The stable hydrogen isotopic composition of sedimentary plant waxes as quantitative proxy for rainfall in the West African Sahel

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Abstract

Various studies have demonstrated that the stable hydrogen isotopic composition (δD) of terrestrial leaf waxes tracks that of precipitation (δDprecip) both spatially across climate gradients and over a range of different timescales. Yet, reconstructed estimates of δDprecip and corresponding rainfall typically remain largely qualitative, due mainly to uncertainties in plant ecosystem net fractionation, relative humidity, and the stability of the amount effect through time. Here we present δD values of the C31 n-alkane (δDwax) from a marine sediment core offshore the Northwest (NW) African Sahel covering the past 100 years and overlapping with the instrumental record of rainfall. We use this record to investigate whether accurate, quantitative estimates of past rainfall can be derived from our δDwax time series. We infer the composition of vegetation (C3/C4) within the continental catchment area by analysis of the stable carbon isotopic composition of the same compounds (δ13Cwax), calculated a net ecosystem fractionation factor, and corrected the δDwax time series accordingly to derive δDprecip. Using the present-day relationship between δDprecip and the amount of precipitation in the tropics, we derive quantitative estimates of past precipitation amounts. Our data show that (a) vegetation composition can be inferred from δ13Cwax, (b) the calculated net ecosystem fractionation represents a reasonable estimate, and (c) estimated total amounts of rainfall based on δDwax correspond to instrumental records of rainfall. Our study has important implications for future studies aiming to reconstruct rainfall based on δDwax; the combined data presented here demonstrate that it is feasible to infer absolute rainfall amounts from sedimentary δDwax in tandem with δ13Cwax in specific depositional settings.

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1. INTRODUCTION

The stable hydrogen isotopic compositions (δD) of sedimentary higher-plant leaf waxes (δDwax) are linked to the δD value of precipitation (δDprecip; summarized by Sachse et al., 2012), and multiple studies have employed δDwax to infer past changes in Northwest (NW) African rainfall (Schefuß et al., 2005; Niedermeyer et al., 2010; Collins...
et al., 2013; Kuechler et al., 2013). In the tropics, the δD value of precipitation (δD_{\text{precip}}) is linked primarily to rainfall intensity (i.e. via the “amount effect”; Dansgaard, 1964; Rozanski et al., 1993), with decreasing values of δD_{\text{precip}} associated with increasing rates of precipitation. This information is recorded in higher-plant leaf waxes, with a fractionation between δD_{\text{precip}} and δD_{\text{wax}} due to metabolic isotope effects. The magnitude of this apparent fractionation, however, differs between plants, a fact that complicates the accurate, quantitative reconstruction of absolute rainfall amounts based on δD_{\text{wax}}. The conventional explanation is that this difference in apparent stable hydrogen isotope fractionation is a function of plant-morphological types (see Sachse et al., 2012), although more recent work suggests a phylogenetic origin (Gao et al., 2014a). Differences in stomatal conductance during photosynthesis and associated variance of leaf water enrichment through leaf transpiration, together with specific carbon allocation strategies of different plants are thought to be of particular importance in this regard (Smith and Freeman, 2006; McInerney et al., 2011; Kahmen et al., 2013a,b; Gao et al., 2014a). Such effects may be of particular importance in arid to semi-arid climates (Feakins and Sessions, 2010a, b), together with evaporative soil water enrichment under low ambient relative humidity. In addition, changes of precipitation source through time and its isotopic composition (e.g. through changes in atmospheric circulation or glacial-interglacial changes in ice volume) exert additional control on δD_{\text{precip}} that is not linked to the amount effect. As all these variables are difficult to assess in the paleorecord, δD_{\text{wax}}-based estimates of past rainfall changes have thus far remained mostly qualitative, i.e. “more” vs. “less” rainfall.

Strictly speaking, the amount effect is a measure of the amount of rainfall during individual precipitation events with rainfall intensity controlling re-evaporation, and, as a consequence, isotopic enrichment of the falling rain (Dansgaard, 1964; Rozanski et al., 1993; Worden et al., 2007; Lee and Fung, 2008; Risi et al., 2008a,b). This effect generally leads to lower δD values (that is stronger D-depletion through reduced re-evaporation) in areas of high precipitation and higher values (D-enrichment through higher re-evaporation) when precipitation is low. This relationship has been found to average -4‰ mm^{-1} day^{-1} (Bony et al., 2008) based on nine tropical marine GNIP (Global Network of Isotopes in Precipitation) stations. Recent studies indicate that e.g. the rainout history of monsoonal moisture (or changes in large-scale atmospheric circulation in general) may exert additional control on local δD_{\text{precip}} (e.g. Dayem et al., 2010; Pausata et al., 2011). This seems to be of particular importance in the equatorial Indo-Pacific realm, whereas the isotopic composition of incoming vapor remains relatively constant in sub-tropical coastal regions (Lee and Fung, 2008).

Sedimentary δD_{\text{wax}} values integrate δD_{\text{precip}} of multiple rainfall events by the formation leaves and associated leaf-wax production (Richardson et al., 2005). Multiple studies show that leaf waxes are produced (and replaced) continuously during the growing season (Pedentchouk et al., 2008; Sachse et al., 2009; Gao et al., 2012, 2015; Gao and Huang, 2013), fuelling debate on whether δD values of leaf waxes in soils represent δD_{\text{precip}} of the last weeks before leaf senescence rather than an integrated record of the growing season. In contrast, other studies indicate little or no wax production after a leaf is fully developed (Sachse et al., 2010; Kahmen et al., 2011a; Tipple et al., 2013). However, as multiple leaves are being produced at different times during the growing season, and as leaf waxes are eroded throughout the rainy season (Baker and Hunt, 1986), sedimentary δD_{\text{wax}} is most likely indicative of the amount of rainfall received during the growing season.

Changes in the amount of rainfall can be associated with changes in both rainfall intensity as well as wet season length. For example, the present-day variability of western Sahel hydroclimate is dominated by the amount of rain that falls during the rainy season rather than by wet-season length or abnormal rainfall during the dry season (Nicholson et al., 2013). On the other hand, long-term changes in western Sahel rainfall such as those induced by millennial-scale ITCZ (intertropical convergence zone) migration and tropical rain belt position have resulted in both changes in rainfall intensity and wet season length (Niedermeyer et al., 2010).

