1 *Multiple plant-wax compounds record differential sources and ecosystem structure in large river*
2 *catchments*

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4 Jordon D. Hemingway^{a,b,*}, Enno Schefuß^c, Bienvenu Jean Dinga^d, Helena Pryer^a, Valier V. Galy^a

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6 ^aDepartment of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution,
7 266 Woods Hole Road, Woods Hole, MA 02543, USA

8 ^bMassachusetts Institute of Technology-Woods Hole Oceanographic Institution Joint Program in
9 Oceanography and Applied Ocean Science and Engineering, 77 Massachusetts Avenue,
10 Cambridge, MA 02139, USA

11 ^cMARUM - Center for Marine Environmental Sciences, Universität Bremen, 28334 Bremen,
12 Germany

13 ^dGroupe de Recherche en Sciences Exactes et Naturelles / Délégation Générale à la Recherche
14 Scientifique et Technologique (GRSEN/DGRST), Ministère de la Recherche Scientifique,
15 Brazzaville, Congo

16 *Corresponding Author. Tel.: +1 508 289 2821. *E-mail address*: jhemingway@whoi.edu (J.D.
17 Hemingway)

Abstract

The concentrations, distributions, and stable carbon isotopes ($\delta^{13}\text{C}$) of plant waxes carried by fluvial suspended sediments contain valuable information about terrestrial ecosystem characteristics. To properly interpret past changes recorded in sedimentary archives it is crucial to understand the sources and variability of exported plant waxes in modern systems on seasonal to inter-annual timescales. To determine such variability, we present concentrations and $\delta^{13}\text{C}$ compositions of three compound classes (*n*-alkanes, *n*-alcohols, *n*-alkanoic acids) in a 34-month time series of suspended sediments from the outflow of the Congo River.

We show that exported plant-dominated *n*-alkanes ($\text{C}_{25} - \text{C}_{35}$) represent a mixture of C_3 and C_4 end members, each with distinct molecular distributions, as evidenced by an $8.1 \pm 0.7\text{‰}$ ($\pm 1\sigma$ standard deviation) spread in $\delta^{13}\text{C}$ values across chain-lengths, and weak correlations between individual homologue concentrations ($r = 0.52 - 0.94$). In contrast, plant-dominated *n*-alcohols ($\text{C}_{26} - \text{C}_{36}$) and *n*-alkanoic acids ($\text{C}_{26} - \text{C}_{36}$) exhibit stronger positive correlations ($r = 0.70 - 0.99$) between homologue concentrations and depleted $\delta^{13}\text{C}$ values (individual homologues average $\leq -31.3\text{‰}$ and -30.8‰ , respectively), with lower $\delta^{13}\text{C}$ variability across chain-lengths ($2.6 \pm 0.6\text{‰}$ and $2.0 \pm 1.1\text{‰}$, respectively). All individual plant-wax lipids show little temporal $\delta^{13}\text{C}$ variability throughout the time-series ($1\sigma \leq 0.9\text{‰}$), indicating that their stable carbon isotopes are not a sensitive tracer for temporal changes in plant-wax source in the Congo basin on seasonal to inter-annual timescales.

Carbon-normalized concentrations and relative abundances of *n*-alcohols (19 – 58% of total plant-wax lipids) and *n*-alkanoic acids (26 – 76%) respond rapidly to seasonal changes in runoff, indicating that they are mostly derived from a recently entrained local source. In contrast, a lack of correlation with discharge and low, stable relative abundances (5 – 16%) indicate that *n*-alkanes better represent a catchment-integrated signal with minimal response to discharge seasonality. Comparison to published data on other large watersheds indicates that this phenomenon is not limited to the Congo River, and that analysis of multiple plant-wax lipid classes and chain lengths can be used to better resolve local vs. distal ecosystem structure in river catchments.

1. Introduction

Since their discovery (Eglinton et al., 1962; Eglinton and Hamilton, 1967), the information recorded in the composition of aliphatic plant-wax lipids has been utilized extensively as a recorder of terrestrial ecosystem structure both in modern settings (Diefendorf et al., 2011; Bush and McInerney, 2013) and the geologic past (see Pancost and Boot, 2004; Eglinton and Eglinton, 2008; Freeman and Pancost, 2014 for review). Much attention has been focused on long-chain (i.e. greater than ~23 carbons) saturated *n*-alkanes, such that the detection of distinct homologue distributions among plant functional types (PFTs) has led to the use of homologue ratios as a tracer for *n*-alkane sources and ecosystem composition (Ficken et al., 2000; Pancost et al., 2002; Bingham et al., 2010). Such ratios have been frequently utilized in geologic records to infer past ecosystem changes, assuming a straightforward relationship between *n*-alkane production and PFT coverage. However, it has recently been recognized that mixing of *n*-alkanes is likely nonlinear with respect to ecosystem composition, as the absolute production rate of these compounds varies greatly by PFT and between individual species within the same PFT (Rommerskirchen et al., 2006; Vogts et al., 2009; Diefendorf et al., 2011; Magill et al., 2013a; Bush and McInerney, 2013; Garcin et al., 2014). To circumvent these issues, the simultaneous measurement of additional *n*-alkyl lipid classes (i.e. *n*-alcohols and *n*-alkanoic acids) should provide complementary information on plant-wax, and thus terrestrial organic carbon, sources and variability (e.g. Chikaraishi and Naraoka, 2006; Jansen et al., 2006; Diefendorf et al., 2011; Galy et al., 2011; Tao et al., 2015).

Gas chromatography coupled to isotope ratio mass spectrometry (GC-IRMS) allows for the stable carbon isotope ($\delta^{13}\text{C}$) analysis of individual compounds (Hayes et al., 1989; Hayes, 1993). Due to their differential fractionation of ^{13}C during photosynthesis, such measurements enable the determination of relative contributions by C_3 , C_4 and crassulacean acid metabolism photosynthetic pathways to individual lipids (Collister et al., 1994; Hobbie and Werner, 2004 and references therein). However, it has been shown that competing factors such as light and water stress can cause secondary fractionation effects (e.g. Graham et al., 2014), potentially complicating interpretation of $\delta^{13}\text{C}$ compositions and changes thereof.

Combining $\delta^{13}\text{C}$ and distribution data, therefore, provides an additional constraint on the mixing of plant-wax lipid sources in environmental samples. For example, $\delta^{13}\text{C}$ differences

between homologous lipids of the same compound class as high as ~6‰ have been observed in fluvial sediments due to increasing influence of C₄ grasses at longer chain lengths (Freeman and Colarusso, 2001; Galy et al., 2011; Hötzel et al., 2013; Wang et al., 2013a; Agrawal et al., 2014). In contrast, differences in ¹³C fractionation between *n*-alkyl lipid classes from the same species have been shown to be negligible (≤1‰) compared to differences between photosynthetic pathways (~13‰; Rommerskirchen et al., 2006; Chikaraishi and Naraoka, 2007; Vogts et al., 2009). Therefore, in addition to their distributions, δ¹³C values of multiple lipid classes should act as a more robust constraint on the sources of plant organic matter in environmental samples (e.g. Chikaraishi and Naraoka, 2006; Diefendorf et al., 2011; Galy et al., 2011; Feng et al., 2013; Tao et al., 2015).

Because of their specificity as a plant biomarker, long-chain *n*-alkyl lipids are ideally suited for reconstructing ecosystem changes recorded in terrestrially dominated lacustrine and marine sediments (Pancost and Boot, 2004; Eglinton and Eglinton, 2008; Castañeda and Schouten, 2011; Freeman and Pancost, 2014). For example, *n*-alkyl lipid δ¹³C measurements have been used for reconstructions such as savannah land cover response to climate change during the last deglaciation (Hughen et al., 2004) and the Miocene C₄ grassland expansion (Freeman and Colarusso, 2001; Hötzel et al., 2013). However, interpretation of individual compound δ¹³C values as a reconstruction of ecosystem land cover is likely complicated by effects such as a nonlinear response to C₃/C₄ coverage (Garcin et al., 2014) and insensitivity to changes within C₃ photosynthetic ecosystems (i.e. woody vs. non-woody; Feakins et al., 2013; Magill et al., 2013a; Magill et al., 2013b).

Additionally, spatial integration is likely not uniform within a river catchment, as changes in plant-wax distribution and isotope signals have been observed during fluvial transit (Galy and Eglinton, 2011; Galy et al., 2011; Ponton et al., 2014). Such non-uniform spatial integration should affect each compound differentially, and will lead to biased reconstructions of catchment land cover depending on which compound is used (e.g. Wang et al., 2013a). In order to properly interpret paleo-environmental plant-wax signals recorded in sedimentary archives it is therefore crucial to better understand how well various classes of fluvially exported *n*-alkyl lipids represent catchment-integrated vegetation coverage, and on what timescales.

2. Background

The Congo River provides an ideal opportunity to address this question. Draining $3.6 \times 10^6 \text{ km}^2$ of central Africa between 15°S - 10°N , the Congo is highly influenced by seasonal monsoonal precipitation due to the north-to-south migration of the inter-tropical convergence zone (ITCZ; Gasse, 2000). Catchment land cover is dominated by nearly equal amounts of closed-canopy evergreen rainforest (31%) and deciduous woodland/shrubland (26%), with lesser amounts of deciduous/montane forest (20%), mixed savannah/grassland (15%) and permanently inundated swamp forest (4%; Mayaux et al., 2004; Still and Powell, 2010). In general, land cover shifts from deciduous woodland/shrubland and mixed savannah/grassland in the headwaters to predominantly evergreen rainforest downstream, although small regions containing woodland/shrubland and savannah/grassland are present near the sampling site (Figure 1a). This corresponds to a shift from a mixed C_3/C_4 signal in both northern and southern hemisphere headwaters to nearly C_3 -exclusive land cover near the equator, especially in the main-stem swamp forest (*Cuvette Congolaise*) and its tributaries (Figure 1b).

Congo River discharge (Q_w) is remarkably stable throughout the year due to a seasonal offset in peak northern- and southern-hemisphere contribution, leading to an annual maximum discharge at Brazzaville/Kinshasa equal to roughly double the annual minimum (Coynel et al., 2005; Spencer et al., 2014). High rainfall in the north of the catchment between May and September and a ~1-2 month transit time corresponds to peak discharge of right-bank tributaries during boreal autumn – i.e. September through November (Bricquet, 1993; Mahe, 1993). Combined with increased flow through the *Cuvette Congolaise*, this leads to the observed annual discharge maximum in December (Figure 2a; Bricquet, 1993). In contrast, peak southern-hemisphere rainfall from November through March increases left-bank tributary discharge and is the source of the secondary discharge maximum observed at Brazzaville/Kinshasa (Figure 2a; Bricquet, 1993; Mahe, 1993), thus leading to the increased southern-hemisphere contribution from February through May (Figure 2b; Bricquet, 1993).

