Biogeosciences Discuss., 12, 2459–2489, 2015
www.biogeosciences-discuss.net/12/2459/2015/
doi:10.5194/bgd-12-2459-2015

Biogeosciences
Discussions
Open Access

Coupled isotopes of plant wax and hemicellulose markers record information on relative humidity and isotopic composition of precipitation

M. Tuthorn[1], R. Zech[2], M. Ruppenthal[3], Y. Oelmann[3], A. Kahmen[4], H. F. del Valle[5], T. Eglinton[2], and M. Zech[1,6]

[1]Department of Soil Physics and Chair of Geomorphology, University of Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany
[2]Geological Institute, ETH Zurich, Sonneggstrasse 5, 8092 Zurich, Switzerland
[3]Geoecology, University of Tübingen, Rümelinstr. 19–23, 72070 Tübingen, Germany
[4]Departement of Environmental Sciences – Botany, University of Basel, Schönbeinstrasse 6, 4056 Basel, Switzerland
[5]Ecología Terrestre, Centro Nacional Patagónico (CENPAT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Boulevard Brown 2825, U9120ACF Puerto Madryn, Argentina
[6]Institute of Agronomy and Nutritional Sciences, Soil Biogeochemistry, Martin-Luther University Halle-Wittenberg, von-Seckendorff-Platz 3, 06120 Halle, Germany

Received: 28 October 2014 – Accepted: 4 December 2014 – Published: 4 February 2015

Correspondence to: M. Zech (michael_zech@gmx.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The δ^2H isotopic composition of leaf waxes is used increasingly for paleohydrological and -climate reconstructions. However, it is challenging to disentangle past changes in the isotopic composition of precipitation and changes in evapotranspirative enrichment of leaf water. We analyzed δ^2H on *n*-alkanes and fatty acids in topsoils along a climate transect in Argentina, for which we had previously measured δ^{18}O on plant-derived sugars. Our results indicate that leaf wax biomarker δ^2H values ($\delta^2\mathrm{H}_\mathrm{lipids}$) primarily reflect $\delta^2\mathrm{H}_\mathrm{source\ water}$ (precipitation), but are modulated by evapotranspirative enrichment. A mechanistic model is able to produce the main trends in $\delta^2\mathrm{H}_\mathrm{lipids}$ along the transect, but seems to slightly underestimate evapotranspirative enrichment in arid regions and overestimate it in grass-dominated ecosystems. Furthermore, the (i) coupling of the $\delta^2\mathrm{H}_\mathrm{lipid}$ and $\delta^{18}\mathrm{O}_\mathrm{sugar}$ biomarker results and (ii) application of biosynthetic fractionation factors allows calculating the δ^2H-δ^{18}O isotopic composition of leaf water along the transect. This also yields the deuterium excess (*d* excess) of leaf water, which mainly reflects evapotranspirative enrichment, and can be used to model relative air humidity (RH). The high correlation of modeled (reconstructed based on biomarker results) and measured RH, as well as the good agreement between modeled and actual δ^2H and δ^{18}O of precipitation along the transect lends support to the coupled $\delta^2\mathrm{H}_\mathrm{lipid}$ and $\delta^{18}\mathrm{O}_\mathrm{sugar}$ biomarker approach for future paleoclimate research.

1 Introduction

Long chain *n*-alkanes and fatty acids are important components of the epicuticular leaf waxes of terrestrial plants (Eglinton, 1967). As leaf waxes can be preserved in sedimentary archives over a long time (Radke et al., 2005; Samuels et al., 2008), they can serve as valuable biomarkers for paleo-environmental and -climate reconstructions (Eglinton and Eglinton, 2008; Zech et al., 2011). The δ^2H isotopic composition of leaf waxes is of particular interest in this regard, because, at least to a first order, it reflects the isotopic composition of precipitation (Sauer et al., 2001; Sachse et al., 2004; Rao et al., 2009), which in turn depends on temperature, humidity, atmospheric circulation, etc. (Gat, 1996; Araguas-Araguas et al., 2000). While there is probably no fractionation of hydrogen isotopes during water uptake by the roots (Ehleringer and Dawson, 1992), several studies have shown that leaf water is enriched in ^{2}H compared to the source water or precipitation (Flanagan et al., 1991; Yakir, 1992; Sachse et al., 2006; Smith and Freeman, 2006; Farquhar et al., 2007; Feakins and Sessions, 2010). This ^{2}H enrichment, which is also recorded in the leaf waxes, can be explained by evapotranspiration and is mainly controlled by relative air humidity (RH), temperature and the isotopic composition of atmospheric water vapor. Potential variations in the degree of evapotranspirative enrichment in the past can make it challenging to reconstruct the isotopic composition of paleoprecipitation from δ^2H biomarker records alone.

Compound-specific δ^2H of lipid biomarkers, especially *n*-alkanes due to their good preservation, are already widely applied in paleoclimate and -hydrological research (Sauer et al., 2001; Schefuss et al., 2005; Pagani et al., 2006; Tierney et al., 2008; Zech et al., 2013). Comparison of $\delta^2\mathrm{H}_{n\text{-alkanes}}$ with $\delta^2\mathrm{H}_{\text{fatty acids}}$ in such research is hardly done so far but may provide additional merits of using fatty acids as an alternative to *n*-alkanes. Similarly, compound-specific δ^{18}O analyses of sugars remain in their infancy, yet hold significant promise (Hener et al., 1998; Juchelka et al., 1998; Werner, 2003; Jung et al., 2005, 2007; Greule et al., 2008; Zech and Glaser, 2009; Zech et al., 2012). Similar to leaf waxes, hemicellulose-derived sugars record the isotopic composition of water used for metabolism, i.e. the isotopic composition of precipitation altered by evapotranspirative ^{18}O enrichment of soil and leaf water (Zech et al., 2013b). Hemicellulose residues can persist in soils (Zech et al., 2012). Given the evaporative ^{2}H and ^{18}O enrichment of leaf water being recorded in both, n-alkanes and hemicellulose-derived sugars the combined plant wax δ^2H and hemicellulose sugar δ^{18}O analyses offer the potential of reconstructing the deuterium excess of leaf water. The *d* excess quantifies the isotopic deviation of water from the Global Meteoric Water Line (GMWL) and may serve as valuable proxy for evapotranspirative enrichment and RH. Furthermore, if leaf water values are defined in a δ^2H-δ^{18}O diagram, sugar and n-alkane isotopic information may enable reconstruction of the isotopic composition of precipitation in paleohydrological studies (Zech et al., 2013a).

This study describes the application of a combined δ^2H and δ^{18}O biomarker approach to modern topsoils sampled along a climate transect in Argentina. The aims of this investigation are to

i. compare the δ^2H values of *n*-alkanes with those of fatty acids, modeled *n*-alkane δ^2H values and δ^{18}O values of sugars and evaluate the dominant climate factors influencing these values,

ii. reconstruct *d* excess using δ^2H values of *n*-alkanes and δ^{18}O values of sugars and assess the potential of reconstructed *d* excess of leaf water as paleoclimate proxy for RH, and

iii. evaluate the potential of the combined δ^{18}O and δ^2H biomarker approach to reconstruct the isotopic composition of precipitation.

2 Material and methods

2.1 Transect description and samples

The investigated transect in Argentina spans from ~ 32 to 47° S, and encompasses 20 sampling localities spanning a large climate and altitudinal (22–964 m) gradient (Fig. 1). Mean annual temperature ranges from 11.4 to 18.0 °C and mean annual precipitation from 185 to 1100 mm. Precipitation shows a systematic southward trend towards more negative δ^{18}O and δ^2H values ($\delta^{18}O_{prec}$ and δ^2H_{prec}, respectively) (Bowen, 2012; GeoINTA, 2012).

The transect is described in detail by Tuthorn et al. (2014). Briefly, it is characterized by warm humid subtropical conditions in the north (Zárate, Buenos Aires Province), pronounced arid conditions in the middle part of the transect and cool temperate conditions in the south (Las Heras, Santa Cruz Province). These markedly contrasting climate conditions are reflected in the vegetation zones of the study area, changing from Humid/Dry Pampa in the north to the Espinal vegetation zone that prevails under semi-arid climate (Burgos and Vidal, 1951), Low Monte semidesert/desert in the most arid region of Argentina (Fernández and Busso, 1997), and Patagonian Steppe in the southernmost part of the transect (Le Houérou, 1996; Paruelo et al., 1998).

