An Acad Bras Cienc (2021) 93(1): e20190638 DOI 10.1590/0001-3765202120190638
Anais da Academia Brasileira de Ciências | *Annals of the Brazilian Academy of Sciences*
Printed ISSN 0001-3765 I Online ISSN 1678-2690
www.scielo.br/aabc | www.fb.com/aabcjournal

GEOSCIENCES

Distribution and origin of sedimentary organic matter in an eutrophic estuary: Pina Sound – NE Brazil

BRUNO V.M. DA COSTA, MARCELO Z. MOREIRA, RODRIGO F. BASTOS & GILVAN T. YOGUI

Abstract: Eutrophic estuaries receive organic matter (OM) inputs from multiple sources. This study evaluated the distribution and origin of sedimentary OM in an eutrophic estuary (Pina Sound, NE Brazil). Thirteen samples were collected in the sublittoral in addition to major local sources. Biochemical (chlorophyll - Chl), elemental [$(C/N)_a$ and C/S ratios] and isotopic ($\delta^{15}N$ and $\delta^{13}C$) analyses were carried out for characterizing OM and redox conditions. The SIAR mixing model was used to quantify contribution from main sources. At Pina Sound, distribution of OM is associated with mud, reflecting the hydrodynamics control on deposition of suspended particles. Microphytobenthic production is limited ([Chl *a*] < 1000 µg/g organic carbon) in the sublittoral where the Chl degradation products prevail (mean [Pheopigments] = 2643 ± 958 µg/g organic carbon). Anoxic conditions (C/S ratio ≈ 2) are typically observed in sediments of deeper portions of Pina Sound. Such sediments receive high organic loads and are subject to poor water renewal. According to SIAR mixing model, sedimentary OM of Pina Sound is composed of, on average: 50% phytoplankton, 24% sewage and 26% C_3 plants. This reflects fertilization of Pina Sound with high loads of untreated sewage. Pina Sound has a great potential to retain sewage-derived OM.

Key words: chlorophyll, mixing model, sewage, stable carbon isotope, stable nitrogen isotope.

INTRODUCTION

Estuaries are ecosystems that retain organic matter (OM) from terrestrial and aquatic sources (Dittmar et al. 2001, Andrews et al. 2008). Additionally, human-impacted estuaries receive nutrients and OM inputs from anthropogenic sources (Mcclelland & Valiela 1998), increasing productivity of aquatic primary producers (Nixon 1995). Such OM inputs are preserved in sedimentary OM (SOM) that reflects proportional contribution from each source (Lesen 2006, Canuel & Hardison 2016). Thus, SOM is an environmental compartment that records the historical inputs of OM to urban estuaries (Andrews et al. 2008, Barcellos et al. 2017) and it contributes to CO_2 sequestration from atmosphere (Watanabe & Kuwae 2015).

Estuaries exhibit a characteristic pattern of OM mixing from terrestrial and marine sources (Gearing 2013). Contribution of terrestrial-derived OM to SOM decreases from upper to lower estuary while marine contribution increases toward the ocean (Gireeshkumar et al. 2013, Sarkar et al. 2016). In contrast, SOM is predominantly derived from aquatic primary producers in eutrophic coastal systems (Zimmerman & Canuel 2001, Carreira et al. 2002, Zhao et al. 2015, Kubo & Kanda 2017). The origin

of SOM has been evaluated using biochemical (chlorophyll and pheopigments), elemental (carbon-to-nitrogen - C/N - ratio) and isotopic (stable carbon and nitrogen isotope ratios - $\delta^{13}C$ and $\delta^{15}N$, respectively) proxies (Hardison et al. 2013, Canuel & Hardison 2016). These proxies allow to quantify the relative contribution from multiple OM sources (C_3 higher plants, phytoplankton, benthic algae and domestic sewage) to SOM (Watanabe & Kuwae 2015, Kubo & Kanda 2017). The relative contribution of bulk sewage-derived OM to human-impacted coastal environments has been scarcely reported in the literature (Tucker et al. 1999, Kubo & Kanda 2017). This gap needs to be filled in order to understanding the fate and the impacts of sewage-derived OM on marine ecosystems (Spano et al. 2014, Roth et al. 2016).

OM is preserved in sediments according to its composition, sedimentary mineralogical composition and redox conditions in interstitial water (Burdige 2007, Arndt et al. 2013, Barber et al. 2017). Redox conditions regulate the early diagenesis of SOM and diagenetic shifts of its isotopic signature (Freudenthal et al. 2001, Lehmann et al. 2002). Water anoxic conditions favor preservation of OM in sediments (Arndt et al. 2013), and have been commonly reported in eutrophic estuaries (Pinckney et al. 2001). Thus, SOM preserved in anoxic conditions is an appropriate record of long-term OM inputs to eutrophic estuaries.

Pina Sound (2 km^2) is an estuary located on the northeastern coast of Brazil (8° S). The sound is delimited by the urban zone of Recife city (218 km^2) whose population increased from 1.3 to 1.6 million inhabitants over the past 20 years (IBGE 2019). Pina Sound receives every day inputs from untreated domestic sewage with an estimated outflow between 0.81 and 2.31 m^3 s^{-1} (IBGE 2011, Zanardi-Lamardo et al. 2016). As a consequence, an eutrophic to hypertrophic and hypoxic to anoxic conditions have been reported at surface and bottom waters of Pina Sound, respectively (Flores Montes et al. 2011, Nascimento et al. 2003, Somerfield et al. 2003). Pina Sound also receives natural OM inputs from local Atlantic forest (~13.4 km^2) and mangrove patches (~3.2 km^2) (Ferreira & Lacerda 2016). The apportionment of OM inputs from natural and anthropogenic sources is important for understanding their impacts on Pina Sound.

This study investigated the distribution and origin of OM in sediments of Pina Sound, northeastern Brazil. Major potential OM sources to the sound were characterized in terms of elemental and isotopic composition. A stable isotope mixing model was employed for estimating the relative contribution of OM sources to SOM of Pina Sound. Additionally, a non-metric multidimensional scaling was performed for visualizing sample grouping according to distribution and sources of OM. Finally, a factor analysis was also performed for identifying major latent dimensions related to distribution, origin and early diagenesis of SOM in Pina Sound.

MATERIALS AND METHODS

Study area

Pina Sound is a tropical ecosystem with mean annual temperature and rainfall of 26 °C and 2450 mm, respectively (Schettini et al. 2016a). The sound is formed by the confluence of Pina, Jordão and Tejipió creeks in addition to the southern branch of Capibaribe River (Fig. 1). Annual mean outflow of Capibaribe is 11 m^3 s^{-1}, ranging from 2 m^3 s^{-1} in the dry season (September to February) to 30 m^3 s^{-1} in the wet season (March to August; Schettini et al. 2016a). Concentration of suspended particulate matter has been reported to be in the range 10-60 mg L^{-1} (Nascimento et al. 2003, Schettini et al. 2016b)