This unique spatial separation of PFTs (Figure 1) and temporal separation of tributary discharge (Figure 2b) should lead to pronounced seasonal variability in exported *n*-alkyl lipid source. Here, we aim to address the following questions regarding *n*-alkyl lipids exported in Congo River suspended sediments:

- (i.) How do exported lipid signals respond to changes in environmental conditions (i.e. discharge) on seasonal to inter-annual timescales?
- (ii.) Are certain lipid classes more representative of specific source regions, and how do lipid classes integrate local vs. distal sources?
- (iii.) How can complementary information obtained from multiple compound classes be used to better reconstruct catchment ecosystem coverage and interpret paleo-environmental records?

To do so, we utilize a 34-month time-series of suspended sediments collected near Kinshasa/Brazzaville between November 2010 and August 2013. We combine *n*-alkane, *n*-alcohol, and *n*-alkanoic acid concentrations, distributions, and $\delta^{13}\text{C}$ values with simultaneous measurements of total suspended sediment (TSS) concentration, %OC, and river discharge to discern seasonal changes in the source of exported plant waxes.

3. Materials and Methods

3.1. Sample collection

Suspended sediment samples were collected once per month from November 2010 through August 2013 near Brazzaville/Kinshasa, just downstream of Pool Malebo and ~300km upstream of the Congo Estuary (4.3°S, 15.3°E; Figure 1). The sampling location is downstream of all major tributaries, capturing >95% of the total Congo River catchment, and the effect of the downstream Congo Rapids on bulk organic geochemical properties has been shown to be minimal (Spencer et al., 2012). Samples are therefore taken to be representative of material exported to the estuary.

A known volume of surface water (~25L) collected near the center of the channel was filtered through a polyethersulfone (PES) membrane filter (Millipore Corporation) with a nominal pore size of 0.22 μm . Filters were dried at 60°C for storage and shipment, and sediments were quantitatively re-suspended in 18M Ω MilliQ water and freeze-dried in pre-combusted glass jars at -40°C (Christ Alpha-L1 equipped with an in-line cold trap) and weighed for TSS concentration. Discharge was measured concurrently with sample collection via a gauging station operated by the Groupe de Recherche en Sciences Exactes et Naturelles (Republic of

Congo) and a rating curve which is periodically updated by Acoustic Doppler Current Profiler (ADCP) transects (Figure 2a). Triplicate transects indicate that precision of discharge measurements is $\pm 5\%$, although overbank flooding during periods of high discharge likely biases measurements towards an underestimate of the true value (Spencer et al., 2014).

3.2. Extraction, separation, and purification of *n*-alkyl lipids

After weighing, sediments were homogenized using an agate mortar and pestle and an aliquot was removed for bulk analysis. One sample (June 2013) contained coarse vegetation debris, which was manually removed using solvent-cleaned forceps and weighed separately (16 mg; not included in extraction). Sediments were then extracted at 100°C for 20 minutes in a microwave accelerated reaction system (MARS, CEM Corporation) in 20mL of dichloromethane (DCM) and methanol (9:1). Total lipid extracts were saponified at 70°C for 2 hours using 0.5M KOH in methanol, after the addition of ~1% 18M Ω MilliQ water to prevent methylation of carboxylic acid functional groups. After the addition of 15mL of water and ~1g pre-combusted NaCl (to increase density difference), “base” fractions were liquid-liquid extracted in 5mL of pure hexane 5 times. Hydrochloric acid was then added until reaching pH 2, and “acid” fractions were extracted using hexane and DCM (4:1) until the organic phase was clear (generally 5 times). Both acid and base fractions were further purified by column chromatography using 1g of Supelclean amino-propyl silica gel (Supelco Analytical) and the following elution scheme: 4mL hexane (F1); 7mL hexane and DCM (4:1, F2); 10mL DCM and acetone (9:1, F3); 14mL 2% (w/w) formic acid in DCM (F4); 18mL DCM and methanol (1:1, F5). Acid and base fractions containing alkanes (F1), alcohols (F3), and alkanolic acids (F4) were recombined to ensure maximum recovery.

To isolate *n*-alkanes, F1_T (acid and base fractions recombined in 1.5mL 2:1 hexane:DCM) was subjected to urea adduction in which 500 μ L of urea-saturated methanol was added and solvent was evaporated using a stream of N₂ gas to promote urea recrystallization (repeated three times). Crystals were rinsed three times with pure hexane to remove the “non adducted” fraction before being dissolved in 15mL MilliQ water and liquid-liquid extracted using pure hexane as described above. Both alcohols and alkanolic acids require derivatization in order to be amenable to gas chromatography. Alcohols were acetylated in 250 μ L of pyridine and acetic anhydride with known isotopic composition (1:1) at 70°C for 1 hour. Alkanolic acids were

trans-esterified in 15mL of HCl and methanol with known isotopic composition (5:95) at 70°C for 12 hours. MilliQ water (15mL) was then added, and fatty acid methyl esters (FAMES) were liquid-liquid extracted into hexane and DCM (4:1) five times. FAMES were further purified by column chromatography using 1g of amino-propyl silica gel eluted with: 4mL hexane (F4_TF1); 7mL hexane and DCM (4:1, F4_TF2); 18mL DCM and methanol (1:1, F4_TF3).

After quantification but before isotope analysis, unsaturated compounds were removed using 0.5g silver nitrate silica gel (Supelco Analytical) in a Pasteur pipette column eluted with: 5mL hexane and DCM (95:5, SN1); 18mL hexane and DCM (4:1, SN2); 5mL DCM and acetone (1:1, SN3). Fractions containing *n*-alkanes (F1_T, adducted), *n*-alcohols (F3_T, SN2), and *n*-alkanoic acids (F4_TF2, SN2) were stored at 4°C until analyzed. Recovery using this protocol is ~90%, as determined by periodically subjecting a known mixture of compounds to the entire procedure.

3.3. Quantification and isotopic measurements

Total organic carbon (%OC) of bulk sediments was measured after decarbonation over HCl fumes at 60°C for 72 hours using a Fisons elemental analyzer coupled to a Finnigan Delta plus IRMS as described in Whiteside et al., 2011. All *n*-alkyl lipids were quantified using a Hewlett Packard 5890 gas chromatograph-flame ionization detector (GC-FID) with a Gerstel PTV injection system, and separated with a VF-1MS capillary column (Agilent Technologies). Temperature program was as follows: ramp to 130°C at 30°C/min, ramp to 320°C at 8°C/min, hold for 7.5min at 320°C (35min total). Samples were analyzed as a single injection and compared to an external standard run at 3 dilutions between every ~5 samples. Uncertainty was calculated using the standard deviation of the best-fit line to the calibration curve.

Compound-specific $\delta^{13}\text{C}$ was determined using a ThermoFisher Scientific Trace GC Ultra with a DB-1MS capillary column (Agilent Technologies) coupled to a Finnigan MAT252 IRMS via a GC/C combustion interface modified for oxygen trickle flow (Merritt et al., 1995; Sessions, 2006). Temperature program was as follows: hold for 3min at 120°C, ramp to 200°C at 30°C/min, ramp to 320°C at 4°C/min, hold for 29.3min at 320°C (70min total). All samples were measured at least in duplicate (triplicate when not limited by low concentrations) and calibrated against pulses of CO₂ gas with a known $\delta^{13}\text{C}$ value. Long-term precision of an external *n*-alkane standard mixture was $\leq 0.2\text{‰}$ ($\pm 1\sigma$ standard deviation). Results for individual compounds after

correction for derivatization agent are reported with uncertainty as $\pm 1\sigma$ of all injections. Data are reported relative to Vienna Pee-Dee Belemnite (VPDB).

3.4. Data analysis

One sample (September 2013) was omitted from the dataset due to contamination by the PES membrane filter, inhibiting the ability to measure bulk %OC. Additionally, one sample (February 2011) returned spurious $\delta^{13}\text{C}$ and concentration values, likely due to improper sampling or influence of a local extreme runoff event, and was thus removed in accordance with Chavenet's criterion (Glover et al., 2011). Regressions were performed as weighted least squares (WLS) using a weighting factor of $1/\sigma_i$ for each sample i (Glover et al., 2011). All data analysis was performed in the Python programming language v.2.7 and ArcGIS for desktop v.10.3.

4. Results

4.1. Environmental parameters

All environmental parameters are presented in Table EA1. Congo River discharge recorded at Brazzaville/Kinshasa during the sampling period ranged from a minimum of $23.2 \times 10^3 \pm 1.1 \times 10^3 \text{ m}^3/\text{s}$ in July 2011 to a maximum of $54.6 \times 10^3 \pm 2.7 \times 10^3 \text{ m}^3/\text{s}$ in December 2011 (Figure 2a). Average discharge for 2011 ($35.3 \times 10^3 \text{ m}^3/\text{s}$) was the fifth-lowest since recording began in 1977, while 2012 and 2013 were closer to long-term average values (Spencer et al., 2012). Seasonally, discharge displays two maxima: a large peak in Nov-Dec-Jan during high flow through northern hemisphere tributaries and the main-stem *Cuvette Congolaise*, and a smaller peak in Mar-Apr-May due to increased flow from southern hemisphere tributaries (Bricquet, 1993; Coynel et al., 2005; Bouillon et al., 2012; Spencer et al., 2012; Spencer et al., 2014). This leads to an estimated range in southern-hemisphere contribution (termed f_{south}) of 31 – 53%, with a median value of 39% (Bricquet, 1993). We classify periods with f_{south} above the median value – i.e. February through May – as being “southern hemisphere dominated,” and all other times as being “main-stem dominated” or “*Cuvette Congolaise* dominated” (Figure 2b). Importantly, the largest southern-hemisphere tributary, the Kasai River, enters the main-stem downstream of the *Cuvette Congolaise* swamp forest.

TSS concentration averaged $21.1 \pm 7.6 \text{ g/m}^3$ throughout the time series, ranging from a

minimum of 10.2 g/m³ to a maximum of 43.6 g/m³ (Figure 2c). TSS are rich in carbon, with an average %OC of 6.1 ± 1.0%, leading to an average particulate organic carbon (POC) concentration of 1.3 ± 0.4 g/m³ with a range of 0.6 – 2.6 g/m³ (Figure 2d). TSS, POC, and %OC ranges reported here agree well with published values, both for the main-stem Congo as well as the Oubangui River at Bangui Station (Figure 1), a major right-bank tributary (Coynel et al., 2005; Bouillon et al., 2012; Bouillon et al., 2014). Congo River suspended sediment %OC increases slightly as a function of discharge ($R^2 = 0.19$, p -value = 0.01; not shown), although POC concentration shows no correlation with discharge (p -value = 0.46; not shown).

