Clim. Past Discuss., doi:10.5194/cp-2017-7, 2017
Manuscript under review for journal Clim. Past
Published: 2 February 2017

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A dual-biomarker approach for quantification of changes in relative humidity from sedimentary lipid D/H ratios

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Abstract

Past climatic change can be reconstructed from sedimentary archives by a number of proxies. However, few methods exist to directly estimate hydrological changes and even fewer result in quantitative data, impeding our understanding of the timing, magnitude and mechanisms of hydrological changes.

Here we present a novel approach based on δ^2H values of sedimentary lipid biomarkers in combination with plant physiological modeling, to extract quantitative information on past changes in relative humidity. Our initial application to an annually laminated lacustrine sediment sequence from western Europe deposited during the Younger Dryas cold period revealed relative humidity changes of up to 15% over sub-centennial timescales, leading to major ecosystem changes, in agreement with palynological data from the region. We show that by combining organic geochemical methods and mechanistic plant physiological models it is possible to extract quantitative ecohydrological parameters from sedimentary lipid biomarker δ^2H data.

1. Introduction

Predicting future changes in the water cycle using state-of-the art climate models is still associated with large uncertainties (IPCC, 2015). This is because we lack a mechanistic understanding of some of the key processes that influence the water cycle, in particular at regional spatial scales. A better mechanistic understanding of drivers and feedbacks within the hydrological cycle can be achieved from

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reconstructing past hydrological changes from sedimentary archives. Stable isotope ratios of meteoric water, expressed as $\delta^{18}O$ and $\delta^{2}H$ (δD) values are an excellent tool in this respect, because their variability is associated with changes in temperature and source water (Bowen, 2008; Gat, 1996). The isotope ratios of precipitation can be recorded in ice core (Alley, 2000), terrestrial and marine paleoclimate archives through a variety of proxies, such as carbonates (Kanner et al., 2013; von Grafenstein et al., 1999), silicates (Tyler et al., 2008) and lipid biomarkers (Sachse et al., 2012).

Despite their potential, the interpretation of the stable isotope ratios from inorganic and organic proxies often allows only a *qualitative* assessment of past hydrological changes while *quantitative* reconstructions of hydrological changes from isotope proxy data, such as precipitation amount or relative humidity, have been difficult to achieve. This is problematic as quantifiable data are necessary for identifying the mechanistic drivers of past hydroclimate changes as well as their continental scale feedbacks and thresholds for example for vegetation changes. Moreover, quantitative data are needed to test the performance of state-of-the art climate models in simulating past and future changes in the hydrological cycle.

The interpretation of isotope proxies is typically not quantitative because multiple drivers can influence meteoric $\delta^{18}O$ and $\delta^{2}H$ values, hampering the assignment of single quantitative relationships between a hydrologic variable and $\delta^{2}H$ values recorded in a geological archive (Alley and Cuffey, 2001). To overcome this limitation, we present a new approach that combines lipid biomarker hydrogen isotope measurements and plant physiological modeling to constrain the influence of multiple drivers on $\delta^{2}H$ values recorded in organic material and allow thus to extract quantitative information about changes in relative humidity from sedimentary archives.

Over the past decade, $\delta^{2}H$ values of lipid biomarkers from photosynthetic organisms have been increasingly used as proxies for reconstructing past changes in the continental hydrological cycle (Feakins, 2013; Rach et al., 2014; Sachse et al., 2012; Schefuss et al., 2011; Seki et al., 2011). In particular *n*-alkanes are ubiquitous in marine and lacustrine sediments and can be preserved over geological timescales (Peters et al., 2007). *n*-Alkanes can be traced back to aquatic or terrestrial sources, where short-chain homologues (nC_{17}-nC_{21}) are primarily synthesized by algae and aquatic plants (Aichner et al., 2010; Ficken et al., 2000), mid-chain n-alkanes (e.g. nC_{23}-nC_{25}) by submerged aquatic macrophytes or mosses (Aichner et al., 2010; Ficken et al., 2000; Gao et al., 2011), and long-chain n-alkanes (>nC_{25}) predominantly by higher terrestrial pants as a protective leaf wax layer on the leaf surface (Bush and McInerney, 2013; Eglinton and Hamilton, 1967).

Algae and submerged aquatic plants directly use lake (or ocean) water as their hydrogen source for lipid synthesis. $\delta^{2}H$ values from *n*-alkanes from aquatic organism ($\delta^{2}H_{aq}$) are thus related to the $\delta^{2}H$ value of the water these organisms live in (Aichner et al., 2010; Sachse et al., 2004) offset by a biosynthetic fractionation (ε_{bio}) between water and *n*-alkanes (Sachse et al., 2012) (Eq. (1)). Laboratory culture studies (Zhang and Sachs, 2007) as well as field studies (Aichner et al., 2010; Sachse et al., 2004) have resulted in strong linear and nearly 1:1 relationships between source water and $\delta^{2}H_{aq}$ (Sachse et al., 2012), but have shown that species specific differences in ε_{bio} do exist (Zhang and Sachs, 2007).

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$$(1)\quad \delta^2H_{aq} = \delta^2H_{precip} + \varepsilon_{bio}$$

Terrestrial plant leaf wax *n*-alkane δ^2H values (δ^2H_{terr}) have also been found to be linearly correlated to the organisms source water δ^2H values, yet not in a 1:1 relationship (Sachse et al., 2012), indicating additional influences on δ^2H_{terr} values. Recent greenhouse experiments and field studies have revealed that in particular the evaporative ^2H enrichment of leaf water shapes δ^2H_{terr} values (Kahmen et al., 2013a; Kahmen et al., 2013b). Soil water evaporation in the upper soil layers has been shown to be less significant for δ^2H_{terr}, as plants usually access the deeper, isotopically unenriched, soil layers (Dawson, 1993). As such, δ^2H_{terr} is affected mainly by the δ^2H value of plant source water (i.e. precipitation), the biosynthetic fractionation and leaf water deuterium enrichment (Δ^2H_e) (Eq. (2)).

$$(2)\quad \delta^2H_{terr} = \delta^2H_{precip} + \Delta^2H_e + \varepsilon_{bio}$$

Systematic differences in δ^2H_{terr} values have been observed for different plant types (especially between grasses and trees) (Diefendorf et al., 2011; Kahmen et al., 2013b), possibly indicating differences in either ε_{bio} (Sachse et al., 2012) or the fraction of leaf water used for lipid biosynthesis (Kahmen et al., 2013b) or yet unidentified factors. As such, vegetation changes in sedimentary records have been suggested to affect δ^2H_{terr} values and "vegetation corrections" have been proposed (Feakins, 2013).