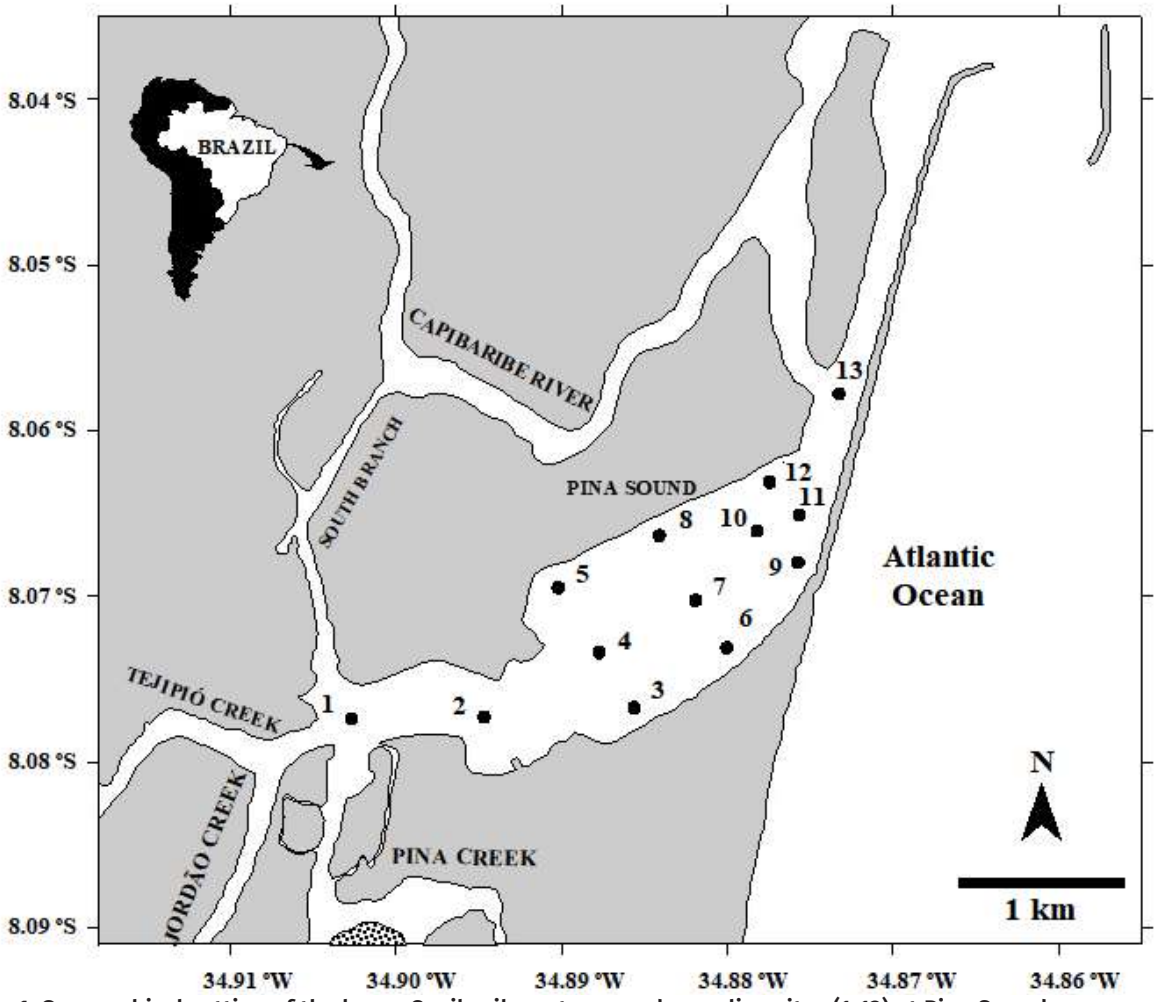

Figure 1. Geographical setting of the lower Capibaribe estuary and sampling sites (1-13) at Pina Sound, northeastern Brazil. The dotted area depicts a mangrove patch.

and mean sedimentation rate is estimated to be 0.45 cm year^{-1} (Xavier et al. 2017). The sound is a shallow depositional environment with sand bars and mud flats exposed during low tide (Feitosa et al. 1999). In the dry season, algal mats grow on mud flats (Santos et al. 2009) while they are not observed during wet season. Mats are mainly composed of cyanobacteria but may also contain diatoms (Santos et al. 2009, Valença et al. 2016), and are visually identified by their typical blue-green color. In Pina Sound, estuarine phytoplankton production ranges between 2.70 and 256 mg m^{-3} throughout the year (Feitosa et al. 1999, Nascimento et al. 2003).

Sampling

Surface sediment (top 10 cm) was collected using a stainless steel van Veen grabber from 13 sites at Pina Sound in December 2014 (Fig. 1). In the laboratory, samples were homogenized and frozen at -20 °C until further analysis.

Three potential sources of OM in the sound were sampled: algal mats (AM), suspended particulate OM (SPOM) from an untreated sewage outfall and leaves from higher C_3 plants (HP) - terrestrial plants and mangrove. Marine phytoplankton production in the adjacent shelf was not considered as an important OM source to Pina Sound. Marine primary production is about

an order of magnitude lower than estuarine production, with concentrations ranging between 0.05 and 5 mg m^{-3} throughout the year (Resurreição et al. 1996). Elemental and isotopic signatures of estuarine phytoplankton were reported by Costa (2018). Costa (2018) sampled estuarine SPOM during complete tidal cycles at lower and middle portions of the Capibaribe River estuarine system. The AM samples (n = 5) were taken from mud flats during low tide using a stainless steel spatula. Samples of estuarine SPOM (n = 11) and SPOM from untreated sewage (n = 13) were collected in a plastic bottle (250 mL) and cooled until filtration in the laboratory. Fresh leaves of terrestrial plants (n = 3) and mangrove *Avicennia schaueriana* (n = 1) were collected using a stainless steel scissor, stored in aluminum containers and processed in the laboratory as soon as possible.

Grain size analysis

Subsamples of sediment (50 g) were oven dried at 60 °C for at least 96 h. OM was removed with H_2O_2 (10%, v/v) and grain size was determined according to Suguio (1973). Briefly, samples were wet sieved through a 63 µm sieve with distilled water. The fraction > 63 µm was dry sieved for separating sand (63 to 2000 µm) and gravel (> 2000 µm). These fractions were weighed for determining their contribution to the total sediment. The mud fraction (< 63 µm) was added to a graduated cylinder (1 L) containing sodium pyrophosphate (3.75 mmol L^{-1}). Silt (4 to 63 µm) and clay (0.5 to 4 µm) fractions were sampled at specific settling time and depth according to the Stokes' law. These fractions were then weighed for determining their contribution to the mud fraction. Results were plotted on the Pejrup's triangular diagram (Pejrup 1988) which is suitable for classifying sediments according to particle texture and hydrodynamic conditions of the depositional environment.

Chemical analysis

Subsamples of wet sediment were freeze-dried for 24 h in the dark to avoid Chl degradation and ground using mortar and pestle. Pigments were extracted from 0.5 g of sediment (in triplicate) with 10 mL acetone (90%, v/v) for 20 h at -20 °C. Pigments were measured with a spectrophotometer using absorbance readings at 630, 647, 664, 665 and 750 nm. Chl *a* and pheopigments (Pheop) were estimated according to the Lorenzen's equations (Lorenzen 1967). In addition, Chl *b* and *c* (c_1 + c_2) were estimated according to equations reported by Jeffrey & Humphrey (1975). Concentration of sedimentary pigments was OC-normalized in order to assess the microphytobenthos contribution (Moreno & Niell 2004). Analytical precision (standard deviation, SD) ranged from 0.4 to 19 µg g^{-1} dry weight.

For elemental analyses, sediment aliquots (1 g) were weighed in centrifuge tubes and acidified with 10 mL HCl (1 M) for 72 h to ensure complete dissolution of carbonates (Hedges & Stern 1984). After acidification, the aliquots were washed with distilled water and oven dried at 60 °C for 24 h. Carbonate-free sediments were weighed in Sn capsules and analyzed for elemental [total nitrogen (TN), organic carbon (OC) and total sulfur (TS)] and isotopic ($\delta^{15}N$ and $\delta^{13}C$) composition.

Water samples were filtered through Whatman GF/C membrane (Ø = 45 mm) and oven dried at 60 °C for 24 h. One-eighth of each filter was wrapped in tin disk prior to elemental and isotopic analyses. Leaf samples were washed with distilled water for removing salts. Leaf and AM samples were oven dried at 60 °C for at least 24 h and ground using mortar and pestle. Aliquots were weighed in tin capsules. All elemental and isotopic analyses were carried out using an elemental analyzer coupled to an isotope ratio mass spectrometer (EA-IRMS).

The stable N and C isotope ratio values were calculated using delta notation ($\delta^{15}N_{AIR}$ for TN and $\delta^{13}C_{VPDB}$ for OC, respectively) according to Eq. 1 (Coplen 2011).

$$\delta^{13}C \text{ or } \delta^{15}N\ (‰) = \left(\frac{R_{Sample}}{R_{Standard}} - 1\right) \quad (1)$$

C/N atomic ratio - $(C/N)_a$ - and C/S weight ratio were calculated according to Hedges & Stern (1984) and Berner & Raiswell (1984), respectively. Average precision of sample replicates was 0.09% and 0.30‰ for elemental and isotopic analysis, respectively.

Modeling

The SIAR mixing model (version 4.0) was used for quantifying OM contribution from natural and anthropogenic sources (Parnell et al. 2008). Model input data were $(C/N)_a$, $\delta^{13}C$ and $\delta^{15}N$ values of sediment and potential local OM sources (including their respective standard deviation), and discrimination factors (DF). This parameter is the magnitude of change in signatures during early diagenesis (Bond & Diamond 2011). DF was assumed to be 0 in OM $(C/N)_a$ ratio and $\delta^{13}C$, and DF ranging from -5 to +5‰ in OM $\delta^{15}N$. This is the range of DF values observed by Lehmann et al. (2002) during laboratory experiments. The model was run through 5 x 10^5 iterations using the 'siarsolo' command (Parnell et al. 2008). Output was mean estimate of the contribution from each source and its 95% credible interval.

Statistical analysis

Pearson product-moment correlation was performed for investigating relationships between sedimentary elemental contents and isotopic ratios. Linear regression between TN and OC was performed for confirming prevalence of organic nitrogen (ON) in the sedimentary N pool. The critical level of significance for all statistical tests was set at $\alpha = 0.05$.