The stable carbon isotopic composition of sedimentary leaf waxes (δ^{13}C_{\text{wax}}) has proven to be a valuable measure of the underlying type of vegetation (C_{3} or C_{4} photosynthetic pathway; Huang et al., 2000; Schefuß et al., 2003; Vogts et al., 2012). Although this does not account for all possible changes in vegetation – in particular the large variability within C_{3} plants (trees, shrubs, C_{3} grasses etc.) cannot be resolved – it nevertheless reflects vegetation changes in semi-arid to arid settings such as NW Africa reasonably well. This is because here, the major plant types contributing leaf waxes to the sedimentary record are tropical grasses (C_{4}) together with shrubs and trees (both C_{3}). As the abundance of C_{4} plants is sensitive to wet season length and wet season temperature (winter vs. summer rain), both wet season intensity and wet season length can potentially be reconstructed from δ^{13}C_{\text{wax}} (Ehleringer et al., 1997; Niedermeyer et al., 2010; Collins et al., 2013). It is however noteworthy that in the past (e.g. during the last glacial) changes in atmospheric CO_{2} concentration may have affected the C_{3}/C_{4} composition of Sahel vegetation (Ehleringer et al., 1997), introducing a potential bias on inferred changes in rainy season length.

Despite the multiple controls on leaf wax δD values, several studies have attempted to quantify δD_{\text{precip}} from sedimentary δD_{\text{wax}} records. Tierney et al. (2010b) corrected their δD_{\text{wax}} record from Pleistocene sediments from Lake Tanganyika (East Africa) for changes in global ice volume and applied a constant apparent D-fractionation factor for vegetation to derive values of δD_{\text{precip}}. They infer a minor impact of vegetation change at their site on δD_{\text{wax}} but suggest changes in relative humidity over time to be the most critical variable amplifying the amount effect. Feakins (2013) and Feakins et al. (2012) in turn accounted for changing vegetation by pairing δD_{\text{wax}} with pollen and δ^{13}C_{\text{wax}} analysis in Miocene records from the Gulf of Aden and Antarctica. Based on their estimate of vegetation composition through time, they calculated time-varying
net ecosystem fractionation factors and converted their $\delta D_{\text{wax}}$ time series accordingly to infer past $\delta D_{\text{precip}}$. Collins et al. (2013) accounted for changes in $C_3/C_4$ vegetation over time and removed the effect of biosynthetic fractionation from their $\delta D_{\text{wax}}$ record using estimates based on $\delta^{13}C_{\text{wax}}$. Applying modern-day relationships between $\delta D_{\text{precip}}$ and precipitation amount, they provided estimates of past of rainfall anomalies along a N-S transect in West Africa on millennial timescales. They conclude that the most critical variable in their approach is uncertainty about the stability of the $\delta D_{\text{precip}}$-amount effect relationship through time, in particular during the last glacial.

In this study, we test the accuracy of combined analysis of $\delta D_{\text{wax}}$ and $\delta^{13}C_{\text{wax}}$ in tandem with the present-day amount effect to reconstruct total amounts of past precipitation in NW Africa. We use a marine sediment core from offshore Senegal (West African Sahel) covering the past 100 years that overlaps with the instrumental record of rainfall in the catchment area. We estimate changes in vegetation using $\delta^{13}C_{\text{wax}}$, calculate the corresponding ecosystem apparent $D$-fractionation, and convert the $\delta D_{\text{wax}}$ time series accordingly to derive $\delta D_{\text{precip}}$. Our data reveal an accurate quantitative match with the instrumental record of precipitation in the western Sahel during the past 100 years.

2. STUDY AREA

2.1. Western Sahel precipitation and vegetation

The African Sahel is a semi-arid ecosystem in tropical North Africa. It stretches from the Red Sea in the East to the Atlantic coast in the West forming a latitudinal band of varying width between 10 and 20°N. Climate of the western Sahel is characterized by seasonal rainfall brought by the West African monsoon. Total annual rainfall (Fig. 1) and duration of the rainy season increase from the Sahara desert (0–100 mm year$^{-1}$) to the equatorial Guinea coast (>3000 mm year$^{-1}$). Maximum precipitation over the western Sahel occurs from July to September, followed by a dry season for the rest of the year (Nicholson, 2013). Vegetation of the Sahel forms the transition between the Sahara desert in the North and the humid Savannah to the South (Fig. 1). It is characterized by decreasing drought tolerance with decreasing latitude, and comprises both semi desert grassland (100–250 mm year$^{-1}$) dominated by $C_4$ grasses and dry savannah (250–500 mm year$^{-1}$) with sporadic $C_3$ trees and shrubs. Towards the North, landscapes include large grassland steppe plains, intermixed with small seasonal water ponds sustaining evergreen and semi-deciduous dense vegetation cover. Southward, increased annual rainfall permits establishment of a mosaic of woodland and savannah vegetation with evergreen forests along perennial water bodies. On a local scale, land cover is influenced by human activity such as agricultural clearing and charcoal production as well as livestock grazing (Mbow et al., 2015).

From the 1970s to early 1980s, the African Sahel experienced a pronounced period of drought. The severe aridification caused starvation of about 1 million people and 40–50% of the domestic livestock perished. Vegetation cover was reduced during the drought, however, a re-greening of the Sahel has been observed since (Eklundh and Olsson, 2003; Anyamba and Tucker, 2005; Olsson et al., 2005; Nicholson, 2013).

2.2. Defining the catchment area of terrestrial plant waxes

Depending on the season, terrestrial plant waxes can be transported to the marine environment via aeolian dust or by fluvial discharge (e.g. Huang et al., 2000; Eglinton et al., 2002; Schefuß et al., 2003, 2004; Vogts et al., 2012). During the wet period, leaf waxes are eroded by rain (Baker and Hunt, 1986) and flushed into the ocean by fluvial runoff of the Senegal River. During the dry season in turn, when the rivers are dry, plant waxes are mobilized via both soil deflation and abrasion by dust grains and blown offshore (Huang et al., 2000; Schefuß et al., 2003).