4.2. Lipid abundance and distribution

Concentrations of individual homologues, average chain lengths, and carbon preference indices are presented in Tables EA2-EA4.

4.2.1. *n*-Alkanes

Carbon-normalized concentrations of individual plant-wax *n*-alkanes (C₂₃ – C₃₅; odd-numbered homologues) range from a minimum of 3.7 ± 0.8 µg/gOC (C₂₃) to a maximum of 82.1 ± 1.3 µg/gOC (C₂₉; Figure 3a). The sum of the long-chain odd-numbered homologue concentrations (ΣLC_{25-35}) exhibits considerably less variability, ranging from 66.0 – 207.1 µg/gOC. Time-series plots of ΣLC_{25-35} and selected homologue concentrations are presented in Figure 4a-c. ΣLC_{25-35} concentrations show a slight decrease with increasing discharge (Figure 5a), although this relationship is driven by changes in %OC and disappears when considering sediment-normalized concentrations ($R^2 = 0.001$, p -value > 0.05; not shown).

n-Alkanes are consistently dominated by C₂₉ and C₃₁ homologues, contributing up to 33% and 26% to ΣLC_{25-35} , respectively. At only 8-9% each, C₂₅ and C₃₅ are the least abundant homologues, while C₂₇ and C₃₃ contribute 12-13% each. To compare changes in distributions between samples, we compute the average chain length (ACL) as the concentration-weighted average of C₂₅ – C₃₅ odd-numbered homologues:

$$ACL = \frac{25 \times [C_{25}] + 27 \times [C_{27}] + 29 \times [C_{29}] + 31 \times [C_{31}] + 33 \times [C_{33}] + 35 \times [C_{35}]}{\Sigma LC_{25-35}} \quad (1)$$

n-Alkane ACL in our sample set is remarkably stable, with an average of 30.0 ± 0.1 units and a range of 29.6 – 30.2 units, and shows no significant correlation with discharge (Figure 5b). We compute the carbon preference index (CPI) for C₂₅ – C₃₅, defined as:

$$CPI = \frac{1}{2} \left(\frac{\Sigma LC_{25-35}}{\Sigma LC_{24-34}} + \frac{\Sigma LC_{25-35}}{\Sigma LC_{26-36}} \right) \quad (2)$$

ΣLC_{25-35} refers to odd-numbered homologues only while ΣLC_{24-34} and ΣLC_{26-36} refer to even-numbered homologues only (we note that C_{36} was not detected in any sample). *n*-Alkane CPI in our dataset averages 2.9 ± 0.5 , ranging from 2.1 – 4.1, and shows a small yet statistically significant decrease with increasing discharge (Figure 5c).

We additionally calculate P_{aq} , an estimate of macrophyte contribution to *n*-alkanes (Ficken et al., 2000), as:

$$P_{aq} = \frac{[C_{23}] + [C_{25}]}{[C_{23}] + [C_{25}] + [C_{29}] + [C_{31}]} \quad (3)$$

Resulting P_{aq} values in our sample set (Table EA2) average 0.19 ± 0.04 with a range of 0.12 – 0.26, and are uncorrelated with discharge ($R^2 = 0.08$, p -value > 0.05 ; not shown).

4.2.2. *n*-Alcohols

While nominally regarded as a plant-wax lipid, C_{24} *n*-alcohol has been observed in freshwater phytoplankton (Volkman et al., 1998; Volkman et al., 1999; Xu et al., 2007). In our sample set, isotopic evidence indicates that phytoplankton contribute to C_{24} *n*-alcohol (see section 5.3. below), and we therefore omit this compound from our calculations of ACL, CPI, and ΣLC .

Plant-wax *n*-alcohols ($C_{26} - C_{36}$; even-numbered homologues) are considerably more abundant than *n*-alkanes, with individual compound concentrations ranging from 14.6 ± 3.1 $\mu\text{g/gOC}$ (C_{36}) to 163.0 ± 8.0 $\mu\text{g/gOC}$ (C_{28} ; Figure 3b). ΣLC_{26-36} concentrations range from 206.5 – 718.7 $\mu\text{g/gOC}$, and are therefore 3.8 ± 0.9 times higher than corresponding *n*-alkane concentrations. Time series plots of ΣLC_{26-36} and selected homologue concentrations are shown in Figure 6a-c, while Figure 5d shows that ΣLC_{26-36} concentrations decrease as a function of river discharge. Again, this relationship is driven by changes in %OC, as sediment-normalized ΣLC_{26-36} concentrations display no significant relationship with discharge ($R^2 = 0.04$, p -value > 0.05 ; not shown).

n-Alcohols are more evenly distributed than *n*-alkanes, with no single homologue contributing more than 21% or less than 9% of the long-chain total (Figure 3b). ACL is calculated similarly to *n*-alkanes, but using $C_{26} - C_{36}$ even-numbered homologues. Again, ACL shows little variability, with a range of 29.8 – 30.6 units and an average of 30.2 ± 0.2 units. CPI,

calculated as above but using ΣLC_{26-36} in the numerator and $\Sigma LC_{25-35}/\Sigma LC_{27-37}$ in the denominators (noting that C_{37} was not detected in any sample), averages 3.7 ± 0.4 with a range of 3.0 – 4.6. While ACL shows no correlation (Figure 5e), CPI exhibits a strong negative relationship with discharge (Figure 5f).

4.2.3. *n*-Alkanoic acids

As C_{24} *n*-alcohol was omitted from the above calculations, to accurately compare ACL, CPI, and ΣLC across compound classes we remove C_{24} *n*-alkanoic acid from the calculations performed here.

Plant-wax *n*-alkanoic acid concentrations ($C_{26} - C_{36}$; even-numbered homologues) display the highest values and largest variability of all *n*-alkyl lipid classes (Figure 3c). Individual compounds range from 2.7 ± 0.2 $\mu\text{g/gOC}$ (C_{36}) to 457.1 ± 2.3 $\mu\text{g/gOC}$ (C_{28}), with a ΣLC_{26-36} concentration range of 190.2 – 1648.6 $\mu\text{g/gOC}$. Long-chain *n*-alkanoic acids therefore contribute up to ~0.2% of total exported POC, and are 7.1 ± 2.5 times more abundant than *n*-alkanes. Similar to *n*-alkanes and *n*-alcohols, *n*-alkanoic acid carbon-normalized ΣLC_{26-36} concentrations decrease with increasing river discharge (Figure 5g). While this relationship is partially driven by changes in %OC, sediment-normalized values additionally exhibit a statistically significant decrease ($R^2 = 0.19$, $p\text{-value} = 1.4 \times 10^{-2}$; not shown). Time series plots of selected homologues and ΣLC_{26-36} concentrations are plotted in Figure 7a-c.

n-Alkanoic acids display a similar distribution to *n*-alcohols, with C_{26} , C_{28} , and C_{30} all contributing ~20 – 25% of the long-chain total, and decreasing contribution with increasing chain length beyond C_{30} (Figure 3c). Average ACL is 29.5 ± 0.2 , slightly lower than that of *n*-alkanes and *n*-alcohols, and exhibits a slight increase with increasing discharge (Figure 5h). *n*-Alkanoic acid CPI is the highest of all observed compound classes (C_{37} not detected), averaging 4.3 ± 0.5 and shows no correlation with river discharge (Figure 5i). We note that inclusion of C_{24} decreases ACL to 28.4 ± 0.2 and exhibits no effect on CPI (not shown).

4.3. Compound-specific $\delta^{13}\text{C}$

Individual homologue $\delta^{13}\text{C}$ measurements are reported in Tables EA5-EA7.

4.3.1. *n*-Alkanes

n-Alkanes display the largest $\delta^{13}\text{C}$ variability across long-chain homologues of all compound classes studied, with an average max-min value of $8.1 \pm 0.7\text{‰}$ (Figure 3d). However, we note that C_{25} could not be measured in two samples (December 2010, July 2013) and C_{35} could not be measured in one sample (July 2013), as concentrations were too low. All samples show the same general trend with chain length – i.e. C_{25} , C_{27} , and C_{33} near -30‰ , C_{29} and C_{31} near -34‰ , and C_{35} up to $-24.7 \pm 0.1\text{‰}$ (Figure 3d). Temporal variability for each compound in the dataset is $\sim 2.5 - 3.0\text{‰}$ (max-min), as is shown for C_{29} and C_{35} in Figure 4d. $\delta^{13}\text{C}$ values of all compounds are uncorrelated with discharge (p-value > 0.05 ; not shown).

4.3.2. *n*-Alcohols

Low concentrations prevented the measurement of $\delta^{13}\text{C}$ values for C_{36} *n*-alcohol. Additionally, one sample (December 2010) displayed contamination by siloxanes and was omitted. All remaining samples follow the same general pattern, with C_{24} exhibiting the most depleted values, nearly identical values for $\text{C}_{26} - \text{C}_{30}$ and C_{34} , and C_{32} showing the most enrichment, averaging $-31.1 \pm 0.7\text{‰}$ (Figure 3e).

Time series plots of $\delta^{13}\text{C}$ values for C_{24} and C_{28} *n*-alcohols are plotted in Figure 6d. C_{24} $\delta^{13}\text{C}$ values display a strong positive correlation with discharge (Figure 8a), with the most ^{13}C -depleted value ($-36.9 \pm 0.1\text{‰}$) observed during the lowest measured discharge on record (July 2011). In contrast, $\text{C}_{28} - \text{C}_{34}$ $\delta^{13}\text{C}$ values display no correlation with discharge (p-value > 0.05 ; not shown), although C_{26} exhibits a slight positive relationship, mainly driven by three outlier points (Figure 8b). Resulting $\delta^{13}\text{C}$ spread across measured plant-wax *n*-alcohols (i.e. $\text{C}_{26} - \text{C}_{34}$) is therefore $2.6 \pm 0.6\text{‰}$, significantly lower than that for *n*-alkanes, even when only considering analogous homologues (i.e. $\text{C}_{25} - \text{C}_{33}$ *n*-alkane spread of $4.2 \pm 0.6\text{‰}$). While temporal variability within $\text{C}_{26} - \text{C}_{30}$ homologues is $\sim 2.5\text{‰}$, C_{32} and C_{34} are significantly more variable, with a max-min value of $\sim 3.5\text{‰}$.

4.3.3. *n*-Alkanoic acids

C_{36} *n*-alkanoic acid $\delta^{13}\text{C}$ values could not be measured as concentrations were too low, nor could C_{34} in one sample (December 2011). Similar to *n*-alcohols, *n*-alkanoic acids show significantly less spread in $\delta^{13}\text{C}$ values between measured homologues (i.e. $\text{C}_{24} - \text{C}_{34}$; $2.0 \pm 1.1\text{‰}$) than do *n*-alkanes (Figure 3f). C_{24} and C_{26} *n*-alkanoic acids display the largest temporal

variability of all measured compounds – with a range of 5.2‰ and 5.5‰, respectively. In contrast, C₂₈ – C₃₂ temporal variability is ~2.5‰, similar to that for *n*-alkanes and *n*-alcohols, while C₃₄ varies by 3.4‰ (Figure 7d).

