

Exchange between macrophyte and mangrove organic matter input in estuarine systems: drought implications

Paq proxy was applied on mid and long-chain n-alkanes in order to develop an index to assist in the long-term assessment of changes and exchanges between aquatic communities in estuarine environments as a result of increased saline incursion. New boundaries are proposed according to n-alkanes abundance in the leaves of local mangrove tree species for better definition of emergent aquatic plant end-member. Molecular distribution and $\delta^{13}C$ isotopic signatures of n-alkanes were also used to support the parameter. A predominance of odd carbon-numbered long chain (> C27 n-alkanes) indicated a main terrestrial input, although mid-chain n-alkanes (23 and 25 carbons) were also identified. Short-chain n-alkanes (< 19) were absent or found in a very small concentration. Carbon Preference Index and C/N ratio reinforced a terrestrial origin for the sedimentary organic matter. $\delta^{13}C$ signatures of n-alkanes for C23, C25, C29 and C31 were characteristic of mangrove input, ranging from -27.57 ‰ (C23) to -34.40 ‰ (C29) for Piraquê-Mirim River (PM) and from -27.36 ‰ (C23) to -32.84 ‰ (C31) for Piraquê-Açu River (PA) without any particular trend. Paq proxy was successfully used to identify rises in marine macrophytes (mid-chain n-alkanes) input mainly in the confluence and PM probably as consequence of drought periods. The confluence presented a mixing sources of OM. PA was identified as a stable mangrove environment while PM was characterized by pulses of marine macrophytes input and should be managed with care in respect to its catchment for water use and dam constructions as a shortage of fresh water can alter the estuarine ecology.

Keywords: Carbon Isotopes; Alkanes; Mangrove; Macrophyte; Drought.

Alteração entre aporte de matéria orgânica oriunda de macrófitas e de mangues em sistemas estuarinos: implicações de seca

O índice Paq foi aplicado em n-alcenos de cadeia média e longa afim de desenvolver um índice para auxiliar na avaliação de longo prazo de mudanças e trocas entre comunidades aquáticas em ambientes estuarinos como resultado do aumento de intrusão salina. Novos limites são propostos de acordo com a abundância de n-alcenos nas folhas de espécies de mangues locais para uma melhor definição dos limites considerados para plantas aquáticas emergentes. A distribuição molecular e as assinaturas isotópicas $\delta^{13}C$ de n-alcenos também foram utilizadas para corroborar com este novo parâmetro. Uma predominância de cadeia carbônica longa e ímpar (> C27) indicou um aporte terrestre dominante, embora n-alcenos de cadeia média (23 e 25 carbonos) também foram identificados. Os n-alcenos de cadeia curta (<19) estiveram ausentes ou foram encontrados em uma concentração muito baixa. O Índice de Preferência de Carbono e a relação C/N reforçaram uma origem terrestre para a matéria orgânica sedimentar. As assinaturas $\delta^{13}C$ de n-alcenos para C23, C25, C29 e C31 foram características de matéria orgânica oriunda de mangues, variando de -27,57 ‰ (C23) a -34,40 ‰ (C29) para o rio Piraquê-Mirim (PM) e de -27,36 ‰ (C23) a -32,84 ‰ (C31) para o rio Piraquê-Açu (PA), sem qualquer tendência específica. O índice Paq foi utilizado com sucesso para identificar um aumento do aporte de matéria orgânica de macrófitas marinhas (n-alcenos de cadeia média), principalmente na confluência e no PM, provavelmente como consequência de períodos de seca. A confluência apresentou Sources de mistas de matéria orgânica. O PA foi identificado como um ambiente de manguezal estável, enquanto o PM foi caracterizado por pulsos de aporte de macrófitas marinhas e deve ser gerenciado com cuidado em relação à sua captação para uso de água e construções de barragens, uma vez que a escassez de água doce pode alterar a ecologia estuarina.


Palavras-chave: Isótopos de Carbono, Alcanos, Manguezais, Macrófitas, Seca.


Topic: **Desenvolvimento, Sustentabilidade e Meio Ambiente**


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INTRODUCTION

Zonation of mangroves species is site specific as it is controlled by tidal inundation, soil pore water salinity, sediment stability and type and fresh water input (JIMÉNEZ et al., 1985; CARDONA et al., 1998; JIMÉNEZ, 1990; ELLISON, 1993; DUKE et al., 1998; ELSTER, 2000). Salinity is the most obvious influencing factor. Even congeneric species usually occupy distinct positions of intertidal zones due to differential ability of salt tolerance (LIANG et al., 2008). Despite mangroves have been adapted to salinity variations and even found in places with same salinity as the open sea (WOODROFFE, 1982), pore water salinization due to high evaporation rates and low freshwater inflow can result in hypersaline zones where mangroves cannot survive.

Surface water runoff from adjacent uplands and groundwater flow are important factors on hypersaline soil formation due to inhibition of salts accumulation in the pore water (BERTNESS et al., 1992; THIBODEAU, et al., 1998), but halophytic shrubs, herbs and grasses can develop in mangroves when fresh water inflow is too low (ELLISON et al., 1991; RAKOTOMAVO et al., 2010). Less rainfall can decrease mangrove diversity and extent, as mangrove requirements for tolerance of high salinity in soil reduce growth rate and mangrove productivity (FIELD, 1995; GILMAN et al., 2008).

Apart from changes in precipitation pattern, construction of dams upstream in the river may reduce fluvial inputs, nutrients and sediment (DUVIAL et al., 2007; SNOUSSI et al., 2007), resulting in biodiversity losses, alteration in structural aspects and swap of biological communities. A reduction in the fluvial flow may favours marine incursions into the estuary and may change environmental conditions for submerged aquatic vegetation settlement that lives below or at the water surface within estuaries and freshwater environments. It includes seagrasses, freshwater grasses and macroalgae species (KEMP et al., 2004; DENNISON et al., 2008). Seagrasses are aquatic flowering plants that form meadows in near-shore brackish or marine waters in temperate and tropical regions and are able to live and complete their life cycle under submerged and haline conditions (DEN HARTOG et al., 2006).

Seagrass meadows and mangroves have been exposed to different anthropogenic impacts of varying intensity, and they may be vulnerable to different stresses according to climate and coastal dynamics and ecosystems resiliencies (COPERTINO et al., 2016). As drought has becoming an often problem in different places of the world, particularly in southeast Brazil, understand how major organic matter producers stand against fluvial flow shrinkage and rise in marine water intrusion is a matter of coastal management, as such ecosystem supports many others adjacent and provides many services (RÖNNBÄCK, 1999; VO et al., 2012; LEE et al., 2014). As mangrove sediment can provide historic records of past environmental conditions such as sea level change and climate variations, differences in hydrological conditions and productivity can be evaluated. Such differences may result in different organic matter inputs and reflect in the quality and degree of diagenesis of the sedimentary organic matter (JAFFÉ et al., 2001).

