf-water-cellulose model, based on average daily relative humidity at 74% and average mid-day relative humidity at 57% for the calculated $\delta^{18}O$ value of cellulose relative to $f$. In (b), the $\delta^{18}O$ values of cellulose vs. relative humidity are plotted as a function of three $f$ values fixed at 0.2, 0.4, and 0.6.

The slopes in Fig. 4a are negative because less of the isotopic leaf enrichment is transferred to the cellulose with increasing $f$. The average $\delta^{18}O$ value for tree ring cellulose during this period is 28.9‰, which intersects at $f = 0$ for the average daytime relative humidity and $f = 0.38$ for average mid-day relative humidity. If a different biochemical fractionation factor ($\epsilon_{\text{biochem.}}$) were selected, the $f$ value would also reflect this change too. For example if $\epsilon_{\text{biochem.}} = 28\%e$, then the average tree ring cellulose $\delta^{18}O$ value of 28.9‰ would intersect at $f = 0.1$ and $\delta^{18}O$ value increases. The slope of the mid-day relative humidity relationship between $f$ and $\delta^{18}O_{\text{cellulose}}$ is $-0.16\%/\%$, almost twice the average daily humidity relationship with a slope of $-0.10\%/\%$.

In Fig. 4b, the $\delta^{18}O$ value of cellulose vs. relative humidity is plotted as a function of three $f$ values fixed at 0.6, 0.4, and 0.2. The relationship between the modeled cellulose $\delta^{18}O$ values and changing relative humidity is also negative, as would be expected with increased evaporative isotopic enrichment (Fig. 4b). In an extreme case, if $f$ is equal to zero in Eq. (3), i.e. all leaf water would be subject to evaporation and/or no dampening, a slope of $0.38\%/\%$ would be expected, whereas $f$ values of 0.2, 0.4, and 0.6 give slopes of $-0.31\%/\%$, $-0.23\%/\%$, and $-0.15\%/\%$, respectively. These fixed $f$ values also intersect with the average cellulose $\delta^{18}O$ of the Eigentobel trees at different relative humidity values of 68%, 58%, and 37%, respectively. Thus, as the $f$ value decreases, the calculated $\delta^{18}O$ value of cellulose for a given humidity increases. Decreasing the dampening results in an increase in the isotopic enrichment of the calculated cellulose values.

The source-water model of Eq. (6) is used to investigate the relationship between modeled source water and a changing $f$, where the results are plotted in Fig. 5. Here, the average cellulose value from the study period is used to perform the calculation. The relationship between modeled source water and the $f$ factor yields positive slopes for the two different relative humidities from the calibration period, $m = 0.10\%/\%$ for average daily relative humidity (74%) and $m = 0.16\%/\%$ for average mid-day relative humidity.
humidity (57%). The plots shown in Fig. 5 are basically the inverse of Fig. 4a because the source water value is now being calculated instead of using the cellulose value produced from a specific source water. The average δ18O composition of precipitation during the growing season is −8.14‰, and this number corresponds to \( f \) factors of 0 and 0.38 for relative humidity values of average daily and average mid-day, respectively. Thus, as relative humidity changes, \( f \) changes as shown in Fig. 4a. Yet, in Fig. 5, when \( f \) is increased, the isotopic composition of the calculated cellulose also increases, but a decrease in relative humidity causes an increase of the slope between source water and \( f \). Along the lines of these tests, in which \( f \) was determined to be sensitive to changes in relative humidity, we correlated predicted \( f \) values from the source water model with humidity (see below).

5.2. Source water model during the calibration period

We tested the ability of the source water model to reproduce the oxygen isotopic composition of precipitation from the Bern GNIP/SNIHC station during the calibration period. These tests were separated into three different modeling scenarios, all based on the calibration of \( f \) with different climatic parameters (Fig. 6). Humidity and δ18O values in tree ring cellulose have an inverse correlation (Anderson et al., 1998; Burk and Stuiver, 1981; Ramesh et al., 1986; Saurer et al., 1997a, 1997b). Previous work by Anderson et al. (1998) indicates that the Eigentobel spruce trees’ δ18O cellulose record has a higher inverse-correlation with relative humidity from mid-day, rather than the average daily humidity. In the study by Anderson et al. (1998), this relationship was determined by linear regression with all climatic parameters and the isotopic data from the spruce trees.