Since evaporative ^2H enrichment of leaf water only affects terrestrial plants but not aquatic organisms, changes in sedimentary δ^2H_{terr} (Sachse et al., 2006) can be seen as a record of variations in terrestrial evaporative ^2H enrichment over time. Thus, by combining Eq. (1) and (2) under the assumption that ε_{bio} of both aquatic and terrestrial organisms was constant on the temporal and spatial scales of sedimentary integration, the difference between δ^2H_{aq} and δ^2H_{terr} values should mainly reflect the evaporative ^2H enrichment of leaf water (Eq. (3)).

$$(3)\quad \Delta^2H_e = \delta^2H_{terr} - \delta^2H_{aq}$$

Variants of this concept (Sachse et al., 2004) have been used to qualitatively interpret changes in evapotranspiration through the isotopic difference between δ^2H_{terr} and δ^2H_{aq} (i.e. expressed as $\alpha_{TA/wat}$, δ^2H C_{23}–C_{31} and $\varepsilon_{terr\text{-}aq}$ (Jacob et al., 2007; Rach et al., 2014; Seki et al., 2011)). With recent progress in understanding of the determinants of δ^2H_{terr} values and the existing mechanistic understanding of the processes governing leaf water evaporative ^2H enrichment (Craig, 1965; Kahmen et al., 2011b; Sachse et al., 2012), we propose a new framework – which we term the dual-biomarker (DUB) approach - to extract quantitative hydrological information, namely changes in relative humidity (Δrh) from sedimentary records. To illustrate the power of this approach with paleohydrological data, we combine compound-specific hydrogen isotope measurements with plant physiological modeling on a previously published Late Glacial record of δ^2H_{aq} and δ^2H_{terr} from sediments of Lake Meerfelder Maar (MFM), Germany (Rach et al., 2014).

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2. Approach and Model

The DUB approach for quantifying changes in relative humidity from aquatic and terrestrial lipid biomarker δ^2H values is based on the assumption, that lake water evaporation is minimal in small catchment lakes from temperate regions (Sachse et al., 2006). δ^2H_{aq} can thus be regarded as a direct recorder of growing season average precipitation δ^2H values. We further argue that δ^2H_{terr} values largely reflect leaf water δ^2H values as has recently been demonstrated for greenhouse and field grown plants (Kahmen et al., 2013a; Kahmen et al., 2013b). Leaf water in turn is a function of the plant's source water and leaf water evaporative ^2H enrichment. We argue that soil water evaporation is negligible as recently suggested by several observational studies and a global assessment (Jackson et al., 1996; Jasechko et al., 2013; Kahmen et al., 2013a) and that precipitation is the ultimate water source of aquatic organisms and terrestrial plants. In terrestrial plants however, the source water becomes more enriched in deuterium due to plant transpiration before it is used for lipid biosynthesis. As such, the isotopic difference between δ^2H_{terr} and δ^2H_{aq} ($\varepsilon_{terr\text{-}aq}$) can be attributed to mean leaf water evaporative ^2H enrichment (Δ^2H_e) (Sachse et al., 2004). Based on recent field and greenhouse studies we further assume, that $\varepsilon_{terr\text{-}aq}$ captures a growing season signal, probably biased towards the earlier summer months in temperate climate zones as the majority of leaf waxes is produced during leaf development with suggested integrational periods between weeks (Kahmen et al., 2013b; Tipple et al., 2013) and several months (Sachse et al., 2015).

The major variables controlling leaf water isotope enrichment are well understood and mechanistic models have been developed based on the Craig-Gordon evaporation model (Craig, 1965) that allow to accurately predict or reconstruct leaf water Δ^2H_e values based on environmental and physiological input variables (Barbour, 2007; Farquhar et al., 2007; Ferrio et al., 2009; Kahmen et al., 2011b) (Eq. (4))

$$(4)\quad \Delta^2H_e = \varepsilon_+ + \varepsilon_k + (\Delta^2H_{wv} - \varepsilon_k)\frac{e_a}{e_i}$$

Δ^2H_e is determined by the equilibrium isotope fractionation between liquid and vapor (ε_+), the kinetic isotope fractionation during water vapor diffusion from the leaf intercellular air space to the atmosphere (ε_k), the ^2H depletion of water vapor relative to source water (Δ^2H_{wv}), and the ratio of atmospheric vapor pressure and intracellular vapor pressure (e_a/e_i) and air temperature (T_{air}). In addition, leaf temperature (T_{leaf}), stomatal conductance (g_s) and boundary layer resistance (r_b) are essential secondary input variables for the prediction of e_i and ε_k, respectively. Reformulating Eq. (4) allows expressing e_a as a function of Craig-Cordon variables (Eq. (5)). Since the atmospheric vapor pressure e_a can also be calculated based on rh and e_{sat} (Eq. (6)) we can merge Eq. (5) and (6) to calculate relative humidity (rh) and to estimate quantitative changes in rh (Δrh) (Eq. (7)).

$$(5)\quad e_a = \frac{e_i(\Delta^2H_e - \varepsilon_+ - \varepsilon_k)}{\Delta^2H_{wv} - \varepsilon_k}$$

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$$(6)\quad \mathrm{rh} = \frac{e_a \cdot 100\%}{e_{sat}}$$

$$(7)\quad \Delta\mathrm{rh} = \frac{e_i(\Delta^2 H_e - \varepsilon_+ - \varepsilon_k) \cdot 100\%}{e_{sat}(\Delta^2 H_{wv} - \varepsilon_k)}$$

Equation (7) illustrates that Δrh can be inferred from a record of past changes in Δ^2H_e (i.e. a record of $\varepsilon_{terr\text{-}aq}$) if the additional variables e_{sat}, e_i, Δ^2H_{wv}, ε_+ and ε_k can be constrained. In the following we discuss the model parameterizations necessary to apply the DUB approach to estimate quantitative changes in rh from sedimentary records.