In order to develop an index to assist in the long-term assessment of changes and exchanges between aquatic communities in estuarine environments as a result of increased saline incursion, a multi-proxy

approach based on *n*-alkanes chain length and their isotopic $\delta^{13}\text{C}$ signature was applied in a typical drowned river valley with Y-shaped morphology, with a main channel towards the mouth (Piraquê-Açu-Mirim Estuarine System - PAMES; Brazil; Figure 1). Both estuarine branches are meandering systems with extensive mangroves and tidal flats (SILVA et al., 2013) with about 15.592 km² around Açu River and about 14.790 km² around Mirim River. The rivers have very different flow regimes due to their different drainage basins and catchment areas (13.69 and 2.59 m³/s; 378.6 and 469.4 km² for PA and PM, respectively; BARROSO et al., 2012; LEITE, 2012), so they have different interactions with the incoming marine flow. The climate of the PAMES region is tropical with seasonal variations of temperature and humidity and an average annual rainfall of ca. 1250 mm (IEMA, 2010). The region presents two well-defined seasonal periods: a rainy season (October to March) with maximum precipitation between November and December (200-250 mm) (LEITE, 2012), average temperatures of ca. 32.4°C (FEITOZA, 1997) and predominance of north-easterly winds (CAMPOS, 2011); a dry period (May to August) with the lowest rainfall June and August (25-50 mm) (ALBINO et al., 2006), and with average temperature of ca. 14.9 °C (FEITOZA, 1997). Although the PAMES has no anthropogenic limitation to block mangrove migration, the natural barrier of the Barreiras Formation (MARTIN et al., 1996) could restrict mangrove migration in case of sea level rise.

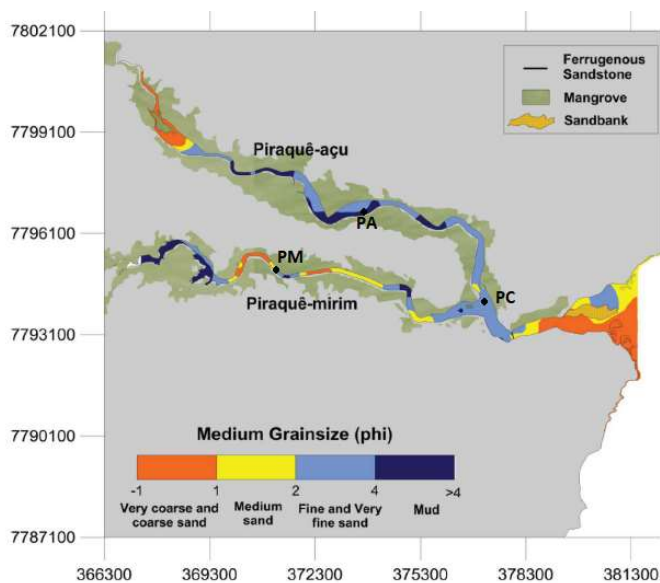


Figure 1: Map of Piraquê-Açu and Piraquê-Mirim Estuarine System (PAMES; Modified after Silva et al., 2014). Coring sites are indicated as black dots on the map.

MATERIALS AND METHODS

Sampling

Three sediment cores were collected in February 2010 with a push corer in the main channel at three different sites (Figure 1): Piraquê-Açu River upstream (PA, 74 cm length), Piraquê-Mirim River upstream (PM, 50 cm length) and at the confluence (PC, 96 cm length). Sampling sites were selected using seismic data of the channel bottom where the sediment layers showed little disturbance. All cores were frozen (-20 °C) and then sliced at 2 cm intervals. The first 10 centimetres were sliced at 1 cm interval. Samples were then freeze-dried (under vacuum at -60 °C) and stored (-20 °C) until analysis.

Elemental composition (C/N molar ratio)

Freeze-dried and macerated sediments (ca. 100 mg) were decarbonated by acid treatment (HCl 10 %) and the carbonate content was determined by gravimetry. Elemental analyses were carried out using a Costech ECS 4010 analyser for quantification of organic carbon and total nitrogen present in the sediment and mean values were taken (S.D < 10 % of the mean).

n-Alkanes analysis

Freeze-dried sediments (ca. 1 g) were macerated and sonicated with dichloromethane (DCM): methanol (9:1 v/v) (3 x 15 min). Extracts were combined and concentrated *in vacuo* (to ca. 1 mL) and transferred to a small vial. Sulphur was removed with pre-activated copper (HCl 37 %, followed by double-distilled water, methanol and DCM wash). The residue was dissolved in DCM and any residual water was removed by drying the extract over anhydrous sodium sulphate. *n*-Alkanes (apolar fraction) were recovered with 4 mL of hexane using a small silica gel column (70-230 microns; Pasteur pipette), with lipid extracts dispersed on alumina. All solvents were distilled or HPLC grade. Sodium sulphate and silica gel were extracted with DCM (24 h) and heated (400°C; 12h).

Quantification and identification were performed on a Trace Gas Chromatograph 2000 Series (ThermoQuest) coupled to a Mass Spectrometer ThermoQuest Finnigan Triple-Stage Quadrupole 7000 with electron impact ionization. A silica capillary column (60m, 0.25 mm, 10µm Agilent J & W DB-5MS) was used with helium as carrier gas at a constant flow. The injections were made manually on the on-column mode and the column flow rate was 1.2 mL/min. The oven heating program began at an initial temperature of 60 °C for 1min, followed by a ramp from 170 °C at 6 °C / min and after, 315 °C at 2.5 °C / min hold by 12min. The MS electron impact was operated in the full scan mode in a range from 50 to 600 Thompsons per second and ionization energy of 70 eV. The ion source temperature was 215 °C and the interface, 320 °C. Data was processed using Xcalibur software. Compounds were identified either by comparison of their mass spectra and relative retention indices with those available in the literature and/or by comparison with authentic standards. Quantitative data were calculated by comparison of peak area of the internal standard 5α (H)-cholestane using the total ion current chromatogram. A lipid standard containing a mixture of compounds (fatty acids, coprostanol, epicoprostanol, cholesterol, cholestanol, stigmastanol, stigmasterol, 37:2 ketone, C₂₀ and C₂₄ alcohols, and 5α (H)-cholanic acid) was injected before each batch of samples to determine response factors for quantification. Samples were corrected with individual blanks when needed, although in most cases lipid levels were insignificant (<1 % of the sample values). Concentrations were normalized to total organic carbon (TOC) content of the sediments.

