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Key Points:

- Biomarkers in transit reflect precipitation throughout the river catchment
- Terrestrial biomarkers integrate sources over the entire studied river catchment
- Leaf waxes work well in fluvial systems as hydrological proxies

Supporting Information:

- Readme
- Text S1
- Table S1
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- Table S3

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Leaf wax biomarkers in transit record river catchment composition

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Abstract Rivers carry organic molecules derived from terrestrial vegetation to sedimentary deposits in lakes and oceans, storing information about past climate and erosion, as well as representing a component of the carbon cycle. It is anticipated that sourcing of organic matter may not be uniform across catchments with substantial environmental variability in topography, vegetation zones, and climate. Here we analyze plant leaf wax biomarkers in transit in the Madre de Dios River (Peru), which drains a forested catchment across 4.5 km of elevation from the tropical montane forests of the Andes down into the rainforests of Amazonia. We find that the hydrogen isotopic composition of leaf wax molecules (specifically the C_{28} *n*-alkanoic acid) carried by this tropical mountain river largely records the elevation gradient defined by the isotopic composition of precipitation, and this supports the general interpretation of these biomarkers as proxy recorders of catchment conditions. However, we also find that leaf wax isotopic composition varies with river flow regime over storm and seasonal timescales, which could in some cases be quantitatively significant relative to changes in the isotopic composition of precipitation in the past. Our results inform on the sourcing and transport of material by a major tributary of the Amazon River and contribute to the spatial interpretation of sedimentary records of past climate using the leaf wax proxy.

1. Introduction

Large variations in precipitation δD values trace hydrological processes [*Gat*, 1996] and are encoded in the δD values of plant biomarkers [*Sachse et al.*, 2012]. Sedimentary archives of plant biomarkers therefore carry evidence of past variability in hydroclimate [e.g., *Schefuss et al.*, 2005; *Tierney et al.*, 2008]. However, accurately interpreting such records relies on understanding how environmental conditions are encoded in plant biomarker isotopic composition and eventually recorded in sedimentary archives. Systematic *D* depletion in precipitation with elevation [*Dansgaard*, 1964; *Gonfiantini et al.*, 2001] as well as during the progressive rainout (Rayleigh distillation) over the continents [*Dansgaard*, 1964] may impart substantial isotopic gradients within river catchments. Erosional and transport processes can variably sample from different areas within river basins [*Walling et al.*, 1999; *Jones and Frostick*, 2002; *Garzanti et al.*, 2007; *Just et al.*, 2014], and in-stream transformations of organic material can lead to preferential loss of some organic compounds and preservation of others during transport [*Aufdenkampe et al.*, 2007]. The combination of erosional sourcing and in-stream reworking is expected to influence the isotopic composition of plant biomarkers delivered to and preserved in marine [e.g., *Schefuss et al.*, 2005, 2011] and lacustrine [e.g., *Tierney et al.*, 2008; *Kirby et al.*, 2013] sedimentary records. Interpretation of paleoclimate records derived from fluvially transported biomarkers would benefit from systematic efforts to test whether river sediment carries plant biomarkers with an isotopic composition that is representative of the catchment area upstream from a given site and to explore the extent to which hydrological processes (e.g., associated with seasonal or storm changes in flow regime) might introduce variability in the associated biomarker signal.

To address these problems, we employ one of the widely used palaeohydrology proxies, the δD composition of terrestrial plant biomarkers, which generally reflects the δD of precipitation [*Sachse et al.*, 2012, and references therein]. The *D* depletion in precipitation with elevation imparts an isotopic gradient to plant biomarkers [*Jia et al.*, 2008; *Peterse et al.*, 2009; *Ernst et al.*, 2013; *Bai et al.*, 2014], making it possible to differentiate sources from across elevation gradients in mountainous catchments. In this study, we specifically consider plant leaf waxes (e.g., C_{28} *n*-alkanoic acid), which have previously been used as tracers of terrestrial plant organic matter sourcing and transport in rivers [*Galy and Eglinton*, 2011]. In the Ganges basin, leaf waxes carried by rivers draining the Himalayan headwaters have low δD values, reflecting biomarkers