2.2.1. Northernmost source of plant waxes

Due to the northeasterly trade winds that prevail over NW Africa during the dry season (Sarmthein et al., 1981), the northernmost source of plant-wax contribution is set by the direction and angle of wind vectors during northern hemisphere winter. We consider the most important wind fields to be those at the onset of the dry season as this is when leaf waxes are still abundant. At the onset of the dry season (October; Supplementary Fig. 1), wind vectors over the study site are steepest, oriented almost parallel to the NW African coast. As the steepest angle of wind sets the northernmost possible source of plant waxes, we anticipate plant wax sourcing of up to 17°N which, on average, is the northernmost extension of vegetation before it transitions into the Sahara Desert (Tucker and Nicholson, 1999). We do not expect significant contribution of leaf waxes from vegetation sources North of the Sahara, as $Pinus$ pollen (an indicator for plant contribution from northernmost Africa) are absent in marine core top sediments at our study site (Hooghiemstra and Agwu, 1986).

2.2.2. Southernmost source of plant waxes

The southernmost extension of the catchment is set by the Senegal River drainage basin and sediment mixing on the shelf. We presume that plant waxes transported by the river that make it to the marine environment are dominantly sourced from vegetation and soils along its final course towards the ocean. In addition, due to strong coastal currents (Mittelstaedt, 1991), additional plant wax contribution to the study site from marine sediment dispersion south of the river mouth must be considered. We therefore set the southernmost limit of plant waxes derived by sediment mixing and lateral advection to 14.5°N. This is where the continental tip of Dakar separates the NW African shelf into a northern and a southern segment.

In summary, we infer a catchment extending latitudinally from 14.5°N to 17°N (Fig. 1). The easternmost extension of the catchment, in turn, cannot be defined precisely. However, it has been shown that plant waxes transported by the low-level northeasterly trade winds represent the vegetation underlying the final section of the air-mass trajectory before
offshore transport (Simoneit et al., 1989; Schefuß et al., 2003). Due to the latitudinal, homogeneous zonation of vegetation and precipitation and \( \delta^{18}D_{\text{precip}} \) (compare Fig. 1) we consider the precise eastern termination of the catchment inconsequential for the purpose of our study and set an arbitrary limit of 500 km from the coastline (11.5°W).

### 2.3. \( \delta^{18}D_{\text{precip}} \) in the catchment area

\( \delta^{18}D \) values of rainfall in the catchment area are driven by rainfall intensity (”amount effect”; Dansgaard, 1964; Rozanski et al., 1993; Worden et al., 2007; Risi et al., 2008a,b), exhibiting decreasing values of \( \delta^{18}D_{\text{precip}} \) with increasing rainfall amount (Fig. 1). As there is no instrumental record of \( \delta^{18}D_{\text{precip}} \) that covers the time span of our record, and as the spatial coverage of weather stations that continuously monitor both precipitation and \( \delta^{18}D_{\text{precip}} \) within the catchment area is poor (compare Fig. 1), we provide a seasonal mean \( \delta^{18}D \) value of modern-day precipitation as derived from the waterisotopes.org database (Bowen and Revenaugh, 2003). This value represents an interpolated, precipitation-amount weighted mean \( \delta^{18}D_{\text{precip}} \) and serves as a reference to compare with reconstructed values of \( \delta^{18}D_{\text{precip}} \) in Section 5.3.

### 3. MATERIALS AND METHODS

#### 3.1. Sediment core

Marine multicore GeoB9501-4 was retrieved from the continental shelf off NW Africa (16°50’N, 16°44’W), approximately 50 km north of the Senegal River mouth at
3.2. Plant wax n-alkane extraction, separation and quantification

3–6 g of freeze-dried, finely ground sediment were extracted in an accelerated solvent extractor (ASE-200, Dionex) at 1000 psi and 100 °C using a 9:1 (v/v) mixture of dichloromethane (DCM) and methanol (MeOH). An internal standard (squalane) was added to the total lipid extracts (TLE), which were subsequently dried via rotary evaporation. Asphaltenes were removed from the TLE by elution over a Na2SO4 pipette column with n-hexane. The hexane soluble fraction was dried again and then saponified with 6% KOH in MeOH at 85 °C for 2 h. This step was included to disintegrate the complex plant-wax matrix in order to free n-alkanes embedded in alcohol-fatty acid esters (for further information on the chemistry of plant waxes see Koch and Enskat, 2008). Then, 2 mL of milliQ water were added and neutral lipids (NL) were extracted with hexane (3×) from the aqueous alkaline solution. Alkanes were isolated from the NL by silica-gel column chromatography (Silica 60, Merck) using hexane, and further purified by AgNO3-silica column chromatography again using hexane as eluent to obtain saturated hydrocarbon fractions.

n-Alkanes were analyzed by gas chromatography/flame ionization detection (GC/FID) on an Agilent HP 5890 II equipped with a Restek Rxi 5 ms column (30 m × 0.25 mm × 0.25 μm). The injector was operated in splitless mode at 300 °C. The GC oven was held at 60 °C for 2 min, ramped to 150 °C at 20 °C min⁻¹, and was then ramped at 4 °C min⁻¹ to a final temperature of 320 °C, which was held for 11 min. Target compounds were identified by comparing their retention times to a standard mixture containing the corresponding n-alkanes. n-Alkane abundances were quantified using the FID peak areas calibrated against an external n-alkane standard. The precision of GC/FID quantification is within 5% based on replicate analyses of the n-alkane standard throughout the course of the study. The carbon preference index (CPI) was calculated after Bray and Evans (1961).

3.3. Isotope analyses

Because of the low abundance of individual plant-wax n-alkanes, successive pairs of samples were combined (e.g. samples 2 + 3, 4 + 5, etc.) for δD and subsequent δ13C analysis. For most samples, duplicate analysis was achieved.