During a field campaign in March and April 2010, mixed topsoil samples (A_h-horizons) from maximum 51 cm depth were collected in triplicate replication from the 20 sample sites along the transect. The soil samples were air-dried in the field and later in an oven at 50 °C. While sampling site heterogeneity was checked for the $\delta^{18}O_{sugar}$ analyses (Tuthorn et al., 2014), the field replications were merged to one composite sample per study site for δ^2H_{lipid} analyses.

2.2 Compound-specific δ^2H analyses of *n*-alkanes and fatty acids

For δ^2H analyses of *n*-alkane and fatty acid biomarkers, an Accelerated Solvent Extractor (Dionex ASE 200) was used to extract free lipids from the dried soil samples with dichloromethane (DCM) and methanol (MeOH; 9 : 1) according to Zech et al. (2013). The total lipid extracts were separated over pipette columns filled with ~ 2 g aminopropyl. *n*-Alkanes were eluted with hexane, more polar lipids with DCM : MeOH (1 : 1), and free fatty acids with diethyl ether:acetic acid (19 : 1). The *n*-alkanes were further purified using zeolite (Geokleen) pipette columns. The zeolite was dried and dissolved in HF after eluting branched- and cyclo-alkyl compounds with hexane, and the straight-chain (*n*-alkyl) compounds were then recovered by liquid–liquid extraction with hexane. For samples 1–12, an additional purification step with silver nitrate columns was carried out in order to eliminate unsaturated compounds. The chromatograms of the other sampled displayed no requirement for this purification step.

Fatty acids were methylated using 5 % HCl in methanol at 80 °C for 12 h. Subsequently, liquid–liquid extraction with 5 % NaCl and hexane was used to retrieve fatty acid methyl esters (FAMEs). FAMEs were purified by elution with dichloromethane over SiO_2 columns (~ 2 g).

5α androstane and hexamethylbenzene was used for quantification of the compounds on an Agilent Technologies 7890A gas chromatograph (GC) equipped with a VF1 column (30 m, 0.25 mm i.d., 0.25 µm film thickness) and a flame ionization detector (FID). Compound-specific δ^2H values of the long-chain *n*-alkanes and FAMEs were determined based on at least triplicate analyses on a gas chromatograph-pyrolysis-isotope ratio mass spectrometer (GC-pyrolysis-IRMS, Delta V, ThermoFisher Scientific, Bremen, Germany). The A4 standard mixture (provided by Arndt Schimmelmann, Indiana University, USA) was run three times per sequence at three different concentrations. All results are reported after normalization using multi-linear regression (Paul et al., 2007) and simple mass-balance correction of the FAMEs for the isotopic composition of the methanol used for derivatisation. Long-term precision of the analyses was monitored using a laboratory standard (oak, *n*-C_{29}). The standard was analyzed in every sequence and yielded a mean value of −147.2 ‰ with a SD of ±1.7 ‰ across all sequences run for this study.

2.3 Modeling of leaf water ^{2}H enrichment

The empirical data analyses were combined with mechanistic model simulations of $\delta^2H_{\text{leaf water}}$ in order to better detect and evaluate how the dominant climate variables (air temperature and relative air humidity) influence ^{2}H enrichment in lipids. The ^{2}H enrichment of leaf water due to evapotranspiration can be predicted by using mechanistic models originally developed for isotope fractionation processes associated with evaporation from water surfaces by Craig and Gordon (1965). These models were adapted for plants by Dongmann et al. (1974) and subsequently Farquhar and Lloyd (1993). Evaporative ^{2}H enrichment of the leaf water (Δ^2H_e) at the evaporative surface in the mesophyll is given by the equation:

$$\Delta^2H_e = \varepsilon^+ + \varepsilon_k + \left(\Delta^2H_{WV} - \varepsilon_k\right)\frac{e_a}{e_i}, \tag{1}$$

where ε^+ is the equilibrium fractionation between liquid water and vapor at the air–water interfaces (Bottinga and Craig, 1969), ε_k is the kinetic fractionation during water vapor diffusion from leaf intercellular air space to the atmosphere, Δ^2H_{WV} is the isotopic difference of the water vapor and the source water, and e_a/e_i is the ratio of ambient to intercellular vapor pressure (Craig and Gordon, 1965). This basic calculation was modified by including a Péclet effect that accounts for opposing fluxes of source water entering the leaf through the transpiration flow and the back-diffusion of isotopically enriched water from the sites of evaporation (Farquhar and Lloyd, 1993):

$$\Delta^2H_{\text{leaf water}} = \frac{\Delta^2H_e(1-e^{-\varphi})}{EL/CD}. \quad (2)$$

The quotient of EL/CD represents the Péclet number (φ) where E is the transpiration rate, L is the effective path length, C is the molar concentration of water and D is the diffusivity of ^2H_2O. The model approach we used followed that of Kahmen et al. (2011b), where the Péclet-modified Craig Gordon model is reduced to three input variables: air temperature, atmospheric vapour pressure and source water δ^2H. This simplified model is based on the assumption that leaf temperature equals air temperature and that atmospheric vapor δ^2H is in equilibrium with source water δ^2H (Kahmen et al., 2011b). Transpiration rates are estimated using relative humidity and air temperature (retrieved from GeoINTA, 2012) and assuming a mean stomatal conductance of $0.15\,\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$. Based on reports for a large number of species in the literature (Kahmen et al., 2008, 2009; Song et al., 2013), we used an average value of 20 mm for L and kept it constant across the transect. For our simulation of leaf water δ^2H values we obtained the model input variables air temperature, atmospheric vapor pressure and source water δ^2H from GeoINTA (2012) and Bowen (2012), respectively.

The isotopic composition of the leaf water can be estimated according to Eq. (3):

$$\delta^2H_{\text{leaf water}} = \Delta^2H_{\text{leaf water}} + \delta^2H_{SW}, \quad (3)$$

where $\Delta^2H_{\text{leaf water}}$ is the bulk leaf water evaporative enrichment and δ^2H_{SW} is the hydrogen isotope ratio of source/xylem water.

2.4 The conceptual model for a coupled δ^{18}O-δ^2H approach

In a δ^{18}O-δ^2H diagram, the distance of reconstructed leaf water to the Global Meteoric Water Line (GMWL) defines the deuterium excess ($d = \delta^2H - 8 \cdot \delta^{18}O$). Observed deviation is caused by the kinetic effect resulting in slower diffusivity of the $^1H^1H^{18}O$ molecules compared to the $^2H^1H^{16}O$ molecules. More humid conditions and less evapotranspiration are reflected by lower d values, and more arid conditions and more evapotranspiration are reflected by higher d values. Using a Craig–Gordon model adapted by Gat and Bowser (1991), the d excess of leaf water can be used to calculate RH values normalized to the temperature of leaf-water:

$$\mathrm{RH} = 1 - \frac{\Delta d}{(\varepsilon_2^* - 8 \cdot \varepsilon_{18}^* + C_k^2 - 8 \cdot C_k^{18})} \tag{4}$$

where Δd represents the difference in d excess between leaf-water and source water. According to Merlivat (1978), experimentally determined kinetic isotope fractionation equals 25.1 and 28.5 ‰ for C_k^2 and C_k^{18}, respectively, considering that these are the maximum values of kinetic fractionation during molecular diffusion of water through stagnant air. Equilibrium isotope enrichments ε_2^* and ε_{18}^* as functions of temperature can be calculated using empirical equations of Horita and Wesolowski (1994).

The combined δ^{18}O-δ^2H biomarker approach also allows reconstruction of the isotopic composition of plant source water, which can be considered as an approximation for δ^2H_{prec} and $\delta^{18}O_{\text{prec}}$. In Fig. 5 these are given by the intercepts of the individual evaporation lines (EL) with the GMWL. The slope value of 2.82 that is used for the EL has been observed in previous experiments on evaporating leaf water (Allison et al., 1985; Walker and Brunel, 1990; Bariac et al., 1994). For further details on modelling coupled δ^{18}O-δ^2H biomarker results the reader is referred to Zech et al. (2013a).

3 Results and discussion

3.1 Comparison of $\delta^2H_{n\text{-alkanes}}$ and $\delta^2H_{\text{fatty acids}}$

The C_{29} and C_{31} *n*-alkane homologues were sufficiently abundant in all samples to be measured for their hydrogen isotopic composition. The δ^2H values range from −155 to −222 ‰ and reveal a similar trend between *n*-C_{29} and *n*-C_{31} along the investigated transect (Table 1 and Fig. 2). While the northern and middle part of the transect is characterized by relatively high δ^2H values (∼ −160 ‰), the southern part of the transect is characterized by considerably more negative δ^2H values (∼ −210 ‰).