In the first scenario, \( f \) is fixed at 0.4, or 60% dampened, which was chosen because it generated the most reasonable values compared to the δ18O precipitation data from Bern (Fig. 6a). Yet, this relationship has a correlation of \( r = 0.48 \) (> 95% confidence level) between the modeled data and the precipitation station. This relationship is worse than the original data’s regression with the station of \( r = 0.64 \) (Fig. 3). In general, the first-order trend of the modeled data does fit the station’s data, but differences between the two are usually > 1‰.

In order to test whether the \( f \) is related to any of the parameters (climate and tree ring index) during the calibration period, we solved the source water model for \( f \), by inputting the δ18O data from Bern for the \( \delta_{\text{sw}} \) term (Table 1). Solving for \( f \) in this manner allows the model to produce a perfect 1:1 correlation with the station’s data on an annual basis. The calculated \( f \) values range from 0.49 to 0.27, with an average of about 0.40. These 1:1 \( f \) values were then correlated with two different subsets of the parameters (Table 2), which showed significant relationships: (1) a linear regression relationship with mid-day relative humidity (\( r = 0.50 \)) and (2) a multiple regression relationship with mid-day relative humidity, average temperature, and the tree-ring width index (\( r = 0.71 \)). A plot of \( f \) is shown in Fig. 2 for the entire record (1913 to 1995), which was calculated using the above multi-regression relationship. These new relationships for \( f \) were then incorporated into the source water model (Fig. 6b and c). The model coupling \( f \) with humidity yields a better
Fig. 6. A comparison of three different models with the Bern GNIP/SNIHC precipitation data: (a) fixed $f$ at 0.40, $r = 0.48$, (b) $f$ coupled with mid-day relative humidity via linear regression, $r = 0.66$, (c) multi-regression $f$ using average temperature, mid-day relative humidity, and tree-ring width index, $r = 0.78$ (see Table 2).
Table 2
Linear regression and multi-regression relationships with $f$ between relative humidity (RH) and average temperature, and the tree-ring width index (TRX)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$r$</th>
<th>Confidence level (%)</th>
<th>Equation for $f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-day RH</td>
<td>0.50</td>
<td>99</td>
<td>$-1.18$ (RH) + 1.06</td>
</tr>
<tr>
<td>Mid-day RH, avg. temp., TRX</td>
<td>0.71</td>
<td>&gt; 99</td>
<td>$-1.47$ (RH) + 0.03 (temp.) + 0.11 (TRX) + 0.62</td>
</tr>
</tbody>
</table>

The model giving the highest correlation coefficient was used to calculate the source water from the entire Eigentobel $\delta^{18}O$ cellulose record, which represents precipitation utilized by the trees during the growing season from 1913 to 1995 (Fig. 7). The modeled precipitation record’s first-order trend has two main enrichment-depletion cycles. The first cycle occurs between 1913 and 1931 with a total shift of over 3‰. This interval is followed by the second enrichment–depletion cycle from 1931 to 1995, obtaining a maximum of $-4.5‰$ in 1947, after which the data show a general depletion trend. Three second-order enrichment–depletion cycles are superimposed on the second first-order trend. The most significant of these cycles occurs from 1936 to 1954, with a total shift magnitude of 5‰. The other two cycles occur from 1954 to 1982 and 1982 to 1995, with both having total isotopic shifts of about 3‰.

6. Discussion

6.1. Model—approach, testing, and calibration

The data presented here show that, using a source-water model modified from the original Dongmann et al.’s (1974) leaf-water model com-

![Graph](image-url)
bined with a calibrated $f$ factor, it is possible to reconstruct the isotopic composition of the precipitation used by a tree. The tests of the model using the average climate parameters (Figs. 4 and 5) indicate that the $^{18}$O composition of plant cellulose is very sensitive to changes in $f$ and relative humidity conditions. Of course, the sensitivity to relative humidity is well known because it is the main control on isotopic evaporative enrichment in plants (see Section 2). Yet, the combined relationship between $f$ and relative humidity is important when calculating the isotopic composition of source water and/or the isotopic composition of cellulose. As would be expected, when $f$ increases, the sensitivity of the calculated $\delta^{18}$O cellulose values to changes in relative humidity decreases (Fig. 4b). One might ask, why should $f$ be variable? The $f$ value in itself is a bit of an unknown quantity and has been thought previously to correct for the overestimation of evaporative enrichment in the leaf water model (Buhay et al., 1996; Saurer et al., 1997a). Following the approach of Allison et al. (1985) and Aucour et al. (1996), the $f$ factor accounts for the inhomogeneous nature of leaf-water, where not all water is subject to evaporation. This view is supported by Yakir et al.’s (1994) experimental results indicating that leaf water is “compartmentalized” and that photosynthetic water is not directly subject to evaporation. Saurer et al. (1997a) proposes a combined approach to the $f$ factor (considered as a dampening factor), where it accounts for both the reduction of the overestimation of leaf water-evaporative enrichment and the probable isotopic exchange between metabolites and stem water, prior to cellulose formation (DeNiro and Cooper, 1989; Farquhar et al., 1998; Sternberg et al., 1986).