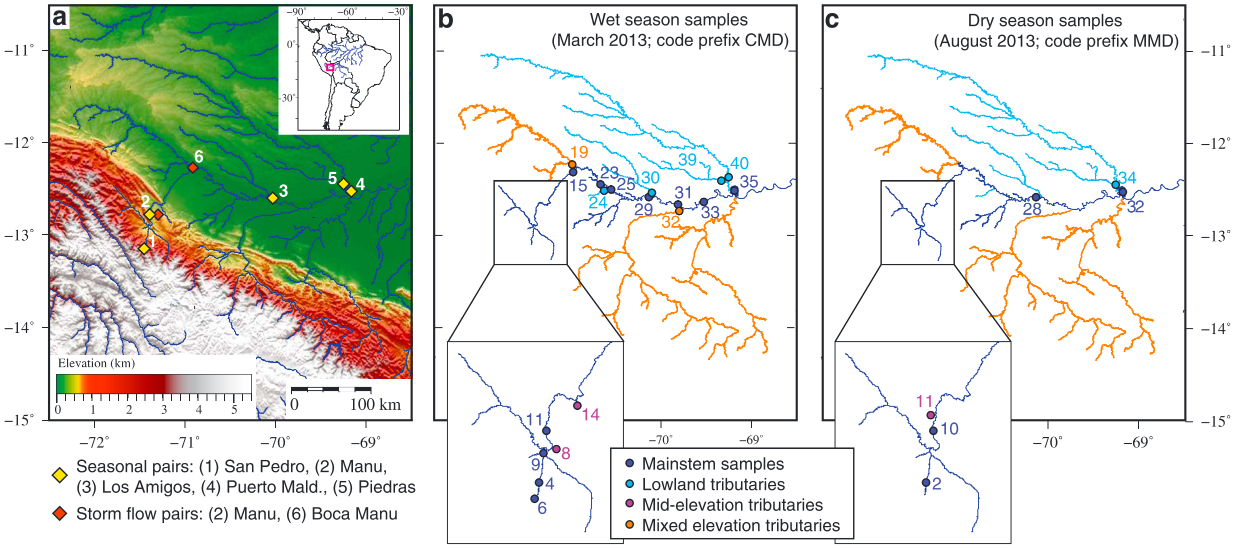

Figure 1. (a) Digital elevation model of the study area (derived from SRTM data) and location of the main sampling sites on the Madre de Dios River, part of the Amazon drainage system (inset). Yellow diamonds show sites with seasonal sample pairs; red diamonds show sites of paired samples through storm flow (Table 1). (b) Madre de Dios River network with sample numbers and locations for the wet season field campaign (sample code prefix CMD). Main stem in dark blue, lowland tributaries in light blue, midelevation tributaries magenta, and mixed elevation tributaries in orange. (c) Sample numbers and locations for the dry season field campaign (sample code prefix MMD). Fewer samples were collected in the dry season compared to the wet season because of much lower sediment concentrations.

encoded with high-elevation precipitation, while waxes at the Ganges outlet have higher δD values characteristic of biomarkers formed from precipitation at low elevations [*Galy et al.*, 2011]. Globally, the isotopic composition of leaf waxes in modern plants, soils, and lake sediments correlates with the composition of local precipitation [*Sachse et al.*, 2012]. These comparisons as well as biomarker isotopic studies in soils across elevation gradients [*Jia et al.*, 2008; *Peterse et al.*, 2009; *Ernst et al.*, 2013; *Bai et al.*, 2014] provide general calibration of biomarker δD to record precipitation δD. Here—for the first time—we systematically test whether rivers in a tropical mountain basin carry biomarkers with a composition that consistently reflects their catchment area, across the elevation profile and between seasons and storms.

2. Summary of Approach, Study Site, and Methods

We have investigated the signals resulting from fluvial integration of terrestrial plant leaf wax biomarkers in a large tropical river catchment. We followed the Madre de Dios River along an elevation gradient of 4.5 km, from the Eastern Cordillera of the central Andes into the Amazonian floodplain within Peru. The Madre de Dios is an almost entirely forested tropical river catchment with both mountainous terrain and extensive floodplains (27,830 km^2; 212–5505 m above sea level (masl); 822 masl mean elevation; Figure 1). We collected samples of stream waters and of particulate organic matter (POM) from the river main stem and its tributaries. Previous studies on this river [*Clark et al.*, 2013] and other Amazon tributaries [*Townsend-Small et al.*, 2008] suggest that organic matter fluxes and sources in the Andean headwaters change under different flow conditions, but these studies did not include biomarker data which have potential to further elucidate sourcing. Meanwhile, several other studies have explored the lignin biomarker composition in river organic matter from the Andes-Amazon system [*Hedges et al.*, 2000; *Aufdenkampe et al.*, 2007], yielding important insights into sources and transformation of woody plant biomass. However, this previous plant biomarker work has not considered hydrogen isotopes which have considerable potential to fingerprint the source of terrestrial plant organic matter across the elevation gradient, and which can be accessed by the study of plant leaf wax hydrogen isotopic compositions. In this study we compare the hydrogen isotope values of stream waters to those of leaf wax *n*-alkanoic acids from river POM and show that leaf wax biomarkers in transit are broadly representative of catchment-averaged precipitation.