Unlike *n*-alcohols, C₂₄ *n*-alkanoic acids do not show ¹³C-depletion relative to longer chain homologues during periods of low discharge (p-value > 0.05; not shown). In addition, C₂₄ – C₂₆ *n*-alkanoic acids are ¹³C-enriched relative to C₂₄ *n*-alcohol by 3.9 ± 1.1‰ and 4.3 ± 1.3‰, respectively. C₂₄ and C₂₈ δ¹³C values show a small yet statistically significant enrichment with increasing discharge (Figure 8c, 8d), while all other compounds are uncorrelated (p-value > 0.05; not shown).

4.4. Correlations between homologues and compound classes

WLS regression correlation coefficients (r) and significance p-values for concentrations and δ¹³C values of each compound are presented in Tables 1-3.

Within each *n*-alkyl compound class, concentrations of all long-chain homologues exhibit statistically significant positive correlations, with r ranging from 0.52 – 0.94 for *n*-alkanes, 0.71 – 0.98 for *n*-alcohols, and 0.70 – 0.99 for *n*-alkanoic acids. In contrast, concentrations of long-chain homologues between different compound classes are uncorrelated or display weak positive correlation (r ≤ 0.75). Concentrations of both C₂₃ and C₂₅ *n*-alkane are statistically uncorrelated with their corresponding (i.e. n + 1) *n*-alkanoic acids. Additionally, C₂₃, C₂₅, and C₃₅ *n*-alkane concentrations are uncorrelated with those of C₂₈ – C₃₄ *n*-alkanoic acid; C₃₆ *n*-alcohol is uncorrelated with C₃₀ – C₃₆ *n*-alkanoic acid; and C₂₉ *n*-alkane is uncorrelated with C₃₆ *n*-alcohol, indicating a decoupling between the sources of these compounds.

In general, δ¹³C values between all long-chain homologues exhibit less correlation than do concentrations. Within each compound class, r exhibits a range of -0.02 – 0.75 for *n*-alkanes, -0.09 – 0.50 for *n*-alcohols, and -0.55 – 0.79 for *n*-alkanoic acids. Similar ranges are observed between compound classes: -0.09 – 0.78 between *n*-alkanes and *n*-alcohols, -0.16 – 0.63 between *n*-alkanes and *n*-alkanoic acids, and -0.35 – 0.58 between *n*-alcohols and *n*-alkanoic acids. Interestingly, δ¹³C values between C₂₆ and C₃₄ *n*-alkanoic acids display a statistically significant negative correlation, while all other significant correlations are positive.

Lastly, δ¹³C values are generally either uncorrelated with concentrations or display a statistically significant negative correlation. C₂₇ – C₃₃ *n*-alkane, C₂₄ *n*-alcohol, and C₂₄ *n*-alkanoic

acid $\delta^{13}\text{C}$ values all exhibit significant negative correlation with increasing concentrations of most measured compounds, while C_{25} *n*-alkane, C_{35} *n*-alkane, $\text{C}_{28} - \text{C}_{30}$ *n*-alcohol, and C_{34} *n*-alcohol $\delta^{13}\text{C}$ values are statistically uncorrelated with the concentrations of all compounds. In contrast to other compound classes, some *n*-alkanoic acid $\delta^{13}\text{C}$ values exhibit significant positive correlation with concentrations: C_{30} $\delta^{13}\text{C}$ values correlate positively with $\text{C}_{33} - \text{C}_{35}$ *n*-alkane and C_{36} *n*-alcohol concentrations, C_{32} $\delta^{13}\text{C}$ values correlate positively with C_{36} *n*-alcohol concentrations, and C_{34} $\delta^{13}\text{C}$ values correlate positively with C_{36} *n*-alkanoic acid concentrations.

5. Discussion

5.1. *n*-Alkane homologues variably record a spatially integrated signal

Contrary to *n*-alcohols and *n*-alkanoic acids, Congo River carbon-normalized *n*-alkane concentrations are relatively low compared to other large rivers studied (van Dongen et al., 2008; Galy et al., 2011; Tao et al., 2015). In addition to vascular plants, petrogenic sources can also contribute to alkanes, especially even chain-length saturated homologues due to the low CPI value (~ 1.0) of rock-derived sources as compared to plant waxes (Eglinton and Hamilton, 1967; Brooks and Smith, 1969). Low concentrations prevented the measurement of even chain-length $\delta^{13}\text{C}$ values in our samples, however CPI values between 2.1 – 4.1 indicate that *n*-alkanes are dominated by a vascular plant signal. Additionally, the Congo catchment is composed mainly of Neoproterozoic craton lithology and exhibits low catchment relief, precluding a significant contribution of outcropped sedimentary rocks to Congo River suspended sediments (Milliman and Farnsworth, 2011; Galy et al., 2015).

Due to their lack of functional groups, *n*-alkanes are more resistant to diagenetic degradation within soils and sediments than are *n*-alkanoic acids and *n*-alcohols (Cranwell, 1981; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993; Sinninghe Damsté et al., 2002; van Dongen et al., 2008). For example, Hoefs et al. (2002) show that *n*-alkanes exhibit $\sim 3\times$ higher preservation factors than do *n*-alkanoic acids upon re-exposure of anoxic sediments to oxygen, while Canuel and Martens (1996) and Sun and Wakeham (1994) calculate lower degradation rates for *n*-alkanes than for functionalized lipids in both oxic and anoxic surface sediments. These results are consistent with observed pre-aging of *n*-alkanes prior to fluvial export, as

indicated by ^{14}C -derived ages of plant-wax *n*-alkanes in suspended sediments from other large rivers (e.g. Gustafsson et al., 2011; Tao et al., 2015).

Congo River suspended sediment *n*-alkanes exhibit significantly lower CPI values than do *n*-alcohols and *n*-alkanoic acids (Figure 5c, 5f, 5i), suggesting increased exposure to diagenesis (Meyers and Ishiwatari, 1993). Additionally, a compilation of individual African forb, grass, shrub, and tree leaves indicates significant overlap in long-chain (i.e. ΣLC_{25-35} , ΣLC_{26-36}) plant-wax concentrations and CPI values between compound classes (Table 4). We note that African plant *n*-alkanoic acid concentration measurements are lacking ($n = 25$; Table 4), potentially leading to the higher mean and median values for this compound class. Inclusion of measurements from shrubs, grasses, and forbs raised in botanical gardens (Gao et al., 2014) lowers this mean value to 406 $\mu\text{g/g}$ dry leaf weight (inter-quartile range of 18 – 643 $\mu\text{g/g}$ dry leaf weight, $n = 72$), nearly identical to the mean of African plant *n*-alkanes and *n*-alcohols. Therefore, barring extreme biases against the transfer of plant-wax *n*-alkanes into soils and subsequent entrainment into streams, their low and stable relative contribution to total *n*-alkyl lipids in suspended sediments ($\leq 16\%$; Figure 9a, 10a) agrees with relatively stronger exposure to diagenesis as compared to *n*-alcohols and *n*-alkanoic acids.

n-Alkane concentrations, ACL, CPI, and $\delta^{13}\text{C}$ values show little to no correlation with discharge (Figure 4, 5a-5c), indicating that exported *n*-alkane signals do not respond to environmental changes on seasonal timescales. In contrast, if *n*-alkanes were dominated by a recently entrained local signal, discharge should exhibit a strong control on molecular concentration/distribution and/or isotopic composition due to temporal variability in northern vs. southern hemisphere tributary contributions and their corresponding PFT signatures (Figure 1, 2b). However, this is not observed. This lack of correlation between *n*-alkane concentration, ACL, and discharge likely explains the similarly low and invariant P_{aq} values (Table EA2), as *Cuvette Congolaise* macrophytes do not contribute significantly to exported *n*-alkanes during periods of high northern hemisphere discharge.

Differences in isotopic composition between homologues contain additional information related to residence time and end-member contribution in river systems with stable ecosystems and discharge source regions. Integration over multiple source regions with unique *n*-alkane homologue distributions should result in large $\delta^{13}\text{C}$ variability with chain length. For example, Agrawal et al. (2014) observed a consistent increase in $\delta^{13}\text{C}$ values with chain length of up to

~6‰ between C₂₄ and C₃₂ *n*-alkanoic acids in a sediment core taken from the Ganges floodplain at the base of the Himalayas. Additionally, they describe a unique “bimodal” concentration distribution with a maximum at C₂₄ and with significantly lower C₂₆/C₂₈ and higher C₃₀/C₃₂ concentrations than would be expected based on the distributions in modern Ganges suspended sediments (Galy et al., 2011). Taken together, Agrawal et al. (2014) use these results as evidence for degradation of Himalayan C₃ *n*-alkanoic acids and replacement by local floodplain C₄-derived compounds, and conclude that C₂₆/C₂₈ better retain a headwater signal while C₃₀/C₃₂ exhibit significant overprinting due to higher production of the longer-chain homologues by local C₄ grasses.

In the Congo River, integration of *n*-alkanes over multiple source regions should result in a similarly large δ¹³C difference across homologues and lower correlation between homologue concentrations, as is observed (Figure 3d, 4d; Table 1). Depleted δ¹³C values for C₂₉ and C₃₁ *n*-alkane confirm the importance of a C₃ source to these compounds, while relatively ¹³C-enriched C₃₃ and, especially, C₃₅ values indicate a larger contribution by C₄ grasses with increasing chain length. This agrees with measurements of individual plant leaves, as African graminoids have been shown to produce higher relative concentrations of C₃₃ (C₃₅ not measured) as compared to African trees and forbs (Rommerskirchen et al., 2006; Vogts et al., 2009). Using a typical end-member *n*-alkane isotopic value of -35‰ for C₃ and -22‰ for C₄ plants (e.g. Castañeda and Schouten, 2011), this results in a C₄ contribution as high as 69 ± 6% to C₃₅ *n*-alkane and as low as 8 ± 4% to C₂₉ *n*-alkane, while remote-sensing results indicate that catchment-wide C₄ graminoid coverage is ~14% (Figure 1b; Still and Powell, 2010). However, we note that remote sensing likely underestimates C₄ coverage in forested areas, as C₄ plants are masked by C₃ forest canopy.

