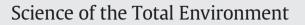
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Land-use impacts on fatty acid profiles of suspended particulate organic matter along a larger tropical river



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HIGHLIGHTS

• We investigated the efficiency of fatty acids (FAs) as indicators of land-use impacts.

FA profiles suggested considerable inputs of domestic sewage.

• Saturated and sewage FAs were correlated with urbanization in a larger tropical river.

• FAs were the most efficient indicators of urban impact.

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ABSTRACT

Land-use change, such as agricultural expansion and urbanization, can affect riverine biological diversity and ecosystem functioning. Identifying the major stressors associated with catchment land-use change is a prerequisite for devising successful river conservation and restoration strategies. Here, we analyzed land-use effects on the fatty acid (FA) composition and concentrations in suspended particulate organic matter (SPOM) along a fourth-order tropical river, the Rio das Mortes. Thereby, we aimed at testing the potential of fatty acids in riverine suspended particulate organic matter (SPOM-FAs) as indicators of land-use change in tropical catchments, and at identifying major human impacts on the biochemical composition of SPOM, which represents an important basal energy and organic matter resource for aquatic consumers. River water SPOM and total FA concentrations ranged between 2.8 and 10.2 mg dry weight (DW) L^{-1} and between 130.6 and 268.2 µg DW L^{-1} , respectively, in our study. Urbanization was the only land-use category correlating with both FA composition and concentrations, despite its low contribution to whole catchment (1.5–5.6%) and riparian buffer land cover (1.7–6.6%). Higher concentrations of saturated FAs, especially C16:0 and C18:0, which are the main components of domestic sewage, were observed at sampling stations downstream of urban centers, and were highly correlated to urbanization, especially within the 60 m riparian buffer zone. Compared to water chemical characteristics (inorganic nutrients, dissolved oxygen, pH, and specific conductance) and river habitat structural integrity, FA variables exhibited a higher variability along the investigated river and were more strongly correlated to urban land use, suggesting that SPOM-FA profiles may be an efficient indicator of urban land-use impacts on larger tropical rivers. High total FA concentrations in the SPOM of urbanized tropical rivers may represent high-energy biochemical subsidies to food webs, potentially leading to changes in functional ecosystem characteristics, such as bacterial and suspension-feeder production.

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1. Introduction

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Streams and rivers supply important ecosystem services, such as drinking water supply, fish production, opportunity for recreational activities, and the collection, transport and processing of pollutants and contaminants originating from the surrounding landscape (Millennium Ecosystem Assessment, 2005). Land-use changes in river basins, as a result of agricultural intensification and expansion, as well as urbanization, can affect various characteristics of river ecosystem

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integrity, such as water quality, community structure, and primary and secondary production, organic matter decomposition, ecosystem metabolism and energy fluxes (Allan, 2004; Young et al., 2008; Rosa et al., 2013). Accordingly, one of the greatest challenges faced by aquatic ecologists nowadays is to identify the specific impact mechanisms of land-use change and to determine their effects on abiotic, biotic, and functional characteristics of lotic ecosystems.

Besides altering channel morphology, habitat diversity and hydrodynamic features (Gücker et al., 2009), agricultural land use can lead to organic and nutrient enrichment in lotic systems, due to fertilization practices, cattle feces, and riparian clearcutting, with profound consequences for stream ecosystem functioning (Sweeney et al., 2004; Silva-Junior et al., 2014). Urbanization also affects the integrity of lotic ecosystems, by altering water quality, channel structure and habitat diversity, and biotic community structure among others (Chadwick et al., 2006). Untreated sewage discharge resulting from the absence of waste water treatment plants, is a common reality in many tropical countries, including Brazil, and is among the most severe problems related to urbanization, contributing substantial organic matter and nutrient loads to streams and rivers (Dodds, 2006; Smith et al., 2006; Gücker et al., 2006). Another frequent problem associated to the expansion of urban centers is the enhanced surface runoff generated by impervious surfaces, carrying substantial contaminant loads and causing hydrodynamic stress to the biotic community (Walsh et al., 2005).

Larger rivers subjected to land-use change may exhibit changes in the quantity and quality of transported particulate organic carbon, depending on the type of land cover change (Young and Huryn, 1999). Two reviews on the global carbon cycle estimated that inland waters receive around 2.9 Pg C y^{-1} of organic carbon from the terrestrial landscape (Battin et al., 2008; Tranvik et al., 2009), of which approximately 27% are particulate organic carbon (Alvarez-Cobelas et al., 2012). Considering the small fraction of the earth surface covered by freshwater ecosystems, this rate is surprisingly high and may represent a large fraction of total terrestrial net ecosystem production (Cole et al., 2007). Recent estimates of total C dioxide emissions from inland waters of around 2.1 Pg C y^{-1} (1.8 Pg C y^{-1} of those from running waters; Raymond et al., 2013) may point to a high organic C transformation potential by aquatic microbial communities. This transformation potential may depend on C lability and origin (Guillemette and Del Giorgio, 2011), and may affect both the quantity and the stoichiometric and biochemical quality of terrestrial organic C that is exported downstream. Thus, the roles of different stressors related to agricultural and urban land use in catchment organic matter transport and processing must be disentangled in order to understand the mechanisms of terrestrialaquatic coupling and the role of larger rivers in assimilating and processing terrestrial organic material.