The δ^2H values of the fatty acids *n*-C_{22}, *n*-C_{24}, *n*-C_{26}, *n*-C_{28} and *n*-C_{30} range from −128 to −225 ‰ (Table 1 and Fig. 2). In general, there is a good overall agreement between the *n*-alkanes and the fatty acids ($R = 0.96$, $p < 0.001$, $n = 20$; for the weighted means), both showing much more negative δ^2H values in the south than in the northern and middle portions of the transect (Table 1, Fig. 2). Interestingly, the longer homologues *n*-C_{28} and *n*-C_{30} are systematically enriched by 3 to 43 ‰ compared to the *n*-alkanes. The same was observed by Chikaraishi and Naraoka (2007), reporting on *n*-alkanes being depleted in ^{2}H relative to the corresponding *n*-alkanoic acid. Reasons for this trend remain vague at this point, but may be relate to metabolic pathways, seasonal differences in homologue production, or differences in homologue sources. Roots, for example, have also been suggested as a source of long-chain *n*-fatty acids (Bull et al., 2000). Shorter homologues, have been suggested to be not only plant-derived, but also of bacterial origin (Matsumoto et al., 2007; Bianchi and Canuel, 2011). Similarly, soil microbial overprinting of long chain *n*-alkanes and fatty acids cannot be excluded (Nguyen Tu et al., 2011; Zech et al., 2011).

The consistent δ^2H pattern revealed by the *n*-alkanes and fatty acids along the north–south climate transect does not solely reflect the δ^2H isotopic composition of precipitation. Especially in the middle part of the transect, δ^2H of the lipid biomarkers shows a pronounced offset (Fig. 3). Given that *n*-alkanes are considered to primarily reflect leaf signals and are most widely applied in paleoclimate and paleohydrological studies, we will principally refer to δ^2H of long chain *n*-alkanes in further discussion and calculations.

3.2 Evapotranspirative ^{2}H enrichment of leaf water

Assuming a consistent biosynthetic fractionation of −160 ‰ for the *n*-alkane and fatty acids biosynthesis in plants (Sessions et al., 1999; Sachse et al., 2006), we estimated the isotopic composition of leaf water using our *n*-alkane and fatty acids δ^2H values along the transect/gradient (Fig. 3). Note that an average biosynthetic fractionation factor of ∼ −200 ‰ was reported by Sessions et al. (1999) for short- and mid-chained fatty acids synthesized mostly by unicellular/multicellular marine alge. By contrast, there are hardly any biosynthetic fractionation factors reported for long-chained fatty acids of higher plants. Given that our δ^2H*n*-alkanes and fatty acids values are very similar, using a biosynthetic fractionation factor of −160 ‰ for both lipids seems appropriate.

Estimated leaf water δ^2H values suggest a pronounced ^{2}H enrichment of leaf water compared to precipitation (up to +62 ‰). This finding highlights the role of aridity for evapotranspiration and isotopic enrichment of leaf waxes, in good agreement with prior studies (Sachse et al., 2006; Feakins and Sessions, 2010; Douglas et al., 2012; Kahmen et al., 2013a).

Figure 4 illustrates the overall good agreement between $\delta^2\mathrm{H}_{\text{leaf water}}$ values inferred from the measured *n*-alkanes and fatty acids, and $\delta^2\mathrm{H}_{\text{leaf water}}$ values calculated using the Peclet-modified Graig–Gordon model. The correlations are highly significant ($r = 0.88$, $p < 0.001$, $n = 20$, for *n*-alkanes and $r = 0.93$, $p < 0.001$, $n = 20$ for fatty acids), suggesting that the model correctly implements the most relevant processes related to evapotranspirative enrichment of leaf water. While predicting the overall trend in leaf water δ^2H along the transect with reasonable accuracy, the model does not capture site-to-site excursions in the *n*-alkane-derived leaf water δ^2H values from this overall trend. As such, additional influences that are not captured by the model, such as evaporative ^{2}H enrichment of soil water can possibly explain the underestimation of the modeled $\delta^2H_{\text{leaf water}}$ values in the middle part of the transect (Fig. 4). In contrast, the model might overestimate $\delta^2H_{\text{leaf water}}$ in the northern and the southern part of the transect. The corresponding ecosystems, the Humid Pampa and the Patagonian Steppe, respectively, are grasslands, whereas the middle part of the transect is dominated by shrubland. Grass-derived lipids have been shown to be less strongly affected by evaporative leaf water ^2H enrichment than those of trees or shrubs (McInerney et al., 2011; Yang et al., 2011; Sachse et al., 2012; Kahmen et al., 2013b), and hence the overestimation of the model may be due to plant species effects (Pedentchouk et al., 2008; Douglas et al., 2012). The more pronounced offsets in Patagonia could additionally be attributed to a seasonality effect. The growing season in Patagonia is not year-round but mainly in spring.

In order to assess the sensitivity of the model to the input parameters, we varied vapor pressure of air by ±5 hPa and mean annual temperature by ±5 °C. While changes in temperature have only negligible effects on the modeled δ^2H isotopic composition of leaf water, changes in RH yield difference of up to ~ 30 ‰ (Fig. 4). Different climatic conditions during the spring growing season in Patagonia could thus readily explain the overestimation of the evapotranspirative enrichment in the model.

Evapotranspirative enrichment of leaf water has also been observed in $\delta^{18}O$ values of hemicellulose-derived arabinose, fucose and xylose analysed in topsoils along the investigated transect (Tuthorn et al., 2014). Model sensitivity tests of ^{18}O enrichment of leaf water using PMCG model corroborate the observations presented here that air humidity is the key factor defining the $^{18}O/^2H$ enrichment of leaf water.

3.3 Combining $\delta^{18}O$ sugar and $\delta^2H_{n\text{-alkane}}$ biomarker analyses

A conceptual model for the combined interpretation of $\delta^2H_{n\text{-alkane}}$ and $\delta^{18}O_{\text{sugar}}$ biomarkers can be illustrated in a $\delta^{18}O$-δ^2H diagram (Fig. 5). The model is based on the assumption that the investigated *n*-alkane and hemicellulose biomarkers are primarily leaf-derived and reflect the isotopic composition of leaf water. With regard to the topsoil transect investigated here, this assumption is reasonable and supported by leaf water modeling (for δ^2H in Sect. 3.2, and for δ^{18}O see Tuthorn et al., 2014). Accordingly, the isotopic composition of leaf water can be reconstructed from the isotopic composition of the biomarkers by applying an average value according to various studies of the biosynthetic fractionation factors resulting in −160 ‰ (Sessions et al., 1999; Sachse et al., 2006) and +27 ‰ (Sternberg et al., 1986; Yakir and DeNiro, 1990; Schmidt et al., 2001; Cernusak et al., 2003) for δ^2H and δ^{18}O, respectively (Fig. 5).

3.3.1 Reconstructed RH values along the climate transect and comparison with actual RH values

The reconstructed *d* excess values of leaf water along the investigated transect range from −67 to −178 ‰ and reveal a systematic trend towards more negative values in the south (Fig. 6). The reconstructed RH values calculated using the leaf water *d* excess values according to the above-described Craig–Gordon model range from 16 to 65 %, with one extremely low value of 5 % (Fig. 6). Reconstructed RH values follow the systematic *d* excess trend and correlate significantly ($r = 0.79$, $p < 0.001$, $n = 20$) with the actual modern RH values retrieved from GeoINTA (2012), which generally validates the δ^{18}O-δ^2H conceptual model.

However, as depicted by Fig. 6, the reconstructed RH values systematically underestimate the actual (modern) RH values. This is especially pronounced for the three southernmost locations (18–20) and may be attributed to several causes. First, the applied model calculations do not account for evaporative enrichment of soil water. In the δ^{18}O-δ^2H diagram, the soil water enrichment shifts the source water (simplified to “reconstructed precipitation” in Fig. 5 and our model) along the evaporation line and thus leads to too negative *d* excess values and an underestimation of RH. Second, the reconstructed source water lies on the GMWL in the model, while local meteoric water lines and thus actual precipitation may have a *d* excess offset from the GMWL (*d* excess of GMWL = 10 ‰). In our case, this effect should be negligible, as *d* excess values of precipitation along the transect are only on the order of 4.8–11 ‰ (Bowen, 2012). Third, given that leaf waxes considered to be formed mostly during early stages of leaf ontogeny (Kolattukudy, 1970; Riederer and Markstaedter, 1996; Kahmen et al., 2011a; Tipple et al., 2012) they may not necessarily reflect the mean annual isotopic composition of precipitation in regions with pronounced seasonality, but rather the isotopic composition of precipitation during the growing season. As well, compared to the annual (modern) RH values, growing season RH yields up to 9 % (CRU, 2013) lower values in Patagonia where seasonality is especially pronounced. Fourth, reconstructed RH values will be also underestimated if *n*-alkanes do not fully incorporate the evapotranspirative ^{2}H enrichment of leaf water, which is the case for grasses (Sect. 3.2; McInerney et al., 2011; Kahmen et al., 2013b). In the δ^{18}O-δ^{2}H diagram, leaf water would thus plot lower than the simple Craig–Gordon model predicts, and *d* excess would be too negative.