Data were *log* transformed [log(50 + x)] and normalized previously multivariate analysis (Hair et al. 2006). Potential relationships among variables (mud content, OC, sedimentary pigments (Chl *a* + Pheop), $(C/N)_a$, $\delta^{13}C$, C/S, Pheop/Chl *a* and $\delta^{15}N$) were summarized using a factor analysis (FA) (Hair et al. 2006). Factors with eigenvalues above 1 were extracted using the principal component (PC) method followed by varimax rotation (Kaiser 1970, Hair et al. 2006). Two non-metric multidimensional scaling (MDS) plots were constructed using the Euclidian distance similarity matrix (Clarke & Warwick 2001). MDS plots evaluated sample grouping according to sand content and OM contribution from HP.

RESULTS

Granulometric composition, sedimentary organic matter distribution and redox conditions

Pina Sound sediments exhibited sand and mud contents ranging from 7 to 80% and from 16 to 91%, respectively (Table I). Samples were separated according to their sand content into two groups: sandy sediments with higher (≥ 45%) sand content collected mostly from central portions of Pina Sound, and sediments with lower sand (< 45%) content collected mainly from bank portions (Fig. 1). Samples had a predominance of clay in the mud fraction and they were plotted along hydrodynamic section II of Pejrup's triangular diagram (Fig. 2).

Mean sedimentary TN and OC was 0.28% (range: 0.07 to 0.44%) and 2.40% (range: 1.01 to 3.42%), respectively (Table I). TN was significantly ($F_{1,11}$ = 21.1, p = 0.001) and linearly correlated to OC, with a zero intercept. Mean sedimentary Chl *a* and Pheop were 459 μg g^{-1} OC (range: 192 to 1003 μg g^{-1} OC) and 2643 μg g^{-1} OC (range: 1321 to 4642 μg g^{-1} OC), respectively (Table I). Predominance

Table I. Sedimentary mud, elemental composition [total nitrogen (TN), organic carbon (OC) and total sulfur (TS)], pigments (chlorophyll a (Chl *a*) and pheopigments (Pheop)) and isotopic signature ($\delta^{15}N$ and $\delta^{13}C$) of sediment samples collected from Pina Sound, northeastern Brazil. C/S and $(C/N)_a$ ratios are showed.

Station	Bathymetry	Sand	Mud	TN	OC	TS	[Chl *a*]	[Pheop]	Pheop/ Chl *a*	$(C/N)_a$	C/S	$\delta^{15}N$	$\delta^{13}C$
	(m)	(%)	(%)	(%)	(%)	(%)	(μg g^{-1} OC)	(μg g^{-1} OC)				(‰)	(‰)
1	1.1	54	38	0.23	2.07	1.25	192	2347	12.3	11	1.66	4.53	-24.19
2	2.2	53	37	0.21	2.32	1.11	276	1321	4.8	13	2.09	2.68	-24.10
3	2.9	29	69	0.39	2.64	1.11	445	2702	6.1	7.9	2.37	2.13	-24.37
4	1.8	48	43	0.12	2.10	1.11	742	4642	6.3	20	1.90	1.44	-23.46
5	1.1	38	61	0.29	2.75	1.27	271	1786	6.6	11	2.17	3.64	-24.12
6	4.4	26	47	0.31	2.19	0.61	506	3239	6.4	8.2	3.59	2.43	-24.14
7	1.8	16	84	0.43	3.16	1.05	481	3241	6.7	8.6	2.99	2.75	-24.20
8	2.0	7	91	0.44	3.42	1.05	1003	3404	3.4	9.1	3.26	2.67	-23.69
9	2.7	25	75	0.35	2.35	0.74	533	2404	4.5	7.8	3.16	2.75	-23.38
10	0.7	80	16	0.16	1.01	0.11	696	3725	5.4	7.5	9.58	1.69	-24.16
11	3.3	57	33	0.25	2.72	0.92	289	1765	6.1	13	2.96	3.29	-25.20
12	3.8	51	46	0.07	1.60	0.54	315	2033	6.4	26	2.98	4.72	-23.83
13	10	18	82	0.41	2.90	1.36	213	1752	8.2	8.2	2.13	4.57	-24.50

of Pheop was expressed using Pheop/Chl *a* ratio, which exhibited mean value of 6.40 (range: 3.39 to 12.3; Table I). Mean sedimentary Chl *b* and *c* was 96 μg g^{-1} OC (range: 31 to 191 μg g^{-1} OC) and 408 μg g^{-1} OC (range: 155 to 695 μg g^{-1} OC), respectively.

Mean TS and C/S ratio were 0.94% (range: 0.11 to 1.36%) and 3.14 (range: 1.66 to 9.58), respectively (Table I). C/S ratio was lower than 2.5 in sediments from upper sound (sites 1-5) and at the confluence with the Capibaribe River main stem (site 13; Fig. 1). Site 10 showed the lowest TS content and the highest C/S ratio (Table I) because it was collected from a sand bar exposed to the atmosphere during low tides.

Elemental and isotopic signatures of OM sources

HP, sewage-derived SPOM, AM and estuarine phytoplankton were considered as potential OM sources. Local HPs have the highest $(C/N)_a$ ratio and the lowest $\delta^{13}C$ and $\delta^{15}N$ values (Table II). The lowest $(C/N)_a$ value and the highest $\delta^{13}C$ and $\delta^{15}N$ values were reported in AM samples collected from the intertidal zone of Pina Sound (Table II). Sewage-derived SPOM exhibited intermediate $(C/N)_a$, $\delta^{13}C$ and $\delta^{15}N$ values (Table II). Elemental and isotopic signatures of phytoplankton collected in the Capibaribe River estuary are reported by Costa (2018). According to the author, phytoplankton had mean $(C/N)_a$, $\delta^{13}C$ and $\delta^{15}N$ values around of 6.67 ± 0.33, -25.83 ± 1.37‰ and -1.57 ± 1.18‰, respectively, in the middle estuary, and 6.22 ± 0.39, -21.14 ± 1.95‰ and +3.36 ± 3.53‰, respectively, in the lower estuary.

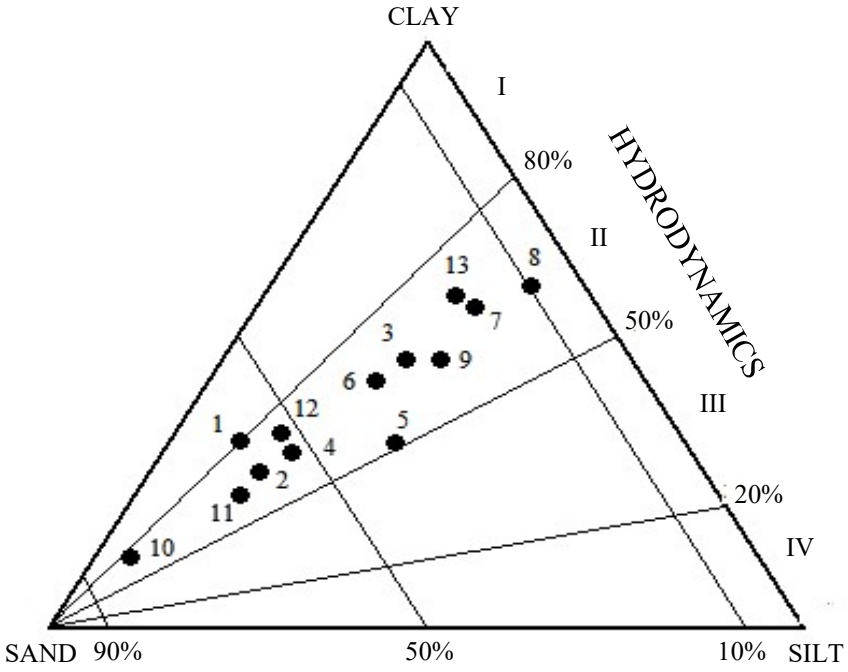

Figure 2. Pejrup's triangular diagram showing classification of estuarine sediments from Pina Sound, northeastern Brazil. Sections I to IV indicate increasing hydrodynamic conditions in the estuary.

Table II. Elemental - $(C/N)_a$ ratio - and isotopic ($\delta^{13}C$ and $\delta^{15}N$) signatures of local potential OM sources to Pina Sound. Legend: SD = standard deviation. SPOM = suspended particulate organic matter.

Sources	$(C/N)_a$ ratio			$\delta^{13}C$ (‰)			$\delta^{15}N$ (‰)		
	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*
Higher C_3 plants	20.8	4.44	4	-29.25	2.23	4	2.40	1.91	4
Sewage-derived SPOM	9.19	1.13	13	-20.73	1.32	13	3.59	3.14	13
Algal mats	7.26	0.27	5	-17.16	1.06	5	4.73	0.93	5

SPOM/SOM signatures and SIAR mixing model

Local surface SPOM exhibited mean $(C/N)_a$, $\delta^{13}C$ and $\delta^{15}N$ values of 7.32 ± 0.95, -22.68 ± 2.11‰ and -2.68 ± 1.42‰, respectively. SOM exhibited $(C/N)_a$ values higher than 10 in sandy sediments with the exception of sample from site 10 (Table I). In muddy sediments, mean $(C/N)_a$ value was 8.70 (range: 7.80 to 11.1) (Table I). A narrow range of signatures was observed for SOM $\delta^{13}C$ and $\delta^{15}N$ values (Table I). Mean $\delta^{13}C$ and $\delta^{15}N$ values were -24.10‰ (range: -25.20 to -23.38‰) and +3.02‰ (range:+1.44 to +4.72‰), respectively (Table I). No correlation was found between sedimentary $\delta^{15}N$ and $\delta^{13}C$ in Pina Sound (Pearson product-moment correlation analysis, r = -0.26, p = 0.39, n = 13).