Steep topography in conjunction with the South American Low Level Jet, which carries humid winds westward over the Amazon basin, drives high annual precipitation over the eastern flank of the Andes [*Killeen et al.*, 2007].

The high precipitation supports productive tropical montane cloud forests and tropical lowland forests [*Girardin et al*., 2010; *Malhi*, 2012]. Above the tree line (3.5 kmasl) [*Girardin et al*., 2014], vegetation is dominated by *puna* grasses. From 1.5 to 3.5 kmasl, tropical montane cloud forest (mean annual temperature (MAT) 11–18°C) has a high species diversity, including *Weinmannia* spp. among the higher vascular plants; although tree ferns and bryophytes are present, we have established that they do not substantially contribute the biomarkers studied here. Below 1.5 kmasl, precipitation peaks, productivity increases, and lowland forest taxa appear (e.g., Anacardiaceae, Moraceae, and Myristicaceae) [*Huaraca Huasco et al*., 2014]. The lowland forest $<$1.0 kmasl (MAT 26°C) in the Madre de Dios floodplain is notably characterized by high biodiversity [*Malhi et al*., 2014]. There is a pronounced seasonality in the amount of precipitation associated with the South American monsoon [*Fu et al*., 1999] that greatly affects river flow regime. The Madre de Dios region receives 1.5 to 5 m yr^{-1} precipitation (peaking at 1.5 km), seasonally fluctuating from very humid (wet season) to humid (dry season) [*Killeen et al*., 2007].

River catchment areas were determined using a flow routing algorithm in Geographic Resources Analysis Support System (GRASS) geographic information system software, using Shuttle Radar Topography Mission (SRTM)-derived digital elevation data with a spatial resolution of 3 arc sec (~90 m). Samples were collected in two field campaigns in March and August 2013, wet and dry season, respectively. Small stream water samples were collected, and their isotopic composition was taken as representative of the time-integrated water isotopic composition of local precipitation across the elevation gradient (discussed in detail below). Water δD measurements were made by laser absorption spectrometry, with instrumental uncertainty of ~0.4‰ (see supporting information). Large volume (60–180 L) river water samples were collected from the main stem and tributaries using bucket sampling from the middle of the river, accessed either from the bank or by small boat where rivers were navigable. Samples were filtered through polyethersulfone filters to recover the suspended particle load ($>$0.2 μm) containing the POM. The sediment was subsequently sieved in the lab to isolate the 0.2–1000 μm fraction and exclude large plant debris that was only found in one sample (out of 25) in minor amounts ($<$1% by weight). Soil samples were taken from well-studied, representative plots in the catchment (see supporting information). The soil samples were collected from the mineral soil horizon, immediately below the organic horizon, which occurs at variable depths across the catchment ranging from 23 cm in the uplands to 1 cm below the surface in the lowlands. All sediment and soil samples were processed to isolate long chain *n*-alkanoic acids. Biomarker δD values were analyzed using a Thermo Scientific Trace gas chromatograph coupled via Isolink pyrolysis furnace to a Delta V Plus mass spectrometer [*Feakins et al*., 2014] (see supporting information). The results are reported using conventional delta notation (δD ‰) on the Vienna Standard Mean Ocean Water- Standard Light Antarctic Precipitation scale. Data are reported for the C_{28} *n*-alkanoic acid as it is sufficiently abundant and thought to be derived exclusively from terrestrial leaf waxes [e.g., *Eglinton and Hamilton*, 1967].