Our data indicate that, for the Eigentobel spruce trees, the $f$ is different depending on relative humidity conditions (see Fig. 4a). When relative humidity is high (using the daily average value of 74%), $f$ must be equal to zero in order to calculate correctly the average $\delta^{18}$O value of the cellulose from our trees. When relative humidity is low (57% using the mid-day relative humidity), $f$ must be equal to 0.38 to predict correctly the average Eigentobel cellulose $^{18}$O composition (Fig. 4a). The response would be similar if another $e_{\text{biochem.}}$ were to be selected other than 27‰, and the absolute values would be shifted accordingly. Therefore, when relative humidity is above 74%, the model will not correctly predict the mean value of the tree ring cellulose over the calibration period. Yet, the model’s values predicted from a relative humidity > 74% would fall within the range of our measured values. The $f$ value is defined as a factor (variable) that can only range between 0 and 1, and this range of values does work with our calibration data, but not necessarily with all scenarios. A similar relationship is observed between the source-water $\delta^{18}$O values and $f$ in Fig. 5, where the high and low relative humidity values give slopes of 0.10‰/% and 0.16‰/%, respectively. These two examples indicate that $f$ is variable for our study area and dependent on humidity conditions. Potentially, this relationship will also hold true at other locations in different geographic areas.

At low relative humidity, the transpiration rate is relatively high when plants are not water-limited, and this can influence $f$, as explained by leaf water inhomogeneity (Yakir et al., 1994) and the advection–diffusion approach of Farquhar and Lloyd (1993). According to these models, high transpiration rates tend to reduce the enrichment because the leaf is flushed with unenriched soil water and thus does not allow the build-up of the full enrichment due to transpiration. This explanation is also supported by the experimental findings of Flanagan et al. (1991). Additionally, this concept of higher transpiration rates, occurring during periods of low relative humidity and resulting in a decrease in the isotopic enrichment, matches our model results. When humidity is low (57%), we find that a higher $f = 0.38$ is required, as compared to $f = 0$ applied for a relative humidity of 74% (to correctly model our data). Thus, one reason for the dependence of $f$ on relative humidity could be the influence of changes in transpiration rate.

Anderson et al. (1998) indicated that the Eigentobel spruce trees were more sensitive to changes in mid-day relative humidity than the average daily value. Our testing of the model in this study supports this previous conclusion. Additionally, the predicted $f$ value of 0.38, calculated from the cellulose model using the mid-day relative humidity of the correlation period (57%), can be potentially explained by a decrease in stomatal conductance (Eq. (3) and Fig. 4a). It is known that when trees are under water-
limited conditions, a decrease in mid-day transpiration rates occurs caused by partial stomatal closures (Larcher, 1995). This decrease in mid-day transpiration rates has previously been observed in spruce trees from Switzerland (Häsler et al., 1991; Herzog et al., 1998). A decrease in stomatal conductance, leading to a decrease in the amount of leaf water which would be evaporated, would also support the results of the cellulose model shown in Fig. 4a. During mid-day, when relative humidity is lower than the daily average, trees respond by partial stomatal closure to conserve water. Flanagan et al. (1991) indicate that it would also be possible to explain the over-prediction of the isotopic enrichment from the leaf-water, due to a “patchy pattern of stomatal closure” across a leaf. They propose that water in cells near open stomata would be more isotopically enriched than in those located near closed stomata, when some of leaves’ stomata close in response to low humidity conditions. Changes in the extent of stomatal closure would explain why the model predicts a $f$ of 0.38, indicating 38% of the leaf water (at a relative humidity of 57%) is not subject to evaporative isotopic enrichment.

Under changing environmental conditions, such as changes in relative humidity and available moisture, a plant will react with a change in physiological processes, resulting in a variable $f$ (dependent on the plant’s response). Both of the above explanations are plausible. Although the mechanisms are different, both result in the same isotopic response. In general, $f$ is responding to changes in humidity, which is the major control on the evaporative enrichment in leaf-water. More experimental and calibration work will be required to give further insight into the physiological mechanisms that are controlling these processes with both laboratory and field based studies. For example, a field-based study combining the measurement of transpiration rates (accompanied by all the necessary meteorological data) and isotopic measurements of soil water, leaf-water, stem water, newly formed twigs, and $\delta_{18}O$ over the entire growing season at water stressed and non-stressed sites would help to better understand what is controlling $f$.