Finally, the δ^{18}O biosynthetic fractionation factor of $\sim +27$ ‰, which has been reported for cellulose, may underestimate the actual fractionation factor of hemicelluloses (Tuthorn et al., 2014; Zech et al., 2014), which would result in reconstructed leaf water values plotting too far to the right in the δ^{18}O-δ^{2}H diagram. This can be explained with the loss of a relatively ^{18}O-depleted oxygen atom attached to C-6 during pentose biosynthesis (C-6 decarboxylation; Altermatt and Neish, 1956; Harper and Bar-Peled, 2002; Burget et al., 2003), and is in agreement with the recent finding that about 80 % of the oxygen atoms at the C-6 position are isotopically exchanged during cellulose synthesis (Waterhouse et al., 2013). In contrast, the value of +27 ‰ would be an overestimation in cases where significant amounts of stem or root-derived sugars contribute to the soil sugar pool, because up to 40 % of the oxygen atoms being biosynthesized in leaves are exchanging with non-enriched root/stem water during cellulose biosynthesis in roots/stems (Sternberg et al., 1986; Gessler et al., 2009). However, given that this would result in an overestimation of reconstructed RH values (the opposite is observed, Fig. 6), we suggest that the majority of the sugar biomarkers along the topsoil transect investigated here are leaf-derived and not stem-/root-derived.

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3.3.2 Comparison of reconstructed and actual δ^2H_{prec} and $\delta^{18}O_{prec}$ values

Values of $\delta^{18}O_{prec}$ and δ^2H_{prec} reconstructed as the intercepts of the individual evaporation lines (EL) with the GMWL in the $\delta^{18}O$-δ^2H diagram (Fig. 5) range from −7 to −22 ‰ and from −47 to −166 ‰, respectively. They correlate significantly (Fig. 7; $r = 0.90$, $p < 0.001$, $n = 20$, and $r = 0.88$, $p < 0.001$, $n = 20$ for $\delta^{18}O_{prec}$ and δ^2H_{prec}, respectively) with the actual δ^2H_{prec} and $\delta^{18}O_{prec}$ values as derived from Bowen (2012). While the reconstructed $\delta^{18}O_{prec}$ and δ^2H_{prec} values, like the reconstructed RH values, generally validate our conceptual model, they appear to systematically underestimate the actual $\delta^{18}O$ and δ^2H values of the precipitation water (Fig. 7).

The uncertainties discussed above for the observed offset of reconstructed vs. actual RH values can also affect the accuracy of reconstructed $\delta^{18}O_{prec}$ and δ^2H_{prec} values. As well, the actual values for the isotopic composition of precipitation as reported by Bowen (2012) show a confidence interval (95 %) ranging from 0.2 to 1.2 ‰, and from 2 to 11 ‰ for δ^2H_{prec} and $\delta^{18}O_{prec}$, respectively. Here, we would like to emphasize the possible influence of seasonality. As reported for sugar biomarkers (Tuthorn et al., 2014), we suggest that leaf waxes as well likely reflect the humidity and the isotopic composition of spring and summer precipitation rather than mean annual values. Accounting for these seasonality effects, the apparent offsets would be reduced. Future modeling studies should therefore pay particular attention to seasonality, and consider using climate parameters of the growing season instead of annual means.

4 Conclusions

The hydrogen isotopic composition of leaf wax *n*-alkanes and *n*-alkanoic (fatty) acids extracted from topsoils along a transect in Argentina varies significantly, with δ^2H values ranging from −155 to −222 ‰ and −128 to −225 ‰, respectively. These δ^2H values broadly parallel variations in the hydrogen isotopic composition of precipitation, but are modulated by evaporative ^{2}H enrichment of leaf water. A mechanistic leaf water model correctly simulates the overall trends. Sensitivity tests show that relative humidity exerts a stronger influence on evaporative enrichment than temperature.

Based on the premise that *n*-alkanes and hemicellulose biomarkers are primarily leaf-derived, we reconstruct $\delta^2\text{H}_{\text{leaf water}}$ and $\delta^{18}\text{O}_{\text{leaf water}}$, respectively, which in turn allows assessment of the *d* excess of leaf water. The large calculated range in *d* excess along the transect (−67 to −178 ‰) can be used to calculate/model RH; modeled RH correlates significantly with empirical modern RH along the transect. Despite this overall correlation, we observe a systematic underestimation of RH, which we attribute to limitations of the combined δ^{18}O-δ^2H conceptual model. Similarly, $\delta^{18}\text{O}_{\text{prec}}$ and $\delta^2\text{H}_{\text{prec}}$ calculated/modeled from biomarker isotopic compositions significantly correlate with modern precipitation.

The novel combined δ^2H-δ^{18}O biomarker approach has great potential for paleohydrological and paleo-climate reconstructions. In principle, it allows determination of *d* excess of past leaf water, thus constraining evaporative enrichment, as well as the isotopic signal of past precipitation.

Acknowledgements. We kindly thank B. Huwe (University Bayreuth) and L. Zöller (University Bayreuth) for logistic support. This study was partly financed by the SIBAE COST Action ES0806, the German Research Foundation (DFG Oe516/2-1 and ZE 844/1-2), and the Swiss National Science Foundation (SNF Ambizione PZ00P2_131670). This publication was funded by the German Research Foundation (DFG) and the University of Bayreuth in the funding programme Open Access Publishing.

References

Allison, G. B., Gat, J. R., and Leaney, F. W. J.: The relationship between deuterium and oxygen-18 delta values in leaf water, Chem. Geol., 58, 145–156, 1985.

Altermatt, H. A. and Neish, A. C.: The biosynthesis of cell wall carbohydrates: III. Further studies on formation of cellulose and xylan from labeled monosaccharides in wheat plants, Can. J. Biochem. Phys., 34, 405–413, 1956.

Araguas-Araguas, L., Froehlich, K., and Rozanski, K.: Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture, Hydrol. Process., 14, 1341–1355, 2000.

Bariac, T., Gonzales-Dunia, J., Katerji, N., Bethenod, O., Bertolini, J. M., and Mariotti, A.: Spatial variation of the isotopic composition of water (^{18}O, ^{2}H) in the soil-plant-atmosphere system, Chem. Geol., 115, 317–333, 1994.

Bianchi, T. and Canuel, E. A.: Chemical Biomarkers in Aquatic Ecosystems, Princeton University Press, Princeton, 2011.

Bottinga, Y. and Craig, H.: Oxygen isotope fractionation between CO2 and water, and the isotopic composition of marine atmospheric CO_2, Earth Planet. Sc. Lett., 5, 285–295, 1969.

Bowen, G. J.: The Online Isotopes in Precipitation Calculator, version 2.2, available at: http://www.waterisotopes.org (last access: 9 January 2015), 2012.

Bull, I. D., Nott, C. J., van Bergen, P. F., Poulton, P. R., and Evershed, R. P.: Organic geochemical studies of soils from the Rothamsted classical experiments – VI. The occurrence and source of organic acids in an experimental grassland soil, Soil Biol. Biochem., 32, 1367–1376, 2000.

Burget, E., Verma, R., Mølhøj, M., and Reiter, W.: The biosynthesis of L-arabinose in plants: molecular cloning and characterization of a golgi-localized UDP-D-xylose 4-epimerase encoded by the MUR4 gene of arabidopsis, Plant Cell, 15, 523–531, 2003.

Burgos, J. J. and Vidal, A. L.: Los climas de la República Argentina, segun la nueva clasificación de Thornthwaite, Meteoros, 1, 1–32, 1951.

Cernusak, L. A., Wong, S. C., and Farquhar, G. D.: Oxygen isotope composition of phloem sap in relation to leaf water in *Ricinus communis*, Funct. Plant Biol., 30, 1059–1070, 2003.

Chikaraishi, Y. and Naraoka, H.: δ^{13}C and δD relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants, Org. Geochem., 38, 198–215, 2007.

Craig, H. and Gordon, L. I.: Deuterium and oxygene-18 variations in the ocean and the marine atmosphere, in: Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures, edited by: Tongiorgi, E., Spoleto, Italy, 9–130, 1965.

