Marine Pollution Bulletin 102 (2016) 206–209

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Edited by Bruce J. Richardson

The objective of BASELINE is to publish short communications on different aspects of pollution of the marine environment. Only those papers which clearly identify the quality of the data will be considered for publication. Contributors to Baseline should refer to 'Baseline–The New Format and Content' (*Mar. Pollut. Bull.* **60**, 1-2).

Trace metal concentrations in tropical mangrove sediments, NE Brazil

Brígida Miola [a,c,*], Jáder Onofre de Morais [b], Lidriana de Souza Pinheiro [b]

[a] *Programa de Pós-graduação em Ciências Marinhas Tropicais, Brazil*
[b] *Instituto de Ciências do Mar, Universidade Federal do Ceará, P.O BOX. 3207, 60165-081 Fortaleza, CE, Brazil*
[c] *Universidade de Fortaleza, Campus P.O. BOX 1321, 60811-905 Fortaleza, CE, Brazil*

ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 10 November 2015
Accepted 16 November 2015
Available online 20 November 2015

Keywords:
Mangroves
Trace metals
Core sediments
Northeast coast of Brazil

ABSTRACT

Sediment cores were taken from the mangroves of the Coreaú River estuary off the northeast coast of Brazil. They were analyzed for grain size, $CaCO_3$, organic matter, and trace metal (Cd, Pb, Zn, Cu, Al, and Fe) contents. Mud texture was the predominant texture. Levels of trace metals in surface sediments indicated strong influence of anthropogenic processes, and diagenetic processes controlled the trace metal enrichment of core sediments of this estuary. The positive relationships between trace metals and Al and Fe indicate that Cu, Zn, Pb, and Cd concentrations are associated mainly with Al and Fe oxy-hydroxides and have natural sources.

Steadily increasing use of coastal areas for human activities has increased deposition of trace metals in soils and sediments in coastal and estuarine regions. Mangrove forests are ecosystems that act as biogeochemical barriers in the continent–ocean interface, retaining metallic contaminants in their sediments, as shown by several studies in tropical and subtropical regions (Alongi et al. 2004; Harbison 1986; Lacerda et al. 1991). It is important, however, to consider the geochemical behaviors of these metals, which may favor retention or release by the solid phase of sediments to coastal waters. Furthermore, the spatio-temporal variability of their input and the sediment composition can influence the distribution of trace metals (Machado et al. 2002; Silva et al. 2003; Tam and Wong 1995). Trace metals reach estuarine environments in association with particulate material suspended and/or dissolved in the water column of river systems and through atmospheric deposition (Lacerda and Solomons 1998). The deposition and accumulation of trace metals in mangroves are enhanced by the characteristics of these regions, resulting in high concentrations of these elements, even in areas where no significant sources occur (Salomão et al. 2001).

Variations in sediment cores reflect the geochemical history of a given region, including any anthropogenic impacts (Szefer and Skwarzec 1988). Diagenetic reactions are important near the sediment–water interface; they are caused by redox changes and affect metal concentrations in vertical sediment profiles (Santschi et al. 1990; Shaw et al. 1990).

This study examined the geochemistry of mangrove sediments in the Coreaú River estuary in order to assess the enrichment and possible sources of trace metals. The Coreaú River estuary lies on the Camocim municipal area in the Ceará State, Brazil (Fig. 1). There are approximately 35.3 km^2 of mangrove forests, and it is considered to be the second largest mangrove area in Ceará (Rodrigues and Souza Filho 2011).

The cores were taken with a half-open iron bar and with a Merkt/Streif piston corer (Merkt and Streif 1970). The sediment cores (T-1 and T-2) were 240 cm and 315 cm deep, respectively. Samples were taken at 20 cm intervals, resulting in 13 and 17 sub-samples in T-1 and T-2, respectively.

The grain sizes of the sediments were classified as gravel, sand, and mud (silt + clay), according to Suguio (1973). Calcium carbonate ($CaCO_3$) was measured with a modified Bernard calcimeter (Lamas

* Corresponding author at: Programa de Pós-graduação em Ciências Marinhas Tropicais, Brazil.
E-mail address: bmiola@gmail.com (B. Miola).

