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Evaluation of the organic matter sources using the $\delta^{13}C$ composition of individual *n*-alkanes in sediments from Brazilian estuarine systems by GC/C/IRMS

Otávio Luiz Gusso Maioli [a,*], Cristiane Rossi de Oliveira [a,b], Marco Aurélio Dal Sasso [a], Luiz Augusto dos Santos Madureira [b], Débora de Almeida Azevedo [a], Francisco Radler de Aquino Neto [a]

[a] Federal University of Rio de Janeiro, Institute of Chemistry, Ilha do Fundão, Rio de Janeiro 21941-909, RJ, Brazil
[b] Federal University of Santa Catarina, Department of Chemistry, Florianópolis, SC 88040-900, Brazil

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The $\delta^{13}C$ composition of individual *n*-alkanes (from C_{16} to C_{34}) was measured from surface sediments of five Brazilian estuarine systems affected by different organic matter sources, such as harbor area, industries, urban centers and sugar cane crops, in order to determine the origins of the organic matter. The aliphatic hydrocarbon fraction was analyzed by gas chromatography–combustion–isotope ratio mass spectrometry (GC/C/IRMS). The levels of *n*-alkanes in the studied areas ranged from 0.34 to 18.14 μg kg^{-1}, being relatively low in comparison to high polluted environments. The Carbon Preference Index (CPI) calculated in the C_{23}–C_{34} range indicates that *n*-alkanes are mainly inherited from cuticular waxes of higher plants. The $\delta^{13}C$ composition of all *n*-alkanes detected in the sediment samples ranged from −39.6 to −18.3‰ showing different sources for the studied estuarine systems. Through Principal Component Analysis (PCA) it was possible to verify the petrogenic influence in the *n*-alkane sources, especially in the Paraíba do Sul sediment samples. Differences up to 15‰ of the $\delta^{13}C$ values between *n*-alkanes of odd and even carbon number (C_{26} and C_{27}) also indicated mixture of petrogenic and biogenic sources in Paraíba do Sul River. High (less negative) $\delta^{13}C$ *n*-alkane values of odd carbon number were obtained from two sampling sites located close to an ethanol plant, indicating residues discharge of sugar cane (C_4 plant). Influence of C_3 plants that are the main components of dense ombrophile forest was observed in the Itajaí-Açu sediments by the decrease of $\delta^{13}C$ (about 10‰ compared to the Paraíba do Sul River $\delta^{13}C$).

1. Introduction

Sediments can act as an ultimate reservoir for natural and anthropogenic organic matter. Marine coastal areas play an important role in the global carbon cycle, either as sources of organic matter to the open ocean or as carbon sinks in the form of accumulation in sediments (Guo et al., 2007).

Hydrocarbons are generally robust recorders of the origin of organic matter in sediments (Meyers, 2003). The high abundance of hydrocarbons in sediments is a potential source of pollution. Aside from anthropogenic sources, hydrocarbons may also have several natural sources, such as terrestrial plant waxes, marine phytoplankton and bacteria, biomass combustion and diagenetic transformation of biogenic precursors (Gogou et al., 2000). Linear alkanes (*n*-alkanes) may originate from vegetation emissions and incomplete combustion of fossil fuels. The odd-to-even-number *n*-alkane concentration ratios from C_{25} to C_{34}, commonly referred to as the carbon preference index (CPI), have been used to suggest their sources (Bray and Evans, 1961; Peters et al., 2005). The *n*-alkane with the maximum concentration (C_{max}) gives the strongest indication of anthropogenic versus natural recent biological input (Azevedo et al., 2007). Due to *n*-alkanes have non-unique chain length signatures, the carbon isotopic signature can be used to better distinguish among sources (Sikes et al., 2009).