CRU: University of East Anglia-Climate Research Unit, Relative humidity data, available at: http://www.cru.uea.ac.uk/cru/data/hrg/tmc/ (last access: 28. November 2013), 2013.

Dongmann, G., Nürnberg, H. W., Förstel, H., and Wagener, K.: On the enrichment of $H_2^{18}O$ in the leaves of transpiring plants, Radiat. Environ. Bioph., 11, 41–52, 1974.

Douglas, P. M. J., Pagani, M., Brenner, M., Hodell, D. A., and Curtis, J. H.: Aridity and vegetation composition are important determinants of leaf-wax δD values in southeastern Mexico and Central America, Geochim. Cosmochim. Ac., 97, 24–45, 2012.

Eglinton, G. and Hamilton, R. J.: Leaf epicuticular waxes, Science, 156, 1322–1335, 1967.

Eglinton, T. I. and Eglinton, G.: Molecular proxies for paleoclimatology, Earth Planet. Sc. Lett., 275, 1–16, 2008.

Ehleringer, J. R. and Dawson, T. E.: Water uptake by plants: perspectives from stable isotope composition, Plant Cell Environ., 15, 1073–1082, 1992.

Farquhar, G. D. and Lloyd, J.: Carbon and oxygene isotope effects in the exchange of carbon dioxide between terrestrial plants and the atmosphere, in: Stable Isotopes and Plant Carbon–Water Relations, edited by: Ehleringer, J. R., Hall, A. E., and Farquhar, G. D., Academic Press, Inc., San Diego, 47–70, 1993.

Farquhar, G. D., Cernusak, L. A., and Barnes, B.: Heavy water fractionation during transpiration, Plant Physiol., 143, 11–18, 2007.

Feakins, S. J. and Sessions, A. L.: Controls on the D/H ratios of plant leaf waxes in an arid ecosystem, Geochim. Cosmochim. Ac., 74, 2128–2141, 2010.

Fernández, O. A. and Busso, C. A.: Arid and semi-arid rangelands: two thirds of Argentina, CERZOS and Departamento de Agronomia, Universidad Nacional del Sur, 8000 Bahía Blanca, Argentina, RALA Report 200, 41–60, 1997.

Flanagan, L. B., Comstock, J. P., and Ehleringer, J. R.: Comparison of modeled and observed environmental influences on the stable oxygen and hydrogen isotope composition of leaf water in *Phaseolus vulgaris* L., Plant Physiol., 96, 588–596, 1991.

Gat, J. R.: Oxygen and hydrogen isotopes in the hydrologic cycle, Annu. Rev. Earth Pl. Sc., 24, 225–262, 1996.

Gat, J. R. and Bowser, C.: The heavy isotope enrichment of water in coupled evaporative systems, in: Stable Isotope Geochemistry: A Tribute to Samuel Epstein, edited by: Taylor, H. P., O'Neil, J. R., and Kaplan, I. R., The Geochemical Society, Lancester, 159–168, 1991.

GeoINTA: Instituto Nacional de Technologia Agropecuaria Visualizador Integrado, available at: http://geointa.inta.gov.ar/visor/ (last accessed 1. August 2012), 2012.

Greule, M., Hänsel, C., Bauermann, U., and Mosandl, A.: Feed additives: authenticity assessment using multicomponent-/multielement-isotope ratio mass spectrometry, Eur. Food Res. Technol., 227, 767–776, 2008.

Harper, A. and Bar-Peled, M.: Biosynthesis of UDP-xylose. Cloning and characterization of a novel Arabidopsis gene family, UXS, encoding soluble and putative membrane-bound UDP-glucuronic acid decarboxylase isoforms, Plant Physiol., 130, 2188–2198, 2002.

Hener, U., Brand, W. A., Hilkert, A. W., Juchelka, D., Mosandl, A., and Podebrad, F.: Simultaneous on-line analysis of 18O/16O and 13C/12C ratios of organic compounds using GC-pyrolysis-IRMS, Z. Lebensm. Unters. F. A, 206, 230–232, 1998.

Horita, J. and Wesolowski, D. J.: Liquid–vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature, Geochim. Cosmochim. Ac., 58, 3425–3437, 1994.

Huang, Y., Shuman, B., Wang, Y., and Webb, T.: Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test, J. Paleolimnol., 31, 363–375, 2004.

Juchelka, D., Beck, T., Hener, U., Dettmar, F., and Mosandl, A.: Multidimensional gas chromatography coupled on-line with isotope ratio mass spectrometry (MDGC-IRMS): progress in the analytical authentication of genuine flavor components, J. High Res. Chromatog., 21, 145–151, 1998.

Jung, J., Sewenig, S., Hener, U., and Mosandl, A.: Comprehensive authenticity assessment of lavender oils using multielement/multicomponent isotope ratio mass spectrometry analysis and enantioselective multidimensional gas chromatography-mass spectrometry, Eur. Food Res. Technol., 220, 232–237, 2005.

Jung, J., Puff, B., Eberts, T., Hener, U., and Mosandl, A.: Reductive ester cleavage of acyl glycerides-GC-C/P-IRMS measurements of glycerol and fatty alcohols, Eur. Food Res. Technol., 225, 191–197, 2007.

Kahmen, A., Simonin, K., Tu, K. P., Merchant, A., Callister, A., Siegwolf, R., Dawson, T. E., and Arndt, S. K.: Effects of environmental parameters, leaf physiological properties and leaf water relations on leaf water δ^{18}O enrichment in different Eucalyptus species, Plant Cell Environ., 31, 738–751, 2008.

Kahmen, A., Dawson, T. E., Vieth, A., and Sachse, D.: Leaf wax *n*-alkane δD values are determined early in the ontogeny of *Populus trichocarpa* leaves when grown under controlled environmental conditions, Plant Cell Environ., 34, 1639–1651, 2011.

Kahmen, A., Hoffmann, B., Schefuss, E., Arndt, S. K., Cernusak, L. A., West, J. B., and Sachse, D.: Leaf water deuterium enrichment shapes leaf wax n-alkane δD values of angiosperm plants II: Observational evidence and global implications, Geochim. Cosmochim. Ac., 111, 50–63, 2013a.

Kahmen, A., Schefuß, E., and Sachse, D.: Leaf water deuterium enrichment shapes leaf wax *n*-alkane δD values of angiosperm plants I: Experimental evidence and mechanistic insights, Geochim. Cosmochim. Ac., 111, 39–49, 2013b.

Kolattukudy, P.: Cutin biosynthesis in *Vicia faba* leaves – effect of age, Plant Physiol., 46, 759–760, 1970.

Le Houérou, H. N.: Climate change, drought and desertification, J. Arid Environ., 34, 133–185, 1996.

Matsumoto, K., Kawamura, K., Uchida, M., and Shibata, Y.: Radiocarbon content and stable carbon isotopic ratios of individual fatty acids in subsurface soils: implication for selective microbial degradation and modification of soil organic matter, Geochem. J., 41, 483–492, 2007.

McInerney, F. A., Helliker, B. R., and Freeman, K. H.: Hydrogen isotope ratios of leaf wax n-alkanes in grasses are insensitive to transpiration, Geochim. Cosmochim. Ac., 75, 541–554, 2011.

Merlivat, L.: Molecular diffusivities of $H_2^{16}O$,$HD^{16}O$, and $H_2^{18}O$ in gases, J. Chem. Phys., 69, 2864–2871, 1978.

Nguyen Tu, T. T., Egasse, C.I., Zeller, B., Bardoux, G.r., Biron, P., Ponge, J.-F.o., David, B., and Derenne, S.: Early degradation of plant alkanes in soils: a litterbag experiment using 13C-labelled leaves, Soil Biol. Biochem., 43, 2222–2228, 2011.

Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., and Schouten, S.: Arctic hydrology during global warming at the Paleocene/Eocene thermal maximum, Nature, 442, 671–675, 2006.

Paruelo, J. M., Beltrán, A., Jobbágy, E., Sala, O. E., and Golluscio, R. A.: The climate of Patagonia: general patterns and controls on biotic processes, Ecologia Austral, 8, 85–101, 1998.

Paul, D., Skrzypek, G., and Fórizs, I.: Normalization of measured stable isotopic compositions to isotope reference scales – a review, Rapid Commun. Mass Sp., 21, 3006–3014, 2007.

Pedentchouk, N., Sumner, W., Tipple, B., and Pagani, M.: delta C-13 and delta D compositions of n-alkanes from modern angiosperms and conifers: an experimental set up in central Washington State, USA, Org. Geochem., 39, 1066–1071, 2008.