3. Effect of Elevation on Hydrogen Isotopes

The hydrogen isotope composition of meteoric water becomes systematically more depleted with increasing elevation in the Madre de Dios catchment [*Horwath*, 2011; *Lambs et al*., 2012]. To capture the representative composition of time-averaged meteoric water across the elevation gradient, we measured water isotope data from small upland streams and lowland tributaries ($\delta D_{\mathrm{stream}}$), each of which were selected for their restricted elevation range and so reflect the local water composition at the sampling site (we do not consider data from the main stem or large tributaries, which reflect the mixture of water from widely distributed elevations within each catchment). Over the 4.2 km elevation range from which we collected small streams and tributaries, measured $\delta D_{\mathrm{stream}}$ values range by 92‰ in the wet season and 107‰ in the dry season (Figure 2). Upland $\delta D_{\mathrm{stream}}$ values (representative of meteoric water) show little seasonal variability, even though precipitation isotopes vary significantly on seasonal timescales (100‰ seasonal range in precipitation composition, see *Horwath* [2011] and *Lambs et al*. [2012]). This lack of variability in upland $\delta D_{\mathrm{stream}}$ can be explained by groundwater mixing [*Clark et al*., 2014]. Lowland tributaries sampled in this study display up to 30‰ seasonal variability, reflecting an attenuated signal of seasonal variability in precipitation isotope composition in the lowland (C. P. Ponton, unpublished data, 2014 and precipitation seasonality at Manaus from *Global Network of Isotopes in Precipitation database, International Atomic Energy Agency/World Meteorological Organization* [2014]). The seasonal differences in $\delta D_{\mathrm{stream}}$ in the lowlands, but not at the high elevations, result

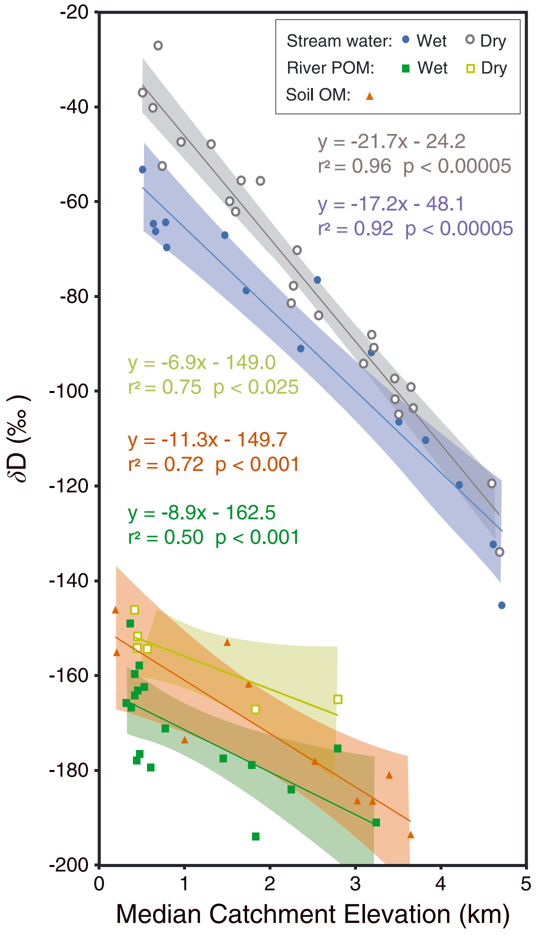

Figure 2. Relationship between δD and elevation. $\delta D_{\mathrm{stream}}$ samples (solid circles, wet season; open circles, dry season) and δD_{POM} samples (solid squares, wet season; open squares, dry season) plotted against the median elevation of the catchment upstream of the sampling site. δD_{soil} (triangles) plotted against the elevation of sample collection. Shadings represent 95% confidence intervals on linear regressions.

in a steeper gradient in $\delta D_{\mathrm{stream}}$ with elevation during the dry versus the wet season (-22‰ km^{-1} in the wet season versus -17‰ km^{-1} in the dry season; Figure 2).

Hydrogen isotopic compositions of plant waxes isolated from mineral soil horizons (δD_{soil}) within the catchment similarly show inverse correlations with sampling elevation (a range of 47‰ over an elevation range of 3.4 km) suggesting that precipitation isotopes exert the primary control on the hydrogen isotopic composition of leaf wax preserved in soils. However, the δD_{soil} elevation slope (-11 ± 5‰ km^{-1}) is attenuated relative to the $\delta D_{\mathrm{stream}}$ elevation slope (-17 ± 3‰ km^{-1} and -22 ± 2‰ km^{-1} for wet and dry season, respectively). This decrease in the offset between $\delta D_{\mathrm{stream}}$ and δD_{soil} with elevation is caused by a systematic decrease in the net or "apparent" fractionation between water and sedimentary plant waxes ($\varepsilon_{\mathrm{wax/water}}$) with elevation (Table S3 in the supporting information) where

$$\varepsilon_{\mathrm{wax/water}} = (\delta D_{\mathrm{wax}} + 1)/(\delta D_{\mathrm{water}} + 1) - 1 \qquad (1)$$