3.3.1. δD measurements

The δD values of individual n-alkanes were measured using a Thermo Trace GC ULTRA coupled to a Thermo Finnigan DELTA+ XP isotope-ratio mass spectrometer via a pyrolysis furnace operated at 1430 °C at the California Institute of Technology in Pasadena, USA. The GC oven was equipped with a Zebran ZB-5 ms column (30 m × 0.25 mm × 1 μm; Phenomenex). The GC oven was programmed at 100 °C for 20 s, ramped at 20 °C min⁻¹ to 200 °C, ramped at 2 °C min⁻¹ to 240 °C, at 5 °C min⁻¹ to 320 °C which was held for 10 min, and then ramped at 5 °C min⁻¹ to a final temperature of 340 °C which was held for 20 min. Data processing and the H2+ correction were done using Isodat v2.2 software as described by Sessions et al. (2001) using a H2 reference gas with known hydrogen isotopic composition.

To monitor system performance, a CH4 reference gas was measured with every sample run, revealing a mean deviation from the known δD value of 5‰ and a precision of 2‰ (n = 48). Replicate analysis of the internal standard (squalane) across all measurements corroborated a precision of 2‰ (n = 49). All δD values are reported as permil (‰) deviations from the VSMOW standard.

3.3.2. δ13C measurements

δ13C values of individual n-alkanes were measured at the Center for Marine Environmental Sciences (MARUM) in
Bremen, Germany. A Thermo Trace GC Ultra equipped with an Agilent DB-5 column (30 m × 0.25 mm × 0.25 μm) and coupled to a Finnigan MAT 252 via a modified combustion interface operated at 1000 °C was set at 120 °C for 3 min and then ramped at 5 °C min⁻¹ to a final temperature of 320 °C which was held for 15 min. Data processing was done using Isodat software v3.0 using a CO₂ reference gas with known isotopic composition. A standard mixture containing 14 compounds was measured every six samples and yielded a mean standard deviation of 0.1‰ (n = 11) with a mean deviation from the known δ¹³C values of 0.4‰. The internal standard (squalane) showed a mean standard deviation of 0.1‰ (n = 49) with a mean deviation from the known δ¹³C value of 0.3‰. Samples were run in duplicate; the difference between duplicate runs on average was 0.1‰. All δ¹³C values are reported in permil (‰) relative to the VPDB standard.

3.4. Instrumental record of precipitation in the catchment area

Annual mean precipitation of the catchment area was taken from the CRU TS3.22 dataset (New et al., 1999; Harris et al., 2014). This dataset is a gridded time-series of mean monthly meteorological variables interpolated from a global compilation of weather station records. For simplicity, we hereafter refer to the gridded time-series as “instrumental record”.

80–90% of the total annual precipitation within the catchment area occurs during the rainy season from July to September, with only little or no rainfall throughout the rest of the year. We therefore consider rainfall amounts during the rainy season as representing annual mean rainfall. We note that comparing a reconstruction of seasonal rainfall (this study) with annual mean rainfall amounts (instrumental record) may introduce a level of inaccuracy as 10–20% of total annual precipitation may fall outside the rainy season. However, interannual changes regarding the exact onset and end of the rainy season in the instrumental dataset lead to an underestimation of the true amount of rainfall during the rainy season, which is calculated using a fixed analytical JAS window. We therefore chose the instrumental record of annual mean rainfall for comparison with our reconstruction of seasonal rainfall.

Previous studies have demonstrated that wetting or drying of the western Sahel depends on rainfall intensity during the wet season rather than on its duration or exceptional rainfall during the dry season (Nicholson, 1981; Dennett et al., 1985; Nicholson and Palao, 1993; Grist and Nicholson, 2001). For our calculations in Section 5.3 we therefore assume a continuous wet season length of three months throughout the record, corresponding to a total of 90 days.

4. RESULTS

4.1. n-Alkane abundances and CPI

Concentrations of individual long-chain n-alkanes (n-C<sub>27</sub>-C<sub>33</sub>) were mostly low with n-C<sub>31</sub> being the most abundant homologue throughout the record (between 100 and 500 ng g⁻¹ dry sediment, on average 210 ± 73 ng g⁻¹; Table 1). Values of CPI vary between 3.9 and 4.9 and display no systematic variation throughout the record.

4.2. Isotopic composition

For most samples, the n-C<sub>29</sub> alkane could not be separated from an unknown, coeluting compound, while abundances of the n-C<sub>27</sub> and n-C<sub>33</sub> alkanes were too low for isotope analysis. We therefore report values of δD and δ¹³C for the n-C<sub>31</sub> alkane only, which was the most abundant and cleanly separated compound throughout the record. Isotope data are provided in Table 2.

4.2.1. δD<sub>Wax</sub>

Mean δD values of the n-C<sub>31</sub> alkane span a range of 16‰, varying between −138‰ and −154‰ across the study interval (Fig 2). The oldest part of the record shows two periods of relative D-depletion of about 5‰ from 1925 to 1935 AD and from 1950 to 1965 AD, followed by a gradual increase of 10‰ (D enrichment) which plateaus around 1975 AD until the end of the record.

4.2.2. δ¹³C<sub>Wax</sub>

Mean δ¹³C values of the n-C<sub>31</sub> alkane vary by about 1‰ between −24.4‰ and −25.5‰ (Fig 2). They display two intervals of ¹³C depletion of about 0.25‰ from 1925 to 1935 AD and from 1950 to 1965 AD. From ~1970 AD on, δ¹³C values decrease continuously by about 0.8‰.

5. DISCUSSION

5.1. δ¹³C variability and vegetation type

Previous studies have shown that changes in vegetation can potentially drive changes in the net isotopic fractionation between precipitation and leaf waxes, complicating the interpretation of δD<sub>Wax</sub> as proxy for precipitation (Sachse et al., 2012 and references therein). It is therefore crucial to understand potential biases arising from changes in plant ecosystem composition in order to produce an accurate estimate of rainfall amount based on δD<sub>Wax</sub>. Starting 1979, vegetation cover of the Sahel has been monitored systematically through remote sensing. This has shown reduced vegetation cover during periods of lowered precipitation during the 1980s followed by a re-greening of the Sahel from 1982 to 2012 (Tucker et al., 1985; Eklundh and Olsson, 2003; Herrmann et al., 2005; Mbow et al., 2015). These studies are based on the remote sensing data product NDVI (“Normalized Difference Vegetation Index”; Tucker, 1979), which measures the fraction of photosynthetically active radiation absorbed by plants and is proportional to green leaf area. However, while changes in vegetation greenness as quantified by NDVI are indicative of changes in vegetation cover, NDVI cannot distinguish among different types of vegetation or identify changes in species composition (compare Karlson and Ostwald, 2016).