n-Alkanes specific isotope analysis

Compound Specific Isotope Analysis (CSIA) was carried out on a Delta V Advantage (Thermo Fisher, Bremen) coupled with an Ultra Trace auto sampler TriPlus with ConFio IV interface and 1 µL splitless mode

injection into a silica capillary column (J&W Scientific DB5, 30 m, 0.25 mm di, 0.25 μ film thickness). The oven heating program had an initial temperature of 45 °C for 1 min followed by a ramp up to 295 °C at 6 °C/min for 15 minutes. The injector was held at 280 °C. Ultra-pure helium was used as carrier gas at a constant flow rate of 1.4 ml/min. The Gas Chromatograph was operated in the back flush mode during the initial period of solvent elution while helium was passed in the opposite direction through the reactor combustion. Isotopic compositions represent the mean of duplicate or triplicate analyses and standard deviations were $\leq 0.5\%$. The CO₂ reference gas was calibrated externally relative to the standard Vienna Pee Dee Belemnite (VPDB) in a double mass spectrometer inlet. The results are presented in per mil (‰) to VPDB standard. Data were acquired and processed using ISODAT software. External standards containing fatty acids (Arndt Schimmelmann, Indiana University) $\delta^{13}\text{C}$ values precisely known were analysed at each batch sample.

RESULTS AND DISCUSSION

n-Alkanes distribution

C/N ratios for PM (23.52 to 53.95; Figure 2) and for PA (23.28 to 32.25; Figure 3) cores were greater than 20 and indicate a major input of terrestrial organic matter, while PC (15.44 to 34.45; Figure 4) profile presented intermediate values (15.44 to 18.86) mainly on the top (first 6 cm), suggesting a phytoplankton organic matter deposition rise in more recent sediments (values between 4 and 10 are an indicative of phytoplankton origin and values > 20 of terrestrial input) (MEYERS et al., 1993; MEYERS, 1997). A smooth rising trend of phytoplankton input was also identified in the PM core from base to the top, as C/N ratio presented a progressive reduction.

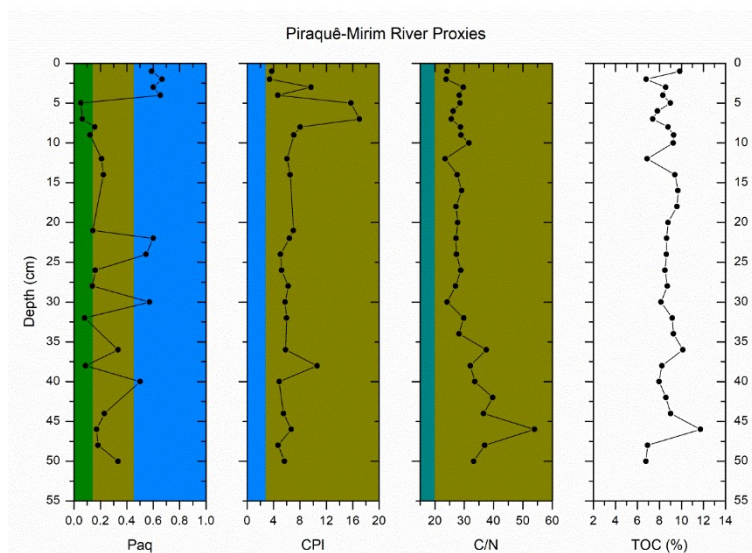


Figure 2: Piraquê-Mirim Proxies are described as $\text{Paq} = (\text{C}_{23} + \text{C}_{25}) / (\text{C}_{23} + \text{C}_{25} + \text{C}_{29} + \text{C}_{31})$; Carbon Preference Index = $0,5 * (\sum \text{Odds } \text{C}_{25} \text{ to } \text{C}_{33} / \sum \text{Evens } \text{C}_{24} \text{ to } \text{C}_{32}) / (\sum \text{Odds } \text{C}_{25} \text{ to } \text{C}_{33} / \sum \text{Evens } \text{C}_{26} \text{ to } \text{C}_{34})$, C/N ratio and Total Organic Carbon (%). Green colour represents terrestrial input, brown represents mangrove input, blue represents marine input and cyan represent mixed environment.

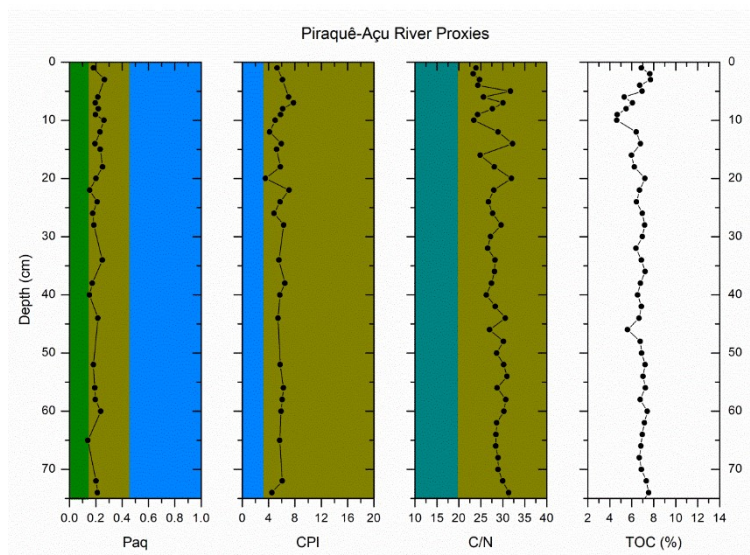


Figure 3: Piraquê-Açu Proxies are described as $Paq = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$; Carbon Preference Index = $0,5 * (\sum \text{odd } C_{25} \text{ to } C_{33} / \sum \text{even } C_{24} \text{ to } C_{32}) / (\sum \text{odd } C_{25} \text{ to } C_{33} / \sum \text{even } C_{26} \text{ to } C_{34})$, C/N ratio and Total Organic Carbon (%). Green colour represents terrestrial input, brown represents mangrove input, blue represents marine input and cyan represent mixed environment.

