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Origin, transport and deposition of leaf-wax biomarkers in the Amazon Basin and the adjacent Atlantic

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Abstract

Paleoenvironmental studies based on terrigenous biomarker proxies from sediment cores collected close to the mouth of large river systems rely on a proper understanding of the processes controlling origin, transport and deposition of biomarkers. Here, we contribute to the understanding of these processes by analyzing long-chain *n*-alkanes from the Amazon River system. We use the δD composition of long-chain *n*-alkanes from river bed sediments from the Amazon River and its major tributaries, as well as marine core-top samples collected off northeastern South America as tracers for different source areas. The $\delta^{13}C$ composition of the same compounds is used to differentiate between long-chain *n*-alkanes from modern forest vegetation and petrogenic organic matter. Our $\delta^{13}C$ results show depleted $\delta^{13}C$ values (−33 to −36‰) in most samples, indicating a modern forest source for most of the samples. Enriched values (−31 to −33‰) are only found in a few samples poor in organic carbon indicating minor contributions from a fossil petrogenic source. Long-chain *n*-alkane δD analyses show more depleted values for the western tributaries, the Madeira and Solimões Rivers (−152 to −168‰), while *n*-alkanes from the lowland tributaries, the Negro, Xingu and Tocantins Rivers (−142 to −154‰), yield more enriched values. The *n*-alkane δD values thus reflect the mean annual isotopic composition of precipitation, which is most deuterium-depleted in the western Amazon Basin and more enriched in the eastern sector of the basin. Samples from the Amazon estuary show a mixed long-chain *n*-alkane δD signal from both eastern lowland and western tributaries. Marine core-top samples underlying the Amazon freshwater plume yield δD values similar to those from the Amazon estuary, while core-top samples from outside the plume showed more enriched values. Although the variability in the river bed data precludes quantitative assessment of relative contributions, our results indicate that long-chain *n*-alkanes from the Amazon estuary and plume represent an integrated signal of different regions of the onshore basin. Our results also imply that *n*-alkanes are not extensively remineralized during transport and that the signal at the Amazon estuary and plume includes refractory compounds derived from the western sector of the Basin. These findings will aid in the interpretation of plant wax-based records of marine sediment cores collected from the adjacent ocean.

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1. INTRODUCTION

The past climate evolution of the Amazon Basin and its implications for the global carbon cycle are the subjects of ongoing debate (Phillips et al., 2009; Cheng et al., 2013; D'Apolito et al., 2013; Gloor et al., 2015). For an improved understanding of past Amazonian climates, environmental archives such as marine sediment cores are of great importance. Terrestrial organic matter (OM) transported by rivers and deposited offshore can provide valuable information on the continental climate and vegetation history. The analysis of specific molecular plant-wax compounds such as long-chain *n*-alkanes has proven useful for the reconstructions of past vegetation and climate conditions (e.g. Rieley et al., 1991; Pancost and Boot, 2004). For example, the hydrogen isotopic composition (δD) encoded in plant-wax compounds can be used to infer the isotopic composition of meteoric water, assuming that other variables are controlled for (e.g. Sauer et al., 2001; Schefuß et al., 2005; Tierney et al., 2008; Sachse et al., 2012; Fornace et al., 2014). The stable carbon isotope composition ($\delta^{13}C$) from the same compounds varies among vegetation types that utilize either the C3 or the C4 photosynthetic pathways and can be used as an indicator of the relative contributions of these two types of vegetation (e.g. Bird et al., 1995; Huang et al., 2001). Alternatively, $\delta^{13}C$ enrichment in long-chain *n*-alkanes may also signal the presence of highly degraded compounds derived from fossil petrogenic sources (Lichtfouse and Eglinton, 1995). In extensive river catchments like the Amazon Basin, a thorough insight into the sources and the transport processes of OM is necessary to appropriately interpret the signal encoded in plant-waxes accumulated in sediment archives. Apart from sourcing from plant organic matter, either directly or via soils, long-chain *n*-alkanes biomarkers can also be of petrogenic origin from eroded sedimentary rocks (Ishiwatari et al., 1994). Biological degradation during transport can alter and overprint the isotopic signal recorded by plant waxes, biasing primary climate- and vegetation-related signals (Galy et al., 2011). The source region of plant waxes may also be unevenly distributed in a river catchment (Galy et al., 2011). Additionally, the source region may vary temporally and contribute compounds from different sectors of a catchment depending on the seasonality of rainfall (Ponton et al., 2014).

So far, knowledge on sources and transport of plant waxes in the Amazon River and its major tributaries is restricted to the Andean headwaters. In the Madre de Dios River, an Andean tributary of the Madeira River, Ponton et al. (2014) found that δD of long-chain fatty acids reflect an integrated signal along an altitudinal gradient. Their findings imply that leaf waxes accumulated downstream and that the sourcing of leaf-waxes is independent of the provenance of inorganic sediment. Similar findings have also been reported by studies using $\delta^{13}C$ analyses of bulk particulate organic carbon (POC) and lignin from Andean and lowland tributaries (e.g. Hedges et al., 2000; McClain and Naiman, 2008). $\delta^{13}C$ analyses of POC also revealed mixed contributions from Andean (30–50%) as well as lowland (50–70%) OM sources (Quay et al., 1992; Hedges et al., 2000; McClain and Naiman, 2008). Both findings suggest that unlike inorganic sediment that is mainly sourced in the Andes, OM might be mainly lowland sourced (Meade et al., 1985; Bouchez et al., 2014). Radiocarbon dating of POC revealed that while lowland sourced OM is modern, Andean sourced material contains up to 80% of old petrogenic material derived from sediments (e.g. Mayorga et al., 2005; Townsend-Small et al., 2007; Clark et al., 2013; Bouchez et al., 2014). During transport, a considerable amount of OM is remineralized to CO_2 and CH_4 (e.g. Mayorga et al., 2005; Sawakuchi et al., 2014). The study of lignin, for instance, revealed that up to 90% of lignin transported in the Amazon is remineralized during transport (Ward et al., 2013). This raises the question whether leaf waxes in the Amazon River are also mainly lowland or Andean sourced, whether they are partially of petrogenic origin and whether compounds from the western sectors of the Amazon Basin are remineralized during transport to the Amazon estuary.

Here we evaluate the stable isotopic composition (δD and $\delta^{13}C$) of long-chain *n*-alkanes from river bed sediment samples to study their source regions and transport mechanisms. Furthermore, we use the Al/Si ratio as a grain size proxy (Bouchez et al., 2011) and the Fe/K ratio to trace the origin of inorganic sediment in some samples (Govin et al., 2014). Finally, we study the offshore deposition of plant waxes from the Amazon Basin using marine core-top samples to identify suitable areas for paleoclimate studies.

2. MATERIALS AND METHODS

2.1. Study area

The Amazon is the largest drainage basin on Earth. With its most remote sources located in the high Andes, the Amazon River eventually discharges some 3000 km farther east into the western equatorial Atlantic Ocean (Fig. 1). The Amazon River drains large parts of tropical South America, and its catchment is mostly covered by rainforest. The large western tributaries, the Madeira River and the Solimões River are generally classified as white water rivers carrying vast quantities of suspended sediment mostly derived from the Andes (Gibbs, 1967). The Negro River, the largest lowland tributary, is a black water river with little suspended sediment but a high dissolved organic carbon (DOC) load (Konhauser et al., 1994). The next two largest lowland tributaries, the Tapajós River and the Xingu River are clear water rivers which carry little organic and inorganic sediment (Moreira-Turcq et al., 2003).