http://dx.doi.org/10.1016/j.marpolbul.2015.11.039
0025-326X/

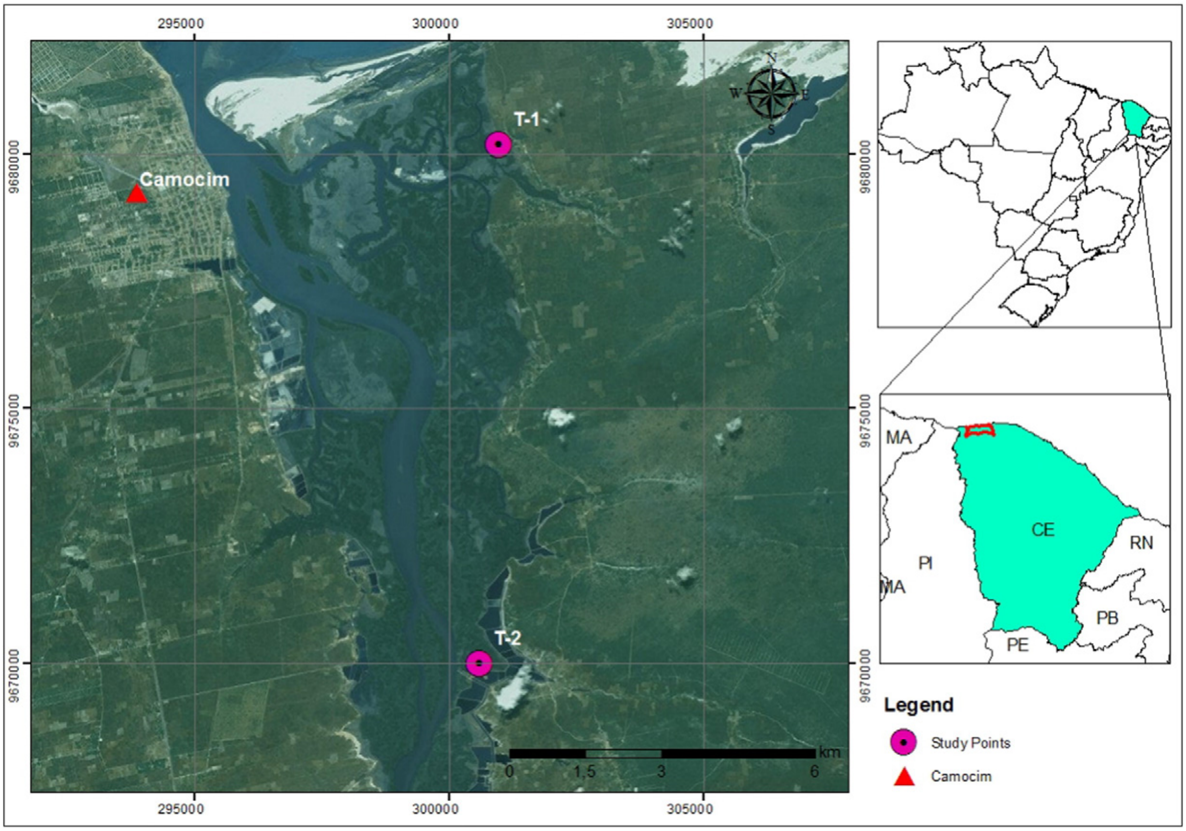

Fig. 1. Study area and core sample locations (T-1 and T-2) of estuary of Coreaú River, NE coast of Brazil.

et al. 2005). The organic matter (OM) was determined using the method of Loring and Rantala (1992). The concentrations of following elements were measured: Cu, Al, Pb, Zn, and Fe. Trace metals were quantified by Atomic Emission Spectrometry with Induced Plasma (ICP OES) using the ICP-OES Vista MPX Model. Analysis was performed at the INNOLAB Brazil Ltda Laboratory, Rio de Janeiro. The results were expressed as $mg \cdot kg^{-1}$ dry sediment.

Textural data of T-1 and T-2 are presented as the percent composition of mud (Table 1). The sediments were predominantly silt and clay. T-1 showed low percentages of mud in the top layers (28.2%). There was a decrease in mud fraction (20 cm, 93.7%; 40 cm, 84%) towards the bottom of the core (220 cm, 10%).

Table 1
Vertical distribution of mud (silt + clay) in core samples (T-1 and T-2) from the Coreaú River estuary, NE coast of Brazil.

Depth (cm)	T-1 mud (%)	T-2 mud (%)
0	28.2	63.05
20	93.7	78.2
40	84	98.8
60	24.1	98.5
80	22.3	97.6
100	23.3	98.82
120	48.5	98.5
140	49.8	97
160	45.9	43.5
180	45.6	76.5
200	41.4	78.3
220	10.0	92.8
240	34.8	45
260	–	38.2
280	–	45.3
300	–	29.5
315	–	51.7
Average	42.4	72.4

The mud fractions in T-2 reached up to 99%. There was a decrease in mud fraction from 240 to 280 cm. At these depths, the sediment contained high concentrations of gravel, represented by the shell fragments.

T-2 was located near a shrimp farm that releases effluent directly into a channel of the Coreaú River estuary. This fact may be responsible