A cross-plot of $(C/N)_a$ and $\delta^{13}C$ values indicated that local SPOM and SOM samples are constrained to a polygon formed by three sources: HP, estuarine SPOM and sewage-derived SPOM (Fig. 3). Apparently, AM is not an important OM source to Pina Sound sediments (Fig. 3). According to the SIAR mixing model, mean contributions of sources to SPOM were

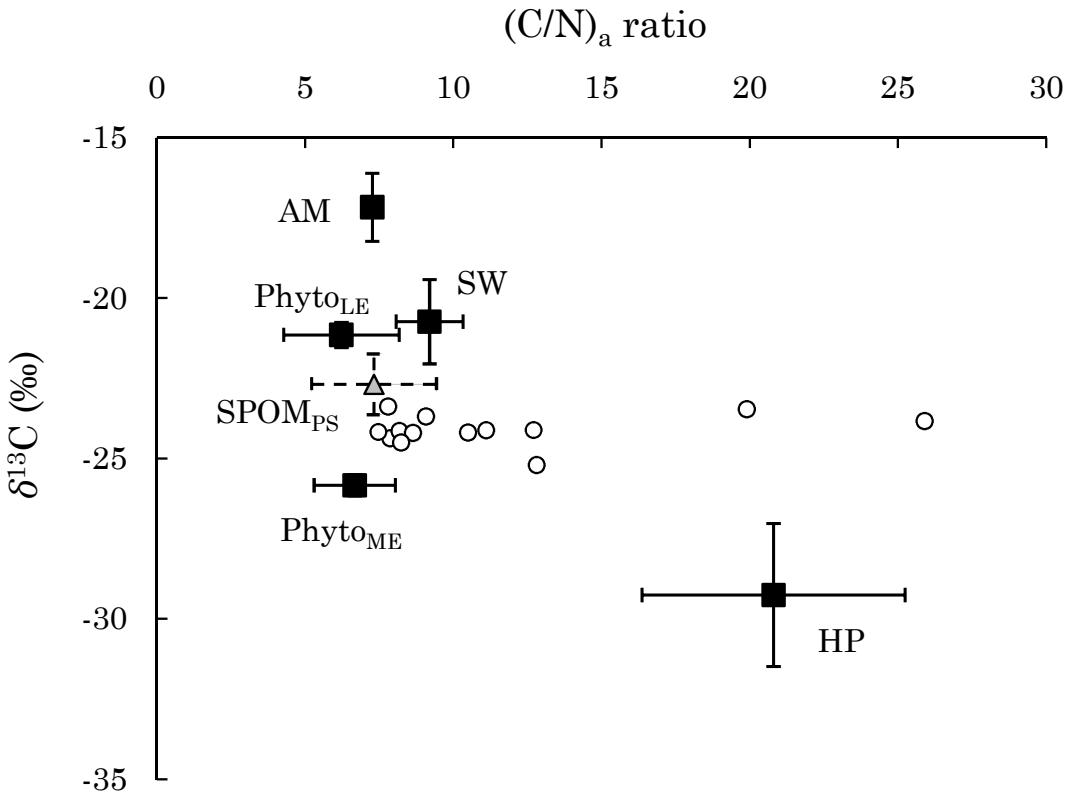

Figure 3. Cross-plot of $(C/N)_a$ versus $\delta^{13}C$ (‰) depicting end members (filled squares), suspended particulate organic matter (SPOM, filled triangle) and surface sediments (open circles) from Pina Sound, northeastern Brazil. Error bars denote standard deviation. Legend: AM = algal mats; SW = sewage suspended particulate organic matter; $Phyto_{LE}$ = estuarine phytoplankton in lower Capibaribe River estuary; $Phyto_{ME}$ = estuarine phytoplankton in medium Capibaribe River estuary; HP = higher C_3 plants. Data of estuarine phytoplankton were reported by Costa (2018).

77% (range: 41 to 93%), 19% (range: 4 to 52) and 4% (range: 2 to 9%) for estuarine phytoplankton, sewage and HP-derived OM, respectively (Fig. 4). Similarly, mean contributions to SOM were 50% (range: 13 to 72%), 24% (range: 11 to 29%) and 26% (range: 7 to 77%) for estuarine phytoplankton, sewage and HP-derived OM to SOM, respectively (Fig. 4). Relative contributions from each OM source did not vary substantially across the range (-5 to +5‰) of DF values used in the SIAR mixing model.

Factor analysis and MDS ordination

FA extracted three components that explained 81% of the data variance. PC1 accounted for 35% of the total variance and showed high, positive loadings for mud, OC and sedimentary pigments, and high negative loading for C/S (Fig. 5a). PC2 (28% of the total variance) exhibited high negative loadings for Pheop/Chl *a* and $\delta^{15}N$, and positive loading for C/S (Fig. 5a). PC3 (18% of the total variance) exhibited high positive loadings for $\delta^{13}C$ and $(C/N)_a$. MDS plot separated samples with high (sites 1, 2, 4, 10, 11 and 12) and low (sites 3, 5, 6, 7, 8, 9 and 13) sand content (Fig. 5a). Correspondingly, MDS also separated samples with high (sites 1, 2, 4, 5, 11 and 12) and low (sites 3, 6, 7, 8, 9, 10 and 13) OM contribution from HP (Fig. 5b).

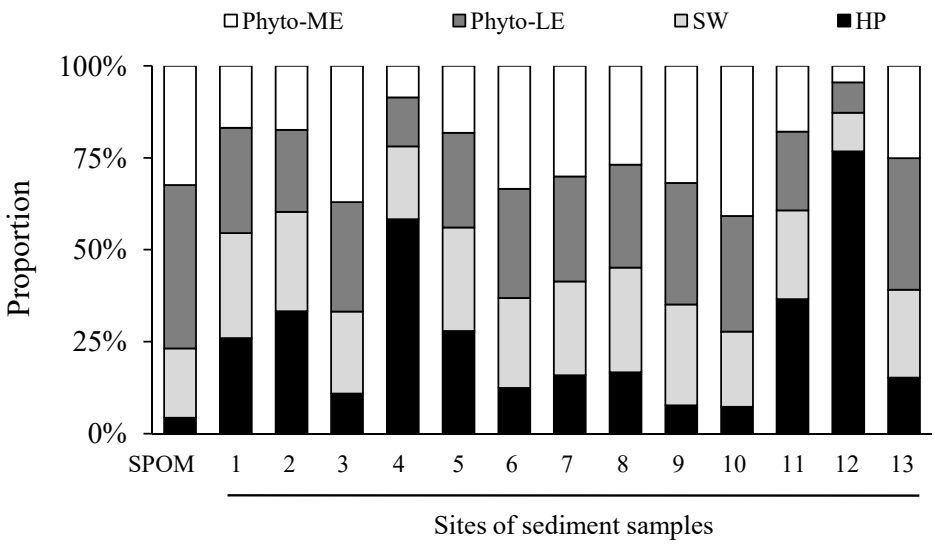

Figure 4. Relative contribution of natural and anthropogenic sources to suspended particulate organic matter (SPOM) and sediments collected from Pina Sound. Legend: Phyto-ME = estuarine phytoplankton in medium Capibaribe River estuary; Phyto-LE = estuarine phytoplankton in lower Capibaribe River estuary; SW = sewage suspended particulate organic matter; HP = higher C_3 plants.