Radke, J., Bechtel, A., Gaupp, R., Püttmann, W., Schwark, L., Sachse, D., and Gleixner, G.: Correlation between hydrogen isotope ratios of lipid biomarkers and sediment maturity, Geochim. Cosmochim. Ac., 69, 5517–5530, 2005.

Rao, Z., Zhu, Z., Jia, G., Henderson, A. C. G., Xue, Q., and Wang, S.: Compound specific δD values of long chain n-alkanes derived from terrestrial higher plants are indicative of the δD of meteoric waters: evidence from surface soils in eastern China, Org. Geochem., 40, 922–930, 2009.

Riederer, M. and Markstaedter, C.: Cuticular waxes: a critical assessment of current knowledge, in: Plant Cuticules – An Integrated Functional Approach, edited by: Kerstiens, K. G., BIOS Scientific Publishers, Oxford, 1996.

Sachse, D., Radke, J., and Gleixner, G.: Hydrogen isotope ratios of recent lacustrine sedimentary *n*-alkanes record modern climate variability, Geochim. Cosmochim. Ac., 68, 4877–4889, 2004.

Sachse, D., Radke, J., and Gleixner, G.: δD values of individual *n*-alkanes from terrestrial plants along a climatic gradient - Implications for the sedimentary biomarker record, Org. Geochem., 37, 469–483, 2006.

Sachse, D., Billault, I., Bowen, G. J., Chikaraishi, Y., Dawson, T. E., Feakins, S. J., Freeman, K. H., Magill, C. R., McInerney, F. A., van der Meer, M. T. J., Polissar, P., Robins, R. J., Sachs, J. P., Schmidt, H.-L., Sessions, A. L., White, J. W. C., West, J. B., and Kahmen, A.: Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms, Annu. Rev. Earth Pl. Sc., 40, 221–249, 2012.

Samuels, L., Kunst, L., and Jetter, R.: Sealing plant surfaces: cuticular wax formation by epidermal cells, Annu. Rev. Plant Biol., 59, 683–707, 2008.

Sauer, P. E., Eglinton, T. I., Hayes, J. M., Schimmelmann, A., and Sessions, A. L.: Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions, Geochim. Cosmochim. Ac., 65, 213–222, 2001.

Schefuss, E., Schouten, S., and Schneider, R. R.: Climatic controls on central African hydrology during the past 20,000 years, Nature, 437, 1003–1006, 2005.

Schmidt, H.-L., Werner, R. A., and Rossmann, A.: ^{18}O pattern and biosynthesis of natural plant products, Phytochemistry, 58, 9–32, 2001.

Sessions, A. L., Burgoyne, T. W., Schimmelmann, A., and Hayes, J. M.: Fractionation of hydrogen isotopes in lipid biosynthesis, Org. Geochem., 30, 1193–1200, 1999.

Smith, F. A. and Freeman, K. H.: Influence of physiology and climate on δD of leaf wax *n*-alkanes from C3 and C4 grasses, Geochim. Cosmochim. Ac., 70, 1172–1187, 2006.

Sternberg, L., DeNiro, M. J., and Savidge, R. A.: Oxygen isotope exchange between metabolites and water during biochemical reactions leading to cellulose synthesis, Plant Physiol., 82, 423–427, 1986.

Tierney, J. E., Russel, J. M., Huang, Y., Sinninghe Damsté, J. S., Hopmans, E. C., and Cohen, A. S.: Northern Hemisphere controls on tropical southeast african climate during the past 60,000 years, Science, 322, 252–255, 2008.

Tipple, B. J., Berke, M. A., Doman, C. E., Khachaturyan, S., and Ehleringer, J. R.: Leaf-wax *n*-alkanes record the plant-water environment at leaf flush, P. Natl. Acad. Sci. USA, 110, 2659–2664, 2013.

Tuthorn, M., Zech, M., Ruppenthal, M., Oelmann, Y., Kahmen, A., Valle, H.c. F.d., Wilcke, W., and Glaser, B.: Oxygen isotope ratios (18O/16O) of hemicellulose-derived sugar biomarkers in plants, soils and sediments as paleoclimate proxy II: Insight from a climate transect study, Geochim. Cosmochim. Ac., 126, 624–634, 2014.

Walker, C. D. and Brunel, J.-P.: Examining evapotranspiration in a semi-arid region using stable isotopes of hydrogen and oxygen, J. Hydrol., 118, 55–75, 1990.

Waterhouse, J. S., Cheng, S., Juchelka, D., Loader, N. J., McCarroll, D., Switsur, V. R., and Gautam, L.: Position-specific measurement of oxygen isotope ratios in cellulose: isotopic exchange during heterotrophic cellulose synthesis, Geochim. Cosmochim. Ac., 112, 178–191, 2013.

Werner, R.: The online $^{18}\mathrm{O}/^{16}\mathrm{O}$ analysis: development and application, Isot. Environ. Healt. S., 39, 85–104, 2003.

Yakir, D.: Variations in the natural abundance of oxygen-18 and deuterium in plant carbohydrates, Plant Cell Environ., 15, 1005–1020, 1992.

Yakir, D. and DeNiro, M. J.: Oxygen and hydrogen isotope fractionation during cellulose metabolism in *Lemna gibba* L., Plant Physiol., 93, 325–332, 1990.

Yang, H., Liu, W., Leng, Q., Hren, M. T., and Pagani, M.: Variation in n-alkane δD values from terrestrial plants at high latitude: implications for paleoclimate reconstruction, Org. Geochem., 42, 283–288, 2011.

Zech, M. and Glaser, B.: Compound-specific δ^{18}O analyses of neutral sugars in soils using gas chromatography-pyrolysis-isotope ratio mass spectrometry: problems, possible solutions and a first application, Rapid Commun. Mass Sp., 23, 3522–3532, 2009.

Zech, M., Pedentchouk, N., Buggle, B., Leiber, K., Kalbitz, K., Markovic, S. B., and Glaser, B.: Effect of leaf litter degradation and seasonality on D/H isotope ratios of n-alkane biomarkers, Geochim. Cosmochim. Ac., 75, 4917–4928, 2011.

Zech, M., Werner, R. A., Juchelka, D., Kalbitz, K., Buggle, B., and Glaser, B.: Absence of oxygen isotope fractionation/exchange of (hemi-) cellulose derived sugars during litter decomposition, Org. Geochem., 42, 1470–1475, 2012.

Zech, M., Tuthorn, M., Detsch, F., Rozanski, K., Zech, R., Zoeller, L., Zech, W., and Glaser, B.: A 220 ka terrestrial δ^{18}O and deuterium excess biomarker record from an eolian permafrost paleosol sequence, NE-Siberia, Chem. Geol., 360–361, 220–230, 2013a.

Zech, M., Tuthorn, M., Glaser, B., Amelung, W., Huwe, B., Zech, W., Zöller, L., and Löffler, J.: Natural abundance of ^{18}O of sugar biomarkers in topsoils along a climate transect over the Central Scandinavian Mountains, Norway. J. Plant Nutr. Soil Sc., 176, 12–15, 2013b.

Zech, M., Mayr, C., Tuthorn, M., Leiber-Sauheitl, K., and Glaser, B.: Oxygen isotope ratios (^{18}O/^{16}O) of hemicellulose-derived sugar biomarkers in plants, soils and sediments as paleoclimate proxy I: Insight from a climate chamber experiment, Geochim. Cosmochim. Ac., 126, 614–623, 2014.

Zech, R., Zech, M., Markovic, S., Hambach, U., and Huang, Y.: Humid glacials, arid interglacials? Critical thoughts on pedogenesis and paleoclimate based on multi-proxy analyses of the loess-paleosol sequence Crvenka, Northern Serbia, Palaeogeogr. Palaeocl., 387, 165–175, 2013.

Table 1. δ^2H values of individual leaf wax *n*-alkanes and fatty acids. Measurements were carried out in at least triplicate (SD = standard deviation).

