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Effect of aridity on $\delta^{13}C$ and δD values of C_3 plant- and C_4 graminoid-derived leaf wax lipids from soils along an environmental gradient in Cameroon (Western Central Africa)

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ABSTRACT

The observation that the hydrogen isotope composition (δD) of leaf wax lipids is determined mainly by precipitation δD values, has resulted in the application of these biomarkers to reconstruct paleoclimate from geological records. However, because the δD values of leaf wax lipids are additionally affected by vegetation type and ecosystem evapotranspiration, paleoclimatic reconstruction remains at best semi-quantitative. Here, we used published results for the carbon isotope composition ($\delta^{13}C$) of *n*-alkanes in common plants along a latitudinal gradient in C_3/C_4 vegetation and relative humidity in Cameroon and demonstrated that pentacyclic triterpene methyl ethers (PTMEs) and *n*-C_{29} and *n*-C_{31} in the same soil, derived mainly from C_4 graminoids (e.g. grass) and C_3 plants (e.g. trees and shrubs), respectively. We found that the δD values of soil *n*-C_{27}, *n*-C_{29} and *n*-C_{31}, and PTMEs correlated significantly with surface water δD values, supporting previous observations that leaf wax lipid δD values are an effective proxy for reconstructing precipitation δD values even if plant types changed significantly. The apparent fractionation (ε_{app}) between leaf wax lipid and precipitation δD values remained relatively constant for C_3-derived long chain *n*-alkanes, whereas ε_{app} of C_4-derived PTMEs decreased by 20‰ along the latitudinal gradient encompassing a relative humidity range from 80% to 45%. Our results indicate that PTME δD values derived from C_4 graminoids may be a more reliable paleo-ecohydrological proxy for ecosystem evapotranspiration within tropical and sub-tropical Africa than *n*-alkane δD values, the latter being a better proxy for surface water δD values. We suggest that vegetation changes associated with different plant water sources and/or difference in timing of leaf wax synthesis between C_3 trees of the transitional class and C_3 shrubs of the savanna resulted in a D depletion in soil long chain *n*-alkanes, thereby counteracting the effect of evapotranspiration D enrichment along the gradient. In contrast, evaporative D enrichment of leaf and soil water was significant enough to be recorded in the δD values of PTMEs derived from C_4 graminoids, likely because PTMEs recorded the hydrogen isotopic composition of the same vegetation type.

1. Introduction

The observation that the hydrogen isotope composition (δD) of *n*-alkanes correlates with precipitation δD values over a large spatial scale (e.g. Sauer et al., 2001; Sachse et al., 2004, 2012; Garcin et al., 2012) has resulted in their widespread use for reconstructing past climate (e.g. Hou et al., 2008; Mügler et al., 2010; Sinninghe Damsté et al., 2011; Schefuss et al., 2011; Handley et al., 2012; Guenther et al., 2013). However, because *n*-alkane δD values can be additionally affected by secondary factors such as vegetation type (e.g. Krull et al., 2006; Sachse et al., 2012) or ecosystem evapotranspiration (e.g. Smith and Freeman, 2006; Sachse et al., 2010; Kahmen et al., 2013a,b), paleoclimatic reconstruction based on their integrated isotopic signal in geological records remains qualitative or semi-quantitative. By measuring the carbon isotope composition ($\delta^{13}C$) and δD values of lipids specifically derived from

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C_3 plants (e.g. trees or shrubs) and C_4 graminoids (e.g. grass) in soil from a latitudinal gradient in C_3/C_4 vegetation and aridity of Cameroon, we aimed to determine the reliability of lipid δD values as paleo-precipitation and ecosystem paleo-evapotranspiration proxies.

Plant water source δD value and subsequent evaporative D enrichment of leaf water mainly control leaf wax lipid δD value (e.g. Sachse et al., 2012; Kahmen et al., 2013a,b). Recently, it has been demonstrated that evaporative D enrichment of leaf water, which is expected to be greater under arid conditions, is linearly related to the D enrichment of *n*-alkanes in both C_3 trees and C_4 graminoids grown under controlled conditions in climate chambers (Kahmen et al., 2013a). These results allow quantifying the D enrichment of *n*-alkanes driven by leaf water evaporative D enrichment and thus might potentially be applied to contemporary plants as ecohydrological proxies for evapotranspiration (Kahmen et al., 2013b). It has been demonstrated that evaporative D enrichment of leaf water occurs to a lower extent in C_4 graminoids than in C_3 plants, resulting in cultured plants to lower *n*-alkane δD values (by 50‰) in C_4 graminoids than in C_3 plants (Kahmen et al., 2013a). However in arid ecosystems, water in the upper soil layers is commonly D-enriched relative to the water in deeper soil layers (e.g. Schulze, 1986; Dawson and Pate, 1995; Oliveira et al., 2005). Because shallow rooted C_4 graminoids (e.g. grass) typically access more D-enriched water than deeper rooted C_3 plants (e.g. trees or shrubs), stratification in soil water δD values might result alternatively in heavier *n*-alkanes in C_4 graminoids than in C_3 plants (Krull et al., 2006). Consequently, intrinsic factors related to different plant physiology between C_3 plants and C_4 graminoids may either increase or decrease the effects of aridity on their leaf wax lipid δD values (e.g. Bi et al., 2005; Chikaraishi and Naraoka, 2006, 2007; Smith and Freeman, 2006). Without better knowledge of the effect of these factors on the integrated plant lipid δD values in geological records, quantitative interpretations will remain limited.