Spatially, C₄-bearing savannah and woodland/shrubland ecosystems are mostly located at the northern and southern extremes of the catchment, above 5°N and between 5-10°S, while C₃-dominated evergreen forest, deciduous/montane forest, and swamp forest occupy the central region (Figure 1). This geographic separation indicates a variable apparent integration region for *n*-alkane homologues, with the longest chain-length *n*-alkanes biasing toward headwater regions due to higher production by graminoids. Additionally, observed negative correlations between C₂₇ – C₃₃ *n*-alkane concentrations and δ¹³C values (Table 3) are further evidence for an overprinting of distal C₄ sources during transit. This relationship is strongest for C₂₉ and C₃₁ (r =

-0.74, -0.65), consistent with significant production of these compounds in C₃ trees and forbs (Rommerskirchen et al., 2006; Vogts et al., 2009). In contrast, C₃₅ δ¹³C values are uncorrelated with concentration, further indicating a predominantly headwater C₄ source to this compound, irrespective of concentration. While regions of mosaic savannah/grassland and deciduous woodland/shrubland exist near the sampling site, especially in left-bank tributaries (Figure 1), this contribution is likely minimal. If local C₄ sources were important, this would lead to ¹³C-enrichment of all *n*-alkane homologues, especially during periods of predominantly southern hemisphere discharge, which is not observed (Figure 4d).

Biasing of C₃₃ and C₃₅ *n*-alkanes toward a headwater C₄ signal agrees with time series measurements of the Oubangui River at Bangui Station (4°21.8' N, 18°33.1' E; Figure 1). Bouillon et al. (2012) show enriched POC δ¹³C values (-26.2 ± 0.4‰, n = 11) during periods of high discharge, when autochthonous production is negligible, as this headwater tributary contains significant amounts of dry woody savannah ecosystem coverage. Additionally, enriched POC δ¹³C values up to -22.8‰ have been reported for a small savannah tributary to the Oubangui River, while the nearby savannah-dominated Niari River exhibits POC δ¹³C values as high as -18.6‰ (Mariotti et al., 1991; Bouillon et al., 2014). In contrast, the Congo main-stem near Brazzaville displays more depleted POC δ¹³C values, averaging -28.2 ± 0.4‰ (n = 5; Spencer et al., 2012).

Additional evidence for variable spatial integration of *n*-alkane homologues comes from a positive correlation between the δ¹³C values of *n*-alkanoic acids/*n*-alcohols and their corresponding *n*-alkanes (i.e. carbon number - 1), as decarboxylation and dehydration of functionalized *n*-alkyl lipids has been shown to occur rapidly in sediments (Cranwell, 1981; Sun and Wakeham, 1994; Sun et al., 1997; Hoefs et al., 2002). Such relationships are especially strong between C₃₀/C₃₂ *n*-alcohol and *n*-alkanoic acid and C₂₉/C₃₁ *n*-alkane (r up to 0.75; Table 2), indicating that diagenetic contribution by functionalized C₃ plant waxes contributes to the overprinting of these compounds during transit. Taken together, the observed depleted δ¹³C values, negative correlations between δ¹³C and concentration, and positive δ¹³C correlations with corresponding functionalized lipids indicate that C₂₉ and C₃₁ *n*-alkane exhibit significant overprinting during fluvial transit and bias toward a more local signal. In contrast, enriched δ¹³C values and weaker correlation between δ¹³C and concentration for C₃₃ and, especially, C₃₅ *n*-alkanes are strong evidence that these homologues better retain a headwater signal.

5.2. *n*-Alcohols and *n*-alkanoic acids are controlled by recently entrained local sources

Contrary to *n*-alkanes, carbon-normalized concentrations of plant-wax *n*-alcohols and *n*-alkanoic acids in Congo River POC are equal to or greater than the highest observed values in any large river system to date (Saliot et al., 2001; van Dongen et al., 2008; Galy et al., 2011; Tao et al., 2015). Such high *n*-alcohol:*n*-alkane (3.8 ± 0.9) and *n*-alkanoic acid:*n*-alkane (7.1 ± 2.5) ratios in suspended sediments contrast with the overlapping range in concentrations between compound classes found in African plants (Table 4). Additionally, despite an identical range in CPI for *n*-alkanes and *n*-alcohols (no *n*-alkanoic data exist) in individual African plant leaves (Table 4), both functionalized compound classes exhibit higher CPI values than do *n*-alkanes in suspended sediment (Tables EA2-EA4), as diagenetic degradation has been shown to lower CPI (Meyers and Ishiwatari, 1993).

Assuming no pervasive biases against the transfer of *n*-alkanes into soils and subsequent entrainment into streams, high concentrations and CPI values of functionalized lipids relative to *n*-alkanes, despite similar input composition from plants (Table 4), supports the hypothesis that exported *n*-alcohols and *n*-alkanoic acids are mostly sourced from local surface soils with less exposure to diagenesis prior to export. Functionalized wax lipids are known to experience rapid diagenetic dehydration and decarboxylation in sediments (Meyers and Eadie, 1993; Sun and Wakeham, 1994; Canuel and Martens, 1996; Sun et al., 1997). For example, Sun et al. (1997) report that 90% of ^{14}C -labeled C_{16} *n*-alkanoic acids (labeled in the methyl position) are degraded due to decarboxylation within 80 days during incubation experiments. While C_{16} *n*-alkanoic acid is produced ubiquitously in the environment, rapid degradation has additionally been observed for plant-wax-specific *n*-alkanoic acids (i.e. $\text{C}_{26} - \text{C}_{30}$) and *n*-alcohols ($\text{C}_{26} - \text{C}_{30}$) upon re-exposure of sediments to oxygen (Hoefs et al., 2002). *n*-Alkanoic acids and *n*-alcohols frequently exhibit the lowest preservation of all lipids in marine and lacustrine sediments and have been observed to degrade at faster rates than bulk OC (Cranwell, 1981; Meyers and Ishiwatari, 1993). However, lipid preservation is additionally a function of sediment mineralogy, as sorptive interactions with mineral surfaces have been shown to stabilize labile OC (e.g. Keil et al., 1994; Mayer 1994).

Isotopic evidence further indicates a predominantly local source, as these compound classes exhibit depleted $\delta^{13}\text{C}$ values for all plant-wax homologues (average $\leq -31.3\text{‰}$ and -

30.8‰, respectively; Figure 3e-f). Using a C₃ end-member value of -35‰ and a C₄ end-member value of -22‰, as above (Castañeda and Schouten, 2011), this leads to a minimum C₃ contribution to *n*-alcohols of $73 \pm 5\%$ (C₃₂) and $68 \pm 6\%$ to *n*-alkanoic acids (C₂₆). However, this is likely an underestimate, as relatively enriched $\delta^{13}\text{C}$ values for individual C₃ angiosperm lipids have been reported (i.e. up to -30‰; Diefendorf et al., 2011; Garcin et al., 2014). Isotopic evidence therefore indicates that functionalized lipids are predominantly sourced from local C₃ ecosystems, as C₄ land cover is mostly limited to distal headwater regions (Figure 1b). Similar to *n*-alkanes, regions of mosaic savannah/grassland and deciduous woodland/shrubland near the sampling site likely do not contribute significantly to exported *n*-alcohols and *n*-alkanoic acids, as this would lead to a ^{13}C -enrichment during southern hemisphere dominated discharge periods, which is not observed (Figure 6d, 7d, 8).

Unlike longer chain homologues, autochthonous production of C₂₄ *n*-alcohol has been observed in freshwater phytoplankton (Volkman et al., 1998; Volkman et al., 1999; Xu et al., 2007) and is likely a significant source of this compound in our sample set. This is supported by depleted $\delta^{13}\text{C}$ values (Figure 3e) and a strong positive relationship with discharge (Figure 8a). If dissolved inorganic carbon (DIC) is ^{13}C -depleted relative to atmospheric CO₂, autochthonous contribution will lead to lower observed $\delta^{13}\text{C}$ values for C₂₄ *n*-alcohol, especially during periods of low discharge when phytoplankton production is highest. While no DIC $\delta^{13}\text{C}$ values exist at our sampling site, low- and rising-water values at Bangui station average $-10.0 \pm 2.2\%$ (n = 30; Bouillon et al., 2012; Bouillon et al., 2014). Additionally, C₂₄ *n*-alcohol $\delta^{13}\text{C}$ values are strongly correlated with those of C₂₂ *n*-alcohol ($R^2 = 0.75$, p-value = 4.0×10^{-10} ; not shown), the dominant lipid in freshwater phytoplankton (Volkman et al., 1998; Volkman et al., 1999; Xu et al., 2007), and are uncorrelated with longer chain-length values (p-value > 0.05; not shown). While a slight $\delta^{13}\text{C}$ vs. discharge correlation is observed for other compounds (i.e. C₂₆ *n*-alcohol, C₂₄ and C₂₈ *n*-alkanoic acid; Figure 8), these homologues are consistently ~3-5‰ enriched relative to C₂₄ *n*-alcohol, indicating minimal autochthonous contribution.

Further evidence for a local, C₃ signal to functionalized *n*-alkyl lipids comes from the fact that $\delta^{13}\text{C}$ values show significantly weaker negative correlation with lipid concentrations than do *n*-alkanes, with the exception of C₂₄ *n*-alcohol and C₂₄ *n*-alkanoic acid (Table 3). As with *n*-alkanes, a negative correlation would indicate addition of C₃ material to a background C₄ signal during transit. However, this is not the case, especially for longer chain-length homologues (i.e.

C₂₈₊), indicating negligible contribution by C₄-dominated headwater ecosystems to measured compounds and therefore a smaller apparent integration region than is observed for *n*-alkanes, especially C₃₃ and C₃₅. African C₄ graminoids exhibit similar *n*-alcohol and *n*-alkanoic acid production rates as African forbs, shrubs, and trees (Ali et al., 2005a; Rommerskirchen et al., 2006; Vogts et al., 2009), indicating that this signal is not due to a source effect. Rather, it is likely the result of quantitative diagenetic degradation of headwater functionalized *n*-alkyl lipids during fluvial transit (Cranwell, 1981; Meyers and Ishiwatari, 1993; Sun et al., 1997; Hoefs et al., 2002; van Dongen et al., 2008). In addition, a low spread in $\delta^{13}\text{C}$ values across plant-wax chain-lengths (Figure 3e-f) and strong positive correlations between homologue concentrations (Table 1) precludes significant spatial integration of multiple PFTs with unique molecular distribution and isotope composition (c.f. Agrawal et al., 2014).