Saturation vapor pressure e_{sat} (Eq. (8)) as well as the equilibrium fractionation factor ε_+ (Eq. (9)) are a function of temperature. The atmospheric pressure term (e_{atm}), which is also needed for calculation of e_{sat}, describes the atmospheric pressure depending on the elevation above sea level (0 meters = 1013 hPa).

$$(8)\quad e_{sat} = \frac{1.0007 + 3.46 \cdot e_{atm}[hPa]}{1000000} \cdot 6.1121 \cdot exp\left(\frac{17.502 \cdot T_{air}[°C]}{240.97 + T_{air}[°C]}\right)$$

$$(9)\quad \varepsilon_+ = \left[exp\left(\frac{24.844 \cdot 1000}{(273.16 + T_{air}[°C])^2} - \frac{76.248}{273.16 + T_{air}[°C]} + 0.052612\right) - 1\right] \cdot 1000$$

For accurate estimates of e_{sat} as well as ε_+ information on air temperature (T_{air}) during the growing season is thus required. Estimates of past T_{air} variability can be derived from paleotemperature proxy data to estimate e_{sat} and ε_+ (e.g. chironomids (Heiri et al., 2014; Heiri et al., 2007), MBT/CBT (Blaga et al., 2013)). In particular chironomid records, thought to represent spring and summer temperatures, provide an ideal proxy of past mean growing season temperatures in this respect (Heiri et al., 2007). Note that e_{sat} also depends on the atmospheric pressure (Eq. (8)), which can be estimated from elevation above sea level and is treated as a constant in the model. Leaf-internal vapor pressure e_i on the other hand is a function leaf temperature (T_{leaf}). We assume for our calculations that T_{air} is a good estimate of a growing season average T_{leaf} and e_i can thus be calculated as:

$$(10)\quad e_i = 6.13753 \cdot exp\left(T_{air}[°C] \cdot \frac{18.564 - \frac{T_{air}[°C]}{254.4}}{T_{air}[°C] + 255.57}\right)$$

We are aware that T_{leaf} can exceed air temperature in situations of extreme drought, when transpiration and evaporative cooling is reduced, or in bright and sunny conditions (Leuzinger and Korner, 2007; Scherrer et al., 2011). However, on cloudy days as well as on days with wind, T_{leaf} typically equals T_{air} (Jones, 2013). Given the spatial and temporal integration of leaves in sedimentary records (covering decadal to millennial timescales) it is thus unlikely that single drought events, where T_{leaf} would exceed

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T_{air} dominate the overall relationship between T_{leaf} and T_{air} and we thus assume that using T_{air} as a proxy for T_{leaf} introduces little error into our calculations.

Another parameter affecting leaf water isotope enrichment is the ^{2}H-depletion of water vapor relative to source water (Δ^2H_{wv}). In temperate climates liquid water and atmospheric water vapor are often in isotopic equilibrium, especially when longer (annual to decadal) timescales are investigated (Jacob and Sonntag, 1991). We therefore assume that Δ^2H_{wv} equals the equilibrium isotope fractionation between vapor and liquid ε_+.

$$(11)\quad \Delta^2H_{wv} = -\varepsilon_+$$

In the model, Δ^2H_{wv} can thus be replaced by $-\varepsilon_+$ (Eq. (11)).

The kinetic isotope fractionation (ε_k) depends on the plant physiological variables stomatal conductance (g_s) and boundary layer resistance (r_b) (Eq. (12)) (Kahmen et al., 2011b).

$$(12)\quad \varepsilon_k = \frac{16.4 \cdot \frac{1}{g_s[mol/m^2/s]} + 10.9 \cdot r_b[mol/m^2/s]}{\frac{1}{g_s[mol/m^2/s]} + r_b[mol/m^2/s]}$$

No direct proxies exist to reconstruct these plant physiological variables from sedimentary records, but paleovegetation data can be used to parameterize the model with biome-averaged values for g_s and r_b that are inferred from modern plants (Klein, 2014). We note that these plant physiological variables exert only minor control on the model outcome, expected to lie within the analytical error of δ^2H lipid measurements (Kahmen et al., 2011b), see also discussion below.

The latest iterations of leaf water models also include a Péclet effect, which describes the ratio of convectional versus diffusional flow of water in the leaf (Eq. (4))(Kahmen et al., 2011b). We did, however, not include the Péclet effect in our calculations because we assume that variations in the Péclet effect are minimal over time (Kahmen et al., 2009; Song et al., 2013) in particular for angiosperm species.

When combining Eq. (9), (10), (11) and (12) with Eq. (7), we obtain a model for Δrh that requires only four input variables: $\varepsilon_{terr\text{-}aq}$, air temperature (T_{air}) as well as literature-derived values for stomatal (g_s) and boundary layer conductance (r_b) to calculate Δrh:

$$(13)\quad \Delta rh = e_i'(T_{air}) \cdot \left(\frac{\Delta^2H_e}{-e_{sat}'(e_{atm}, T_{air})\left(\varepsilon_+'(T_{air}) + \varepsilon_k'(g_s, r_b)\right)} + \frac{1}{e_{sat}'(e_{atm}, T_{air})} \right) \cdot 100\%$$

Since we use $\varepsilon_{aq\text{-}terr}$ ($=\Delta^2H_e$) as an input variable, which is representative of leaf water isotope enrichment above source water and not absolute δ^2H leaf water values, Eq. (13) predicts changes in rh (Δrh) but not rh directly. In theory, Eq. (13) would also allow the calculation of rh values directly, if absolute δ^2H_{precip} and $\delta^2H_{leafwater}$ was available. The current lack of experimentally determined biosynthetic fractionation factors for the respective aquatic and terrestrial plants prevents this approach, but future experimental research may result in robust estimates of ε_{bio}, enabling the reconstruction of absolute rh values (Zhang et al., 2009).

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3. Uncertainties and sensitivity tests

Although the DUB approach for estimating Δrh is based on only four input variables, these variables still have to be derived from other proxies and our assumptions are associated with uncertainties. To evaluate the robustness of our DUB approach for predicting Δrh in the context of these uncertainties, we tested the sensitivity of the model to uncertainties in the four key input variables T_{air}, $\varepsilon_{terr\text{-}aq}$, g_s and r_b. In these sensitivity analyses we used a leaf water model, where all secondary variables (e_i, e_k,e_+,e_{sat}) are coupled to the primary input variables T_{air}, T_{leaf}, g_s and r_b (Kahmen et al., 2011b). We performed this test under a range of dramatically different climatic and ecological settings reflected by the climate conditions of Lista (Norway), Koblenz (Germany), Genoa (Italy) and Perth (Australia) that differ in mean growing season temperatures and prevailing vegetation types. While the vegetation in Norway and Australia is dominated by conifers and Mediterranean shrubland respectively, the prevailing vegetation in Germany and Italy are broad leaf tree species. As baseline values for the sensitivity tests we set T_{air} in the analyses to the growing season mean temperatures of each site, which was 9.4°C, 15°C, 17.2°C and 20.4°C for Lista, Koblenz, Genoa and Perth respectively (IAEA/WMO, 2006). Leaf water evaporative enrichment $\varepsilon_{terr\text{-}aq,}$ (Δ^2H_e) was set to 25‰ (Lista), 35‰ (Koblenz), 45‰ (Genoa) and 55‰ (Perth), which reflects average growing season leaf water enrichment values for the tested environments (Kahmen et al., 2013a). Base line data for plant physiological variables were biome typical estimates that we obtained from the literature (Jones, 2013; Klein, 2014): stomatal conductance (g_s) for Lista and Koblenz was set to 0.25 mol/m^2/s, while for Genoa and Perth the preset values were 0.45 and 0.35 mol/m^2/s, respectively (Klein, 2014). Boundary layer resistance (r_b) for Lista and Perth was set to 0.5 m^2s/mol, while for Koblenz and Genoa this variable was set to 1.0 m^2s/mol (Jones, 2013).