The remote-sensing results have been combined with field studies, revealing that re-greening of the Sahel is linked
to recovery of the herbaceous layer (grasses) as well as to changes in land-use management such as cropping, manuring and livestock grazing (Tappan et al., 2004; Olsson et al., 2005; Dardel et al., 2014). In agreement with the above, several studies show a decline in tree cover and tree diversity in the western Sahel (Senegal) with a concurrent increase in shrub abundance in some locations (Wezel and Lykke, 2006; Gonzalez et al., 2012; Herrmann and Tappan, 2013). Other studies in turn observe the opposite and link the observed greening of the Sahel to recovery of trees and shrubs (Brandt et al., 2015; Kaptue ´ et al., 2015 ). The picture that emerges is a heterogeneous pattern of greening (and local browning) depending on the specific sites that have been studied together with varying impacts of land use change (charcoal production, agricultural expansion, grazing etc.), soil and topographic diversity, and local climate conditions (Mbow et al., 2015). To our knowledge, there is no comprehensive literature data on changes in grasses vs. trees/shrubs available that would allow inferences on the development of the ratio of C3/C4 plants in the study area.

Values of $\delta^{13}C_{\text{wax}}$ provide a means to control for influences on $\delta D_{\text{wax}}$ from changes in ecosystem composition (C3 shrubs and trees vs. C4 grasses). Mean $\delta^{13}C$ values of the n-C31 alkane vary between $-24.5 \pm 2.3 \permil$ and $-25.5 \pm 2.6 \permil$ with a mean value of $-24.8 \pm 0.1 \permil$ (Fig 2). Applying end member carbon isotopic compositions of C4 and C3 leaf-wax n-alkanes of $-21.7 \pm 2.3 \permil$ and $-35.2 \pm 2.6 \permil$, respectively (Castaneda et al., 2009), this corresponds to an ecosystem composition of $77 \pm 1.9 \permil$ C4 grasses throughout the record ($\sigma$ is based on C3/C4 endmember error propagation on weighted mean). This finding is in agreement with

<table>
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<th>n-C29 (ng g$^{-1}$)</th>
<th>n-C31 (ng g$^{-1}$)</th>
<th>n-C33 (ng g$^{-1}$)</th>
<th>CPI (C25-33)</th>
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Table 1 n-Alkane concentrations in dried sediment, carbon preference index (CPI) after Bray and Evans (1961), and normalized C31 index (Schefuß et al., 2003).
modern observational data of grassland-dominated savanna in the presumed catchment area (White, 1983; Mayaux et al., 2004), corroborating earlier studies on sedimentary δ13Cwax as proxy for C3/C4 vegetation on the adjacent continent (e.g. Vogts et al., 2012). This further implies that δ13Cwax (which will be used in Section 5.3 to estimate the relative proportion of C3 and C4 plants within the catchment) is a reasonable indicator of plant composition (C3/C4) in an arid summer-rainfall region such as the African Sahel.

The δ13Cwax record displays two periods of 13C depletion of about 0.3‰ coinciding with two periods of D-depletion of about 5‰ in the δDwax record from 1925 to 1935 AD and from 1950 to 1965 AD (Fig 2). Despite being at the limit of significance, these shifts might indicate an ecosystem change towards a (very slight) increase of C3 plants producing leaf-wax n-alkanes that are more depleted in 13C compared to those of C4 grasses. Given a range of on average 13‰ in δ13C and ~20‰ in δD (Sachse et al., 2012) between C3 and C4 plants (see above), a shift of 0.3‰ in δ13C (which corresponds to just a 2‰ increase in C3 vegetation) cannot explain a 5‰ shift in δD based solely on vegetation type. Changes in δDwax should therefore largely reflect changes in δDprecip. We note, however, that possible changes in water use efficiency (WUE) during periods of increased humidity could have influenced δ13Cwax as well (e.g. Larcher, 2003; Hou et al., 2007), potentially masking the true magnitude 13C depletion in response to an increase in C3 vegetation.

A larger shift in δ13Cwax of about −1‰, however, occurs from 1970 AD onwards towards the end of the record. If this reflects a shift of vegetation towards C3 plants, this could at most explain a 1.5‰ D enrichment in the δDwax record (based on apparent fractionation factors for C4 grasses, C3 dicots provided in Sachse et al., 2012). However, whereas there is evidence for a decrease of vegetation cover during the drought of the 1970s and 1980s (e.g. Anyamba and Tucker, 2005; Herrmann et al., 2005), there is no evidence for a concurrent increase of C3 plants. The most important driver of δ13Cwax over the course of the record, however, is changes in the atmospheric 13C concentration through anthropogenic fossil fuel emissions (Suess, 1955; Keeling, 1979). From 1900 to 2008, atmospheric 13CO2 has decreased by about 1.5‰ (Friedli et al., 1986; Keeling, 2010). Therefore, the decrease in δ13C since ~1970 must, at least partly, be attributed to the “Suess effect” (Suess, 1955; Keeling, 1979). If we correct δ13Cwax for the Suess Effect between 1978 and 2008, which is the time interval covered by direct measurements of atmospheric δ13C, the δ13Cwax record increases from −25.0‰ to −24.2‰. This would correspond to an increase of C4 vegetation from 77% to 81%. The extent to which this agrees with observational data, however, is difficult to assess. As mentioned above, there is equivocal evidence for the nature of the Sahel re-greening. In addition, δ13Cwax may be further compromised from 1970 on as rising atmospheric CO2 concentrations influence stomatal conductance of C3 plants and therewith affect 13C discrimination during photosynthesis, which may mask the effect of C4 on δ13Cwax.

As this effect cannot be quantified at this point, and as overall changes in δ13Cwax are small given the physiological range of δ13Cwax of 13‰, we assume no significant change in the ratio of C3 over C4 plants throughout the interval covered by our record.