Another potential factor accounting for apparent changes in $f$ and/or the overall dampening between the tree record and the Bern isotope data is any change in local hydrology. The study by Buhay and Edwards (1995) shows how important a hydrologic setting is on a tree ring record. They investigated trees located in both groundwater discharge and recharge zones. Tree located near recharge zone will be more hydrologically influenced by precipitation falling during the growing season (Buhay and Edwards, 1995). In contrast, trees growing near discharge zones utilized more homogenized groundwater, which consists of precipitation falling on an annual basis, dependent on flow velocities. When a tree utilizes ground water instead of soil water, the growing season’s signal will be muted by the addition of more negative winter and fall precipitation. Even late season snow events or residual infiltration can cause a dampening in the isotopic signal of soil water the trees use. The study of soil water at a site near Bern by Hesterberg and Siegenthaler (1991) indicated that the seasonal isotopic signal was strongly dampened. Canopy interception and re-evaporation would also affect any tree ring record.

However, the correlation between the Eigentobel spruce trees and the Bern station (Fig. 3) suggests that the trees are using precipitation during the growing season (Anderson et al., 1998) and that the dampening in the soil water may be relatively minor, but nevertheless important. Additionally, spruce trees have shallow root systems, which supports the assumption that the trees have access to soil water and not homogenized groundwater. Saurer et al. (1997b) also observed a similar relationship between beech trees growing near Bern and the Bern station. In fact, Anderson et al. (1998) have previously shown that their spruce data have a correlation of $r = 0.71$ with Saurer et al.’s (1997b) yearly beech record between 1971 to 1992. Both of these records are sensitive to the growing season’s precipitation.

The results of the source-water model shown in Fig. 6 indicate the effects that the three different approaches of determining $f$ can have on the correlation with the oxygen-isotope precipitation data from Bern. The $f$ values calculated using the Bern $\delta^{18}O$ precipitation values in Table 1 also indicate that this parameter is variable at our study area over time. The version of the source-water model with a fixed $f$ at 0.4 has the poorest correlation with the isotopic composition of precipitation, with an $r = 0.48$ (Fig. 6a). The version of the model, where $f$ is coupled to changes in relative humidity (Table 2), shows a good
correlation with the Bern data \((r = 0.66)\) over the calibration period. However, this correlation is the same as that achieved with the raw cellulose data (non-modeled) compared with the precipitation station (Figs. 3 and 6b), and thus does not improve the true relationship between calibration data and modeled data. The multiple regression model of \(f\), based on average temperature, mid-day relative humidity, and tree-ring width index, incorporated into the source-water model yielded the best relationship \((r = 0.78)\) with the calibration data. The addition of the tree-ring width index and temperature within the multiple regression of the \(f\) equation (Table 2) helped to improve the correlation over the calibration period significantly compared to using only the humidity relationship. The addition of temperature probably helps modulate the \(e_w\) factor by affecting the leaves’ heat transfer, which Buhay et al. (1996) have indicated is an important component, but estimates of leaf temperatures are next to impossible to determine for the past archives. The boundary layer near the stomata is controlled by airflow over a leaf. This airflow is in turn controlled by external forces such as wind and by differences in density of air between the leaf (and leaf-water) and the air near its surface due to changes in the heat transfer flux (Buhay et al., 1996). Hence, our model does not take into account the actual leaf temperature. The tree-ring width index provides a general indicator of plant dry matter and health, but previous correlation of the width index with climate parameters yielded no significant relationships (Anderson et al., 1998). When more data sets are available from other investigations, it will be more feasible to better assess the relationship between tree-ring width index and \(f\).