The temperature sensitivity tests were performed by increasing and decreasing the respective T_{air} values for a location by 0.5°C, 1°C, 2°C and 5°C. For the $\varepsilon_{terr\text{-}aq,}$ (Δ^2H_e) the respective $\varepsilon_{terr\text{-}aq,}$ (Δ^2H_e) values were varied by ± 5‰, 10‰, 15‰ and 20‰ for each location. The plant physiological variables (g_s and r_b) were varied by ±0.1, ±0.2, ±0.4 and in maximum by ±0.6 mol/m^2/s and ±0.6 m^2s/mol, respectively. These tested variations in plant physiological variables cover the expected variation in g_s and r_b for the local vegetation at a site.

The sensitivity analyses showed similar results for all four tested environments (Fig. 1). This suggests a similar behavior of the model under very different climate and ecological conditions. The DUB model is most sensitive to changes in $\varepsilon_{terr\text{-}aq}$ (i.e. Δ^2H_e) and T_{air}, while the plant physiological variables (g_s, r_b) showed only minor effects on Δrh (Fig 1). Specifically, a change of ±20‰ in $\varepsilon_{terr\text{-}aq}$ (i.e. Δ^2H_e) resulted in a change ±20% in Δrh. A ±5°C change in T_{air} resulted in a 3% change in Δrh. Varying g_s and r_b within the specified limits caused only changes in Δrh of 0.01 to 0.5% (Fig. 1), suggesting low model sensitivity to plant physiological variables. The difference in calculated Δrh for sites with low (e.g. Lista) and high (e.g. Perth) growing season mean temperature were smaller than the regional model sensitivity of the different input variables and are therefore negligible. Our sensitivity analyses shows that the most critical variables for estimating changes in relative humidity with our model are $\varepsilon_{terr\text{-}aq}$ and T_{air} (Fig 1).

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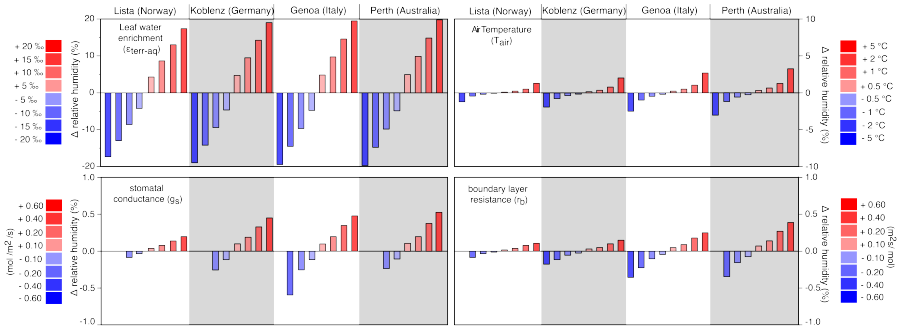

Fig 1. Sensitivity analyses for major model input variables ($\varepsilon_{terr\text{-}aq}$, T_{air}, g_s and r_b) on resulting Δrh values tested for four different climatic and ecological environments (Norway, Germany, Italy and Australia). Bars represent the effect on model output (Δrh) for each tested environment and its variation when the respective input variable will be varied by the marked value. Missing bars (i.e. for negative g_s and r_b) results from a bigger (negative) variation than the preset value (below 0).

4. Application: Reconstructing quantitative changes in Δrh during the Younger Dryas (YD) in Western Europe

To illustrate the potential of the DUB approach for estimating changes in rh over time, we applied the model using a previously published high-resolution dataset of δ^2H_{terr} and δ^2H_{aq} values from lake Meerfelder Maar (MFM) in W-Germany (Rach et al., 2014). This record was interpreted to depict significant hydroclimate variability during the onset and the termination of the Younger Dryas (YD) period in Western Europe between ca. 13.100 and 11.000 years BP. The availability of additional different proxy data, such as palynological data (Brauer et al., 1999a; Litt and Stebich, 1999), enables a robust parameterization of the DUB model for the MFM sediment record. In addition, annual varves and a high temporal sampling resolution (decades) allow the evaluation of the timing of climatic and ecosystem changes - an ideal setting to illustrate the power of the DUB approach. A detailed description of the record and the available proxy data are given in Rach et al. (2014). Briefly, the annually laminated sediments of MFM covering the YD period contain abundant aquatic (nC_{23}) and higher terrestrial (nC_{29}) lipid biomarkers (*n*-alkanes). Based on the pollen record, the nC_{23} alkane can be related to the aquatic submerged plant *Potamogeton sp.* and the nC_{29} alkane to leaves originating from the terrestrial angiosperm trees *Betula* sp. and *Salix* sp. with input from grasses (Brauer et al., 1999a; Diefendorf et al., 2011). For the DUB approach we use the isotopic difference between δ^2H values of the nC_{29} and of nC_{23} alkanes ($\varepsilon_{terr\text{-}aq}$) as a measure for leaf water ^2H enrichment (Δ^2H_e).

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288 **4.1 Model parameterization for the MFM application**

289 **4.1.1 Temperature**

290

291 Since, no paleotemperature proxy data are directly available for MFM, we use a high-resolution
292 chironomid based temperature reconstruction from a nearby location, lake Hijkermeer in the
293 Netherlands, ca. 300 km N of MFM (see the Appendix). The Hijkermeer record is interpreted as a
294 record of mean July temperatures for Western Europe with an mean error of about 1.59°C (Heiri et al.,
295 2007). Since leaf wax synthesis occurs most likely during the early part of the growing season (spring
296 and summer) (Kahmen et al., 2011a; Sachse et al., 2015; Tipple et al., 2013), the Hijkermeer record
297 might slightly overestimate spring temperatures. However, when reconstructing Δrh during the
298 Younger Dryas, it is important that paleotemperature data capture the changes in temperature before
299 and during that period, rather than absolute temperatures.