This reduction in $\varepsilon_{\mathrm{wax/water}}$ could be due to changes in plant water fractionations [*Feakins and Sessions*, 2010; *Kahmen et al.*, 2013] or biosynthetic fractionations [*Sessions et al.*, 1999; *Sachse et al.*, 2012] perhaps associated with environmental influences, or due to changes in species distribution with elevation [*Malhi et al.*, 2014; *Girardin et al.*, 2014; *Huaraca Huasco et al.*, 2014]. These effects could be distinguished by measuring the hydrogen isotope composition of leaf waters and waxes extracted from plant samples across the elevation gradient. Other isotope effects could be associated with leaf litter decomposition, or storage of biomarkers synthesized under prior different climatic regimes—and each of these could exert systematic biases with elevation. These effects could be elucidated with leaf litter degradation studies and compound-specific radiocarbon analysis of biomarkers stored in soils and transported in rivers.

Hydrogen isotopic compositions of plant waxes isolated from river POM samples (δD_{POM}) span a range similar to δD_{soil}: 48‰ over an altitude range of 2.8 km (for river samples, altitude refers to the median elevation of the catchment upstream, not the sampling elevation). With the median catchment elevation δD_{POM} values exhibit a negative correlation ($r^2 = 0.50$, $p < 0.001$). The elevation dependency (slope) of δD_{POM} (-9 ± 5‰ km^{-1} wet season and -7 ± 6‰ km^{-1} dry season) is statistically identical to that of δD_{soil} (-11 ± 5‰ km^{-1}), and the soil and POM data overlap across the entirety of the elevation gradient. The similarities between δD_{POM} and δD_{soil} indicate that the composition of leaf waxes in river sediments is, to first order, representative of the composition of the average leaf wax sources in each catchment. Several processes may contribute to explaining why leaf waxes isolated from the river sediments are similar to the average catchment sources, including the distribution of elevations within each catchment and the effectiveness of erosional integration of this distribution [*Nichols et al.*, 2009], the effect of grain size sorting on the partitioning of biomarkers [*Prahl et al.*, 1994], and the role of degradation and loss of leaf waxes during transport [*Hedges et al.*, 2000; *Aufdenkampe et al.*, 2007]. While we have established here that biomarker isotopic composition reflects the

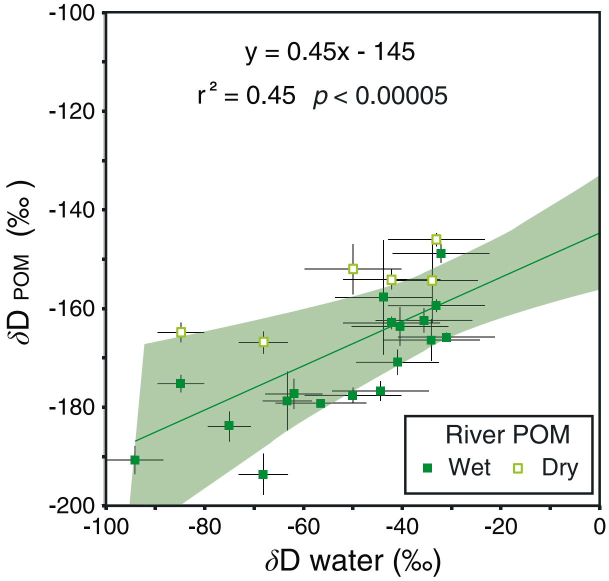

Figure 3. Relationship between δD_{POM} and δD of precipitation (δD_{water}), both for the median catchment elevation. δD_{water} for each catchment was estimated using the linear regression for dry season stream water samples (from Figure 2). Solid squares for wet season samples; open squares for dry season. The correlation coefficient of this relationship is the same whether δD_{water} is calculated for dry season or wet season precipitation, or the average of the two. Vertical error bars are 1 standard deviation instrument precision, and horizontal bars are the propagated uncertainties from the linear regression in Figure 2.

upstream catchment area, further work on leaf wax abundances and sediment particle surface area might make it possible to tease apart the relative roles of each of these processes.