The $^{12}C/^{13}C$ ($\delta^{13}C$) isotope ratio in natural materials varies slightly as a result of isotopic fractionation during physical, chemical and biological processes, being highly diagnostic of key environmental processes (Boutton et al., 1996; Meyers, 2003). Both ^{13}C composition of organic matter and *n*-alkane distributions in sediments from Plum Island, a salt marsh from Massachusetts, USA, indicated that the marsh plants could contribute predominantly to the amount of organic matter in sediments (Wang et al., 2003). In the same way, the $\delta^{13}C$ values of organic matter averaging −21‰

* Corresponding author.
E-mail addresses: otaviomaioli@mma.gov.br, otaviomaioli@iq.ufrj.br (O.L.G. Maioli), rossi.cristiane@yahoo.com.br (C.R. de Oliveira).

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point to the influence of organic matter transported from the C_4 plants dominated savannas in the northern fringe of the Orinoco River, Venezuela (Medina et al., 2005). The $^{12}C/^{13}C$ analysis of *n*-alkanes is also a direct way to discriminate among C_3, C_4 and CAM plants (carbon fixation pathway during photosynthesis) contribution to sediments. The *n*-alkane $\delta^{13}C$ values between −31‰ and −39‰ are associated to plants that use the Calvin–Benson cycle (C_3) (Schefub et al., 2003). On the other hand, plants utilizing the Hatch–Slack cycle (C_4) have *n*-alkanes $\delta^{13}C$ values ranging from −18‰ to −25‰ (Schefub et al., 2003). A third type of plants is based on the Crassulacean Acid Metabolism (CAM). These type of plants can use both fixation pathways and their *n*-alkanes $\delta^{13}C$ values are intermediate, −25‰ to −27‰ (Collister et al., 1994). The ($\delta^{13}C$) values of individual *n*-alkanes (C_{16}–C_{33}) varied between −22.6‰ and −34.2‰ in short sediment cores from Mundaú-Manguaba estuarine–lagoon system (MMELS) collected in 2007 at three sites, suggesting a dominance of ^{12}C-enriched *n*-alkanes that originated from C_3 plants and lacustrine algae (Silva et al., 2012).

Traditionally, the difference in characteristic chain lengths of marine and terrestrial plants made the distribution of *n*-alkanes an effective biomarker tool for assessing biogenic sources of organic matter in terrestrial and marine ecosystems. However, significant mangrove, marine macrophyte, and/or riparian–aquatic inputs introduce sources with non-unique *n*-alkane compositions to the system, making the effective determination of sources by only *n*-alkane chain length data difficult in such complex environments (Sikes et al., 2009). Additionally, $\delta^{13}C$ is used to determine origin and identify sources of oil spills and oil pollution, ocean-transport bitumen and characterization of refractory wastes at heavy-oil contaminated sites (Meyer-Augenstein, 1999; Philp et al., 2002).

According to Tanner et al. (2010), $\delta^{13}C$ values of *n*-alkanes are minimally affected by degradation in Morse River, USA. Although *n*-alkanes can be biodegraded in the sediments, there is no influence on the $\delta^{13}C$ signature of these compounds.

Gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) is a highly specialized instrumental technique used to establish the relative ratio of light stable isotopes of carbon ($^{13}C/^{12}C$) in individual compounds separated from complex mixtures of components, such as *n*-alkanes (Silva et al., 2008). The desire to study $\delta^{13}C$ isotope abundance of sedimentary hydrocarbons on molecular levels was one of the driving forces behind the development of GC/C/IRMS (Hayes, 1993; Meyer-Augenstein, 1999).

The $\delta^{13}C$ composition of *n*-alkanes (from C_{16} to C_{34}) was measured in surface sediments from three estuarine systems in Santa Catarina State, one lagoon in Alagoas State and one river in Rio de Janeiro State. The mentioned estuarine systems are impacted by different activities such as urbanization, industrialization, harbor activities and sugar cane plantation. The aim of this study was to evaluate the impact of these anthropogenic activities in these estuarine systems and to determine origins of the sedimentary organic matter.