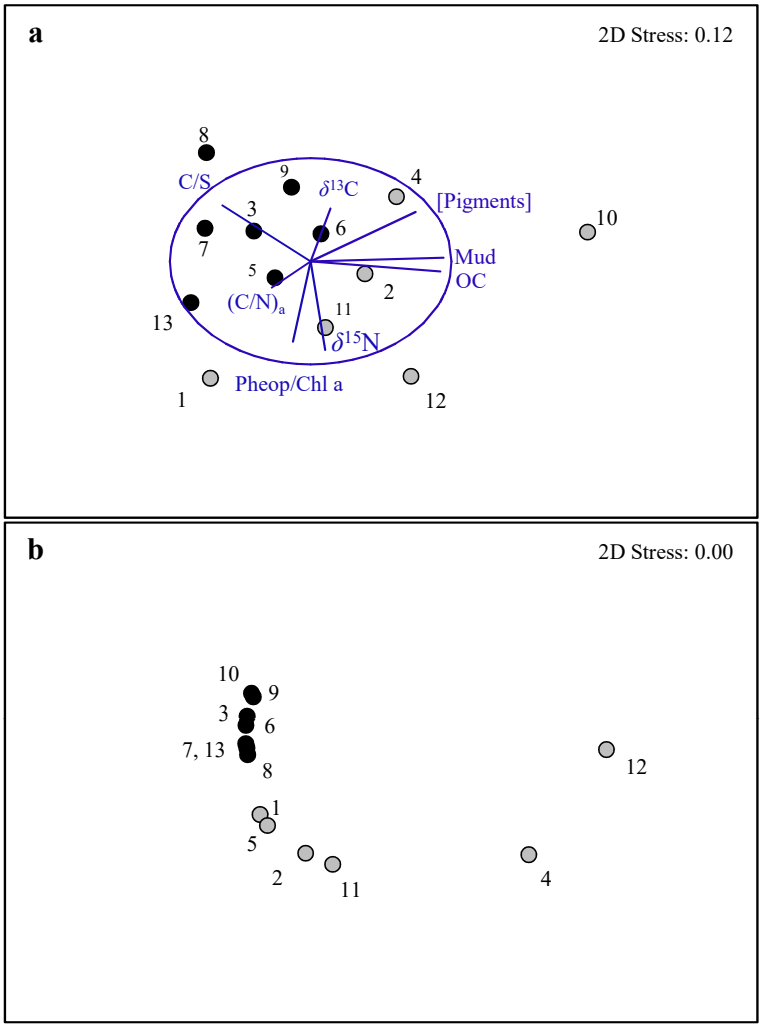

Figure 5. Factor analysis loading plot (a) and MDS plots (a, b) of sediments collected from Pina Sound, northeastern Brazil. Sediment samples were grouped according to their sand content (a) and organic matter contribution from higher C_3 plants (b). Black circles depict samples with low sand content or contribution from higher plants while gray circles depict the inverse situation. Legend: Pheop/Chl *a*: pheopigments-to-chlorophyll a ratio; $(C/N)_a$ = carbon-to-nitrogen ratio; Mud = sedimentary mud content; OC = organic carbon; [Pigments] = sum of concentrations of pheopigments and chlorophyll *a*; C/S = carbon-to-sulfur ratio.

DISCUSSION

Distribution of SOM, redox conditions and diagenesis of labile OM

Distribution of SOM in Pina Sound was evaluated by bulk parameters (TN and OC contents) and pigment (Chl *a*, *b* and *c*) contents. Bulk TN and OC parameters were significantly related, indicating that TN is a good estimate for organic nitrogen. This allows the use of $(C/N)_a$ to infer SOM sources (Hedges et al. 1986). A strong relationship between TN and OC has been commonly reported for organic-rich estuarine sediments, and indicates sorption of SOM onto clay minerals (Andrews et al. 1998, Resmi et al. 2016, Sarkar et al. 2016).

Sedimentary Chl is a proxy for both planktonic and benthic primary production (Burford et al. 1994). Low concentrations (< 2000 μg g^{-1} OC) indicate that subtidal sediments at Pina Sound have limited microphytobenthic production (Moreno & Niell 2004) and sedimentary pigment content is related to planktonic primary production (Lesen 2006). Chl *b* is a proxy for OM inputs from green algae, euglenophytes and higher plants, while Chl *c* indicates OM inputs from dinoflagellates, diatoms and chrysophytes (Leavitt 1993). At Pina Sound, dinoflagellates and diatoms are the most abundant groups of planktonic primary producers (Santiago et al. 2010). In contrast, green algae and euglenophytes exhibit a small abundance in the phytoplanktonic community at Pina Sound (Santiago et al. 2010). Thus, higher plants are likely the main Chl *b* source to SOM.

Redox conditions at the sediment-water interface were evaluated using TS and C/S ratio as proxies (Berner & Raiswell 1983, 1984). Boundary TS and C/S values for oxic marine sediments are 0.6% and 2.8, respectively (Goldhaber 2005). Under anoxic conditions, sedimentary TS tends to increase while C/S tends to decrease (Berner & Raiswell 1983, Goldhaber 2005). Bottom water anoxic conditions are commonly reported for eutrophic estuaries (Pinckney et al. 2001, Bricker et al. 2008), including Pina Sound (Nascimento et al. 2003, Somerfield et al. 2003). This is related to the balance between sewage discharges and estuarine hydrodynamic conditions (Cardoso-Mohedano et al. 2016), which regulate the dispersal and dilution of sewage. At Pina Sound, sewage discharges (0.81-2.31 m^3 s^{-1}) can be similar to river discharge during dry season (≤ 2 m^3 s^{-1}) (Schettini et al. 2016a). At Pina Sound, sulfur proxies indicated predominantly anoxic conditions at sites 1-5 and 13 (TS > 1.1% and C/S < 2.4). This is probably related to OM input from streams that drain into the sound (see Fig. 1) and receive high loads of untreated sewage. At sites 6-12, sulfur proxies (TS < 1% and C/S ratio > 3) indicated predominantly oxic conditions at the sediment-water interface. At these sites, mesotides and shallow depths (ca. ~ 2.7 m) facilitate wastewater dilution, leading to oxic conditions in sediment. According to Valença & Santos (2013), there is a high density of macrobenthic fauna (up to 40,000 individuals m^{-2}) in surface sediments of the lower sound, which is additional evidence for predominantly local oxic conditions.

Diagenesis of labile OM was evaluated using Pheop/Chl *a* ratio (Rasiq et al. 2016). Such ratio indicated a prevalence of chlorophyll degradation products in sediments of Pina Sound. This might be primarily related to analysis of ancient sediments deposited during the last 20 years (Xavier et al. 2017), which record past planktonic primary production of Pina Sound. Additionally, low light conditions are prevalent in surface sediments from sublittoral zone of Pina Sound (Nascimento et al. 2003). Thus, microphytobenthos does not have an important contribution to surface SOM from sublittoral. Microphytobenthos have been found to play an

important role in primary production of bottom sediments where the Pheop/Chl *a* ratio is close to 1 (Hardison et al. 2013, Valença & Santos 2013, Gontharet et al. 2015).

Signatures of OM sources

At Pina Sound, potential OM sources exhibited distinct elemental and isotopic signatures (Fig. 3 and Table II). Local HPs and sewage-derived SPOM showed $(C/N)_a$, $\delta^{13}C$ and $\delta^{15}N$ values similar to signatures reported in the literature (Dover et al. 1992, Kuramoto & Minagawa 2001, Waldron et al. 2001, Gearing 2013, Francisquini et al. 2014). The $\delta^{13}C$ values of AM were similar to the mean $\delta^{13}C$ (-17‰) reported for marine benthic algae (France 1995, Bouillon et al. 2011, Noh et al. 2019). In contrast, $\delta^{15}N$ of AM was higher than that reported for marine N-fixing cyanobacteria ($\delta^{15}N$ ca. 0‰) (Yamamuro et al. 1995). This suggests assimilation of dissolved inorganic nitrogen derived from nitrogen-rich wastewaters discharged into Pina Sound (Rejmánková et al. 2004).

At Capibaribe River estuarine system, estuarine phytoplankton exhibits striking differences in isotopic signatures along the estuarine gradient (Costa 2018). ^{13}C and ^{15}N-depleted signatures of phytoplankton in middle estuary suggest fixation of dissolved inorganic carbon (DIC) and assimilation of NH_4^+ from depleted pools, respectively (Waser et al. 1998, Montoya 2007, Bouillon et al. 2011). Conversely, ^{13}C and ^{15}N-enriched signatures of phytoplankton in lower estuary suggest fixation of marine DIC and NO_3^-, respectively (Montoya 2007, Bouillon et al. 2011). Thus, both depleted and enriched signatures should be included in the mixing model in order to obtain accurate OM contributions from estuarine phytoplankton.

Origin of SPOM and SOM

At Pina Sound, SPOM and SOM are mixtures of OM from HPs, estuarine phytoplankton and sewage-derived SPOM. Apparently, AM is not an important OM source to Pina Sound (Fig. 3). Low contribution of AM is likely a consequence of their seasonal growth (September to February) on restricted areas (intertidal mud flats).

Sedimentary $\delta^{15}N$ and $\delta^{13}C$ were not significantly related. A positive correlation between these proxies tend to be observed in estuaries dominated by OM inputs from terrestrial C_3 plants and marine algae (Middelburg & Nieuwenhuize 1998, Gearing 2013). Conversely, the lack of correlation between $\delta^{15}N$ and $\delta^{13}C$ has been related to either high OM inputs from a third source (Wada 2009) or diagenetic shifts in $\delta^{15}N$ of organic nitrogen (Kurian et al. 2013). At Pina Sound, inputs of untreated domestic sewage (an anthropogenic source) are likely the major reason.