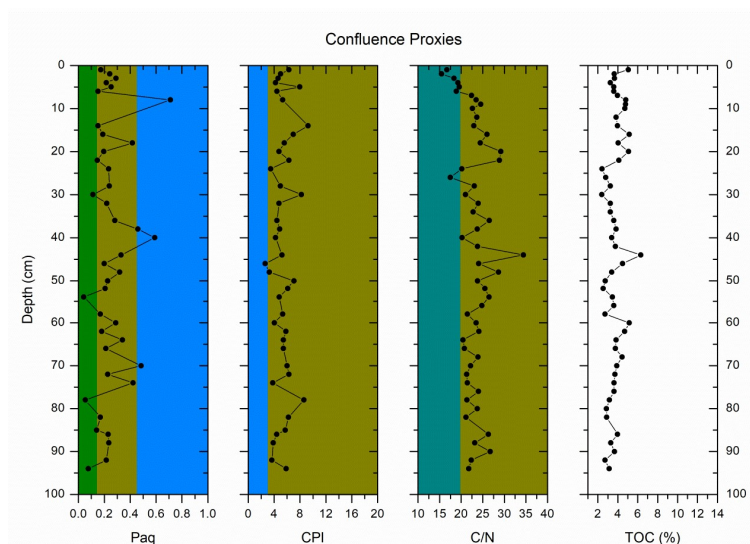


Figure 4: Confluence Proxies are described as $Paq = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$; Carbon Preference Index = $0,5 * (\sum \text{odd } C_{25} \text{ to } C_{33} / \sum \text{even } C_{24} \text{ to } C_{32}) / (\sum \text{odd } C_{25} \text{ to } C_{33} / \sum \text{even } C_{26} \text{ to } C_{34})$, C/N ratio and Total Organic Carbon (%). Green colour represents terrestrial input, brown represents mangrove input, blue represents marine input and cyan represent mixed environment.

The most abundant *n*-alkanes in the three cores were those of long-chain length (> 25 carbons) with a strong dominance of odd over even and a unimodal distribution with a maximum at C₂₉ homologue (Figures 5, 6 and 7), implying a major input of higher plants (EGLINTON et al., 1967) due to its great abundance in cuticular waxes (CRANWELL, 1973; REDDY et al., 2000; WANG et al., 2003). The great abundance of C₂₇ and C₃₁ homologues is also an indicative of higher plant waxes input (EGLINTON et al., 1967; CRANWELL, 1973). As the surrounded vegetation is composed by mangroves, another higher plant source is unlikely and allows long-chain *n*-alkanes to be used as mangrove markers to the estuary, reflecting on higher values of CPI (> 3), indicating an input prevalence of *n*-alkanes from higher plants waxes (BRAY et al., 1961; CHIKARAIISHI et al., 2003; EGLINTON et al., 1967; VAN DONGEN et al., 2008) for the three cores (4.69 to 10.59 for PM; 1.92 to 7.8 for PA; 2.63 to 9.26 for PC; Supplementary Data 1; Figure 2, 3 and 4).

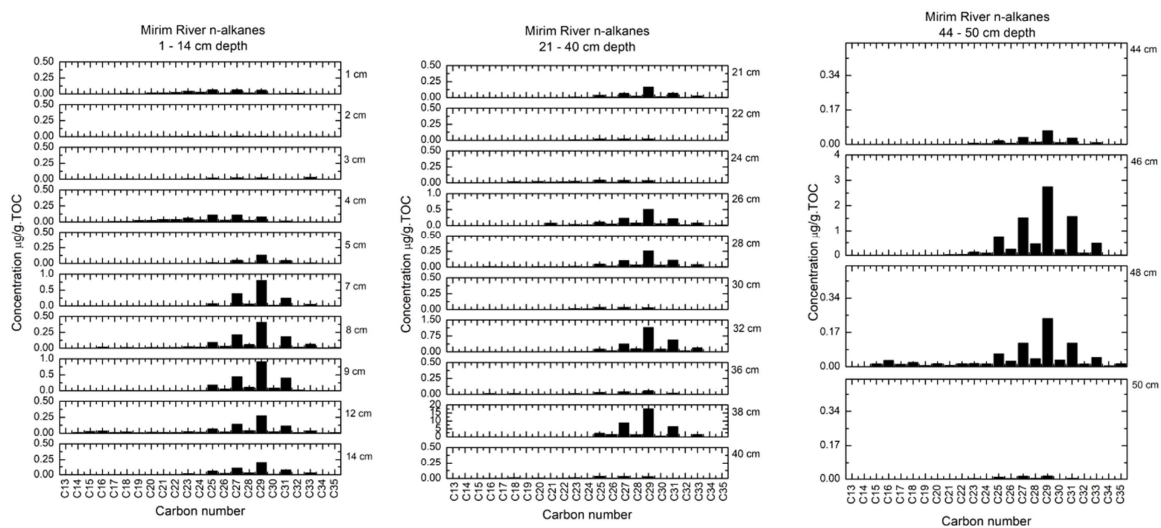


Figure 5: n-Alkanes abundance ($\mu\text{g/g.TOC}$) for Piraquê-Mirim River. Y-axes are not standardized while X-axes range is from 13 to 35 carbons.

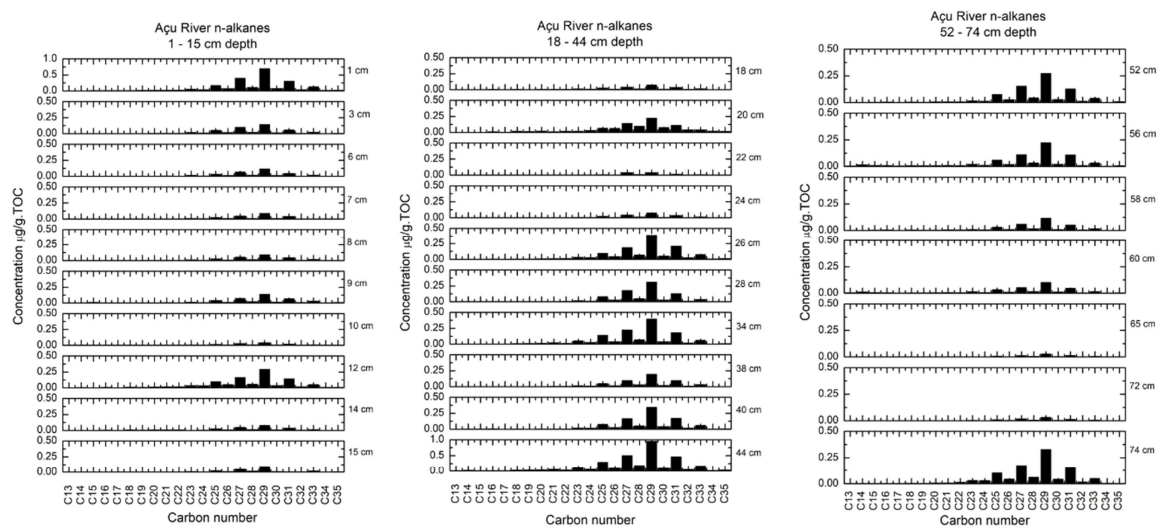


Figure 6: n-Alkanes abundance ($\mu\text{g/g.TOC}$) for Piraquê-Açu River. Y-axes are not standardized while X-axes range is from 13 to 35 carbons.

