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Dual isotope evidence for sedimentary integration of plant wax biomarkers across an Andes-Amazon elevation transect

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Abstract

Tropical montane regions tend to have high rates of precipitation, biological production, erosion, and sediment export, which together move material off the landscape and toward sedimentary deposits downstream. Plant wax biomarkers can be used to investigate sourcing of organic matter and are often used as proxies to reconstruct past climate and environment in sedimentary deposits. To understand how plant waxes are sourced within a wet, tropical montane catchment, we measure the stable C and H isotope composition ($\delta^{13}C$ and δD) of *n*-alkanes and *n*-alkanoic acids in soils along an elevation transect and from sediments within the Madre de Dios River network along the eastern flank of the Peruvian Andes, draining an area of 75,400 km^2 and 6 km of elevation. Soils yield systematic trends in plant wax $\delta^{13}C$ (+1.75 and +1.31‰ km^{-1}, for the C_{29} *n*-alkanes and C_{30} *n*-alkanoic acids respectively in the mineral horizon) and δD values (−10 and −12‰ km^{-1}, respectively) across a 3.5 km elevation transect, which approximates trends previously reported from canopy leaves, though we find offsets between $\delta^{13}C$ values in plants and soils. River suspended sediments generally follow soil isotopic gradients defined by catchment elevations ($\delta^{13}C$: +1.03 and +0.99‰ km^{-1} and δD: −10 to −7‰ km^{-1}, for the C_{29} *n*-alkanes and C_{30} *n*-alkanoic acids respectively) in the wet season, with a lowering in the dry season that is less well-constrained. In a few river suspended sediments, petrogenic contributions and depth-sorting influence the *n*-alkane $\delta^{13}C$ signal. Our dual isotope, dual compound class and seasonal sampling approach reveals no Andean-dominance in plant wax export, and instead that the sourcing of plant waxes in this very wet, forested catchment approximates that expected for spatial integration of the upstream catchment, thus with a lowland dominance on areal basis, guiding paleoenvironmental reconstructions in tropical montane regions. The dual isotope approach provides a cross-check on the altitudinal signals and can resolve ambiguity such as might be associated with vegetation change or aridity in paleoclimate records. Further, the altitude effect encoded within plant waxes presents a novel dual-isotope biomarker approach to paleoaltimetry.

Keywords: Plant wax; Leaf wax; Biomarker; Hydrogen isotope; Carbon isotope; Andes; Amazon; Paleoaltimetry; Source-to-sink

1. INTRODUCTION

The transport of organic carbon (OC) by large river systems is a crucial component of the Earth's carbon cycle. Rivers erode and transport plant, soil and rock-derived (petrogenic) OC across the landscape, and that which survives degradation may be deposited in sedimentary basins. Among the world's river systems, the Amazon River is the

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largest in terms of drainage area (6.4 million km^2) and discharge (200,000 m^3 s^{-1}) (Meybeck and Ragu, 2012), and its export of particulate organic carbon (POC; *c.* 11.6 Tg yr^{-1} to the Atlantic) represents *c.* 6% of the global riverine POC input to the oceans (Richey et al., 1990; Beusen et al., 2005; Galy et al., 2015). Understanding the sourcing, degradation, and transport of POC in the Amazon fluvial system is thus significant in budgeting the global carbon cycle, and has been extensively studied in both the lowland mainstreams and Andean head waters (Hedges et al., 2000; Townsend-Small et al., 2005; Townsend-Small et al., 2008; Clark et al., 2013; Bouchez et al., 2014). The Andes Mountains represent just 11% of the Amazon River catchment area, but may account for 90% of rock-debris exported from the Amazon River to the Atlantic Ocean (Meade et al., 1985). While globally, biospheric OC export generally scales with sediment load (Galy et al., 2015), POC carried by the lowland Amazon River is thought to be dominantly sourced from lowland forests implying a near-complete degradation of Andean-derived POC in transit or swamping by more extensive lowland contributions (Mayorga et al., 2005). The biospheric OC represents carbon fixed from the atmosphere, and if it escapes oxidation in transit (Hedges and Oades, 1997; Cole et al., 2007) and is sequestered in ocean sediments for up to 10^8 yrs, it represents a long-term sink of atmospheric CO_2 (France-Lanord and Derry, 1997; Galy et al., 2007). In contrast, if biospheric carbon decomposes in soils (Koven et al., 2017) or in transit (Richey et al., 2002), CO_2 is returned to the atmosphere relatively rapidly, on decade-century timescales, related to the age of carbon in soils (Trumbore, 1993) and in rivers (Townsend-Small et al., 2007; Clark et al., 2013). Sourcing and degradation processes within the catchment need to be understood to determine which regions contribute to marine repositories both for carbon budget and paleoclimate applications. Yet, many prior source-to-sink carbon cycle studies are based upon bulk POC, which is a complex mixture of components with diverse age, residence time, degradation potentials and geochemical signatures that can be difficult to tease apart (Mayorga et al., 2005).