4. Do Fluvial Biomarkers Record a Representative Isotopic Composition of Source Waters?

As the soil data show that sedimentary leaf waxes primarily record the isotopic composition of precipitation, analysis of the river sediments allows us to test catchment sourcing to elucidate the nature of the hydroclimate recorder carried by the river. We consider precipitation isotopic composition based on our two-season sampling from small streams and lowland tributaries as the best available means to determine the average of temporally variable precipitation isotopes from a given elevation. This is useful since both stream and plant waters have been shown to carry an isotopic signal that is a time average of highly variable precipitation [*McDonnell*, 2014]. While this simplifies consideration of plant water sources, the isotopic composition of streams represents our best present constraint on seasonally averaged precipitation and plant water sources. Furthermore, we have confirming data that in this catchment dry season plant stem waters follow the dry season stream regression across the elevation profile (S. J. F. Feakin, unpublished data, 2014).

We find a significant relationship ($r^2 = 0.45$, $p < 0.00005$) between δD_{POM} and the inferred δD of the precipitation (δD_{water}) in each catchment (Figure 3). The slope and intercept of this relationship differ slightly depending on whether δD_{water} is calculated for dry season or wet season precipitation, or the average of the two; however, the correlation coefficient is the same in all cases. Seasonality of leaf growth and wax synthesis can impart a bias to average wax isotope composition (e.g., in temperate forests) [*Tipple et al*., 2013]. Leaf production in the Madre de Dios occurs year round, but with a propensity to greater new leaf production at the end of the dry season [*Malhi et al*., 2014; *Girardin et al*., 2014; *Huaraca Huasco et al*., 2014], suggesting leaf waxes should capture an annually integrated signal of meteoric waters with a slight bias to the late dry season. In Figure 3, we consequently plot δD_{water} based on dry season precipitation (i.e., rather than wet season or the average) but emphasize that our primary observation of close correspondence between wax and water composition does not depend on this choice.

Overall, the strong correlation between source water δD_{POM} composition across two seasons and 4.2 km elevation (Figure 3) supports the use of leaf waxes transported by river sediments as recorders of the isotopic composition of precipitation in paleoclimate investigations. We note the strength of the correlation is comparable to that in lake core-top studies elsewhere [cf. *Sachse et al*., 2012], implying that leaf waxes work well in fluvial systems as hydrological proxies. As in spatial correlations from lakes, the slope of δD_{POM} to δD_{water} relationship is $<1-\varepsilon$, which in this case we know represents the gradient in apparent fractionation with elevation.

5. Variability in Biomarker Composition Associated With Flow Regime

Distinct seasonal (Figure 2) and storm variability (Table 1) is superimposed on the δD_{POM} composition that is broadly representative of catchment-averaged precipitation. The interseasonal shift of δD_{POM} values

Table 1. Seasonal and Stormflow Changes in δD_{POM} (‰)

Site	Median Elevation (km)	ID (Wet/Dry)	Wet Season	Dry Season	Difference
San Pedro	2.795	CMD-4/MMD-2	−175 ± 2	−165 ± 2	10 ± 3
Manu	1.830	CMD-11/MMD-10	−193 ± 2	−167 ± 4	26 ± 4
Los Amigos	0.445	CMD-29/MMD-28	−163 ± 2	−154 ± 1	9 ± 2
Puerto Maldonado	0.451	CMD-35/MMD-32	−177 ± 5	−152 ± 2	25 ± 5
Piedras	0.413	CMD-40/MMD-34	−160 ± 1	−146 ± 1	14 ± 1
	Median Elevation (km)	ID (Storm/Normal)	Stormflow	Normal Flow	Difference
Manu	1.830	CMD-13/CMD-11	−174 ± 2	−193 ± 4	−19 ± 4
Boca Manu	1.454	CMD19/CMD-15	−161 ± 3	−177 ± 1	−16 ± 3