This inference is supported by the normalized C31 index (Table 1), which has been proposed as relative measure of n-alkanes deriving from C3 and C4 plants (Schefuß et al., 2003). The range of the index derived from aeolian dust

Table 2

<table>
<thead>
<tr>
<th>Age (C.E.)</th>
<th>Plant wax component</th>
<th>Mean δ13Cwax (% VPDB)</th>
<th>Range (±)</th>
<th>Mean δDwax (% VSMOW)</th>
<th>Range (±)</th>
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<tr>
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<td>n-C31 alkane</td>
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samples along the coast of NW Africa varies from 0.58 offshore the western Sahel (C₄ plant dominated) to 0.1 near the tropical rainforest (C₃ plant dominated). Variation of the n-C₃1 index in our record in turn is small (between 0.54 and 0.58) and is not linked to the temporal evolution of the δ¹³Cwax record, supporting our conclusion of negligible changes in vegetation type throughout the record. We therefore base our estimate of ecosystem net fractionation (Section 5.3) on vegetation comprising an average of 77% C₄ plants. An analysis of the sensitivity of our rainfall reconstruction to δ¹³Cwax is provided in Section 5.3.

5.2. δDwax variability and relative changes of western Sahel precipitation

Based on the importance of the amount effect (Dansgaard et al., 1993; Rozanski et al., 1993; Worden et al., 2007; Risi et al., 2008a,b) in the study area, we attribute periods of D-depletion in our δDwax record to intervals of increased rates of precipitation during the rainy season. Before attempting a quantitative reconstruction of past rainfall amounts in the catchment, we first test to what extent our sedimentary δDwax record relates to relative changes in precipitation amount in the western Sahel in general (i.e. beyond the catchment area). For this purpose we compared the δDwax time series to a spatially integrating rain index for the western Sahel (Fig. 2; Fink et al., 2010). This normalized rainfall index is based on precipitation amount during the rainy season (July to September) between 1921 and 2004 at seven stations west of 8°N across Mauritania, Senegal, Mali, and Guinea, and serves as a relative (not quantitative) measure of changes in precipitation.

Comparison of the two time series reveals a close link between the temporal evolution of the rain index and δDwax. In particular the two periods of increased rainfall from 1925 to 1935 AD and from 1950 to 1965 AD (green bars in Fig. 2), as well as the “Sahel Drought” in the 1970s and ’80s (brown bar in Fig. 2) are well reflected in the δDwax record, together with the slight increase of precipitation in mid 1980 AD. The rain index further indicates that the period of drier conditions around 1940 was less severe than the more recent Sahel Drought, a feature that is captured by the δDwax record as well.

Taken together, the close match between the two records regarding their temporal pattern supports the interpretation that changes in δDwax deposited offshore NW Africa reflect relative changes in rainfall amount, promoting previous applications of δDwax from marine sediments as a relative measure of rainfall changes on the adjacent continent (Schefuß et al., 2005, 2011; Niedermeyer et al., 2010, 2014; Tierney et al., 2010a, 2012; Collins et al., 2013; Kuechler et al., 2013; Tierney and deMenocal, 2013). Next, we turn to converting our δDwax timeseries to a quantitative estimate of rainfall.

5.3. δDwax – total rainfall amounts in the catchment area

Given no evidence for significant changes in vegetation (C₃/C₄) composition, we next attempt to quantitatively reconstruct total precipitation amounts in the catchment based on the δDwax record. The global compilation of Sachse et al. (2012) suggests mean apparent fractionation factors (ε) between precipitation and the C₃ n-alkane leaf waxes of −136 ± 25‰ for C₄ grasses and −110 ± 31‰ for C₃ dicots. Using our estimate of 77% C₄ plants (see Section 5.1) yields an ecosystem fractionation of −130 ± 21‰, whereas our maximum estimates of 81% C₄ plants would correspond to an ecosystem fractionation factor of −131 ± 21‰. We note that Feesink and Sessions (2010a) report a rather constant ε of −90‰ for sub-humid to arid environments in southern California, significantly smaller than our estimate. However, whereas southern California experiences rainfall in winter, our study site is characterized by summer rainfall. This fundamental difference in seasonal rainfall distribution is reflected in the vegetation with southern California hosting a mixed woody Mediterranean type vegetation with little C₄ grasses, opposing the C₃ grass dominated flora of our study site.

The relationship between δDwax and δDprecip is given by

\[ ε = \frac{[\delta D_{wax} + 1]}{\delta D_{precip} + 1} - 1 \]

which can be rearranged to solve for δDprecip

\[ δD_{precip} = \frac{[\delta D_{wax} + 1]}{(1 + ε)} - 1 \]

with omission of the commonly used factor of 1000 following the recommendation of Coplen (2011). The reconstructed values of δDprecip based on a value of ε of −130‰ are shown in Fig 3 and vary between −9‰ and −29‰. To evaluate extent to which reconstructed values of δDprecip correspond to present-day values of δDprecip in the study area, we retrieved δD values of precipitation from the dataset of Bowen and Reavenagh (2003) available on waterisotopes.org. We extracted interpolated monthly values of δDprecip for the sedimentary catchment (see Section 2.3), and averaged δDprecip over the rainy season (Jul, Aug, Sep), yielding a mean value for δDprecip of −25‰. Given a range from −56‰ to 0‰ for annual mean δDprecip across Africa (compare www.waterisotopes.org), this agrees fairly well with the most recent data in the reconstructed δDprecip Record of −20 ± 3‰, supporting the validity of our approach.

Next, we converted values of δDprecip to absolute changes in rainfall using the modern-day relationship between δDprecip and rainfall intensity (“amount effect”, Dansgaard, 1964; Rozanski et al., 1993) of −4.1‰ mm⁻¹ day⁻¹, as calculated by Bony et al. (2008) based on observational data from tropical rainfall stations. Anticipating that δεwax and the derived estimate of δDprecip reflect the average δD value of precipitation during the rainy season with a duration of 90 days (July to September; Nicholson, 2013), we calculated the amount of rainfall during the rainy season as:

\[ \text{Precipitation (mm rainy – season}^{-1}) = (\delta D_{precip} / -4.1‰) \times 90 \]
periods as well as absolute amounts. We consider our rainfall reconstruction accurate if the analytical uncertainty band (i.e. the range between the highest and lowest estimate based on duplicate analyses of δDwax; shaded area in Fig. 3a) encloses the instrumental record. In particular during periods of enhanced precipitation, i.e. from 1925 to 1935 AD and from 1950 to 1965 AD as well as towards the end of the record, reconstructed amounts of precipitation accurately replicate the instrumental record.