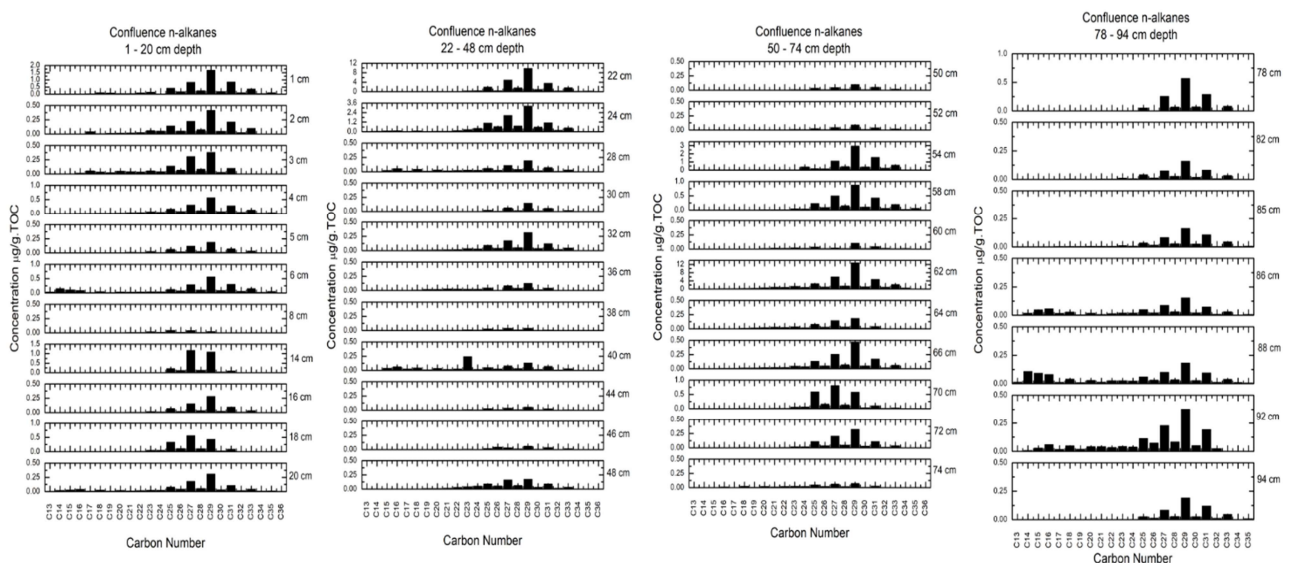


Figure 7: n-Alkanes abundance ($\mu\text{g/g.TOC}$) for Confluence. Y-axes are not standardized while X-axes range is from 13 to 35 carbons.

Supplementary data 1: Data acquired for Piraquê-Mirim (PM), Piraquê-Açu (PA) and Confluence (PC). Blank cells are the core limit. C/N ratio > 20 are indicative of terrestrial origin, while < 10 are indicative of aquatic sources. CPI < 3 are indicative of aquatic origin, while > 3, terrestrial. Paq < 0.15 are indicative of terrestrial inputs; 0.15–0.45 of emergent aquatic plants; > 0.45 are aquatic plants and marine macrophytes.

Depth (cm)	PM			PA			PC		
	CPI	C/N	Paq	CPI	C/N	Paq	CPI	C/N	Paq
1	3.72	24.16	0.59	5.3	23.93	0.18	6.28	16.67	0.17
2	3.4	23.85	0.67	nc	23.28	0.26	5.0	15.44	0.24
3	9.67	29.69	0.6	6.12	24.7	nc	4.61	18.35	0.28
4	4.65	28.34	0.65	nc	24.35	nc	4.22	19.27	0.22
5	15.72	28.58	0.05	nc	31.78	nc	7.96	19.57	0.24
6	17.02	26.27	nc	7.06	25.64	nc	4.43	18.86	0.16
7	8.05	25.63	0.06	7.8	30.07	0.19	nc	22.41	nc
8	7.07	28.71	0.16	6.14	27.66	0.24	5.33	23.47	0.75
9	nc	28.86	0.12	5.85	24.29	0.2	nc	24.52	nc
10	6.05	31.57	nc	5	23.44	0.33	nc	22.62	nc
12	6.51	23.52	0.21	4.15	28.91	0.23	nc	23.64	nc
14	nc	27.63	0.22	5.94	32.25	0.21	9.26	22.95	0.15
16	7.02	29.15	nc	5.21	nc	0.25	6.98	26.01	nc
18	6.4	27.24	nc	5.81	24.89	nc	5.59	24.42	0.2
20	5.06	27.73	nc	3.5	28.09	0.23	4.76	29.19	0.42
22	5.23	27.22	nc	7.1	31.96	0.21	6.3	28.89	0.19
24	6.24	27.36	0.14	5.76	27.94	nc	3.49	20.19	nc
26	5.77	28.83	0.6	4.85	26.71	0.17	nc	17.47	0.15
28	5.96	27.06	0.55	6.3	27.68	0.2	4.99	23.04	0.23
30	nc	24.13	0.16	nc	29.6	0.18	8.21	21.03	nc
32	5.84	29.82	0.14	nc	27.21	0.19	4.76	23.97	0.26
34	10.59	28.24	0.57	5.58	26.57	nc	nc	22.76	0.09
36	4.86	37.51	0.08	nc	28.24	nc	4.46	26.5	0.21
38	nc	32.06	nc	6.49	28.12	0.25	4.86	23.74	nc
40	5.5	33.58	0.33	5.74	27.41	nc	4.23	20.21	0.27
42	6.69	nc	0.09	nc	26.23	0.17	nc	23.81	0.44
44	4.69	39.7	0.5	5.45	28.26	0.16	5.22	34.45	0.59
46	5.66	36.54	nc	nc	30.59	nc	2.63	24.08	nc
48	3.72	53.95	nc	nc	26.98	nc	3.27	28.68	nc
50	3.4	36.98	0.23	nc	30.13	0.22	7.07	23.78	0.36
52				5.76	28.63	nc	6.1	25.52	0.25
54				nc	30.2	nc	4.81	26.45	0.33
56				6.27	30.97	nc	nc	24.79	0.21
58				6.08	28.73	0.18	5.32	21.44	0.19
60				5.89	30.67	nc	4.06	23.47	0.04
62				nc	30.27	0.2	5.84	24.11	nc
64				nc	28.61	0.19	5.43	20.42	0.17
66				5.71	28.45	0.21	5.45	20.74	0.3
68				nc	28.4	nc	nc	23.89	0.18
70				nc	28.91	nc	6	22.22	0.35
72				nc	28.94	0.2	6.28	21.27	nc
74				6.07	30.02	0.21	3.8	21.44	0.41
76				nc	31.34	nc	nc	24.03	nc
78							8.61	21.36	0.05
80							nc	23.72	nc
82							6.21	21.14	0.17
85							5.73	nc	0.13
86							4.41	26.33	0.24
88							3.87	23.15	0.25
90							nc	26.76	nc
92							3.67	22.35	0.21
94							5.88	21.77	0.09