between the wet and the dry season mimics that of water, with dry season δD values on average D enriched relative to wet season values (by 15‰ for POM and 16‰ for streams; Figure 2). The dry season δD_{POM} enrichment is also observed in Figure 3, but we do not use seasonally variable δD_{water} to establish the correlation because this would imply that leaf waxes are synthesized and transported into river POM over seasonal timescales—a scenario that is unlikely because of the timescales of leaf growth and senescence, soil storage, and erosion. Instead, we attribute the seasonal variability in δD_{POM} to less sampling of high-elevation leaf waxes in the dry season, when flow conditions are less conducive to erosion and rapid transport from high to low elevations compared to the wet season. This explanation is consistent with the observation of very low sediment concentrations in the high-elevation rivers during the dry season (Table S1), suggesting that these rivers are transporting very little material to the lowlands at low flow conditions. We also observe a better correlation of δD_{POM} with median catchment elevation in the dry season than in the wet season (Figure 2) when advection from upstream locations plays a role in complicating the nature of the hydrological proxy. However, we note that the wet and dry season data sets have different sampling sizes ($n = 18$ and $n = 6$, respectively).

We opportunistically sampled one storm event at two sites during the wet season and found that δD_{POM} was less depleted during the storm, relative to baseline wet season conditions (Table 1). We suggest that relatively enriched δD_{POM} during storm events reflects sourcing from more local, lower elevations sites, compared to the prestorm transport of material from upstream, because of strong local precipitation events driving enhanced soil erosion near to the sample collection site. We note that the direction of the storm shift (towards local precipitation) is opposite to the seasonality shift (upland precipitation signal) providing an important reminder not to scale between changes in δD_{POM} and river discharge across flow regimes.

The observation of changing δD_{POM} across seasons (changes of 9–26‰ less isotopically enriched at higher flow) and storms (changes of 16–19‰ more enriched at higher flow) demonstrates that transport processes may introduce variability in the source of organic material in rivers and thus may introduce variability in the associated isotopic composition of biomarkers. The magnitude of this flow-related variability is significant compared to the magnitude of changes in the isotopic composition of precipitation recorded in many paleo-archives, which are typically interpreted in terms of changes in hydroclimate [e.g., *Schefuss et al.*, 2005; *Rach et al.*, 2014]. Although storms may be relatively infrequent, they typically account for a significant proportion of the total organic material delivered by rivers because both sediment concentrations and organic carbon concentrations within the sediment increase with increasing discharge [e.g., *Hilton et al.*, 2008]. Thus, storm event transport, if characterized by distinct isotopic composition, may be an important factor in determining the biomarker composition in fluvial-derived deposits.

Variability at the timescale of storm events or seasonal cycles is likely to be averaged at the temporal resolution of most paleorecords that consider intervals of many years, decades, or longer. However, the effects of short-timescale variability in fluvial sourcing should be carefully considered for records with high (e.g., subannual) temporal resolution. Even in records of lower time resolution, the observation of variability associated with fluvial processes may be relevant, especially if these processes have changed in the past as a result of changing regional hydrology. Changes in seasonality may not on their own strongly bias records, since dry season transport of organic material makes up a small proportion of total annual yield (e.g., estimates that the dry season contribution to total annual yields of nonrock-derived organic carbon are in the range of $< 5\%$ for the headwaters of the Madre de Dios) [*Clark*, 2014]. However, both wet season and storm flow conditions are important as agents of organic material transfer [*Clark*, 2014], and our observations show that these two conditions can lead to opposing shifts in biomarker δD, with consequent implications for long-term records from sediments. For example, if the wet season becomes less stormy over the long term, or if the locus of storm activity shifts to higher elevations, the average biomarker composition in sedimentary records might be expected to change (in these examples, toward more depleted δD). Thus, although our data from the Madre de Dios validate the use of fluvially derived biomarker isotopes for paleoclimate reconstructions, they also suggest that attention is warranted to consider the extent to which hydrologic changes, by altering fluvial sourcing, might influence biomarker records.

Acknowledgments

Data used in figures are available in Tables S1, S2, and S3 in the supporting information. This work was supported by funding from the U.S. National Science Foundation award 1227192 to A.J.W. and S.J.F. V.G. was supported by the U.S. National Science Foundation award OCE-0928582. We are grateful to field assistance from M. Torres, A. Robles, and A. Ccahuana. A. Nottingham and P. Meir provided the soil samples. Y. Malhi, J. Huaman, W. Huaraca, and K. Clark are thanked for logistical support and advice, C. Johnson and M. Rincon for technical support, and R. Hilton for constructive discussion. Undergraduate students involved in the lab sample processing included K. McPherson, E. Rosca, and L. Arvin. A. Sessions kindly provided access to the water isotope analyzer. M. Hren and one anonymous reviewer provided insightful comments that greatly improved the manuscript.

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