	$\delta^2H_{n\text{-alkanes}}$				$\delta^2H_{\text{fatty acids}}$									
sampling locality	C_{29} mean (‰)	SD	C_{31} mean (‰)	SD	C_{22} mean (‰)	SD	C_{24} mean (‰)	SD	C_{26} mean (‰)	SD	C_{28} mean (‰)	SD	C_{30} mean (‰)	SD
1	−157	2	−164	2	−155	1	−157	1	−151	1	−153	1	−153	2
2	−166	0	−166	1	−150	0	−155	1	−165	1	−163	1	−161	3
3	−175	1	−179	1	−162	0	−161	1	−165	1	−159	1	−155	0
4	−176	1	−176	1	−162	2	−163	1	−166	1	−165	1	−158	2
5	−178	1	−180	2	−164	0	−165	1	−168	2	−162	1	−159	1
6	−171	2	−172	0	−166	0	−165	2	−169	1	−161	1	−158	1
7	−179	0	−182	0	−170	0	−172	1	−177	0	−169	1	−157	0
8	−162	1	−167	1	−161	1	−161	1	−166	1	−161	1	−158	2
9	−173	1	−168	1	−163	1	−164	0	−168	1	−169	0	−156	1
10	−173	2	−170	2	−159	1	−167	1	−168	0	−159	1	−137	2
11	−170	2	−156	2	−158	0	−169	0	−167	2	−153	4	−147	4
12	−155	1	−176	0	−158	1	−168	1	−172	1	−148	1	−133	1
13	−157	2	−161	1	−158	1	−153	0	−140	1	−135	1	−128	1
14	−158	1	−166	0	−168	1	−183	0	−181	2	−160	2	−147	1
15	−194	2	−193	1	−194	0	−197	0	−191	1	−176	2	−168	2
16	−203	1	−211	1	−204	1	−198	0	−201	0	−193	0	−189	1
17	−218	1	−217	1	−219	1	−220	1	−217	0	−205	1	−204	1
18	−213	1	−202	4	−211	0	−203	1	−204	0	−196	0	−194	0
19	−222	1	−222	1	−220	0	−210	0	−225	1	−212	1	−204	1
20	−220	1	−212	1	−225	0	−221	1	−211	1	−193	3	−195	2

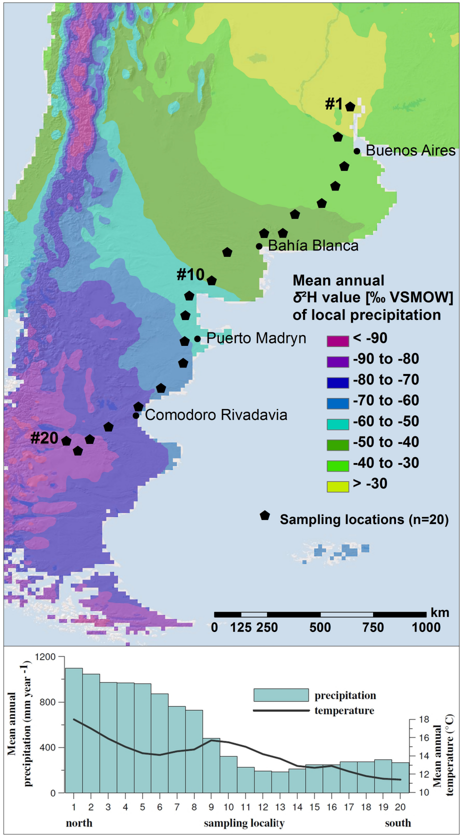

Figure 1. Sampling localities along the investigated transect in Argentina. The colors illustrate the gradient in δ^2H_{prec}, and mean annual temperature and precipitation are shown below.

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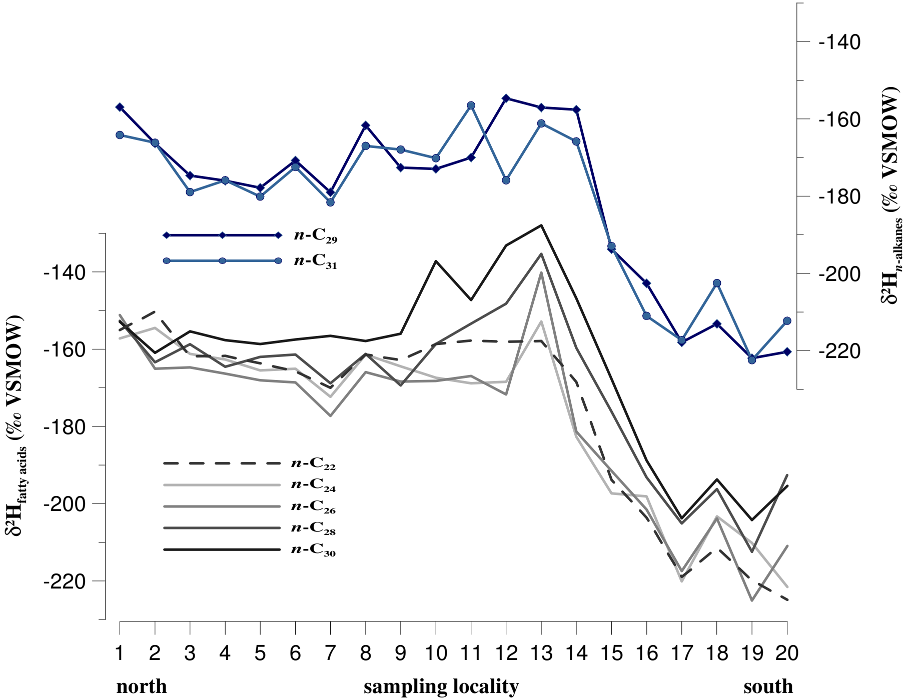

Figure 2. Comparison of δ^2H results of individual leaf wax *n*-alkanes and *n*-alkanoic (fatty) acids along the investigated transect.

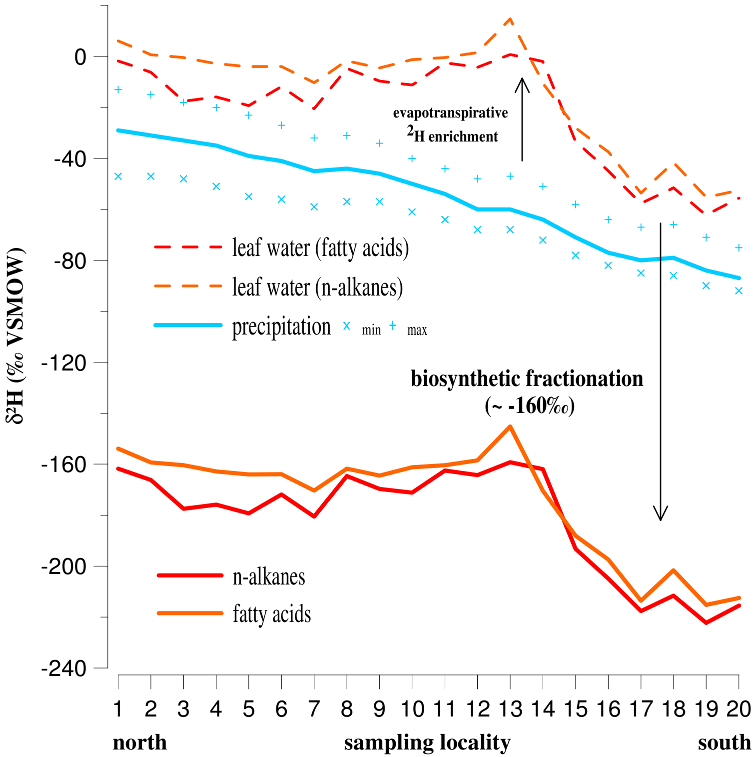

Figure 3. Comparison of measured $\delta^2H_{n\text{-alkanes}}$ (weighted mean of n-C_{29} and n-C_{31}) and $\delta^2H_{\text{fatty acids}}$ (weighted mean of n-C_{22}, n-C_{24}, n-C_{26}, n-C_{28} and n-C_{30}) pattern with δ^2H_{prec} (Bowen, 2012) along the north–south climate transect. Assuming a consistent biosynthetic fractionation of −160 ‰ for the *n*-alkane and fatty acid biosynthesis in plants the isotopic composition of leaf water was inferred.