300

301 **4.1.2 Plant physiological parameters**

302

303 We estimated plant physiological variables (g_s and r_b) based on literature data from the prevalent
304 catchment vegetation inferred from available MFM pollen records (Brauer et al., 1999a; Litt and
305 Stebich, 1999). These suggest that *Betula sp*. and *Salix sp*. were the dominant nC_{29} producing taxa but
306 that grasses became more abundant during the YD (Brauer et al., 1999a; Litt and Stebich, 1999).
307 Reported g_s values for these species growing under humid to arid conditions today range from 0.1 to
308 0.5 mol/m^2/s and boundary layer resistance (r_b) values from 0.95 to 1.05 mol/m^2/s (Klein, 2014;
309 Schulze, 1982, 1986; Turner, 1984). As input variables for our modified model we therefore used mean
310 values, i.e. 0.3 mol/m^2/s for g_s and 1.0 mol/m^2/s for r_b. We used the variance of ± 0.2 mol/m^2/s for g_s
311 and ± 0.1 mol/m^2/s for r_b to calculate the error range of Δrh. We note the low sensitivity of the DUB
312 model outcome to variability in these variables (see Fig. 1, Appendix), as such that Δrh changes of less
313 that 0.1% result from varying g_s by 0.4 mol/m^2/s or r_b by 0.1 mol/m^2/s (Fig. 1).

314

315 **4.2 Estimation of uncertainty**

316

317 The estimation of uncertainty for Δrh is based on a linear error propagation (Eq. (16) - in the
318 Appendix) using specific error ranges for the individual input variables. For each input variable we
319 used their individual reported or estimated error (i.e. for chironomid interfered temperature
320 reconstruction: ± 1.5°C), for $\varepsilon_{aq\text{-}terr}$ the analytical uncertainty (standard deviation) of the respective
321 biomarker δ^2H measurements and for g_s and r_b the observed range of plant physiological parameters
322 between different species (g_s: 0.1-0.5 mol/m^2/s, r_b: 0.95-1.05 m^{2}s/mol). The resulting average error for
323 Δrh estimation during the investigated interval is 3.4% (see above and in the Appendix).

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328 **4.3 Model results for the YD period at MFM**
329
330 Applying the DUB approach to the Late Glacial MFM record we can for the first time estimate the
331 magnitude by which rh changed during a distinct period of abrupt climatic change in the past. Our
332 quantification revealed substantial changes in relative humidity (Δrh) on the order of 30% (Fig 2)
333 during the Late Glacial period, some of which occurred on multi-decadal timescales. To better illustrate
334 these changes we normalized our results to the mean of the period between 12.847 – 12680 BP (mean
335 Allerød) (Fig 2), which is thought to have been warmer and moister than the Younger Dryas (Hoek,
336 2009).
337 In particular, at the onset of the YD at 12.680 years BP, Δrh decreased by 13% +/- 3.4% over 112 years
338 compared to mean Allerød level (Fig. 2). During the YD (from 12.680-11.600 years BP) Δrh values
339 were on average 5% +/- 3.4% lower compared to the mean Allerød level. Furthermore in our high-
340 resolution dataset we observe a division of the YD into two distinct phases: the first part of the YD
341 (12.610-12.360 years BP) was characterized by low but relatively constant Δrh (variability between -
342 8% and -13% and a mean of -10%, compared to Allerød), whereas the variability in Δrh increases after
343 12360 years BP and ranges between -19% and +2% and a mean of -8% compared to Allerød mean
344 values (Fig. 2). Towards the termination of the YD we reconstructed a strong increase in Δrh (up to
345 +20% above the Allerød level) over only 80 years. This increase started about 100 years before the YD
346 – Holocene transition at 11.600 BP (Fig. 2), indicating that hydrological changes lead major ecosystem
347 changes, which formed the basis for the definition of the YD-Holocene boundary (Brauer et al., 1999a;
348 Brauer et al., 1999b). The onset of the Holocene was characterized by substantial variability in Δrh,
349 with a strong increase followed by a decrease to mean Allerød levels 150 years after the transition. The
350 reconstructed magnitude of changes, i.e. a ca. 9% reduction in rh during the YD constitutes a shift from
351 an oceanic to a dry summer climate, comparable to the difference in mean annual rh between Central
352 and Southern Europe today (Center for Sustainability and the Global Environment (SAGE), 2002; New
353 et al., 1999). The overall temporal pattern of reconstructed Δrh changes is in good agreement with
354 proxy data from western Europe (Bakke et al., 2009; Brauer et al., 1999a; Brauer et al., 2008; Goslar et
355 al., 1993), which indicate a shift to drier conditions due to a southward displacement of the westerly
356 wind system chanelling dry, polar air into Western Europe (Brauer et al., 2008; Rach et al., 2014).
357 Our approach reveals for the first time that substantial changes in rh of up to 20% can take place over
358 very short time scales, i.e. several decades, leading to substantial changes in terrestrial ecosystems.
359 While other proxy data reveal qualitative trends in aridification, our approach can be used to identify
360 hydrological thresholds. Applied to high-resolution records, such as annually laminated lake sediments,
361 the DUB approach can even be used to derive rates of hydrological changes and compare those with
362 associated ecological changes (i.e. pollen records).
363

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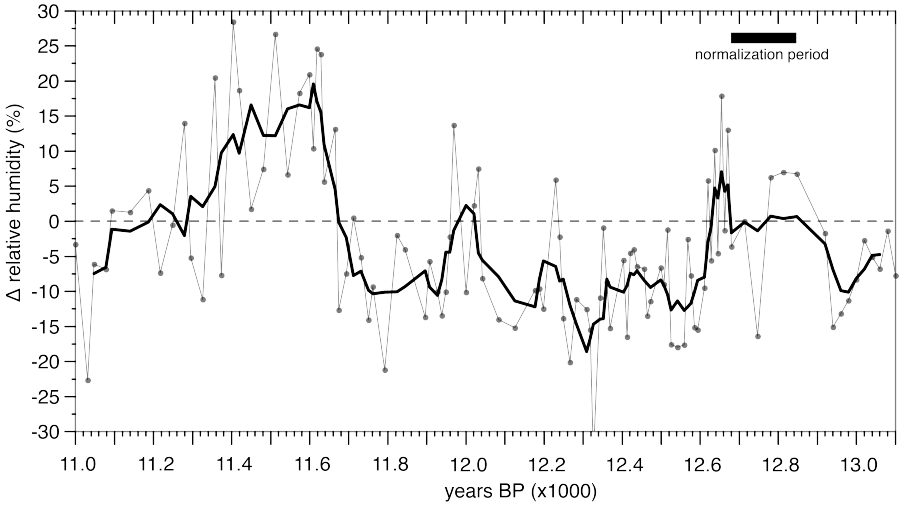

Fig 2. Variability of Δrh during the YD cold period at MFM. The data are normalized to mean Allerød level (12.847 – 12.680 years BP). The bold line marks the moving average.