6.2. Interpretation of record

The modeled \(\delta^{18}O\) values of precipitation for the study period document the changes in the average oxygen isotopic composition for the growing season (May to September) over the last century, from 1913 to 1995 (Fig. 7). Analysis of regional Swiss climatic data reveals that minimum temperatures have increased 2°C since the beginning of the century, outpacing the global warming trend of 0.5°C (Beniston et al., 1994). Our model results indicate that \(\delta^{18}O\) composition of precipitation is not necessarily following this trend. Typically, the \(^{18}O/^{16}O\) ratios of precipitation correlate positively with temperature and negatively with precipitation amount. For example, the relationship between the \(\delta^{18}O\) of precipitation at the Bern GNIP/SNIHC station (during the calibration period) with air temperature and amount of precipitation is 0.50‰/°C \((r = 0.67)\) and −0.15‰/cm \((r = -0.42)\), respectively, based on 12 monthly averages representing each year. A similar relationship of 0.52‰/°C \((r = 0.68)\) is also observed for temperatures averaged over the growing season (May–September). The strongest enrichment–depletion trend in the modeled data occurs between 1936 and 1954, corresponding with the sustained increase in minimum temperatures throughout Switzerland of 1–2°C (Beniston et al., 1994). The correlation of the modeled \(\delta^{18}O\) of precipitation data with the climate station’s average temperature during May to September for the entire record (1913 to 1995) is 0.79‰/°C \((r = 0.56)\), and, between the years of the calibration period (1971 to 1995), relationship is 0.42‰/°C \((r = 0.45)\). These different relationships for the different periods imply that factors other than varying temperature or amount are influencing the values of regional precipitation. Additionally, atmospheric circulation patterns have changed over the last century in Europe. The seasonality of maximum frequency of zonal circulation (westerly air flow) has changed; between 1881 and 1950, the maximum frequency occurred in August, while in the 1980s the maximum shifted to December and January (Bárdossy and Caspary, 1990). This change in airflow regime over the continent can potentially account for the changes after 1950 in our modeled isotope record, by changing the dominant source area of precipitation for central Switzerland. These differences between the entire record and the calibration period potentially indicate that the relationship between \(\delta^{18}O\) of precipitation and temperature has changed through time. Additionally, a change in the relationship between the isotopic composition of precipitation and Swiss average air temperatures could be explained by changes in rainfall patterns over time (Schotterer, oral communication). Our data indicate that, from 1951 to 1995, the relationship of the Eigentobel modeled data with the average temperature of the growing season (May through September) is 0.56‰/°C \((r = 0.40)\), and, from 1913
to 1950, the relationship is $1.22\%e/°C$ ($r = 0.72$). This change in the relationship will need to be confirmed by other studies and proxies of the isotopic composition of precipitation. The oldest GNIP records from Groningen and Vienna date back only to 1961. With our modeled approach, these isotope records could be extended further back in time using this tree ring cellulose proxy. As more tree ring cellulose records are analyzed, the changes recognized in our data may be further verified or refined, leading to a better understanding of the relationship between $δ^{18}O$ of precipitation and temperature for a specific region.

7. Conclusions

Cellulose from annual tree rings provides a high-resolution proxy record from which to reconstruct the isotopic composition of precipitation. Clearly, our reconstruction supports the use of this method to calibrate $f$ with the proper climate and isotope data, which can be applied at other locations to test the spatial variability of the changes observed in our record. The variable $f$ factor in the modified Dongmann model accounts for the suppression of Craig-type evaporative enrichment response in tree ring cellulose (though it goes beyond the original intention by integrating all “upstream” dampening rather than only physiological effects within a tree). These results indicate that the trees studied are responding to changes in environmental variables in a dynamic mode, and not fixed relationships. We find that $f$ is not a constant parameter, but it is inversely related to relative humidity. This relationship could be caused by high transpiration rates reducing leaf-water enrichment, which is in agreement with a recent advection–diffusion model or partial stomatal closures induced by changes in humidity and/or soil moisture conditions. Additionally, changes in many parameters including: $δ_{am}$, soil water mixing, sample pooling, and/or various other factors, will of course affect the Eigentobel cellulose record too. It is difficult to completely estimate the factors affecting our record (and many paleo-records) at a specific time, and, for this reason, we rely on the justification of our approach with reference to the successful application of the model using data from the calibration period. Models must take into account changing conditions affecting a specific proxy, such as our variable $f$ factor.

Data, such as those presented here, can provide the baseline from which to compare other data sets, in order to understand the atmospheric controls on the oxygen isotopic composition of precipitation in the hydrologic cycle. The oxygen isotopic composition of precipitation is an important hydrologic parameter. Using the modeled approach presented here, estimation of the oxygen isotopic composition of tree ring cellulose can be extended further into the past to evaluate changes in the isotopic composition of paleo-precipitation throughout the Holocene. Our data indicate that the relationship between $δ^{18}O$ of precipitation and air temperature has changed over the last century in Switzerland. These changes might be linked to major modes of climate variability related to large-scale atmospheric teleconnection patterns such as NAO, ENSO, etc., which can affect storm tracks, precipitation patterns, and seasonality.

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