We emphasize that the δD-based reconstruction of rainfall amount is not “tuned”, offset, or stretched to match the instrumental record. The net ecosystem fractionation and isotope amount effect are both derived independently. The one significant free parameter in this analysis is selection of the appropriate watershed area over which rainfall data are integrated. Because of the very strong north–south gradient in precipitation, extension of the boundary further northward would result in a decrease in average instrumental rainfall amount, whereas extension further southward results in increase in average precipitation. Nevertheless, the watershed boundaries we use here were chosen based on the prevailing wind fields, the physiography of the Senegal River watershed and the influence of coastal currents, and were not adjusted to fit the precipitation record.

Interestingly, during both onset and peak of the Sahel drought, reconstructed rainfall amounts align with the driest years of the drought (brown bar in Fig. 3). The accuracy of our reconstruction notwithstanding, it is conspicuous that only rainfall minima are recorded by the leaf wax record. At the peak of the drought, i.e. during driest conditions, the catchment received on average about 350 mm rainfall (instrumental record), whereas the reconstructed rainfall record indicates only 250 mm rainfall. This may be coincidental, deriving from the difference in temporal resolution between the two records. However, as the reconstructed record represents at least a four-year running average of precipitation, the observed bias, albeit small, requires further consideration.

It has been demonstrated that leaf water δD enrichment by transpiration has an effect on δDwax, and that this effect may be of particular importance in arid environments through an enhanced water vapor pressure deficit (Sachse et al., 2010; Feakins and Sessions, 2010a; Kahmen et al., 2011b, 2013b; Douglas et al., 2012; Hoffmann et al., 2013). Other studies in turn suggest minor changes in δDwax in response to relative humidity (Hou et al., 2008; Gao et al., 2014b). During the time period covered by our record, we observe only little change in relative humidity during the growing season of 62–66% (Fig. 4; extracted from the CRU dataset; Harris et al., 2014). Moreover, these fluctuations are not correlated with the temporal structure of either the δDwax or the instrumental record of rainfall. It is therefore unlikely that leaf water enrichment via changes in relative humidity could explain the observed bias towards minimum rainfall during the Sahel Drought. This is especially so as the studies mentioned above consider much larger changes in relative humidity than those observed during the study period.

One possible alternative explanation would be a northward expansion of the catchment towards drier sources, e.g. in response to increased dust flux during drier conditions. However, the driest possible northernmost source area of plant waxes has already been included in the definition of the catchment (compare Section 2.2), so this explanation does not seem plausible. A third possible explanation would be an eastward expansion of the catchment towards the interior of the continent during the drought. This also appears unlikely as plant waxes sourced
from more continental sources should be D-depleted (due to the continental effect), which would result in an overestimation of rainfall in our reconstruction. Another candidate would be a change in the amount effect, e.g. the amount has been shown to decrease to $\Delta 15^{\circ}$ by $6.3^{\circ}$ mm day$^{-1}$ in regimes of weak precipitation (that is less than 2–3 mm day$^{-1}$; Bony et al., 2008). This would, however, shift our rainfall reconstruction towards even lower values. A change in the amount effect during the Sahel Drought is therefore unlikely to have biased the reconstructed rainfall record. The final and most likely explanation for the observed bias towards lower values of our rainfall reconstruction, however, is an increase of leaf wax production during periods of reduced precipitation. It has been shown that leaf wax accumulation may increase up to 2.5-fold in response to drought (Cameron et al., 2006). Therefore, enhanced leaf wax production during the Sahel Drought may have resulted in an overrepresentation of D-enriched leaf waxes in the sedimentary $\delta^{2}D$ record.

In summary, our 100-year time series of reconstructed rainfall amount based on $\delta^{2}D$ matches in both timing and amount the instrumental record of rainfall, in particular during periods of increased precipitation. During periods of enhanced aridity such as the “Sahel Drought”, it is unlikely that the reconstructed rainfall record is biased due to the continental effect. Here, a difference of 1% mm$^{-1}$ day$^{-1}$ may change the rainfall reconstruction by 50–200 mm in total (Fig. 4a).

5.4. Sensitivity analysis

To help understand the sensitivity of our rainfall reconstruction to input variables, we plotted the relationships between the size of the amount effect vs. reconstructed rainfall amount (Fig. 4a), net ecosystem fractionation vs. reconstructed amounts of rainfall (Fig. 4b), $\delta^{13}C_{\text{wax}}$ vs. net ecosystem fractionation (Fig. 4c), and $\delta^{13}C_{\text{wax}}$ vs. reconstructed rainfall amount (Fig. 4d). We simulated variations of $\delta^{13}C_{\text{wax}}$ and ecosystem fractionation according to their physiological ranges from $-21.7^{\circ}$ to $-35.2^{\circ}$ and $-110^{\circ}$ to $-136^{\circ}$, respectively (values for the $n$-C$_{31}$ alkane; Castanhera et al., 2009; Sachse et al., 2012). In the absence of an equivalent for the amount effect, we varied its size between arbitrary values of $-2^{\circ}$ to $-6^{\circ}$. Sensitivities to one-permil changes were determined by subsequent regression analysis. All calculations are based on a fixed value for $\delta^{2}D$ of $-145^{\circ}$ and a rainfall period of 90 days. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
However, as the present-day amount effect is a directly measured relationship, such a change is hypothetical – though a change through geologic time is possible. This is very different for ecosystem fractionation as it is calculated using a proxy-based estimate of past vegetation. A change of $\varepsilon$ of one permil results in an average change in seasonal rainfall of 24 mm (note that the correlation is not exactly linear, compare Eq. (2) and (3); Fig. 4b). This makes $\delta^{13}C_{\text{wax}}$ a critical variable for the reconstruction of rainfall; in combination a one-permil shift in $\delta^{13}C_{\text{wax}}$ changes $\varepsilon$ by 1.9‰, leading to an average change of 47 mm in seasonal rainfall (Fig. 4c and d). Yet, the similarity of our rainfall reconstruction with the instrumental record indicates that sedimentary $\delta^{13}C_{\text{wax}}$ allows an accurate estimate of $\varepsilon$, supporting the validity of our approach.