Additionally, we observe large seasonal variability in *n*-alcohol and *n*-alkanoic acid relative contribution (Figure 9), indicating a change in functionalized lipid source in response to seasonal hydrology. This is consistent with the above evidence that these compounds are sourced from recently entrained OC and integrate a mostly local signal. *n*-Alcohol relative contribution displays a statistically significant increase during *Cuvette Congolaise* dominated periods, balanced by an equal decrease in *n*-alkanoic acids (Figure 10). These results agree with literature measurements of individual plants, as macrophytes display considerably higher *n*-alcohol production rates than do other PFTs (Ficken et al., 1998; Ficken et al., 2000; Bugalho et al., 2004; Ali et al., 2005a; Ali et al., 2005b; Aichner et al., 2010; Gao et al., 2011; Diefendorf et al., 2011; Wang and Liu, 2012; Gao et al., 2014).

It has been shown that the Congo main-stem and a range of tributaries bias toward swamp-forest-like chemical properties during periods of high discharge, indicating an increased contribution by this ecosystem to exported organic carbon (Wang et al., 2013b; Mann et al., 2014). These observations, combined with an increase in *n*-alcohol fractional contribution, are strong evidence for a significant increase in *Cuvette Congolaise* contribution to functionalized *n*-alkyl lipids during periods of high northern hemisphere discharge. Thus, our results indicate that this geographically small region (4% coverage; Mayaux et al., 2004) exhibits a dominant control on the composition of exported functionalized *n*-alkyl lipids in response to seasonal changes in hydrology. However, a lack of significant $\delta^{13}\text{C}$ variability across the time series for any

functionalized plant-wax lipid (Figure 6d, 7d) indicates that their $\delta^{13}\text{C}$ values are not a sensitive tracer for changes in *n*-alkyl lipid source on these timescales.

5.3. Comparison to other river basins and global significance

Variable spatiotemporal integration of *n*-alkane homologues and a local, recently entrained *n*-alcohol/*n*-alkanoic acid signal is a feature not limited to the Congo River catchment. For example, isotopic and molecular signals of *n*-alkanes and *n*-alkanoic acids show differential contribution by C_4 grasses during transport in the Ganges River through the floodplain (Galy et al., 2011). Using the data of Galy et al. (2011), we compare the concentration-weighted Himalayan plant-wax signal to that just before the confluence with the Brahmaputra River in Bangladesh, noting that sediment fluxes are nearly identical in all major Himalayan tributaries (Andermann et al., 2012).

Himalayan plant-wax *n*-alkanes ($\text{C}_{25} - \text{C}_{35}$) and *n*-alkanoic acids ($\text{C}_{26} - \text{C}_{34}$) display nearly identical $\delta^{13}\text{C}$ composition, averaging -32.1‰ and -32.3‰ respectively, with similar spread between chain-lengths of 1.8‰ and 1.4‰. In contrast, downstream Ganges *n*-alkanoic acid $\delta^{13}\text{C}$ values are enriched by an average of 1.3‰ relative to *n*-alkanes. Additionally, isotopic spread between chain lengths remains constant for *n*-alkanoic acids (i.e. 1.4‰), but increases to 3.5‰ for *n*-alkanes, while ACL of both compound classes increases by ~1 unit. Combined, these results indicate that C_3 *n*-alkanoic acids sourced in the Himalayan range are quantitatively replaced by a mixed C_3/C_4 floodplain signal independent of chain length. In contrast, *n*-alkanes display differential contribution by a floodplain signal across chain lengths, with $\text{C}_{33}/\text{C}_{35}$ showing the most influence. Quantitative *n*-alkanoic acid replacement during floodplain transit agrees with the results of Agrawal et al. (2014), which already show significant overprinting near the base of the Himalayan range. Thus, despite large differences in sediment erosion rates and biospheric carbon yields between the Congo and Ganges rivers (Galy et al., 2015), exported plant waxes display similar behavior in these two catchments.

In addition to the Ganges River, a large spread in *n*-alkane $\delta^{13}\text{C}$ values with chain-length has been observed in settings such as Cameroonian lacustrine and Washington margin surface sediments (Feng et al., 2013; Garcin et al., 2014) and a Zambezi River sedimentary archive (Wang et al., 2013a). Differential contribution by C_3/C_4 plants to *n*-alkanes with chain length therefore appears to be a common phenomenon. We suggest that $\delta^{13}\text{C}$ measurement of multiple

n-alkane chain lengths can be used to address nonlinear PFT mixing during transport (Garcin et al., 2014), as C₃₃ and, especially, C₃₅ bias almost exclusively toward a C₄ end-member, opposite to C₂₉ and C₃₁.

Additionally, differential sourcing between compound classes (i.e. functionalized vs. *n*-alkanes) appears to be common in river catchments spanning multiple ecosystems. Thus, in addition to *n*-alkanes, measurement of *n*-alcohols and *n*-alkanoic acids in river sediments and fluvially dominated sedimentary archives can be utilized to address geospatial PFT distribution within the catchment, as functionalized lipids will bias toward a local signal (e.g. Galy et al., 2011; Ponton et al., 2014; this study).

6. Conclusion

We report concentrations and $\delta^{13}\text{C}$ values of three classes of dominantly plant-derived *n*-alkyl lipids from a 34-month time series of Congo River suspended sediments. Our results show that *n*-alkanoic acid and *n*-alcohol concentrations are equal to or greater than the highest OC-normalized concentrations in large fluvial systems reported to date. In contrast, *n*-alkanes concentrations are lower than those reported in other major rivers. Spread in *n*-alcohol and *n*-alkanoic acid $\delta^{13}\text{C}$ values between long-chain homologues is lower than observed in other major rivers, while *n*-alkanes exhibit up to ~8‰ enrichment with increasing chain length.

These data indicate that *n*-alkanoic acids and *n*-alcohols are sourced from local, C₃-dominated ecosystems, consistent with the idea that high reactivity of functional groups precludes significant spatial integration of these compounds. In contrast, *n*-alkane homologues variably integrate over a wide range of ecosystems with increasing contribution by distal C₄-dominated savannah and woodland/shrubland source regions to the longest chain-length compounds. Strong seasonal shifts in relative *n*-alkanoic acid and *n*-alcohol concentrations indicate that functionalized lipids respond rapidly to changes in hydrological regime. This signal, however, is not reflected in $\delta^{13}\text{C}$ values. During periods of highest northern hemisphere discharge, an increase in fractional *n*-alcohol contribution and decrease in *n*-alkanoic acid contribution suggest a strong bias towards a local swamp-forest signal. *n*-Alkanes are less affected by seasonal changes in discharge, further indicating that these compounds integrate over a larger source region.

Consequently, we suggest that simultaneous measurement of multiple *n*-alkyl lipid classes and chain lengths in down-core samples will likely provide better geospatial resolution for paleo-ecosystem reconstruction due to their differential integration regions and C₃/C₄ biases.

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924

Table Captions

Table 1: Weighted least squares regression correlation values (r) and significance p -values between all measured C_{23+} n -alkyl lipid concentrations. Statistically significant (p -value ≤ 0.05) correlations are bolded.

Table 2: Weighted least squares regression correlation values (r) and significance p -values between all measured C_{25+} n -alkyl lipid $\delta^{13}C$ values. Statistically significant (p -value ≤ 0.05) correlations are bolded.

Table 3: Weighted least squares regression correlation values (r) and significance p -values between all measured C_{23+} n -alkyl lipid concentrations vs. C_{25+} $\delta^{13}C$ values. Statistically significant (p -value ≤ 0.05) correlations are bolded.

Table 4: Summary statistics of plant-wax n -alkane, n -alcohol, and n -alkanoic acid (ΣLC_{25-35} , ΣLC_{26-36}) concentration and CPI data from African plant leaves ($\mu g/g$ dry leaf weight).

Figure Captions

Figure 1: Map of the Congo catchment upstream of sampling location showing (a.) land cover according to European Commission Joint Research Centre (Mayaux et al., 2000) and (b.) $\%C_3$ vs. $\%C_4$ vegetation (Still and Powell, 2010). Our sampling location is marked as a red circle. For reference, Bangui Station (Coynel et al., 2005; Bouillon et al., 2012; Bouillon et al., 2014) is marked as a white diamond.

Figure 2: Time series plots of (a.) Congo River discharge (Q_w), (b.) monthly fractional contribution by southern hemisphere tributaries (f_{south}) as estimated by Bricquet (1993) (repeating for multiple years), (c.) TSS concentration, and (d.) POC concentration measured at Brazzaville/Kinshasa during the sampling period. Southern hemisphere dominated periods are defined when f_{south} is greater than the median value of 39%, and are indicated by gray boxes.

Figure 3: Violin plots of *n*-alkane, *n*-alcohol, and *n*-alkanoic acid (a. – c.) POC-normalized concentrations and (d. – f.) $\delta^{13}\text{C}$ values for individual long-chain homologues. Violin plots represent the temporal distribution of values throughout the time-series using a Gaussian kernel density function. Mean values are marked as black circles, and median values are marked as horizontal black lines.

Figure 4: Time series plots of *n*-alkane concentrations – (a.) C_{29} , (b.) C_{35} , (c.) ΣLC_{25-35} – and $\delta^{13}\text{C}$ values – (d.) C_{29} (solid line) and C_{35} (dashed line). Selected homologues are chosen to represent the increasing influence by C_4 grasses with increasing chain length. Dark gray shading represents $\pm 1\sigma$ uncertainty, and light gray shading represents 95% confidence interval (CI). Periods when $f_{\text{south}} > 39\%$ are indicated by gray boxes.

Figure 5: Correlations between $\Sigma\text{LC}_{25-35}/\Sigma\text{LC}_{26-36}$ concentrations, ACL, and CPI vs. Congo River discharge (Q_w) measured at Brazzaville/Kinshasa for *n*-alkanes (a. – c.), *n*-alcohols (d. – f.), and *n*-alkanoic acids (g. – i.). Error bars on individual points represent $\pm 1\sigma$ uncertainty. Black line is the WLS best-fit line, dark gray shading represents $\pm 1\sigma$ regression uncertainty, and light gray shading represents the 95% CI. Samples collected when $f_{\text{south}} > 39\%$ are plotted as white squares, and samples collected when $f_{\text{south}} \leq 39\%$ are plotted as black circles.

Figure 6: Time series plots of *n*-alcohol concentrations – (a.) C_{24} , (b.) C_{28} , (c.) ΣLC_{26-36} – and $\delta^{13}\text{C}$ values – (d.) C_{24} (solid line) and C_{28} (dashed line). Selected homologues are chosen to represent the autochthonous contribution to C_{24} and C_3 plant dominance of longer homologues. Dark gray shading represents $\pm 1\sigma$ uncertainty, and light gray shading represents 95% CI. Periods when $f_{\text{south}} > 39\%$ are indicated by gray boxes.

Figure 7: Time series plots of *n*-alkanoic acid concentrations – (a.) C_{28} , (b.) C_{34} , (c.) ΣLC_{26-36} – and $\delta^{13}\text{C}$ values – (d.) C_{28} (solid line) and C_{34} (dashed line). Selected homologues are chosen to represent the similar C_3 -like isotopic composition across all long-chain homologues. Dark gray shading represents $\pm 1\sigma$ regression uncertainty, and light gray shading represents 95% CI. Periods when $f_{\text{south}} > 39\%$ are indicated by gray boxes.