4.4 The effect of vegetation change on $\varepsilon_{terr\text{-}aq}$ and the estimation of Δrh

Numerous studies have established that vegetation changes can also affect the sedimentary leaf wax δ^2H record, since significant differences in the net or apparent fractionation (ε_{app}) between source water and lipid δ^2H values exist among different plant types, in particular between monocot and dicot (all grasses) plants (Kahmen et al., 2013b; Tipple et al., 2013). Since the YD period at MFM was characterized by an increased amount of grasses, we tested, how vegetation changes may affect Δrh reconstructions through the DUB approach. For this we have developed two approaches to "correct" δ^2H_{terr} values, based on either a constant offset between monocot and dicot ε_{app} (Sachse et al., 2012) or a lower sensitivity of grass derived leaf wax δ^2H values to leaf water isotope enrichment (Kahmen et al., 2013b). Both approaches assume that palynological reconstructions are representative of leaf wax producing plants and that both monocots and dicots produce similar quantities of *n*-alkanes.

We used available palynological data to quantify the relative distribution of major tree vegetation (*Betula*, *Salix*) and grasses over the investigated period (Fig. 3B), expressed as the fraction of tress and grasses, f_{trees} and f_{grass}, assuming that leaf waxes and pollen share a similiar transport pathway in this small, constrained crater catchment.

4.4.1 Correction - case 1 – constant difference in ε_{app} between monocots and dicots

The first vegetation correction for reconstructed leaf water enrichment ($\varepsilon_{terr\text{-}aq}$*) is based on the assumption of a constant offset in biosynthetic isotope fractionation (ε_{bio}) between trees and grasses. Observational evidence shows that leaf wax lipid δ^2H values (δ^2H_{terr}) from C3 monocots are on average 34‰ more negative that from C3 dicots (non-grasses) when growing at the same site (Sachse et al.,

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2012). This value is based on an observed mean difference between apparent isotope fractionation (i.e. The isotopic difference between source water and leaf wax n alkanes, ε_{app}) values of C3 dicots (-111‰) and C3 monocots (-141‰) within a global dataset (Sachse et al., 2012).

The difference between monocot and dicot *n*-alkane δ^2H could potentially affect our modeled Δrh values, especially since an 23% increase in grass abundance in the MFM catchment during the YD has been suggested by pollen studies (Brauer et al., 1999a; Litt and Stebich, 1999).The causes for these differences in ε_{app} have been hypothesized to be due to species-specific differences in biosynthetic fractionation (Sachse et al., 2012) or temporal differences in leaf wax synthesis during the growing season (Tipple et al., 2013). Both scenarios would result in a more or less constant isotopic offset between monocots and dicots growing under the same climatic conditions.

Assuming a mean isotopic difference of -34‰ between trees and grasses (Sachse et al., 2012), we calculated a vegetation weighted correction value (-34*f_{grass}) for each data point. This value is then subtracted from $\varepsilon_{terr\text{-}aq}$, and results in the vegetation corrected $\varepsilon_{terr\text{-}aq}$* value (Eq. (14)). Similar approaches for a pollen based vegetation reconstruction have been recently proposed and applied (Feakins, 2013; Wang et al., 2013).

$$\varepsilon_{terr-aq}{}^{*} = \varepsilon_{terr-aq} - (-34 \cdot f_{grass}) \quad (14)$$

4.4.2 Correction - case 2: different sensitivity to leaf water isotope enrichment in dicot vs. monocot leaf wax δ^2H values

The second vegetation correction ($\varepsilon_{terr\text{-}aq}$**) is based on the assumption that the isotopic difference between monocot and dicot leaf wax n alkanes is not constant, but dependant on environmental conditions (Kahmen et al., 2013b). Previous greenhouse studies imply that the difference in ε_{app} between dicots and monocots is variable depending with a change in humidity conditions (Kahmen et al., 2013b). In a high humidity climate chamber treatment (80% rh) monocots and dicots showed similar values for ε_{app} (-220‰ and -214‰ respectively) whereas in a low humidity treatment ε_{app} for monocots was substantially lower compared to dicots (-205‰ and -125‰ respectively) (Kahmen et al., 2013b), a finding that is in disagreement with the two hypotheses proposed above. Rather, the latter study hypothesized that grasses use a mixture of enriched leaf water and unenriched xylem water for lipid synthesis (Kahmen et al., 2013b). This hypothesis would imply, that leaf wax *n*-alkane δ^2H values of monocots do not record the full magnitude of the evaporative leaf water enrichment signal, but only a fraction (Sachse et al., 2009). A recent greenhouse study on grass derived *n*-alkane δ^2H values of a broad spectrum of C3 and C4 grasses support this idea (Gamarra et al., 2016). Gamarra et al. suggest that the differences between *n*-alkane δ^2H values from grasses and *n*-alkane δ^2H values from dicotyledonous plants are caused by an incomplete transfer of leafwater Δ^2H to the *n*-alkanes. As such, also a sedimentary record of *n*-alkanes derived partly from grasses would underestimate mean ecosystem leaf water enrichment. Under dry conditions this fraction was estimated to be ca. 18% for C3 grasses, based on one grass species (Wheat) studied (Kahmen et al., 2013b). The data from Gamarra et al. show that for C3 grasses only 38 – 61% of the leaf water evaporative ^2H-enrichment

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signal (depending on the species) was transferred to leaf wax *n*-alkane δ^2H values. To work with a conservative value and not to overestimate a potential leaf water enrichment signal in grass dervied *n*-alkane δ^2H values we decided to use the data from Kahmen et al. (2013) for the wheat C3 grass. As such our correction approach would rather underestimate changes in relative humidity and represents as such the lower limit of reconstructed changes.

Under the assumption of different sensitivities to leaf water isotope enrichment of *n*-alkane δ^2H values in monocot and dicot plants (Kahmen et al., 2013b) we developed a correction for $\varepsilon_{terr\text{-}aq}$ based on the experimentally determined mixing ratio between leaf water and unenriched xylem water in wheat, a C3 grass (Kahmen et al., 2013b), essentially by weighing the fraction of grass cover with a factor of 0.18: (Fig. 3B) (Eq. (15)).

$$(15)\quad \varepsilon_{terr-aq}{}^{**} = \left(f_{trees} \cdot 1 + f_{grass} \cdot 0.18\right) \cdot \varepsilon_{terr-aq}$$

4.5 Comparison of results from uncorrected ($\varepsilon_{terr\text{-}aq}$) and corrected ($\varepsilon_{terr\text{-}aq}$*, $\varepsilon_{terr\text{-}aq}$) values**

Results from the raw (Δrh) and both vegetation corrected scenarios (Δrh* and Δrh**) are within the calculated error range of 3.4% of Δrh (Fig. 3A) during the Allerød and the Early Holocene, but diverge by up to 10% during the YD, when C3 grass vegetation was estimated to have increased from 28% to 52% in the catchment of MFM (Fig. 3B). Vegetation corrected results (case 1 Fig. 3A) showed on average a 7% stronger decrease for Δrh* and only a 2% stronger decrease for Δrh** compared to uncorrected results. As such Δrh** values (case 2) are within the error range of uncorrected Δrh during the entire record.