Estuarine phytoplankton was the major OM source to both SPOM and SOM, reflecting the eutrophic to hypertrophic condition commonly observed in surface waters of Pina Sound (Flores Montes et al. 2011). High phytoplankton contribution suggests sewage fertilization effect on planktonic primary production. The contribution of sewage-derived OM at Pina Sound was higher than that reported for Tokyo Bay (10%) (Kubo & Kanda 2017). Differences in sewage-derived SOM between Pina Sound and Tokyo Bay likely reflect local treatment of sewage and hydrodynamic conditions of these marine-influenced systems.

The mixing model revealed that on average HP-derived OM in Pina Sound comprises 26% of local SOM (Table III). Contribution of that source to Pina Sound SOM is lower than those reported for other estuaries and coastal zones (Table III). This is likely related to the small area occupied by Atlantic forest (13.4 km^2) and mangrove patches

Table III. Apportionment of organic matter sources in coastal sediments around the world. Figures in brackets represent 95% confidence interval. Legend: HP = higher C_3 plants; SIAR = stable isotope analysis in R; ME = mixing equation reported by Gireeshkumar et al. (2013); nc = not calculated.

Local	Phytoplankton	Sewage	HP	Model	Reference
Pina Sound (NE Brazil)	50 (4 - 41)	24 (11 - 29)	26 (7 - 77)	SIAR	This study
Tokyo Bay (Japan)	68 (64 - 72)	10 (5 - 15)	21 (15 - 27)	SIAR	Kubo & Kanda (2017)
Cochin estuary (India)	nc	nc	(13 - 74)*	ME	Gireeshkumar et al. (2013)
Yellow River mouth (China)	nc	nc	(40 - 50)*	ME	Liu et al. (2015)
Vembanad estuary (India)	nc	nc	(< 2 - 60)*	ME	Sarkar et al. (2016)

***Footnote*: *Range of values.**

(3.2 km^2) in the highly urbanized Recife city (218 km^2) (Ferreira & Lacerda, 2016). Additionally, MDS indicated a high contribution of HP to sandy sediments (see Fig. 5). This suggests the accumulation of large (> 63 µm) HP-derived detritus in the sand fraction (Megens et al. 2002).

Major factors controlling SOM

FA was used to infer major latent factors which may be related to distribution and origin of SOM in Pina Sound. PC1 indicated that SOM distribution was regulated by sedimentary mud content (Fig. 5a), reflecting hydrodynamics control on deposition of fine-grained (silt and clay) suspended particles. This has been commonly observed in estuarine and coastal ecosystems (Keil et al. 1994, Fagherazzi et al. 2014). Estuaries are retention zones for fine-grained suspended particles (Schettini et al. 2013). This has been previously observed along the longitudinal axis of Pina Sound (Maciel et al. 2016), resulting in high local sedimentation rate (0.45 cm $year^{-1}$) of fine-grained suspended particles (Xavier et al. 2017). At Pina Sound, calm hydrodynamic conditions are prevalent according to indicated by the Pejrup's triangular diagram (Fig. 2) (Pejrup 1988). FA also indicated that anoxic conditions were inversely related to SOM content (Fig. 5a), reflecting the control of dissolved oxygen concentrations on preservation of sedimentary OC (Goldhaber 2005).

PC2 is likely related to OM degradation/preservation that is directly influenced by sediment redox conditions (Lehmann et al. 2002). Low C/S ratio indicates anoxic sediments that facilitate OM preservation. In contrast, high Pheop/Chl *a* along with high $\delta^{15}N$ reflect OM degradation. A positive shift in $\delta^{15}N$ of SOM may be related to selective removal of labile organic compounds (e.g. Chl *a*) or microbial fractionation during degradation of N compounds (Freudenthal et al. 2001). On average, Chl *a* is ^{15}N-depleted by 5‰ when compared to the total biomass of marine primary producers (Sachs et al. 1999). Thus, selective degradation of Chl *a* would result in ^{15}N enrichment of the non-degraded biomass of primary producers. Intense N isotope fractionation occurs during microbial assimilation of aminoacids, altering the $\delta^{15}N$ value of bulk SOM (Macko & Estep 1984,

Lehmann et al. 2002). For instance, Lehmann et al. (2002) reported an increase in $\delta^{15}N$ (ca. 4‰) during degradation of planktonic algae under oxic conditions after 21 days.

PC3 probably reflects the conservative mixing of protein-rich and ^{13}C-depleted OM from estuarine phytoplankton (mean C/N = 6.5 and mean $\delta^{13}C$ = -23.49‰), and ^{13}C-enriched OM from sewage SPOM (mean C/N = 9.2 and $\delta^{13}C \approx$ -20.73‰).

CONCLUSIONS

Distribution of SOM is regulated by hydrodynamic conditions in Pina Sound. Sediments from subtidal zone have limited microphytobenthic production with predominance of chlorophyll degradation products. Pina Sound exhibits non-uniform redox potential at the sediment-water interface, with anoxic conditions prevalent in the upper sound and at the confluence with the Capibaribe River main stem. SOM of Pina Sound is predominantly composed of OM from estuarine phytoplankton and sewage followed by a lower contribution from higher plants. This reflects fertilization of Pina Sound by high loads of untreated domestic sewage. Additionally, Pina Sound has a great potential to retain sewage-derived OM and adsorbed contaminants.

Acknowledgments

B.V.M.C. was funded by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Grant No. 141146/2014-1) and Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE, Grant No. AMD-0035-1.00/15). Chemical analyses were partially funded by CNPq (Grant No. 141146/2014-1) and Multiuser FACEPE (Grant No. APQ-0388-1.08/10).

REFERENCES

ANDREWS JE, GREENAWAY AM & DENNIS PF. 1998. Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary: Hunts Bay, Kingston Harbour, Jamaica. Estuar Coast Shelf Sci 46: 743-756.

ANDREWS JE, SAMWAYS G & SHIMMIELD GB. 2008. Historical storage budgets of organic carbon, nutrient and contaminant elements in saltmarsh sediments: Biogeochemical context for managed realignment, Humber Estuary, UK. Sci Total Environ 405: 1-13.

ARNDT S, JORGENSEN BB, LAROWE DE, MIDDELBURG JJ, PANCOST RD & REGNIER P. 2013. Quantifying the degradation of organic matter in marine sediments: A review and synthesis. Earth-Sci Rev 123: 53-86.

BARBER A, BRANDES J, LERI A, LALONDE K, BALIND K, WANG J & GÉLINAS Y. 2017. Preservation of organic matter in marine sediments by inner-sphere interactions with reactive iron. Sci Rep 7: 1-10.

BARCELLOS RL, FIGUEIRA RCL, FRANÇA EJ, SCHETTINI CA & XAVIER DA. 2017. Changes of Estuarine Sedimentation Patterns by Urban Expansion: the Case of Middle Capibaribe Estuary, Northeastern Brazil. Int J Geosci 8: 514-535.

BERNER RA & RAISWELL R. 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. Geochim Cosmochim Acta 47: 855-862.

BERNER RA & RAISWELL R. 1984. C/S method for distinguishing freshwater from marine sedimentary rocks. Geol 12: 365-368.

BOND AL & DIAMOND AW. 2011. Recent Bayesian stable-isotope mixing models are highly sensitive to variation in discrimination factors. Ecol Appl 21: 1017-1023.

BOUILLON S, CONNOLLY RM, GILLIKIN DP, WOLANSKI E & MCLUSKY D. 2011. Use of Stable Isotopes to Understand Food Webs and Ecosystem Functioning in Estuaries. In: Wolanski E and Mclusky DS (Eds), Treatise on Estuarine and Coastal Science, Waltham: Academic Press, p. 143-173.

BRICKER SB, LONGSTAFF B, DENNISON W, JONES A, BOICOURT K, WICKS C & WOERNER J. 2008. Effects of nutrient enrichment in the nation's estuaries: A decade of change. Harmful Algae 8: 21-32.

BURDIGE DJ. 2007. Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? Chem Rev 107: 467-485.

BURFORD MA, LONG BG & ROTHLISBERG PC. 1994. Sedimentary pigments and organic carbon in relation to microalgal

and benthic faunal abundance in the Gulf of Carpentaria. Mar Ecol Prog Ser 103: 111-117.

CANUEL EA & HARDISON AK. 2016. Sources, Ages, and Alteration of Organic Matter in Estuaries. Annu Rev Mar Sci 8: 409-434.

CARDOSO-MOHEDANO JG, BERNARDELLO R, SANCHEZ-CABEZA JA, PÁEZ-OSUNA F, RUIZ-FERNÁNDEZ AC, MOLINO-MINERO-RE E & CRUZADO A. 2016. Reducing nutrient impacts from shrimp effluents in a subtropical coastal lagoon. Sci Total Environ 571: 388-397.

CARREIRA RS, WAGENER ALR, READMAN JW, FILEMAN TW, MACKO SA & VEIGA A. 2002. Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: An elemental, isotopic and molecular marker approach. Mar Chem 79: 207-227.