2. Materials and methods

2.1. Study areas

The study areas correspond to: Babitonga Bay, Imbituba (open sea) and Itajaí-Açu River, located in the state of Santa Catarina, S-Brazil; Manguaba lagunar estuarine, state of Alagoas, NE-Brazil and, Paraiba do Sul River, state of Rio de Janeiro, SE-Brazil (Fig. 1, Table 1).

The Babitonga Bay estuarine system has an area of 1400 km^2 and is located on Northeast of the Joinville City, the most populated and urbanized town of the State. The bay watershed has a broad environment, where agriculture and mariculture, as well as textile, metal mechanic and foundry factories, coexist in the same area. The São Francisco do Sul Harbor is located inside the Babitonga Bay (BAB), in the Northeast coast of Santa Catarina, at the city of São Francisco do Sul. This bay shelters the last big South American mangrove, being the most important estuarine region of the Santa Catarina State (Cremer et al., 2006). On an open inlet at the Imbituba city is located the Imbituba Harbor (IMB), in the Southern coast of Santa Catarina. Itajaí-Açu River mouth (ITA) is located at the center coast of the State and has a drainage basin of about 15,500 km^2. The Itajaí and Navegantes Harbors are located in its waterfront at their homonym cities. This estuary receives wastewaters and untreated industrial effluents from several cities located in the Itajaí Valley (Pereira Filho et al., 2003).

Manguaba lagunar estuarine (MAN) falls into the category of a choked estuarine–lagoon system, with long residence times of water, a large potential for material recycling and retention, and exhibits eutrophic conditions (Oliveira and Kjerfve, 1993; Souza et al., 2002). Manguaba lagoon has a total surface area of 43 km^2 and a mean depth of around 2 m. The climate in the upper basin is semi-arid and the lower basin is tropical humid, with an annual precipitation around 1500 mm and distinct dry summer (November–March) and wet winter (May–August) conditions. Sugar cane waste effluents are transported by the rivers and urban sewage is introduced into Manguaba lagoon from a number of smaller cities around it (Souza et al., 2002).

Paraíba do Sul (PSR) falls into the category of an estuarine–delta, fed by turbid river waters and is an exporter of materials to the coastal sea. This estuarine system is fed by the 1145 km long Paraíba do Sul River with a mean annual fresh water discharge of 868 m^3 s^{-1} from a watershed of 55,400 km^2, with access to the sea via a primary channel and a secondary channel lined by mangroves. The climate at the coast is tropical humid with an average annual precipitation of 1100 mm and wet summer (October–March) and dry winter (April–September) seasons. The river crosses three of the most important and developed states of Brazil (São Paulo, Minas Gerais and Rio de Janeiro). It supplies water for more than 11 million people of Rio de Janeiro, but it is also used as waste disposal for a very large number of industries along its course. Other human impacts arise from domestic/industrial effluents upriver, partially retained by a cascade of dams. Along its lower course in the coastal plains, it is affected by punctual and diffuse sources of sugar cane monoculture and domestic effluents. Ground water contamination by herbicides and pesticides from sugar cane effluents has been detected in the PSR (Knoppers et al., 1999).

2.2. Sample collection

Surface sediment samples were collected from Paraíba do Sul in July 2006, from Manguaba in August 2006, from Babitonga Bay in October 2007, from Imbituba in April 2008 and from Itajaí-Açu River Mouth in July 2008. A total of five surface sediment samples (0–5 cm) were collected from Manguaba (two in the Manguaba lagoon, two in the channel and one in the Sumaúma River); six from the Paraíba do Sul River – being that two are located in the river (PSR) and four in the river mouth (PSE); two from Babitonga Bay (harbor dockyards); three from Imbituba (harbor area); and four from Itajaí-Açu River mouth – one at the open inlet (ITA-1), two at the harbor dockyards (ITA-2 and ITA-3) and one at the marina area (ITA-4).

Surface sediments (0–5 cm deep) were sampled using a van Veen grab, kept in pre-cleaned aluminum foil containers and stored at −20 °C. Afterwards, the samples were sieved through 63 μm, freeze-dried, extracted and analyzed.