Because isotope fractionation during carbon fixation differs between plant pathways, C_3 and C_4 plants differ in their carbon isotope composition (Farquhar et al., 1989). Commonly, C_3 plant-derived lipids exhibit δ^{13}C values of ca. −35‰ ± 5‰ and C_4 plant-derived lipids ca. −20‰ ± 2‰ (Chikaraishi et al., 2004; Rommerskirchen et al., 2006b). Despite possible ^{13}C enrichment during soil degradation (e.g. Chikaraishi and Naraoka, 2006), plant-derived lipid δ^{13}C values faithfully record the biosynthetic pathway of the producers and have thus been widely used to infer the relative contribution of C_3 and C_4 plants to soil organic matter (e.g. Rommerskirchen et al., 2006b; Diefendorf et al., 2011; Garcin et al., 2014).

The C_4 photosynthetic pathway occurs primarily within monocotyledonous plants and particularly among grasses (Poaceae) and sedges (Cyperaceae) (Ehleringer et al., 1997). Poaceae (graminoids) is a large family including more than 10,000 species that are particularly well represented in drier vegetation zones of tropical Africa (Tieszen et al., 1979). Pentacyclic triterpene methyl ethers (PTMEs) are found in variety of plants. But, because they typically occur in high abundance in C_4 graminoids (Poaceae; e.g. Ohmoto and Natori, 1969; Jacob et al., 2005), they have been used to infer grass contribution in geological records (Jacob et al., 2008; Oyo-Ita et al., 2010). Recently, they have been reported in substantial amount in savanna soil, making them attractive as a potential grass biomarker in C_4-dominated environments (Mendez-Millan et al., 2014).

Garcin et al. (2014) measured bulk and *n*-alkane δ^{13}C values of the common C_3 plants and C_4 graminoids of a climatic and vegetation gradient along a south–north transect in Cameroon. The transect was characterized by a progressive change in vegetation from C_3-dominated rainforest to C_4-dominated dry savanna and by a decrease in relative humidity (RH) from 80% to 45%. By comparing the δ^{13}C values of *n*-alkanes in plants and sediments against the relative abundance of C_3/C_4 plant cover in the region, Garcin et al. (2014) developed a new model to reconstruct C_3 vegetation cover in arid environments based on sedimentary *n*-alkane δ^{13}C records. Here, we have used bulk and *n*-alkane δ^{13}C values of the C_3 plants and C_4 graminoids from the former study to assess the photosynthetic origin of soil *n*-alkanes and PTMEs from the same study sites. By combining the δ^{13}C and δD values of these soil lipids, we aimed to differentiate the combined influences of climate and vegetation types (e.g. mostly C_3 trees and shrubs and C_4 graminoids) on leaf wax lipid δD values in the soil. The reliability of these lipids to record paleo-precipitation δD values and ecosystem evapotranspiration across the studied transect is discussed.

2. Study area

2.1. Climate

On the extreme south of the transect, the Debundscha (Debu), Ossa (Ossa) and Barombi (Baro) sites have a humid and hot climate with mean relative humidity (RH) ca. 85% (New et al., 2002) and mean annual temperature (MAT) ca. 26 °C. Precipitation (ca. 2500–12,000 mm/yr) occurs throughout the year, without a marked dry season (Table 1). Northwards, the length of the dry

Table 1
Climate and soil *n*-alkane and PTME distributions in the sampled lake catchments within different vegetation classes.

Latitude	Site code	Climate			Vegetation		Soil *n*-alkane and PTME distributions					
		RH[b] (%)	MAT[a] (°C)	MAP[a] (mm)	Zone[a]	f_{C3}[b]	Total *n*-alkanes (µg/g)	CPI (16–33)	CPI (25–33)	ACL (16–33)	Total PTMEs (µg/g)	% PTMEs
11.0547	Mora	45	27.2	540	DS	0.06 ± 0.06	270	2	6	24	50	16
10.5082	Rhum	46	22.7	970	DS	0.28 ± 0.25	480	3	8	25	150	24
7.2533	Mamg	57	26.3	1560	TZ	0.58 ± 0.06	340	3	7	26	60	15
7.1307	Tizo	63	21.8	1450	TZ	0.61 ± 0.05	370	4	8	25	100	22
6.6245	Tabe	63	21.7	1450	TZ	0.64 ± 0.04	610	11	18	28	10	2
5.0364	Asso	66	23	1740	TZ	0.69 ± 0.12	310	2	8	22	60	17
8.3909	Mane	77	16	2700	TZ (HA)	0.93[c] ± 0.12	1140	5	7	27	180	14
4.6544	Baro	81	24.9	2550	RF	0.95 ± 0.12	520	5	9	27	4	2
4.1034	Debu	82	25.7	11,700	RF	0.97 ± 0.12	1200	7	9	29	2	1
3.7686	Ossa	82	26.3	2900	RF	0.92 ± 0.19	360	19	20	29	1	1

CPI (16–33) = Σodd C*n*/Σeven C*n*; CPI (25–33) = $((C_{25} + C_{27} + C_{29} + C_{31} + C_{33}/C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33}/C_{24} + C_{26} + C_{28} + C_{30} + C_{32}))/2$; ACL (16–33) = $(\Sigma Cn \times n)/\Sigma Cn$; %PTMEs = ($\Sigma$PTMEs)/$\Sigma$PTMEs + Σ*n*-alkanes) $*$ 100; RH = relative humidity; MAT = mean annual temperature; MAP = mean annual precipitation; RF = rainforest; TZ = transition zone; HA = high altitude site; DS = dry savanna; f_{C3} = predicted areal fraction of C_3 vegetation ± 1 standard deviation.

[a] From Garcin et al. (2012).

[b] From Garcin et al. (2014).

[c] Overestimated.