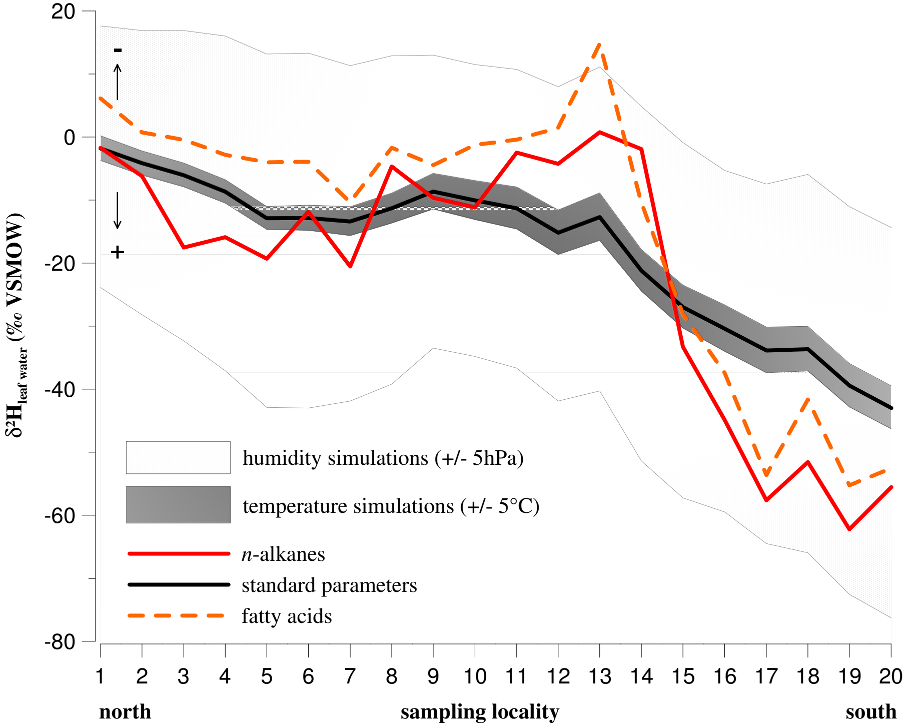

Figure 4. Results of $\delta^2H_{\text{leaf water}}$ model simulations and comparison with measured $\delta^2H_{n\text{-alkanes}}$ and $\delta^2H_{\text{fatty acids}}$. Sensitivity tests for $\delta^2H_{\text{leaf water}}$ are shown for changes in RH and air temperature for all 20 sites along the transect.

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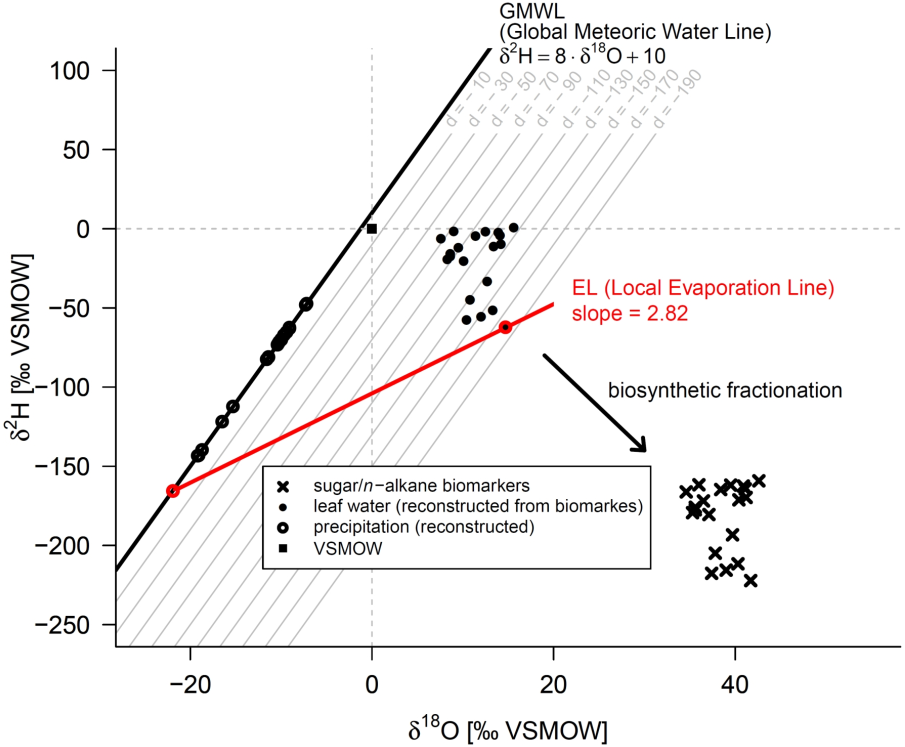

Figure 5. $\delta^{18}O$-δ^2H diagram representing the global meteoric water line (GMWL) and an evaporation line (EL). Data for the $\delta^{18}O$ values of hemicellulose-derived sugars (mean of arabinose, fucose and xylose) and the mean δ^2H values of leaf wax-derived *n*-alkanes (mean of n-C_{29} and n-C_{31}) are displayed. δ^2H and $\delta^{18}O$ values of leaf water are reconstructed using biosynthetic fractionation factors and the distance of reconstructed leaf water to the GMWL defines the deuterium excess ($d = \delta^2H - 8 \cdot \delta^{18}O$). δ^2H and $\delta^{18}O$ values of precipitation for each site are calculated as intersection of the individual ELs (slope 2.82) with the GMWL.

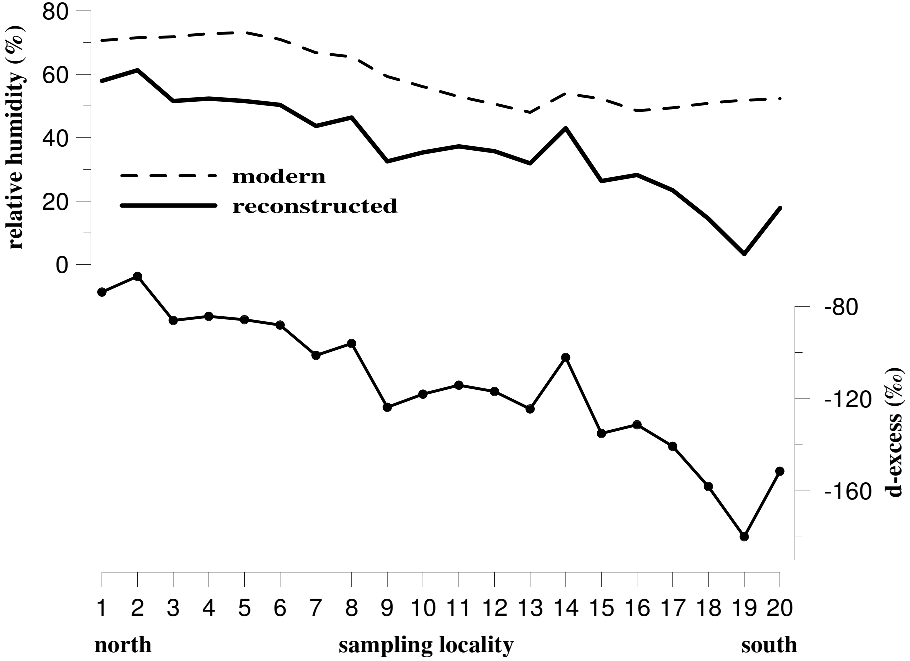

Figure 6. Comparison of reconstructed humidity based on a normalized Craig–Gordon model accounting for deuterium excess and temperature with modern humidity data retrieved for the investigated sites (GeoINTA, 2012). Deuterium excess values were calculated using $\delta^{18}O_{\text{leaf water}}$ reconstructed from terrestrial sugars (Tuthorn et al., 2014) and $\delta^{2}H_{\text{leaf water}}$ reconstructed from *n*-alkanes.

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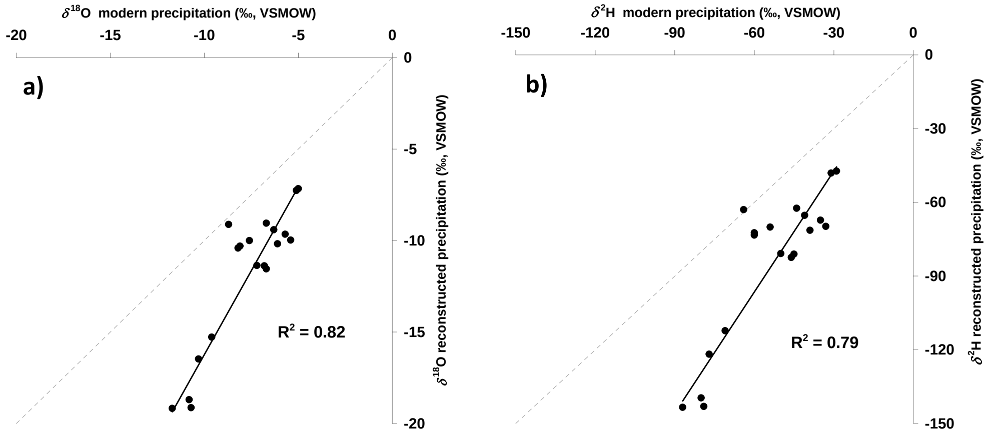

Figure 7. Correlation of $\delta^{18}O_{prec}$ and $\delta^{2}H_{prec}$ reconstructed from the biomarkers with actual modern $\delta^{18}O_{prec}$ and $\delta^{2}H_{prec}$ (from Bowen, 2012), a and b, respectively.