nc = not calculated

$CPI = 0,5 * (\sum Odds C25 \text{ to } C33 / \sum Even C24 \text{ a } C32) / (\sum Odd C25 \text{ to } C33 / \sum Even C26 \text{ to } C34)$

$Paq = [C23 + C25] / [C23 + C25 + C29 + C31]$

Source: Ficken et al. (2000).

Carbon chains between C₁₅ and C₂₅ without odd or even predominance are considered an indicative of reworked autochthonous organic matter (GRIMALT et al., 1990), mainly C₁₅ and C₁₇ homologues (CRANWELL, 1982), or petrogenic input (JAFFÉ et al., 2001). *n*-Alkanes between C₁₄ and C₁₉ can also be considered as an indicative of phytoplankton input (SIKES et al., 2009), mainly C₁₇ homologue (ORO et al., 1967; BLUMER et al., 1971). Short chain *n*-alkanes (< C₂₁) were identified in very low abundance compare to their long-chains counterparts, mostly with C₁₆ and C₁₈ homologues as more abundant and only in some depths at PM (1, 4, 8, 12, 24, and 48 cm; Figure 5), PA (12, 20, 34, 44, 56 and 74 cm; Figure 6) and PC (1-4, 6, 20, 24, 28, 36, 40, 64, 74, 86 – 92 cm; Figure 7).

Because conventional *n*-alkane source apportionment techniques, such as CPI, do not account for mid-chain length sources that can be prevalent in coastal environments, they may suggest low terrestrial inputs (SIKES et al., 2009) or do not account for submerged macrophytes producers. A lesser input of mid chains *n*-alkanes (21, 23 and 25 carbons) was also identified with C₂₅ predominance over C₂₃ in the three cores (except for PC at 40 cm). The presence of *n*-alkanes between C₂₁ and C₂₅ with odd over even predominance is an indicative of a potential input of aquatic macrophytes and/or macroalgae (FICKEN et al., 2000; JEFFÉ et al., 2001; MEAD et al., 2005). Submerged and floating plants present higher abundances of C₂₁, C₂₃ and/or C₂₅ homologues (CRANWELL, 1984; OGURA et al., 1990; VISO et al., 1993) while emergent macrophytes present a similar distribution to higher plants, having as most abundant homologues those with more than 27 carbons (JOHNSON et al., 1955; CRANWELL, 1984). A potential input of *n*-alkanes from aquatic macrophytes (submerged and/or floating) can be better evaluated by a proxy ratio comparing the relative contribution of those derived from macrophytes (C₂₃ to C₂₅) versus emergent and higher plants (C₂₉ to C₃₁; FICKEN et al., 2000).

The proxy Paq is described as $[C_{23}+C_{25}]/[C_{23}+C_{25}+C_{29}+C_{31}]$, where low values (< 0.1) correspond to terrestrial plants, mid values (0.1–0.4) to emergent macrophytes and high values (> 0.4) to submerged/floating macrophytes (FICKEN et al., 2000). Values near the boundaries can be an indicative of a mixed input. Although emergent macrophyte considered in the Paq index was applied for a lacustrine environment, mangrove species also present as majoritarian *n*-alkane the C₂₉ homologue (Table 1). Paq values has been reported between 0.88 and 0.99 for marine macrophytes, 0.24 for *Rizophora. mangle*, between 0.44 and 0.53 for a mix between terrestrial and seagrass input and an increasing trend towards the open sea (MEAD et al., 2005, XU et al., 2006; ANKITA et al., 2017). Some improvement in the Paq boundaries was made by the inclusion of marine macrophytes and mangroves as end-members (SIKES et al., 2009) for its application in coastal environments (Pmar-aq proxy) but did not fit well in the present study.

It seems that the difficult of applying the Paq and Pmar-aq proxies lies on the values for mangrove boundaries. The abundance of *n*-alkanes among the three Brazilian species of mangrove (*Rhizophora mangle*, *Avicennia schaueriana* and *Laguncularia racemosa*) are different and is also variable between leaves maturity (Table 1). While the natural process of decaying promotes an accumulation of *n*-alkanes in senescent leaves, plants under water stress due to salinization and/or drought may produce more *n*-alkanes in their leaves for protection against evapotranspiration (BELLIGOTTI et al., 2007) and shift the Paq values boundaries for

mangroves input. By making an average of Paq for the three mangrove species and for both senescent and green leaves, proxy value for major mangrove input becomes 0.2. Considering the natural standard deviation (± 0.27 in the present work), the proposed boundaries became < 1.5 to terrestrial plants, mid values (1.5–4.5) to emergent aquatic plants (including mangroves) and high values (> 4.5) to aquatic plants and marine macrophytes (Figures 2, 3 and 4).

Table 1: *n*-Alkanes abundance ($\mu\text{g}\cdot\text{g}^{-1}\cdot\text{TOC}^{-1}$) for mangrove leaves. RZ = Rizophora mangle, LA = Laguncularia racemosa, AV = Avicennia schaueriana. G = green leaf, S = senescent leaf.