Figure 8: Correlations between $\delta^{13}\text{C}$ values vs. Congo River discharge (Q_w) measured at Brazzaville/Kinshasa for (a.) C_{24} *n*-alcohol, (b.) C_{26} *n*-alcohol, (c.) C_{24} *n*-alkanoic acid, and (d.) C_{28} *n*-alkanoic acid. Error bars on individual points represent $\pm 1\sigma$ uncertainty. Black line is the WLS best-fit line, dark gray shading represents $\pm 1\sigma$ regression uncertainty, and light gray shading represents the 95% CI. Samples collected when $f_{\text{south}} > 39\%$ are plotted as white squares, and samples collected when $f_{\text{south}} \leq 39\%$ are plotted as black circles.

Figure 9: Time series plots of the fractional contribution to the plant-wax *n*-alkyl lipid total by (a.) ΣLC_{25-35} *n*-alkanes, (b.) ΣLC_{26-36} *n*-alcohols, and (c.) ΣLC_{26-36} *n*-alkanoic acids. Dark gray shading represents $\pm 1\sigma$ regression uncertainty, and light gray shading represents 95% CI. Periods when $f_{\text{south}} > 39\%$ are indicated by gray boxes.

Figure 10: Fractional contribution by (a.) ΣLC_{25-35} *n*-alkanes, (b.) ΣLC_{36-36} *n*-alcohols, and (c.) ΣLC_{26-36} *n*-alkanoic acids plotted vs. Congo River discharge (Q_w) measured at Brazzaville/Kinshasa. Black line is the quadratic WLS regression line. R^2 values and significance p-values for linear (β_1) and quadratic (β_2) parameters are reported for each regression. Samples collected when $f_{\text{south}} > 39\%$ are plotted as white squares, and samples collected when $f_{\text{south}} \leq 39\%$ are plotted as black circles. Uncertainty ($\pm 1\sigma$) is smaller than the symbols for all data points.

- closed-canopy evergreen forest
- deciduous and montane forest
- deciduous woodland/shrubland
- mosaic savannah/grassland
- water bodies
- swamp forest

100% C₄ 100% C₃

Figure 1

Figure 2

Figure 5

n-alcohols

Figure 6

n-alkanoic acids

Figure 7

n-alcohols *n*-alkanoic acids $Q_w (\times 1000 \text{ m}^3/\text{s})$

Figure 8

Figure 9

n-alkane concentrations

n -alcohol concentrations

m-alkanoic acid concentrations

Table 2

		<i>n</i> -alkane $\delta^{13}\text{C}$							<i>n</i> -alcohol $\delta^{13}\text{C}$					<i>n</i> -alkanoic acid $\delta^{13}\text{C}$					
		C25	C27	C29	C31	C33	C35	C24	C26	C28	C30	C32	C34	C24	C26	C28	C30	C32	C34
<i>n</i> -alkane $\delta^{13}\text{C}$	C25 r	--	0.41	0.32	0.53	0.54	0.35	-0.09	0.41	0.21	-0.01	0.09	0.11	0.10	0.10	0.39	0.40	0.19	0.07
	p-val	2.3E-02	8.4E-02	2.5E-03	2.1E-03	5.8E-02	6.2E-01	2.6E-02	2.6E-01	9.5E-01	6.3E-01	5.7E-01	6.0E-01	5.9E-01	3.3E-02	3.0E-02	3.2E-01	7.1E-01	
	C27 r		--	0.54	0.61	0.63	-0.02	0.36	0.37	0.22	-0.02	0.27	0.15	0.42	-0.16	0.22	0.12	0.05	0.05
	p-val		1.4E-03	2.4E-04	1.1E-04	9.0E-01	4.4E-02	4.2E-02	2.3E-01	9.3E-01	1.3E-01	4.3E-01	1.7E-02	3.8E-01	2.2E-01	5.1E-01	7.8E-01	8.0E-01	
	C29 r			--	0.76	0.75	0.45	0.30	0.50	0.33	0.41	0.51	0.06	0.21	0.06	0.10	0.38	0.58	0.22
	p-val			4.3E-07	8.8E-07	1.2E-02	1.1E-01	4.2E-03	6.9E-02	2.1E-02	3.4E-03	7.4E-01	2.4E-01	7.4E-01	5.9E-01	3.4E-02	5.0E-04	2.4E-01	
<i>n</i> -alkane $\delta^{13}\text{C}$	C31 r				--	0.66	0.38	0.02	0.18	0.31	0.25	0.40	0.17	-0.07	0.03	0.10	0.34	0.75	0.36
	p-val				3.8E-05	3.6E-02	9.3E-01	3.2E-01	9.2E-02	1.8E-01	2.4E-02	3.6E-01	7.2E-01	8.9E-01	5.7E-01	5.7E-02	7.3E-07	4.9E-02	
	C33 r					--	0.00	0.23	0.42	0.66	0.36	0.78	0.22	0.18	0.28	0.40	0.53	0.63	0.54
	p-val					9.9E-01	2.0E-01	1.8E-02	5.8E-05	4.7E-02	1.9E-07	2.3E-01	3.2E-01	1.2E-01	2.4E-02	1.9E-03	1.2E-04	1.9E-03	
	C35 r						--	0.56	0.30	0.34	0.19	0.57	0.12	0.17	0.09	0.59	0.18	0.27	0.61
	p-val						1.3E-03	1.0E-01	6.8E-02	3.2E-01	8.9E-04	5.3E-01	3.7E-01	6.3E-01	4.3E-04	3.4E-01	1.4E-01	3.9E-04	
<i>n</i> -alcohol $\delta^{13}\text{C}$	C24 r							--	0.53	0.43	0.44	-0.20	-0.03	0.58	-0.19	0.55	-0.17	-0.23	0.25
	p-val							2.0E-03	1.7E-02	1.2E-02	2.7E-01	8.9E-01	6.6E-04	3.2E-01	1.3E-03	3.6E-01	2.1E-01	1.9E-01	
	C26 r								--	0.41	0.53	0.10	-0.07	0.47	-0.35	0.56	-0.14	0.15	0.42
	p-val								2.2E-02	2.1E-03	5.9E-01	7.2E-01	7.2E-03	5.6E-02	1.1E-03	4.6E-01	4.2E-01	2.1E-02	
	C28 r									--	0.67	0.59	-0.09	0.18	0.13	0.56	0.55	0.54	0.50
	p-val									3.7E-05	4.2E-04	6.5E-01	3.4E-01	4.7E-01	1.0E-03	1.2E-03	1.6E-03	5.0E-03	
<i>n</i> -alcohol $\delta^{13}\text{C}$	C30 r										--	0.49	-0.01	0.23	-0.12	0.35	0.35	0.10	0.45
	p-val										5.0E-03	9.8E-01	2.0E-01	5.3E-01	5.7E-02	5.4E-02	5.9E-01	1.3E-02	
	C32 r											--	0.22	0.51	0.08	0.35	0.55	0.47	0.53
	p-val											2.4E-01	3.1E-03	6.7E-01	5.0E-02	1.5E-03	8.4E-03	2.5E-03	
	C34 r												--	-0.01	-0.01	-0.11	0.35	0.19	0.20
	p-val												9.5E-01	9.6E-01	5.4E-01	5.2E-02	3.0E-01	2.8E-01	
<i>n</i> -alkanoic acid $\delta^{13}\text{C}$	C24 r													--	-0.18	0.45	-0.17	-0.24	0.23
	p-val													3.1E-01	1.1E-02	3.5E-01	1.9E-01	2.0E-01	
	C26 r														--	-0.22	0.25	0.12	-0.55
	p-val														2.2E-01	1.8E-01	5.1E-01	1.2E-03	
	C28 r															--	0.30	0.29	0.73
	p-val															9.3E-02	1.1E-01	3.8E-06	
<i>n</i> -alkanoic acid $\delta^{13}\text{C}$	C30 r																--	0.69	0.79
	p-val																1.4E-05	1.2E-07	
	C32 r																	--	0.52
	p-val																	2.6E-03	
	C34 r																		--
	p-val																		