Fatty acids (FAs) are an important class of lipids, because they represent biomarkers of aquatic organisms (Kaneda, 1991; Ahlgren et al., 1992) and their limitation, synthesis and metabolism have profound consequences for consumer physiology and trophic interactions (Müller-Navarra et al., 2004; Boëchat et al., 2005, 2006). Moreover, the role of FAs in ecosystems has gained attention in recent years, as a result of the necessity to couple ecosystem services to human health, and the importance of essential FAs from aquatic ecosystems for human nutrition has been emphasized (Lands, 2009). However, environmental studies involving FAs in aquatic ecosystems commonly focus on their use as markers for bacterial or algal presence and origin of organic matter (terrestrial, aquatic), as well as indicators of prey nutritional quality for consumers (Arts et al., 2009). FAs have rarely been tested as indicators of human impacts on ecosystems, but could be used as markers for urbanization impacts, such as sewage discharge (Jardé et al., 2005) or as markers for changes in key ecosystem processes, such as the response of primary production to enhanced nutrient availability in agricultural streams (Boëchat et al., 2011).

In this study, we analyzed land-use effects on river SPOM-FAs in a larger tropical catchment. We aimed at identifying major human

impacts on the biochemical quality of SPOM, which represents an important basal energy and organic matter source for aquatic consumers, and may affect several aspects of river ecosystem functioning, such nutrient spiraling, ecosystem respiration, secondary production and energy flux. We hypothesized that catchment land use from river's headwaters to its mouth not only leads to direct anthropogenic matter inputs, but also affects the structural integrity of the surrounding environment, thereby altering natural patterns of allochthonous matter inputs. As a consequence, FA composition and concentrations of SPOM should also change, with potential consequences for trophic linkages and energy fluxes. Moreover, we expected urban land use to directly and profoundly affect FA profiles, for instance due to direct inputs of cooking oils and fecal FAs by sewage discharge. Thus, we hypothesized that FAs would be good indicators of land-use impacts on tropical river ecosystem health, and could be a useful tool for monitoring and restoration efforts in tropical catchments, for which land-use maps are often not available or outdated.

2. Materials and methods

2.1. Study site

The present study was conducted in the Rio das Mortes, a fourthorder tributary to the Rio Grande, in the upper Rio Paraná basin. The Rio das Mortes catchment covers two mesoregions in the Brazilian Federal State of Minas Gerais, the mesoregion of Barbacena and the mesoregion of São João del-Rei, with 27 cities (IBGE, 2007; see Fig. 1 for urban centers in the Rio das Mortes catchment). Land cover in the Rio das Mortes catchment is dominated by native vegetation (52.0% of total catchment area; Fig. S1), agriculture (mainly pasture, 30.2%; crops, 5.6%; open soil and burnt areas, 7.3%; and eucalyptus, 1.3%) and urban land cover (urban areas, 1.2%; roads, 2.0%; railways, 0.2%; and mines, 0.1%). Efficient sewage treatment is largely absent in the Rio das Mortes catchment. Thus, urban land cover had a much larger impact on the water quality of headwater streams of this catchment than its small contribution to total catchment area suggested (Silva-Junior et al., 2014). In order to test the hypothesis that different types of land use will drive changes in SPOM-FA composition and concentration, we selected 11 sampling stations, from the river's headwater to its mouth, including sites located upstream and downstream of urban centers, farmland and pasture areas (Fig. 1). Sampling stations were located in the middle of the river. All sites were sampled in triplicate in the middle of the water column during four campaigns carried out in May and September 2010, and March and June 2011, covering the dry and rainy season.

2.2. Land-use characterization of the Rio das Mortes catchment area

Land use of the Rio das Mortes catchment was categorized into three land cover types, i.e. natural, agricultural and urban land cover, in a previous study (Silva-Junior et al., 2014). Riparian buffer zones of 60, 120, 180, 240, and 300 m width upstream of each sampling site were delimited using the open source software QGIS 2.0. Sub-catchment upstream of each study site was delimited based on hypsometric maps using QGIS 2.0 (Quantum GIS Development Team, 2013). Subsequently, land cover distributions for these sub-catchments as well as the riparian buffer zones were calculated from the previously compiled land-use map. As the relative contributions of each land cover type in riparian buffer zones of different width were highly correlated among each other, and with whole catchment land cover (all $R^2 > 0.99$), only whole catchment land cover, and land cover in the 60 m and the 300 m riparian buffer zone were used in further analyses, e.g. in exploring the relationship between land use, water quality, and fatty acid composition and concentration.

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