Interestingly, both correction approaches, but in particular case 2, level the relatively large variability in uncorrected Δrh at the onset and the termination of the YD, where abrupt vegetation changes occurred. For example, uncorrected Δrh changes were predicted to be up to 35% during the termination of the YD, corresponding to the modern gradient between western Europe and the semi-desert areas in northern Africa (Center for Sustainability and the Global Environment (SAGE), 2002). Vegetation corrected Δrh** values were on the order of 20%, seemingly more reasonably representing local Late Glacial changes (Fig. 3A).

Our analysis shows that vegetation changes have the potential to affect the DUB approach estimates, but a lacking mechanistic understanding of the causes of the differences in δ^2H_{terr} between tree and grass vegetation (Sachse et al., 2012) makes an assessment of the validity of either (or any) correction approach difficult. Tentatively, the lower variability in Δrh** within the YD as well as the less pronounced shift in particular at the onset and termination of the YD (Fig. 3A) provides are more realistic scenario. But as of now, we regard the differences in predictions as the error of quantitative predictions from the DUB approach. This uncertainty is larger during periods characterized by vegetation changes and in our case maximum differences in prediction of Δrh between the Allerød and the YD are on the order of 11% (mean Allerød vs mean YD difference between Δrh and Δrh*).

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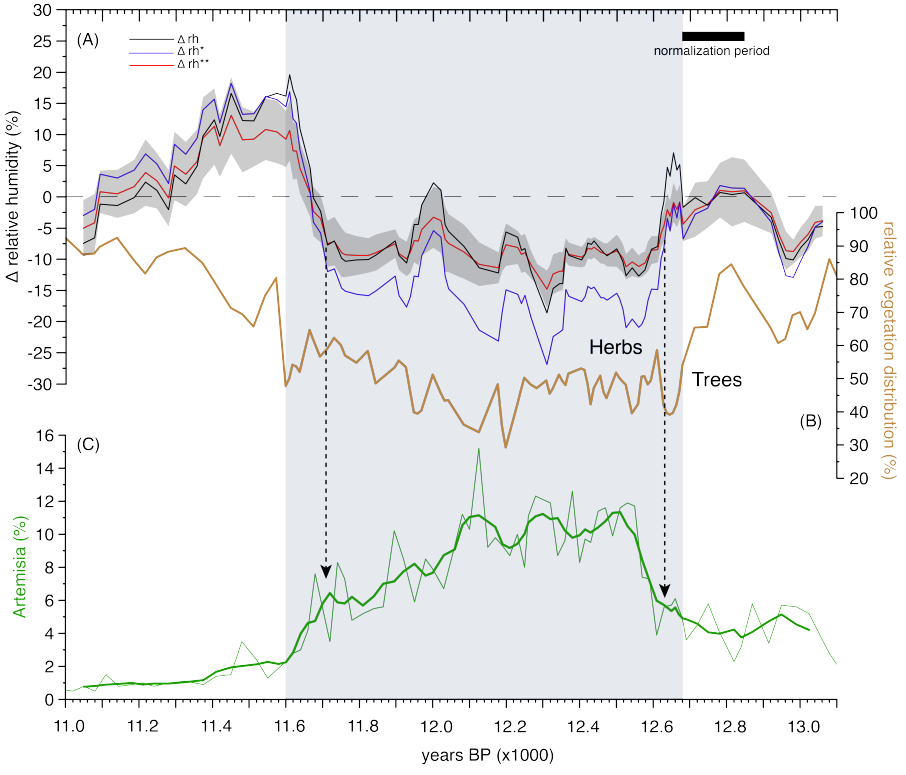

Fig. 3: (A) Reconstructed Δrh variability during the YD period, without vegetation correction (**black line, Δrh**) with vegetation correction assuming a constant offset between C3 dicots and C3 monocots (**blue line, Δrh*),** with vegetation correction assuming different leaf water sensitivities among grasses and trees (**red line, Δrh****). The shaded area marks the error range for Δrh**. **(B)** relative distribution of trees and grasses in the catchment of MFM during the YD from pollen studies (Brauer et al., 1999a; Litt and Stebich, 1999). **(C)** Occurrence of Artemisia pollen in the catchment of MFM during YD (Brauer et al., 1999a; Litt and Stebich, 1999). Arrows highlight the contemporaneous major changes in Δrh and *Artemisia*.

4.6 Comparison of reconstructed Δrh with other proxy data

We can further demonstrate the validity of our approach by direct comparison to other hydroclimate proxies from the MFM record. For example, a classical palynological marker for more arid conditions is *Artemisia* pollen (D'Andrea et al., 2003). In the MFM catchment a prominent increase in the occurrence of *Artemisia* has been used to infer dryer conditions during the YD (Fig. 3C) (Brauer et al., 1999a; Litt and Stebich, 1999), (Bremer and Humphries, 1993; D'Andrea et al., 2003). When comparing the abundance of *Artemsia* pollen % (note that the *Artemisia* abundance data are not part of the vegetation corrections discussed above) to the DUB Δrh record, we observed striking similarities over the whole of the study period (Fig. 3A,C). Inferred wetter conditions during the second phase of

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the YD, or centennial scale excursions to higher Δrh (such as between 12280 and 12170 years BP) go in line with lower *Artemisia* pollen abundance after 12.100 BP. In fact, both independent datasets show an inverse, statistically significant relationship ($p < 0.001$) (Fig. 4A-C), with high *Artemisia* pollen abundance during periods of low Δrh values (Fig. 3A,C). The correlation between Δrh and *Artemisia* is higher for vegetation corrected Δrh* and Δrh** (Fig. 4B,C) than uncorrected Δrh and in particular for Δrh** the variance of the dataset is greatly reduced (Fig. 4C), providing support for the hypothesis that vegetation changes could have affected the record.