Table 3

		<i>n</i> -alkane δ ¹³ C						<i>n</i> -alcohol δ ¹³ C						<i>n</i> -alkanoic acid δ ¹³ C						
		C25	C27	C29	C31	C33	C35	C24	C26	C28	C30	C32	C34	C24	C26	C28	C30	C32	C34	
<i>n</i> -alkane concentrations	C23	r	-0.04	-0.46	-0.36	-0.09	0.10	0.00	0.05	0.35	0.24	0.02	0.18	0.01	-0.40	-0.17	-0.08	0.17	0.29	0.14
		p-val	8.1E-01	8.3E-03	4.5E-02	6.1E-01	5.8E-01	9.9E-01	7.8E-01	5.3E-02	2.0E-01	9.0E-01	3.3E-01	9.5E-01	2.3E-02	3.5E-01	6.8E-01	3.4E-01	1.0E-01	4.5E-01
	C25	r	-0.14	-0.35	-0.49	-0.14	-0.06	-0.12	0.10	0.15	0.09	0.02	0.14	0.11	-0.39	-0.20	-0.07	0.11	0.21	0.10
		p-val	4.5E-01	5.0E-02	4.3E-03	4.3E-01	7.5E-01	5.3E-01	6.0E-01	4.3E-01	6.3E-01	9.2E-01	4.5E-01	5.7E-01	2.6E-02	2.7E-01	7.1E-01	5.5E-01	2.5E-01	5.8E-01
	C27	r	-0.24	-0.41	-0.62	-0.39	-0.47	-0.23	-0.08	-0.09	0.01	-0.05	-0.05	0.17	-0.44	-0.14	-0.14	0.12	0.13	0.00
		p-val	2.0E-01	2.1E-02	1.4E-04	2.7E-02	6.2E-03	2.1E-01	6.9E-01	6.5E-01	9.7E-01	7.7E-01	8.0E-01	3.7E-01	1.1E-02	4.3E-01	4.5E-01	5.1E-01	4.7E-01	9.9E-01
<i>n</i> -alcohol concentrations	C29	r	-0.10	-0.21	-0.74	-0.67	-0.72	-0.25	-0.36	-0.31	-0.08	-0.35	-0.40	-0.06	-0.54	-0.14	-0.05	-0.01	-0.17	-0.10
		p-val	6.2E-01	2.6E-01	1.1E-06	2.8E-05	4.0E-06	1.7E-01	4.4E-02	9.4E-02	6.6E-01	5.2E-02	2.4E-02	7.6E-01	1.3E-03	4.3E-01	8.0E-01	9.6E-01	3.5E-01	5.9E-01
	C31	r	-0.09	-0.35	-0.69	-0.65	-0.68	-0.25	-0.47	-0.29	-0.09	-0.33	-0.31	0.01	-0.50	-0.18	-0.08	0.18	-0.06	0.01
		p-val	6.4E-01	4.6E-02	1.3E-05	5.8E-05	1.7E-05	1.8E-01	8.0E-03	1.2E-01	6.4E-01	7.3E-02	8.6E-02	9.6E-01	3.5E-03	3.1E-01	6.5E-01	3.3E-01	7.4E-01	9.8E-01
	C33	r	-0.08	-0.55	-0.53	-0.48	-0.55	-0.19	-0.47	-0.20	-0.03	-0.22	-0.07	0.12	-0.40	-0.19	-0.10	0.37	0.16	0.14
		p-val	6.9E-01	1.1E-03	1.8E-03	5.1E-03	1.2E-03	3.2E-01	7.7E-03	2.8E-01	8.7E-01	2.4E-01	7.1E-01	5.1E-01	2.4E-02	2.9E-01	5.9E-01	3.6E-02	3.8E-01	4.4E-01
<i>n</i> -alkanoic acid concentrations	C35	r	-0.07	-0.57	-0.33	-0.20	-0.26	-0.02	-0.33	-0.06	0.09	-0.09	0.20	0.15	-0.23	-0.22	0.03	0.36	0.31	0.28
		p-val	7.3E-01	5.8E-04	6.3E-02	2.7E-01	1.6E-01	9.3E-01	7.3E-02	7.5E-01	6.4E-01	6.4E-01	2.8E-01	4.3E-01	2.1E-01	2.2E-01	8.8E-01	4.3E-02	8.7E-02	1.3E-01
	C24	r	-0.31	-0.76	-0.41	-0.54	-0.54	-0.13	-0.64	-0.49	0.12	-0.22	-0.20	-0.10	-0.51	0.14	-0.07	0.24	0.12	0.10
		p-val	9.7E-02	3.5E-07	2.0E-02	1.5E-03	1.3E-03	5.0E-01	1.1E-04	5.0E-03	5.1E-01	2.4E-01	2.7E-01	5.9E-01	3.1E-03	4.5E-01	7.1E-01	1.8E-01	5.2E-01	5.9E-01
	C26	r	-0.27	-0.71	-0.41	-0.57	-0.58	-0.11	-0.50	-0.50	0.10	-0.21	-0.24	-0.11	-0.42	0.11	0.01	0.27	0.03	0.16
		p-val	1.5E-01	4.9E-06	2.1E-02	7.1E-04	5.5E-04	5.5E-01	4.0E-03	4.1E-03	6.0E-01	2.5E-01	2.0E-01	5.7E-01	1.7E-02	5.6E-01	9.4E-01	1.4E-01	8.5E-01	3.8E-01
<i>n</i> -alcohol concentrations	C28	r	-0.24	-0.74	-0.45	-0.59	-0.56	-0.12	-0.58	-0.47	0.16	-0.24	-0.22	-0.13	-0.44	0.10	-0.04	0.31	0.07	0.15
		p-val	2.0E-01	1.2E-06	9.0E-03	3.4E-04	9.6E-04	5.2E-01	5.7E-04	7.1E-03	4.0E-01	2.0E-01	2.4E-01	4.7E-01	1.2E-02	6.0E-01	8.2E-01	8.3E-02	7.2E-01	4.3E-01
	C30	r	-0.26	-0.70	-0.53	-0.66	-0.54	-0.16	-0.45	-0.43	0.23	-0.13	-0.27	-0.15	-0.28	-0.01	0.05	0.24	-0.02	0.16
		p-val	1.6E-01	9.7E-06	1.7E-03	4.6E-05	1.4E-03	4.0E-01	1.2E-02	1.6E-02	2.2E-01	4.8E-01	1.4E-01	4.1E-01	1.2E-01	9.8E-01	7.9E-01	1.9E-01	9.0E-01	3.8E-01
	C32	r	-0.16	-0.69	-0.42	-0.61	-0.50	-0.04	-0.41	-0.31	0.28	-0.14	-0.20	-0.16	-0.21	-0.06	0.14	0.29	-0.04	0.27
		p-val	3.9E-01	1.0E-05	1.5E-02	1.8E-04	3.4E-03	8.2E-01	2.2E-02	9.0E-02	1.3E-01	4.5E-01	2.9E-01	3.8E-01	2.5E-01	7.6E-01	4.3E-01	1.1E-01	8.1E-01	1.4E-01
<i>n</i> -alkanoic acid concentrations	C34	r	-0.22	-0.79	-0.30	-0.52	-0.40	-0.08	-0.53	-0.34	0.33	-0.12	-0.15	-0.19	-0.21	0.04	0.10	0.29	0.13	0.23
		p-val	2.5E-01	7.7E-08	9.8E-02	2.2E-03	2.5E-02	6.7E-01	2.0E-03	6.4E-02	7.3E-02	5.2E-01	4.1E-01	3.0E-01	2.5E-01	8.5E-01	5.9E-01	1.1E-01	4.7E-01	2.1E-01
	C36	r	-0.14	-0.72	-0.07	-0.13	-0.04	-0.04	-0.73	-0.39	0.28	-0.11	0.16	-0.06	-0.29	0.17	-0.03	0.42	0.44	0.20
		p-val	4.5E-01	3.8E-06	7.2E-01	4.9E-01	8.3E-01	8.3E-01	3.4E-06	2.8E-02	1.2E-01	5.5E-01	3.9E-01	7.5E-01	1.1E-01	3.5E-01	8.8E-01	1.8E-02	1.1E-02	2.9E-01
	C24	r	-0.15	-0.73	-0.46	-0.41	-0.57	-0.26	-0.63	-0.55	-0.28	-0.18	-0.13	-0.04	-0.42	-0.02	-0.41	0.00	-0.14	-0.16
		p-val	4.2E-01	2.6E-06	7.5E-03	2.0E-02	6.3E-04	1.6E-01	1.5E-04	1.5E-03	1.3E-01	3.3E-01	4.9E-01	8.4E-01	1.6E-02	9.3E-01	2.0E-02	9.8E-01	4.6E-01	3.8E-01
<i>n</i> -alcohol concentrations	C26	r	-0.13	-0.70	-0.54	-0.45	-0.63	-0.25	-0.62	-0.58	-0.29	-0.22	-0.23	-0.02	-0.48	-0.01	-0.40	0.00	-0.15	-0.20
		p-val	5.0E-01	6.7E-06	1.3E-03	9.2E-03	1.2E-04	1.8E-01	2.0E-04	7.1E-04	1.2E-01	2.3E-01	2.1E-01	9.0E-01	5.2E-03	9.7E-01	2.2E-02	9.9E-01	4.1E-01	2.7E-01
	C28	r	-0.09	-0.71	-0.54	-0.46	-0.63	-0.27	-0.66	-0.59	-0.29	-0.24	-0.25	-0.04	-0.48	0.01	-0.36	0.03	-0.14	-0.20
		p-val	6.4E-01	4.3E-06	1.3E-03	8.2E-03	1.1E-04	1.4E-01	5.4E-05	5.2E-04	1.1E-01	1.9E-01	1.8E-01	8.4E-01	5.6E-03	9.6E-01	4.5E-02	8.5E-01	4.4E-01	2.8E-01
	C30	r	-0.04	-0.64	-0.64	-0.48	-0.64	-0.23	-0.53	-0.56	-0.29	-0.22	-0.32	-0.08	-0.40	-0.05	-0.24	-0.09	-0.32	-0.20
		p-val	8.2E-01	6.8E-05	9.1E-05	5.1E-03	7.6E-05	2.0E-01	2.1E-03	9.5E-04	1.1E-01	2.2E-01	8.4E-02	6.8E-01	2.4E-02	8.0E-01	1.8E-01	6.3E-01	7.7E-02	2.9E-01
<i>n</i> -alkanoic acid concentrations	C32	r	-0.04	-0.59	-0.67	-0.51	-0.66	-0.22	-0.49	-0.55	-0.30	-0.21	-0.31	-0.03	-0.37	-0.06	-0.27	-0.09	-0.37	-0.22
		p-val	8.1E-01	3.7E-04	2.9E-05	2.6E-03	3.8E-05	2.4E-01	4.7E-03	1.5E-03	9.9E-02	2.5E-01	8.5E-02	8.6E-01	3.5E-02	7.4E-01	1.4E-01	6.4E-01	3.9E-02	2.5E-01
	C34	r	-0.05	-0.59	-0.67	-0.50	-0.65	-0.17	-0.47	-0.54	-0.29	-0.20	-0.29	-0.02	-0.31	-0.08	-0.31	-0.05	-0.36	-0.19
		p-val	8.1E-01	3.9E-04	3.0E-05	3.6E-03	5.2E-05	3.5E-01	7.1E-03	1.8E-03	1.2E-01	2.8E-01	1.1E-01	9.3E-01	8.6E-02	6.7E-01	8.8E-02	7.9E-01	4.1E-02	3.1E-01
	C36	r	-0.08	-0.35	-0.50	-0.25	-0.52	0.06	-0.25	-0.38	-0.17	-0.04	-0.11	-0.02	-0.20	-0.69	0.27	-0.06	-0.19	0.54
		p-val	6.6E-01	5.2E-02	3.5E-03	1.6E-01	2.3E-03	7.5E-01	1.8E-01	3.5E-02	3.6E-01	8.2E-01	5.4E-01	9.2E-01	2.7E-01	1.4E-05	1.3E-01	7.3E-01	3.1E-01	1.6E-03

Table 4

African plant-wax concentrations (µg/g dry leaf weight)				African plant
	<i>n</i> -alkanes (ΣLC ₂₅₋₃₅)	<i>n</i> -alcohols (ΣLC ₂₆₋₃₆)	<i>n</i> -alkanoic acids (ΣLC ₂₆₋₃₆)	<i>n</i> -alkanes (ΣLC ₂₅₋₃₅)
Mean	398	535	872	18
Stdev.	556	829	385	28
Median	186	294	837	14
25 th pctle.	125	104	544	9
75 th pctle.	388	708	1131	17
n	176	129	25	111
PFTs	forbs, grasses, shrubs, trees		forbs, grasses, trees	forbs, grasses,
references	Ali et al., 2005a; Rommerskirchen et al., 2006; Vogts et al., 2009; Garcin et al., 2014	Ali et al., 2005a; Rommerskirchen et al., 2006; Vogts et al., 2009	Ali et al., 2005a	Rommerskirchen et al.,

Stdev. = standard deviation

pctle. = percentile

n = number of samples

*no CPI data available for *n* -alkanoic acids