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The sources and accumulation of sedimentary organic matter in two estuaries in the Brazilian Northern coast

Maria P.S.P. Vilhena [a], Marcondes L. Costa [b], José F. Berredo [c,*], Rosildo S. Paiva [d], Marcelo Z. Moreira [e]

[a] Federal Rural University of Amazon-UFRA, Campus Tomé-Açu-PA, PA-451, Km 10, Industrial District, CEP, 68682-000, Para, Brazil
[b] Federal University of Para, Institute of Geosciences, Avenida Augusto Corrêa, 01, CEP, 66075-110, Guamá, Belém-Para, Brazil
[c] Museum Goeldi, Coordination of Earth Sciences and Ecology, Avenida Perimetral, 1901, CEP, 66077-530, Terra Firme, Belém-Para, Brazil
[d] Federal University of Pará, Institute of Biological Sciences, Avenue Augusto Corrêa, 01, CEP, 66075-110, Guamá, Belém-Pará, Brazil
[e] University of São Paulo/Isotopic Ecology Lab. CENA/ - Piracicaba/SP, Brazil

HIGHLIGHTS

- Particulate matter is the main source of sedimentary organic matter (SOM).
- The SOM is derived mainly from the terrestrial and marine entrances.
- $\delta^{13}C$ is a indicator of the sources of organic matter in the Para river.
- Mocajuba River estuary reflect only biogeochemical processes.

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ABSTRACT

The origin of the organic matter was assessed in two estuaries in Eastern Amazon, Brazilian Northern Coast, under different hydrodynamic conditions. The isotopic composition ($\delta^{13}C$; $\delta^{15}N$) and the elementary ratio (C/N) were determined in the sediments, in the suspended particulate material (SPM), as well as in the phytoplankton, plants and oysters. The ($\delta^{13}C$) values have indicated that the sedimentary organic matter is a terrestrial–marine mix composed of terrigenous organic matter (75%) in the Pará River estuary, as well as of marine organic matter (60%) in the Mocajuba River estuary. The estimates of sources recorded through $\delta^{13}C$ data were partially confirmed through the correlation ($\delta^{15}N$) versus C/N, which reflects the action of diagenetic and biological processes on the organic matter composition control. On the other hand, the high carbon content ($\delta^{13}C$) found in Pará River estuary samples is conclusive because it shows isotopic changes due to the anthropogenic processes in the region.

1. Introduction

Estuaries are characterized by the abundance and diversity of organic matter sources of marine and terrestrial origin (Canuel et al., 1995; Zhang et al., 2009). The organic matter dynamics is of great ecological importance to the coastal environment (Zhou et al., 2006), and its sources, destiny and participation in the estuarine processes have been deeply studied (Yunker et al., 1995; Cifuentes and Eldridge, 1998; Canuel, 2001). However, these studies rarely regard the Brazilian Northern coast.

The active zones wherein the dissolved and particulate materials are produced, transformed or naturally removed through physical, chemical and biological processes, develop in estuaries that present intense continent/ocean exchanges (Jaffé et al., 2001). However, despite the natural processes, the significant changes in the material flow in the coastal zone have been attributed to the anthropogenic action. These changes have been made evident by the gradual nitrogen enrichment in the food chains due to high domestic, industrial and agricultural effluent discharges (Cole et al., 2004; Savage, 2005; Lepoint et al., 2008). They may lead to environmental unbalance and directly affect the local biota.

Many techniques such as the isotope analysis ($\delta^{13}C$; $\delta^{15}N$) and the elementary ratio (C/N), which are used as natural tracers, have been used in studies about organic matter dynamics (Zhang et al., 1997; Graham et al., 2001; Goñi et al., 2003). The use of these markers is based on the existing differences between the

* Correspondence to: Museu Paraense Emílio Goeldi, Av. Perimetral, 1901, CEP. 66077-530, Belém-Para, Brazil.
E-mail addresses: sprogene@hotmail.com.br (M.P.S.P. Vilhena), mlc@ufpa.br (M.L. Costa), berredo@museu-goeldi.br (J.F. Berredo), rpaiva@ufpa.br (R.S. Paiva), mmoreira@cena.usp.br (M.Z. Moreira).

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natural abundance of isotopes ($\delta^{13}C$; $\delta^{15}N$) and the elementary ratio (C/N) due to the increased content of terrigenous, marine and anthropogenic organic matter (Goñi and Thomas, 2000; Lepoint et al., 2004). Combined results ($\delta^{13}C$; $\delta^{15}N$) may provide accurate information about the sources of organic matter, as well as characterize the food chain structure in the ecosystems (Vander Zanden et al., 1999; Fredriksen, 2003; McCallister et al., 2004).

Among the main rivers flowing into the Atlantic Ocean, the Amazon River contributes with 6.5×10^9 mol d^{-1} of the total organic carbon and with 6.8×10^8 mol d^{-1} of the total nitrogen associated with the organic matter (Meade et al., 1985), which account for high biomass production (Sousa et al., 2008, 2009). Seventy percent (70%) of the total deposited organic matter is of terrestrial origin; and 30% is of marine origin (Showers and Angle, 1986; Aller et al., 1996). However, little is known about the distribution and sources of sedimentary organic matter, as well as about their influence on the food chain of rivers that have reduced capacity to transport sediments, but that are of great ecological importance for the coastal production. In light of the foregoing, the aim of the present study is to set the sources of organic matter in the estuaries of Pará and Mocajuba rivers, which are important waterways in the Amazon basin and food sources to the local population.