CLARKE KR & WARWICK RM. 2001. Change in marine communities: an approach to statistical analysis and interpretation. Plymouth: Plymouth Marine Laboratory.

COPLEN TB. 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. Rapid Commun in Mass Spectrom 25: 2538-2560.

COSTA BVM. 2018. Origem e degradação da matéria orgânica em um estuário tropical eutrofizado. Ph.D. thesis, Universidade Federal de Pernambuco, Brasil.

DITTMAR T, LARA RJ & KATTNER G. 2001. River or mangrove? Tracing major organic matter sources in tropical Brazilian coastal waters. Mar Chem 73: 253-271.

DOVER CLV, GRASSLE JF, FRY B, GARRITT RH & STARCZAK VR. 1992. Stable isotope evidence for entry of sewage-derived organic material into a deep-sea food web. Nature 360: 153-156.

FAGHERAZZI S, MARIOTTI G, BANKS AT, MORGAN EJ & FULWEILER RW. 2014. The relationships among hydrodynamics, sediment distribution, and chlorophyll in a mesotidal estuary. Estuar Coast Shelf Sci 144: 54-64.

FEITOSA FAN, NASCIMENTO FCR & COSTA KMP. 1999. Distribuição espacial e temporal da biomassa fitoplanctônica relacionada com parâmetros hidrológicos na Bacia do Pina (Recife - PE). Trop Oceanogr 27: 1-13.

FERREIRA AC & LACERDA LD. 2016. Degradation and conservation of Brazilian mangroves, status and perspectives. Ocean and Coast Manage 125: 38-46.

FLORES MONTES MDJ, PAULO JG, NASCIMENTO FILHO GA, GASPAR FL, FEITOSA FA, SANTOS JUNIOR AC, BATISTA TNF, TRAVASSOS RK & PITANGA ME. 2011. The trophic status of an urban estuarine complex in Northeast Brazil. J Coast Res 64: 408-411.

FRANCE RL. 1995. Carbon-13 enrichment in benthic compared to planktonic algae: foodweb implications. Mar Ecol Prog Ser 124: 307-312.

FRANCISQUINI MI, LIMA CM, PESSENDA LCR, ROSSETTI DF, FRANÇA MC & COHEN MCL. 2014. Relation between carbon isotopes of plants and soils on Marajó Island, a large tropical island: Implications for interpretation of modern and past vegetation dynamics in the Amazon region. Palaeogeogr Palaeoclimatol Palaeoecol 415: 91-104.

FREUDENTHAL T, WAGNER T, WENZHOFER F, ZABEL M & WEFER G. 2001. Early diagenesis of organic matter from sediments of the eastern subtropical Atlantic: evidence from stable nitrogen and carbon isotopes. Geochim Cosmochim Acta 65: 1795-1808.

GEARING JN. 2013. The use of stable isotope ratios for tracing the nearshore-offshore exchange of organic matter. In: Janson BO (Ed), Coastal-Offshore Ecosystem Interactions. Lecture Notes on Coastal and Estuarine Studies Series. Berlim: Springer, p. 69-101.

GIREESHKUMAR TR, DEEPULAL PM & CHANDRAMOHANAKUMAR N. 2013. Distribution and sources of sedimentary organic matter in a tropical estuary, south west coast of India (Cochin estuary): A baseline study. Mar Pollut Bull 66: 239-245.

GOLDHABER MB. 2005. Sulfur-rich sediments. In: Mackenzie FT (Ed), Sediments, Diagenesis, and Sedimentary Rocks. Treatise on Geochemistry. Oxford: Elsevier, p. 257-288.

GONTHARET S, ARTIGAS LF, MATHIEU O, LEVÊQUE J, MILLOUX MJ, CAILLAUD J, PHILIPPE S, LESOURD S & GARDEL A. 2015. Effect of emersion/immersion cycles on the elemental and isotopic compositions of the organic matter from surface sediments of an intertidal mud bank (French Guiana): A preliminary study. Rapid Commun Mass Spectrom 29: 2147-2157.

HAIR JF, BLACK B, BABIN BJ, ANDERSON RE & TATHAM RL. 2006. Multivariate data analysis, 6th ed., New Jersey: Prentice Hall, 688 p.

HARDISON AK, CANUEL EA, ANDERSON IC, TOBIAS CR, VEUGER B & WATERS MN. 2013. Microphytobenthos and benthic macroalgae determine sediment organic matter composition in shallow photic sediments. Biogeosciences 10: 5571-5588.

HEDGES JI, CLARK WA, QUAY PD, RICHEY JE, DEVOL AH & SANTOS UDM. 1986. Compositions and fluxes of particulate material in the Amazon River. Limnol and Oceanogr 31: 717-738.

HEDGES JI & STERN JH. 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnol and Oceanogr 29: 657-663.

IBGE. 2011. Atlas de saneamento. Instituto Brasileiro de Geografia e Estatística, Rio de Janeiro.

IBGE. 2019. Population census. Instituto Brasileiro de Geografia e Estatística. Disponível em: http://www.ibge.gov.br.

JEFFREY SW & HUMPHREY GF. 1975. New spectrophotometric equations for determining chlorophylls a, b, c1 and c2 in higher plants, algae and natural phytoplankton. Biochem Physiol Pflanz 167: 191-194.

KAISER HF. 1970. A second generation Little Jiffy. Psychometrika 35: 401-415.

KEIL RG, TSAMAKIS E, FUH CB, GIDDINGS JC & HEDGES JI. 1994. Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. Geochim Cosmoch Acta 58: 879-893.

KUBO A & KANDA J. 2017. Seasonal variations and sources of sedimentary organic carbon in Tokyo Bay. Mar Pollut Bull 114: 637-643.

KURAMOTO T & MINAGAWA M. 2001. Stable Carbon and Nitrogen Isotopic Characterization of Organic Matter in a Mangrove Ecosystem on the Southwestern Coast of Thailand. J Oceanogr 57: 421-431.

KURIAN S, NATH BN, KUMAR NC & NAIR KKC. 2013. Geochemical and Isotopic Signatures of Surficial Sediments from the Western Continental Shelf of India: Inferring Provenance, Weathering and the Nature of Organic Matter. J Sediment Res 83: 427-442.

LEAVITT PR. 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. J Paleolimn 9: 109-127.

LEHMANN MF, BERNASCONI SM, BARBIERI A & MCKENZIE JA. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochim Cosmoch Acta 66: 3573-3584.

LESEN AE. 2006. Sediment organic matter composition and dynamics in San Francisco Bay, California, USA: Seasonal variation and interactions between water column chlorophyll and the benthos. Estuar Coast Shelf Sci 66: 501-512.

LIU D, LI X, EMEIS KC, WANG Y & RICHARD P. 2015. Distribution and sources of organic matter in surface sediments of Bohai Sea near the Yellow River Estuary, China. Estuar Coast Shelf Sci 165: 128-136.

LORENZEN CJ. 1967. Determination of chlorophyll and pheopigments: spectrophotometric equations. Limnol Oceanogr 12: 343-346.

MACIEL DC, SOUZA JRB, TANIGUCHI S, BÍCEGO MC, SCHETTINI CAF & ZANARDI-LAMARDO E. 2016. Hydrocarbons in sediments along a tropical estuary-shelf transition area: Sources and spatial distribution. Mar Pollut Bull 113: 566-571.

MACKO SA & ESTEP MLF. 1984. Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter. Org Geochem 6: 787-790.

MCCLELLAND JW & VALIELA I. 1998. Linking nitrogen in estuarine producers to land-derived sources. Limnol Oceanogr 43: 577-585.

MEGENS L, VAN DER PLICHT J, DE LEEUW J & SMEDES F. 2002. Stable carbon and radiocarbon isotope compositions of particle size fractions to determine origins of sedimentary organic matter in an estuary. Org Geochem 33: 945-952.

MIDDELBURG JJ & NIEUWENHUIZE J. 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. Mar Chem 60: 217-225.

MONTOYA JP. 2007. Natural abundance of 15N in marine planktonic ecosystems. In: Michener R & Lajtha K (Eds), Stable Isotopes in Ecology and Environmental Science. Malden: BlackWell Publishing, p. 176-201.

MORENO S & NIELL FX. 2004. Scales of variability in the sediment chlorophyll content of the shallow Palmones River Estuary, Spain. Estuar Coast Shelf Sci 60: 49-57.

NASCIMENTO FCR, MUNIZ K, FEITOSA FAN, ARAÚJO JP, SILVA, RMS, SILVA GS & FLORES MONTES MJ. 2003. Disponibilidade nutricional da Bacia do Pina e Rio Tejipió (Recife-PE-Brasil) em relação aos nutrientes e biomassa primária (setembro/2000). Trop Oceanogr 31: 149-169.

NIXON SW. 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41: 199-219.

NOH J, YOON SJ, KIM H, LEE C, KWON BO, LEE Y, HONG S, KIM J, RYU J & KHIM JS. 2019. Anthropogenic influences on benthic food web dynamics by interrupted freshwater discharge in a closed Geum River estuary, Korea. Environ Int 131: 104981.