5.5. Implications for paleoclimatic applications

Our study shows that in a dry, highly seasonal environment with a unimodal distribution of rainfall such as the West African Sahel, it is possible to accurately reconstruct rainfall amounts from sedimentary $\delta D_{\text{wax}}$ records. Here, seasonal leaf wax production dominated by shallow rooting Savannah grasses allows an annually distinct recording of $\delta D_{\text{wax}}$. Moreover, it can be expected that leaf waxes are transported to the marine environment on a regular (annual) basis due to seasonal activity of riverine runoff and northeasterly trade winds. The latter may be of particular importance as e.g. Li et al. (2011) found only little correlation of precipitation amount with $\delta D_{\text{wax}}$ from marine sediments receiving terrestrial material from a similarly arid environment as our study site. They conclude that the transport time of leaf wax compounds into the sedimentary record is a crucial component for the application of sedimentary $\delta D_{\text{wax}}$ as proxy for $\delta D_{\text{precip}}$.

Converting $\delta D_{\text{wax}}$ to $\delta D_{\text{precip}}$ and, ultimately, to rainfall amounts requires information on the composition of vegetation ($C_3/C_4$), the length of the growing season, ecosystem apparent fractionation, and the amount effect. Our data show that sedimentary $\delta^{13}C_{\text{wax}}$ is a valuable measure of vegetation composition at the study site. As the seasonality of precipitation is a key factor controlling the ratio of $C_3$ over $C_4$ plants in (sub)tropical arid environments, we infer that information on rainy season length can be deduced from $\delta^{13}C_{\text{wax}}$ as well. Our study further demonstrates that the $\delta^{13}C_{\text{wax}}$ based estimate of the ratio of $C_3/C_4$ plants allows to calculate an accurate apparent ecosystem fractionation.

The sensitivity analysis reveals that accurately estimating $\varepsilon$ is a critical step as our rainfall reconstruction is very sensitive to even small changes. This may be challenging in environments with highly variable $C_3$ species composition (trees – shrubs – $C_4$ grasses) over time. Although such changes are not necessarily recorded in $\delta^{13}C_{\text{wax}}$, pollen data may also help to gain more detailed insight into vegetation structure (Feakins et al., 2012; Dupont et al., 2013; Feakins, 2013). This could be of particular importance for evergreen tropical environments, where changes in $\delta^{13}C_{\text{wax}}$ may relate to changes in canopy closure and light availability rather than the proportion of $C_3$ and $C_4$ plants (Ehleringer et al., 1987).

Controls of $\delta D_{\text{precip}}$ over time are probably of most interest for paleoclimatic applications. These include uncertainties regarding the size of the amount effect, changes of the rainout history of advected moisture, possible mixing/shifting of moisture sources as well as changes in the seasonal distribution (uni- vs. bimodal) of rainfall. The complex control of $\delta D$ values of atmospheric water may be the underlying explanation for that fact that $\delta D_{\text{wax}}$ based estimates of rainfall amounts in tropical East Africa have remained largely quantitative so far (Tierney et al., 2010b, 2011a,b; Konecky et al., 2011; Costa et al., 2014). Similarly, across (sub)tropical locations (including East Africa) such as India, Indonesia and East America, the El Nino Southern Oscillation and the Indian Ocean Zonal Mode exert additional control on $\delta D_{\text{precip}}$ (e.g., Vuille and Werner, 2005; Cobb et al., 2007; Kurita et al., 2009; Dayem et al., 2010; Tierney et al., 2013; Lekshmy et al., 2014). These variables therefore need to be considered carefully when reconstructing precipitation on longer timescales, in particular beyond the Holocene.

6. CONCLUSIONS

We have measured and used a 100-year sedimentary record of $\delta D_{\text{wax}}$ to successfully reconstruct $\delta D$ values of precipitation and, ultimately, total amounts of rainfall. We show that reconstructed $\delta D$ values of precipitation and inferred rainfall amounts provide an accurate quantitative match to the instrumental record of rainfall on the adjacent continent.

Our study offers further evidence that sedimentary $\delta^{13}C_{\text{wax}}$ can be used to estimate the composition of vegetation regarding the proportional contribution of $C_3$ and $C_4$ plants in the NW African Sahel, and that this estimate can be used to calculate an ecosystem net D-isotope fractionation. Despite the considerable variability of $\delta^{13}C_{\text{wax}}$ and net fractionation factors across and within individual $C_3$ and $C_4$ plants, it appears that average values, regardless of considerable standard variations, are good predictors of vegetation characteristics recorded by our marine sediment sequence. The latter in turn integrates vegetation across its catchment and thereby smoothens individual characteristics (see also and Tipple and Pagani, 2013).

We detect no influence of relative humidity on leaf water enrichment during periods of drought. However, whether or not this holds true for studies of more ancient sediments covering a broader range of relative humidity variations than this study needs to be elucidated. In particular, changes in vegetation associated with hydrological shifts bigger than those covered by this study may introduce a bias through changes in water use efficiency. On the other hand it has been suggested that this effect is counterbalanced by opposing effects of changes in vegetation, and that the influence of water use efficiency is captured by the apparent fractionation of different types of vegetation (Hou et al., 2008). However, whether or not this exerts significant control on $\delta D_{\text{wax}}$ needs to be investigated by further studies.
Our study further demonstrates that the amount effect as quantified by Bony et al. (2008) is applicable to reconstruct absolute rainfall amounts for the time period covered by our study. However, for applications that go beyond the recent past uncertainty remains as to whether or not the amount effect has been stable over time and to what extent additional controls on δD_{precip} may have influenced δD_{wax}. This is of particular importance for studies outside the Holocene entering climates with very different-than-present boundary conditions. Here, the rapidly growing advance in hydrosphere isotope modeling may help to assess past differences in the hydrogen isotopic composition of atmospheric water vapor.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.03.034.

REFERENCES


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