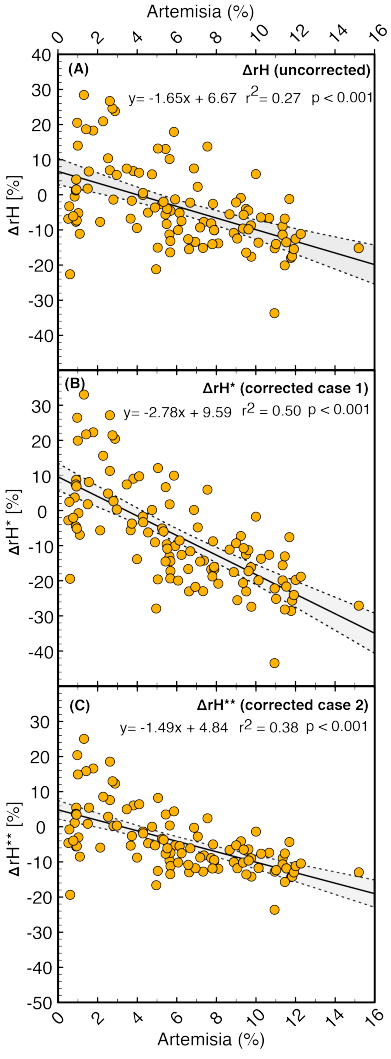

Fig. 4: Correlation plots of normalized reconstructed Δrh vs. *Artemisia* population. (**A**) uncorrected Δrh values vs. *Artemisia*. (**B**) vegetation corrected Δrh values (Δrh*) vs *Artemisia*. (**C**) Vegetation corrected Δrh values (Δrh**) vs *Artemisia*.

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5. Conclusions

We present a novel approach for quantifying paleohydrological changes (i.e. changes in relative humidity) combining sedimentary lipid biomarker δ^2H values from aquatic and terrestrial lipids with mechanistic leaf water isotope modeling. This dual-biomarker approach (DUB) relies on the observation that aquatic and terrestrial organisms within the catchment of small lakes from temperate climate zones use distinct water sources, namely lake (i.e. precipitation) and ^2H-enriched leaf water as a source for their organic hydrogen. By taking advantage of the mechanistic understanding of and available models on leaf water isotope enrichment in terrestrial plants, we show it is possible to extract quantitative information about changes in relative humidity from sedimentary records.

Parameterizing and applying the DUB model to a lacustrine lipid biomarker δ^2H record from western Europe, we find strong and abrupt changes in rh at the onset and the termination of the YD occurring within the lifetime of a human generation. Specifically, our approach showed that shifts in rh of up to 13% +/- 3.4% occurred within only 112 years. This dramatic change corresponds to shifts in average biome rh from oceanic to dry summer climates. Our quantification showed that dry conditions prevailed during the Younger Dryas period with rh being between 8 and 15% lower on average compared to the Allerød, depending on how the possible effect of vegetation changes is accounted for. The pattern but also the magnitude of our rh reconstruction agrees well with other proxy data, such as the increase in the abundance of specific taxa adapted to dry conditions (e.g. *Artemisia*) during that time period.

Our analyses shows that the DUB approach is capable of quantifying past hydrological changes in temperate environments, when additional proxy data, especially on vegetation distribution and paleotemperature exist. We suggest that this approach can be particularly valuable in the future for the validation of climate models and to better understand uncertainties in predictions of future hydrological change under global warming.

Appendix

Error propagation

The uncertainty estimation (Δf, Eq. (16)) for the reconstructed Δrh variability is based on a linear error propagation, which is the most conservative method for error estimations. This Method does not require the same kind of the considered errors and provides therefore the possibility to combine different kinds of errors with their specific ranges (i.e. measuring error, counting error, etc.). The individual error ranges of the independent variables in our approach arise from different sources such as analytical errors (chironomid interfered temperature reconstruction: ± 1.5°C), observed variations of plant physiological parameters between different species (stomatal conductance: 0.1-0.5 mol/m^2/s, boundary layer resistance: 0.95-1.05 m^{2}s/mol) and standard deviation of δ^2H measurements of terrestrial and aquatic *n*-alkanes.

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The specific uncertainty for $\varepsilon_{terr\text{-}aq}$** was preliminary determined by a separate error propagation using the (analytical) standard deviation of the triplicate measurements of the sedimentary *n*-alkane δ^2H values as well as the plant derived *n*-alkane δ^2H measurements by Kahmen et al 2013. The results of these separate error estimation were integrated into the general error estimation of Δrh**.

In contrast to the linear error propagation a less conservative method (Gaussian error propagation) requires a similarity of the errors, i.e. all errors are measurement or counting errors, which is not the case in this study. The mean error when using the Gaussian method is however only 3.2% and therefore only 0.2% smaller than the calculated error using the linear propagation.

$$(16)\quad \Delta f = \left|\frac{\partial rh}{\partial \varepsilon_{terr-aq}}\right| \cdot \Delta {\varepsilon_{terr-aq}}^{**} + \left|\frac{\partial rh}{\partial r_b}\right| \cdot \Delta r_b + \left|\frac{\partial rh}{\partial g_s}\right| \cdot \Delta g_s + \left|\frac{\partial rh}{\partial T_{air}}\right| \cdot \Delta T_{air}$$

Temperature data

The temperature data used for the DUB model parameterization of the MFM case were taken from ref. 35 and constitute reconstructed summer temperatures based on chironomid analyses from Hijkermeer (NL) (Heiri et al. (2007)), which, to our knowledge, constitutes the closest lateglacial paleotemperature record to the MFM site (distance 311km). However, the dataset of the Hijkermeer consists only of 37 data-points between 13.000 BP and 11.000 BP with a temporal resolution varying between 26 to 167 years /sample. Therefore, we determined a new equidistant time-series for the temperature data, fitting data-volume and temporal resolution of our Δ^2H_e record from MFM (106 data-points with an 8 to 33 year-resolution). For calculating the equidistant time series we were using method "interpl" with the specification "linear" in MATLAB (version R2010b).

Vegetation data

Information about Lateglacial vegetation-cover in the catchment area of MFM is based on palynological analyses (Brauer et al. (1999), Litt & Stebich (1999)). We used Pollen percent data also for determining the vegetation distribution between trees and grasses for each datapoint. For using these vegetation data in our model it was necessary to determine an equidistant time-series according to age model of our Δ^2H_e values. For calculating these time series we used also method "interpl" with the specification "linear" in MATLAB (version R2010b).

Author contributions

Oliver Rach conducted model modifications, calculations and wrote the paper. Ansgar Kahmen provided the basic leaf water enrichment model and was responsible for plant physiological part and contributed in writing the paper. Achim Brauer was responsible for lake coring, provided the chronology and stratigraphy for Younger Dryas hydrological reconstruction and wrote the paper. Dirk Sachse conceived the research, acquired financial support and wrote the paper.

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Competing financial interests

The authors declare no competing financial interests.

Acknowledgements

This work was supported by a DFG Emmy-Noether grant (SA1889/1-1) and an ERC Consolidator Grant (No. 647035 *STEEP*clim) to D.S. It is a contribution to the INTIMATE project, which was financially supported as EU COST Action ES0907 and to the Helmholtz Association (HGF) Climate Initiative REKLIM Topic 8, Rapid climate change derived from proxy data, and has used infrastructure of the HGF TERENO program.

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Clim. Past Discuss., doi:10.5194/cp-2017-7, 2017
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