Biological marker molecules, or biomarkers, not only derive from a specific class of organism but also carry signatures of environment. These biomarkers can be variously used to investigate sourcing and track molecules in transit, and they are often used as proxies to reconstruct past climate and environment, which is predicated on understanding sourcing. Biomarkers provide tracers for specific components of terrestrial OC cycling and thus provide a clearer view of sourcing and fluvial integration processes than bulk OC. For example, lignin (Goñi et al., 2000; Aufdenkampe et al., 2007), terpenoids (Medeiros et al., 2012; Giri et al., 2015) and plant wax biomarkers (Galy et al., 2011; Tao et al., 2015; Häggi et al., 2016; Hemingway et al., 2016; Hoffmann et al., 2016; Freymond et al., 2018) have been used in riverine systems to trace biogenic OC derived from vascular plant biomass. In addition, biomarkers for microbial activity have been used to trace bacterial and archaeal components of terrestrial biospheric OC production exported by rivers (Kim et al., 2012; Wagner et al., 2014; Hanna et al., 2016; Hemingway et al., 2017).

Plant wax hydrogen (δD_{wax}) and carbon isotope compositions ($\delta^{13}C_{wax}$) reflect environmental and ecological conditions and thus may be able to reveal sourcing within a catchment, provided it is characterized by a gradient in environmental conditions. The carbon isotopic signatures of plant waxes in river sediment have been used to trace the evolving character of suspended sediment OC between mountain-front tributaries and the river mouth, based on the contrast between C_3 upland vegetation and C_4 lowland vegetation (Galy et al., 2011), between river and estuary (Medeiros et al., 2012) and between C_3 forest and petrogenic sources (Häggi et al., 2016). Sourcing has also been differentiated based on hydrogen isotopes in precipitation that vary spatially within catchments, including with elevation (Galy et al., 2011; Ponton et al., 2014; Häggi et al., 2016; Hoffmann et al., 2016). A few studies are beginning to combine information from different compound classes as erosion and preservation pathways may differ between compounds, for example with diterpenoids (derived from conifers) being over contributed relative to triterpenoids (derived from angiosperms; Giri et al., 2015) or with *n*-alkanoic acids and *n*-alcohols having a more rapid response to changes in runoff and thus more local input relative to *n*-alkanes (Hemingway et al., 2016). Studies of river suspended sediment using radiocarbon have demonstrated the potential for pre-aged carbon to contribute to the *n*-alkane load (including rock-derived sources, that are radiocarbon dead), whereas the radiocarbon ages for the *n*-alkanoic acids suggest considerably less (but not negligible) influence from soil storage (Kusch et al., 2010; Galy and Eglinton, 2011; Tao et al., 2015). However, despite the complementary information provided by different isotope systems and biomarker compounds, few fluvial studies have combined information from C and H isotopes (Galy et al., 2011; Häggi et al., 2016), and fewer have compared *n*-alkane and *n*-alkanoic acid compound classes (Hemingway et al., 2016) or C and H isotope systems in multiple compound classes (Chikaraishi et al., 2005).

In a series of biomarker studies along the eastern flank of the Andes in Perú, the authors of this paper and other collaborators have shown that biomarkers record aspects of environment and that these properties may tag biospheric carbon in fluvial transit. The altitude effect in the isotopic composition of precipitation has been demonstrated locally in precipitation, plant waters, and plant wax *n*-alkanes and *n*-alkanoic acids in the canopy leaves of the modern forest (Feakins et al., 2016a). Similarly, the δD value of plant wax C_{28} *n*-alkanoic acids transported by rivers in the Madre de Dios River network records the altitude effect in soils in the same catchment (Ponton et al., 2014). Lignin biomarkers trace soil degradation and erosion processes represented in river sediments (Feng et al., 2016), and also signal that soil-river is the dominant pathway for most organic carbon including plant waxes (rather than direct input of plant leaves or leaf wax aerosols into the river). More recently it has been shown that plant leaf (Asner et al., 2014) and plant leaf wax *n*-alkane and *n*-alkanoic acids (Wu et al., 2017) are ^{13}C-enriched with altitude. This pattern in bulk leaves has also been seen in other wet tropical montane forests (Körner et al., 1988;