PARNELL AC, INGER R, BEARHOP S & JACKSON A. 2008. SIAR: stable isotope analysis in R. Available at: http://cran.r-roject.org/web/packages/siar/ index.html.

PEJRUP M. 1988. The triangular diagram used for classification of estuarine sediments: a new approach. In: de Boer PL, Van Gelder A and Nio SD (Eds), Tidal-Influenced Sedimentary Environments and Facies. Dordrecht: Reidel, p. 289-300.

PINCKNEY JL, PAERL HW, TESTER P & RICHARDSON TL. 2001. The Role of Nutrient Loading and Eutrophication in Estuarine Ecology A Definition of Eutrophication. Environ Health Perspect 109: 699-706.

RASIQ KT, KURIAN S, KARAPURKAR SG & NAQVI SWA. 2016. Sedimentary pigments and nature of organic matter within the oxygen minimum zone (OMZ) of the Eastern Arabian Sea (Indian margin). Estuar Coast Shelf Sci 176: 91-101.

REJMÁNKOVÁ E, KOMÁRKOVÁ J & REJMÁNEK M. 2004. δ15N as an indicator of N2-fixation by cyanobacterial mats in tropical marshes. Biogeochemistry 67: 353-368.

RESMI P, MANJU MN, GIREESHKUMAR TR, KUMAR CSR & CHANDRAMOHANAKUMAR N. 2016. Source characterisation of Sedimentary organic matter in mangrove ecosystems of northern Kerala, India: Inferences from bulk characterisation and hydrocarbon biomarkers. Reg Stud Mar Sci 7: 43-54.

RESURREIÇÃO MG, PASSAVANTE JZO & MACÊDO SJ. 1996. Estudo da plataforma continental na área do Recife (Brasil): variação sazonal da biomassa fitoplanctônica (08°03'38" Lat. S; 34°42'28" à 34°52'00" Long. W). Trop Oceanogr 24: 39-59.

SACHS J, REPETA D & GOERICKE R. 1999. Nitrogen and carbon isotopic ratios of chlorophyll from marine phytoplankton. Geochim Cosmochim Acta 63: 1431-1441.

SANTIAGO MF, SILVA-CUNHA MGG, NEUMANN-LEITÃO S, COSTA KMP, PALMEIRA GCB, NETO FFP & NUNES FS. 2010. Phytoplankton dynamics in a highly eutrophic estuary in tropical Brazil. Braz J Oceanogr 58: 189-205.

SANTOS PJP, BOTTER-CARVALHO ML, NASCIMENTO AB, MARINHO RGC, CARVALHO PVVC & VALENCA APMC. 2009. Response of estuarine meiofauna assemblage to effects of fertilizer enrichment used in the sugar cane monoculture. Pernambuco, Brazil. Braz J Oceanogr 57: 43-55.

SARKAR A, CHAKRABORTY P & NAGENDER NATH B. 2016. Distribution and nature of sedimentary organic matter in a tropical estuary: An indicator of human intervention on environment. Mar Pollut Bull 102: 176-186.

SCHETTINI CAF, MIRANDA JB, VALLE-LEVINSON A, TRUCCOLO E & DOMINGUES EC. 2016a. The circulation of the lower Capibaribe estuary (Brazil) and its implications in the transport of scalars. Braz J Oceanogr 64: 263-276.

SCHETTINI CAF, PAIVA BP, BATISTA RAL, FILHO JCO & TRUCCOLO EC. 2016b. Observation of an Estuarine Maximum Turbidity Zone in the Highly Impacted Capibaribe estuary, Brazil. Braz J Oceanogr 64: 185-190.

SCHETTINI CAF, PEREIRA MD, SIEGLE E, MIRANDA LB & SILVA MP. 2013. Residual fluxes of suspended sediment in a tidally dominated tropical estuary. Cont Shelf Res 70: 27-35.

SOMERFIELD PJ, FONSECA-GENEVOIS VG, RODRIGUES ACL, CASTRO FJV & SANTOS GAP. 2003. Factors affeting meiofuna community, struture in the Pina Basin, an a urbanized embayment on the coast of Pernambuco, Brazil. J Mar Biol Assoc UK 83: 1209-1213.

SUGUIO K. 1973. Introdução a sedimentologia. São Paulo: Edgar Blucher, 317 p.

TUCKER J, SHEATS N, GIBLIN AE, HOPKINSON CS & MONTOYA JP. 1999. Using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay. Mar Environ Res 48: 353-375.

VALENÇA APMC, CLEMENTE CCC, NEVES JR, SILVA JF, BEZERRA RS, BOTTER-CARVALHO ML, CARVALHO PVVC & SANTOS PJP. 2016. Effects of algal mats on a tropical estuarine benthic system: sediment biogeochemistry and macrofauna. Hydrobiologia 775: 197-211.

VALENÇA APMC & SANTOS PJP. 2013. Macrobenthic community structure in tropical estuaries: the effect of sieve mesh-size and sampling depth on estimated abundance, biomass and composition. J Mar Biol Assoc U.K. 93: 1441-1456.

WADA E. 2009. Stable δ15N and δ13C isotope ratios in aquatic ecosystems. Proc Jpn Acad Ser B - Phys Biol Sci 85: 98-107.

WALDRON S, TATNER P, JACK I & ARNOTT C. 2001. The Impact of Sewage Discharge in a Marine Embayment: A Stable Isotope Reconnaissance. Estuar Coast Shelf Sci 52: 111-115.

WASER NA, YU Z, TADA K, PAUL J, TURPIN DH & CALVERT SE. 1998. Nitrogen isotope fractionation during nitrate, ammonium and urea uptake by marine diatoms and coccolithophores under various conditions of N availability. Mar Ecol Prog Ser 169: 29-41.

WATANABE K & KUWAE T. 2015. How organic carbon derived from multiple sources contributes to carbon sequestration processes in a shallow coastal system? Global Change Biol 21: 2612-2623.

XAVIER DA, SCHETTINI CA, FRANÇA EJ, FIGUEIRA RC & BARCELLOS RL. 2017. Determination of geochemical background values on a tropical estuarine system in a densely urban

area. Case study: Capibaribe estuary, Northeastern Brazil. Mar Pollut Bull 123: 381-386.

YAMAMURO M, KAYANNE H & MINAGAWA M. 1995. Carbon and nitrogen stable isotopes of primary producers in coral reef ecosystems. Limnol Oceanogr 40: 617-621.

ZANARDI-LAMARDO E, NÓBREGA ASC, SANTOS RHA & MACIEL DC. 2016. Fontes e níveis de contaminação do Sistema Estuarino do Rio Capibaribe (Pernambuco/Brasil). Trop Oceanogr 44: 118-131.

ZHAO J, FENG X, SHI X, BAI Y, YU X, SHI X, ZHANG W & ZHANG R. 2015. Sedimentary organic and inorganic records of eutrophication and hypoxia in and off the Changjiang Estuary over the last century. Mar Pollut Bull 99: 76-84.

ZIMMERMAN AR & CANUEL EA. 2001. Bulk organic matter and lipid biomarker composition of Chesapeake Bay surficial sediments as indicators of environmental processes. Estuar Coast Shelf Sci 53: 319-341.

How to cite

COSTA BVM, MOREIRA MZ, BASTOS RF & YOGUI GT. 2021. Distribution and origin of sedimentary organic matter in an eutrophic estuary: Pina Sound – NE Brazil. An Acad Bras Cienc 92: e20190638. DOI 10.1590/0001-3765202120190638.

Manuscript received on May 31, 2019;
accepted for publication on February 17, 2020

BRUNO V.M. DA COSTA[1]
https://orcid.org/0000-0003-4481-4236

MARCELO Z. MOREIRA[2]
https://orcid.org/0000-0001-6769-5570

RODRIGO F. BASTOS[1]
https://orcid.org/0000-0002-9692-4237

GILVAN T. YOGUI[1]
https://orcid.org/0000-0002-4720-3337

[1] Universidade Federal de Pernambuco, Departamento de Oceanografia, Av. Arquitetura, s/n, Cidade Universitária, 50740-550 Recife, PE, Brazil

[2] Universidade de São Paulo, Centro de Energia Nuclear na Agricultura, Av. Centenário, 303, São Dimas, 13416-000 Piracicaba, SP, Brazil

Correspondence to: **Bruno V.M. da Costa**
E-mail: brunovmcosta@gmail.com

Author contributions

B.V.M. Costa and G.T. Yogui conceived the experimental design and collected the samples. B.V.M Costa processed the samples, analysed the data and wrote the manuscript. M.Z. Moreira carried out the isotopic analysis and analyze the data. B.V.M. Costa and R.F. Bastos runned the Bayesian mixing model and analysed the data. M.Z. Moreira, R.F. Bastos and G.T. Yogui reviewed the manuscript.