2. Materials and methods

2.1. Characterizing the study sites

The study was developed in two coastal areas in Northwestern Pará State. The first area is of saline influence and located in the Curuçá region (Lauro Sodré Village), in the estuary of Mocajuba and Tijoca rivers (Fig. 1a). The second area is located in the Barcarena region, which is predominantly composed of fresh water and located in the Pará River estuary, Southwest of Marajó archipelago, close to the confluence of the Tocantins and Pará rivers (Fig. 1b).

The regions have tropical rainy and humid climate. The strongest rainfall happens between January and June (>400 mm/month) and increases the amount of sediments, as well as the volume of fresh water. The reduced recharge of fresh water in the basin (<150 mm/month) and the prevalence of ocean water in the estuaries take place during the dry season — from August to November (Lima and Kobayashi, 1988). These estuaries are strongly influenced by macro- and meso-tides (>4 m) and by the action of waves. They are also associated with mangroves, floodplains, sandbanks and tidal plains (Berrêdo et al., 2008; Vilhena et al., 2009).

The mangroves are represented by mixed woodlands of *Rhizophora mangle* and *Avicennia germinans* in the Mocajuba River estuary. These plant species colonize the muddy sediments belonging to the silt loam Quaternary, which is mineralogically composed of quartz, kaolinite, smectite and illite (Rossetti et al., 1989). This quaternary is daily flooded by the tides. The Pará River estuary presents landscape typical of the Amazon plain, which is constituted by recent silty-sandy sedimentary terrains composed of quartz and kaolinite. In addition, the estuary has many rivers, as well as small drainage systems interconnected with the Marajó Bay (Lima and Kobayashi, 1988). The vegetation cover is composed of lowland and floodland plant species such as *Euterpe oleracea* Mart, *Montrilia fluxuosa* L., *Hevea brasiliensis*, *Manilkara huberi,* and mainly of *Montrechardia arborescens* (L) Shott, which is widely distributed in the region. There is also *Bertholletia excelsa,* which is a dry land forest vegetation (Macedo et al., 2005). Mangrove species such as *R. mangle* and *A. germinans* are found in the river mouth.

The human activities, which are intense in the Pará River estuary, generate great mineral load moves, as well as fuel oil and caustic soda (used in bauxite — aluminum oxide treatments) discharges. There is intense flow of vessels at Vila do Conde terminal. These vessels contribute to the production of industrial, agricultural and domestic effluents.

2.2. Sampling procedures

The collection of bottom sediments, suspended particulate material (SPM), phytoplankton, vegetation and oysters was conducted in the months of most intense rainfall (from January to April) and drought (from August to November). Three collection points were chosen in the Mocajuba River estuary (P1C, P2C and P3C, Fig. 1a). The collections were performed in six points of the Pará River estuary: in the industrial-harbor area, in the Itupanema and Vila do Conde beaches, and in four points (P1B, P2B, P3B and P4B). An anthropogenic influence-free sampling point (sample, control, P5B) was set close to the Barcarena region for comparison purposes. Another sampling point was set in an area highly influenced by anthropogenic activities (Santos et al., 2012). This area was located close to Guajará Bay (P0B), which is an important receptor of Pará River estuary water (Fig. 1b).

2.3. Bottom sediments and suspended particulate material (SPM)

The bottom sediments were collected using a jaw-type steel dredge. Twenty-eight (28) samples were collected, stored in plastic bags and kept at 4 °C. The samples were oven-dried at 50 °C, in laboratory environment, until reaching constant weight, and ground in agate mortar, after drying. Approximately 400 liters of water were stored and decanted for suspended particulate material (SPM) collection. The decanted material was oven-dried at 50 °C and, subsequently, ground in agate mortar.

2.4. Phytoplankton

The phytoplankton samples (10 L volume) were collected during the flood tides; horizontal hauls were performed on the water surface (maximal depth 50 cm), using a standard-type plankton mesh, with mesh opening 64 μm. This mesh opening is the most used one in the Amazonian estuary due to the strong local hydrodynamics (Paiva et al., 2006). Each sample was inspected in binocular microscope after they were washed in deionized water and subjected to wet sieving (mesh opening 20 μm) to remove the contaminant particles (trunks, leaves and shells) or possible zooplankton predators. Next, the samples were frozen and lyophilized.

2.5. Oysters

The oysters from the Mocajuba (*Crassostrea* gasar) and Pará rivers (*Paxyodon ponderosus*) were collected in five sampling points (Fig. 1), in January, April, August and November. The oysters were kept alive up to the time to be taken to the laboratory where their external parts were cleaned in fresh and deionized water. Subsequently, the length and width of the shells were measured and the total wet weight of each animal was recorded. The shells were opened using a stainless steel knife and the tissue was withdrawn using scissors and stainless steel tweezers. This procedure was separately repeated in each animal, according to size (between 5 and 12 cm long), until reaching 10 g of tissue. Next, the samples were lyophilized, ground and macerated in agate mortar.

2.6. Vegetation

The samples of adult *R. mangle* and *M. arborescens sholt* leaves were collected. The leaves were washed in fresh and deionized water in order to remove the adhered sedimentary particles. In addition, they were dried at room temperature, stored in Kraft paper bags and ground in stainless steel spade mill.

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