Carbon number	RZ G	RZ S	LA G	LA S	AV G
C13	nd	nd	nd	0.20	nd
C14	nd	0.10	nd	0.34	nd
C15	nd	0.05	nd	nd	nd
C16	nd	0.12	nd	0.18	nd
C17	nd	nd	nd	0.08	nd
C18	nd	0.06	nd	0.16	nd
C19	nd	0.04	nd	0.13	nd
C20	0.03	0.06	nd	0.27	nd
C21	0.05	0.06	nd	0.24	nd
C22	0.10	0.10	nd	0.26	nd
C23	0.1	0.17	nd	nd	nd
C24	0.10	0.11	nd	0.35	nd
C25	0.16	0.5	0.46	2.37	0.28
C26	0.04	0.08	0.37	1.29	0.49
C27	0.15	0.87	10.78	28.26	8.04
C28	0.06	0.10	0.92	4.91	0.49
C29	0.11	1.09	22.83	83.06	4.78
C30	nd	0.07	nd	1.37	0.10
C31	nd	0.54	nd	2.11	0.9
C32	nd	nd	nd	nd	nd
C33	nd	nd	nd	nd	nd
C34	nd	nd	nd	nd	nd
C35	nd	nd	nd	nd	nd
Paq	0.70	0.29	0.02	0.03	0.05

*nd = not detected;

*Paq = $(C23+C25)/(C23+C25+C29+C31)$

Source: Ficken et al. (2000).

As expected, PA profile is very stable and is kept from the base to the top inside the mangrove boundaries. PM and PC profiles swapped between all three zones, but a greater influence of terrestrial input appears in PM. The core retrieved from the confluence presented the greatest variation of proxies due to rivers meet with the sea, having a high sedimentary dynamic with deposition followed by bottom erosion (SILVA et al., 2014). Despite Piraquê-Açu and Piraquê-Mirim rivers meet in the same estuary they present different catchment area resulting in a distinct fluvial flow and interaction with the income of marine incursions, where Piraquê-Açu holds a greater fluvial flow. A minor river outflow imposes a weak barrier against marine waters incursions, mostly during periods of dry weather, characterized by greater macrophyte inputs (Paq > 0.45) in PM and PC cores. The greater intrusion of marine waters during dry periods can be confirmed by the increase of mean salinity of the water column from 29.38 ± 2.1 to 34.32 ± 1.1 as the rainfall decrease in the PAMES, having a minima (25.66 ± 1.5 in March and 25.82 ± 1.9 in December) in the Piraquê-Açu River and a maxima (36.96 ± 0.6 in September) in the confluence during the winter, when the intrusion of marine waters is stronger (MONTEIRO et al., 2017).

Isotope Analysis

It is important to note that chain length-based parameters cannot distinguish uniquely between submerged macrophytes versus marine sources nor can they distinguish well between riverine delivery of emergent aquatic material versus local coastal mangrove inputs without additional parameters to a better discrimination of the organic detritus (SIKES et al., 2009). In an attempt to enhance our capacity to discriminate among organic matter sources, compound specific carbon stable isotope ratio measurement were performed in the sediment cores on the *n*-alkanes (C₂₃, C₂₅, C₂₉, C₃₁) used to determine the Paq proxy.

Carbon isotope ratios in plants are regulated by photosynthetic fixation of CO₂, making signature of most terrestrial plants typically falls within two groups, C₃ or C₄. Terrestrial and emergent vegetation present similar carbon isotopic composition, while the marine and submerged freshwater vegetation are quite different (MEAD et al., 2005) due to differences in the photosynthetic pathway (O'LEARY, 1981). Although seagrasses are C₃ plants, they use bicarbonate instead of CO₂ as a carbon source, resulting in a C₄-like δ¹³C enriched isotopic signature (BENEDICT et al., 1980; O'LEARY, 1981; HERNANDEZ et al., 2001).

C₄ plants are enriched in δ¹³C, ranging from -18 to -25 ‰, while C₃ plants have a comparatively larger isotopic discrimination, and their values range between -31 to -39 ‰ (DEINES, 1980; COLLISTER et al., 1994; SIMONEIT, 1997). Although organic matter source derived from mangroves (C₃ plants) is considered as a terrestrial input, *n*-alkanes δ¹³C values range between -35 and -21 ‰ (BOUILLON et al., 2008). In contrast, marsh grasses, sea grasses, and marine macrophyte alkanes are more enriched (-13 to -22 ‰; CANUEL et al., 1997; FICKEN et al., 2000; MEAD et al., 2005) and can mask the terrestrial signal in coastal environments by contributing to the enriched isotopic signature of the C₂₃₋₂₅ *n*-alkanes and C₂₅₋₂₇ *n*-alkanes (SIKES et al., 2009), according to each species.

Values of *n*-alkanes δ¹³C signatures for C₂₃, C₂₅, C₂₉ and C₃₁ were inside the proposed limit for mangroves, ranging from -27.57 ‰ (C₂₃) to -34.40 ‰ (C₂₉) for PM and from -27.36 ‰ (C₂₃) to -32.84 ‰ (C₃₁) for PA (Figure 8; Supplementary Data 2) and also presented values similar to previous signals reported for typically mangrove estuarine sites (-27.3 ‰ to -31.9 ‰ for C₂₃ to C₂₉; MEAD et al., 2005), except for C₂₉ homologue (minimum of -34.40 ‰) in the Piraquê-Mirim River. Isotopic signatures of each homologue were enriched by decreasing the carbon chain length, except for C₂₉ in the PM core, where C₂₉ was always heavier than C₃₁. As the major homologue in mangrove leaves is C₂₉, its isotopic enrichment is less significant than for C₂₃ and C₂₅, which is probably mainly derived from marine submerged vegetation. δ¹³C values of *n*-alkanes from sediments cores did not show any particular trend, although C₂₉ and C₃₁ in the PM core presented standard deviation near 1 ‰ probably due to enhanced organic matter production from halophyte marsh grasses (like *Spartina*; Wang et al., 2003). Seagrasses are typically enriched relative to other estuarine producers, with most values between -16 and -12‰ (HEMMINGA and MATEO, 1996), but show remarkable variability in signature over short distances, with more depleted values close to the mangroves, varying almost 10 ‰ in less than 4 km distance (MARGUILLIER et al., 1997; FRANCE et al., 1997; MEAD et al., 2005).

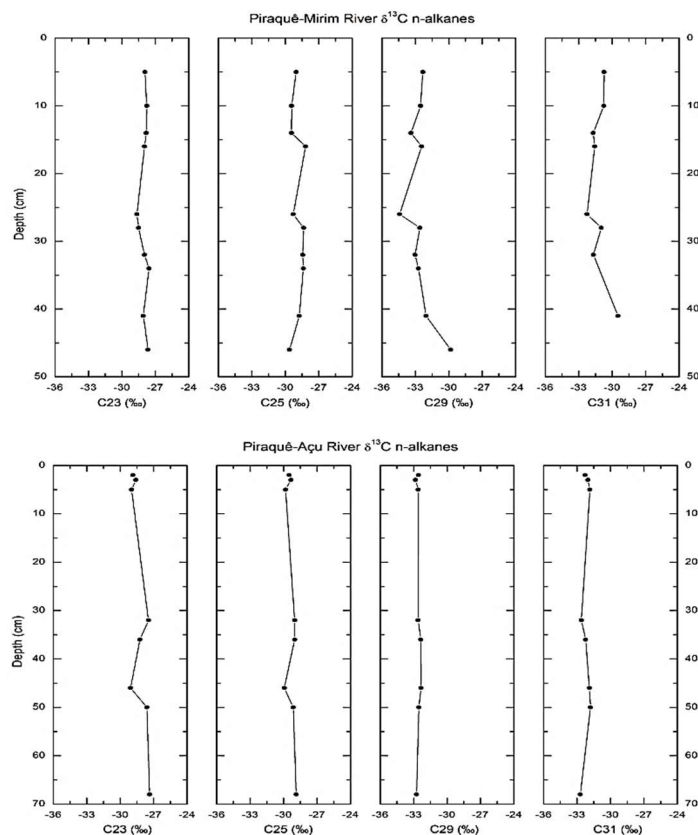


Figure 8: $\delta^{13}\text{C}$ (‰) Signatures of n-alkanes (C_{23} , C_{25} , C_{29} and C_{31}) used on Paq index for Piraquê-Mirim and Piraquê-Açu Rivers. Y-axes are standardized for each river while X-axes are standardized for both rivers.

Supplementary data 2: $\delta^{13}\text{C}$ (‰) signatures of n-alkanes for Piraquê-Mirim (PM), Piraquê-Açu (PA) and Confluence (PC) cores. Minimum and maximum values for each homologue are shown at the end of the table.

Depth (cm)	PM n-alkanes isotopes				PA n-alkanes isotopes			
	$\delta^{13}\text{C}_{23}$ (‰)	$\delta^{13}\text{C}_{25}$ (‰)	$\delta^{13}\text{C}_{29}$ (‰)	$\delta^{13}\text{C}_{31}$ (‰)	$\delta^{13}\text{C}_{23}$ (‰)	$\delta^{13}\text{C}_{25}$ (‰)	$\delta^{13}\text{C}_{29}$ (‰)	$\delta^{13}\text{C}_{31}$ (‰)
2	na	na	na	na	-28.86	-29.5	-32.48	-32.56
3	na	na	na	na	-28.59	-29.35	-32.2	-32.84
4	na	na	na	na	na	-29.35	-32.84	na
5	-27.93	-29.03	-32.32	-30.73	-28.98	-29.82	-32.66	-32.58
10	-27.76	-29.43	-32.53	-30.76	na	na	na	na
14	-27.82	-29.44	-33.39	-31.7	na	na	na	na
16	-27.96	-28.18	-32.43	-31.56	na	na	na	na
26	-28.65	-29.29	-34.4	-32.26	na	na	na	na
28	-28.5	-28.36	-32.59	-30.97	na	na	na	na
32	-27.97	-28.43	-33.03	-31.69	-28.98	-29.82	-32.66	-32.58
34	-27.57	-28.38	-32.71	na	na	na	na	na
36	na	na	na	na	-28.23	-29	-31.52	-32.35
41	-28.08	-28.75	-32.04	-29.47	na	na	na	na
42	na	-28.75	-32.04	na	na	na	na	na
46	-28.08	-28.75	-32.04	-29.47	-29.06	-29.94	-31.48	-32.33
48	na	-29.62	-29.83	na	na	na	na	na
50	na	na	na	na	-27.61	-29.14	-31.27	-32.52
68	na	na	na	na	-27.36	-28.86	-31.02	-32.74
Minimum	-27.57	-28.18	-29.83	-29.47	-27.36	-28.86	-31.02	-32.33
Maximum	-28.65	-29.62	-34.40	-32.26	-29.06	-29.94	-32.84	-32.84

*na = not analysed

Paq proxy and $\delta^{13}\text{C}$ signature for n-alkanes in the Piraquê-Açu River were quite stable, while Piraquê-Mirim River presented greater variation, implying more susceptibility to marine waters intrusion during dry period and the resulted flourishing of submerged macrophyte. Concerns about increasing rate of global climate change and extremely events on submerged macrophytes meadows is generally linked to distribution

shifts and losses as a result of increased temperature stress, water depth and turbidity, and changes in the patterns of sexual reproduction (SHORT et al., 1999) but rarely linked to its invasion into estuarine environments due to the increase in marine waters intrusion as a result of prolonged dryness. In southern Brazil, the relationship between climatic/hydrological parameters and the distribution and abundance of estuarine submerged macrophyte presented high seasonal and interannual variability (COPERTINO, 2010; COPERTINO et al., 2010) with drastic reductions of seagrasses meadows after extreme precipitation and fluvial discharges (MÖLLER et al., 2009). Different from southern Brazil, southeast region has been suffered from prolonged dryness in the last decade, which may result in an invasion of submerged macrophyte into the PAMES, mainly in the Piraquê-Mirim River. Submerged macrophytes present different behavior and ecosystem services in relation to mangrove vegetation, as less efficiency in sediment trapping and protection against flood and erosion. When submerged macrophytes settles in the tidal flat they may inhibit establishment of mangrove seedlings or growth of saplings (CUNHA-LIGNON et al., 2011), resulting in losses of mangrove forest coverage.

CONCLUSIONS

Paq proxy applied on mid and long-chain *n*-alkanes homologues was a useful and enlightening tool, revealing input of submerged macrophyte as a result of marine water intrusion in a complex estuarine system surrounded by a dense mangrove forest. Discussed proxies (C/N ratio, *n*-alkanes abundance, Paq and CPI) complemented each other and allowed the distinction of three different environments for each site in the PAMES: a stable mangrove environment in the Piraquê-Açu River; a mixed source but with mangrove dominance in the confluence; and a mangrove environment periodically disturbed by marine intrusion during dry period in the Piraquê-Mirim River.

The present study concludes that mangrove ecosystem in the Piraquê-Açu River presents greater resilience against drought while mangrove forest in the Piraquê-Mirim River should be managed with care in respect to freshwater catchment and dam construction. Although Paq application was successfully applied, its boundaries must be set carefully due to the natural variability of *n*-alkanes abundance in mangrove leaves as a result of decaying and salinity stress as well in submerged macrophyte species.

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