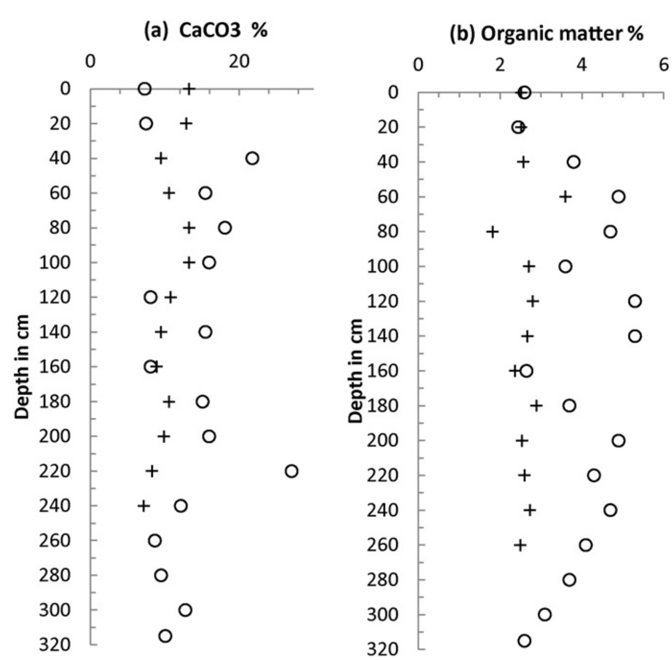

Fig. 2. Vertical profiles of $CaCO_3$ and organic matter in sediments cores (T-1 and T-2) of the Coreaú River estuary, NE coast of Brazil.

for the high mud content of the core samples. According to Godoy (2011), shrimp farms act as large pools of sedimentation because of the water renewal process; the amount of suspended sediment measured at the output of the tanks is less than the amount measured at the input.

The $CaCO_3$ concentration in the sediments varied from 7.2 to 13.3% in T-1 and 7.3 to 27.1% in T-02 (Fig. 2). The highest concentrations of $CaCO_3$ were observed in T-2 (220 cm; 27.1%), where there was a high concentration of gravel. The highest $CaCO_3$ levels were primarily of biogenic origin, resulting from the accumulation of bivalve shell fragments with high levels of carbonates.

The OM ranged from 1.82 to 3.6% in T-1 and 2.45 to 5.3% in T-2 (Fig. 2). Particle size directly influenced the OM content of sediments. This was observed in T-2 as OM decreased from 240 (4.7%) to 315 cm (2.6%); this was associated with decreasing levels of fine sediments in this depth range.

The OM values in the sediments of the Coreaú River estuary were on the same order of magnitude as those noted by Aguiar (2005): from 0.64 to 3.96% in estuary sediments of the Ceará River and 0.86 to 5.23% in the Pacoti River estuary, northeast of Brazil.

Al and Fe had the highest among metals concentrations in T-1 and T-2 (Fig. 3). According to Sageman (2005), the association of trace metals with Al and Fe in estuarine sediment indicates the presence of silicate minerals of terrestrial origin or allochthonous origin (e.g., biotite) generated by leaching or soil erosion.

The concentration of Fe decreased from the surface, suggesting diagenetic enrichment in which the oxy-hydroxides of Fe are partially dissolved in the lower sediment layers. This produces Fe^{2+}, which migrates upward in the sediment column and precipitates near the oxic–suboxic interface (Froelich et al. 1979; Skei and Paus 1979; Santschi et al. 1990; Shaw et al. 1990). The above inference can be supported by high values of Fe in the surface (34.418 $mg \cdot kg^{-1}$) and decreased levels at 20 cm (30.922 $mg \cdot kg^{-1}$) in T-2.

Diagenetic enrichment of Fe in T-1 was noted between 40 cm (49.512 $mg \cdot kg^{-1}$) and 60 cm (10.829 $mg \cdot kg^{-1}$), at which point the concentration started decreasing. This situation also occurred with Al, which had high concentrations at 40 cm (107.103 $mg \cdot kg^{-1}$) and a decreased below 60 cm (19.819 $mg \cdot kg^{-1}$).

The concentrations of Fe and Al found in the surface layers in T-2 (Al: 60.074 $mg \cdot kg^{-1}$and Fe: 34.418 $mg \cdot kg^{-1}$) showed higher levels than T-1 (Al: 17.110 $mg \cdot kg^{-1}$and Fe: 10.326 $mg \cdot kg^{-1}$), which indicates different retention times of these metals in surface sediments between the two sediment cores.

In T-2, there was an increase in the concentration of Fe at the bottom of the core (16.283 $mg \cdot kg^{-1}$ at 240 cm to 49.089 $mg \cdot kg^{-1}$ at 315 cm).

At the surface of the sediment cores, Cu, Zn, Pb, and Cd showed higher values in T-2 than T-1 (Fig. 3). In T-1, the analyzed metals had highest values at 40 cm (Cu: 12.5 $mg \cdot kg^{-1}$; Pb: 19 $mg \cdot kg^{-1}$; Zn:64 $mg \cdot kg^{-1}$, and Cd: 1.1 $mg \cdot kg^{-1}$) as did Fe and Al, suggesting diagenetic enrichment. This hypothesis is well supported because there were decreased levels of metals at 60 cm (Cu: 2.8 $mg \cdot kg^{-1}$; Pb: 3 $mg \cdot kg^{-1}$; Zn: 16 $mg \cdot kg^{-1}$, and Cd: 0.3 $mg \cdot kg^{-1}$).

Values of Cu ranged from 1.8 to 11.1 $mg \cdot kg^{-1}$ in T-1; high concentrations were observed in T-2 (6.3 to 23 $mg \cdot kg^{-1}$). Lacerda et al. (2004) measured Cu concentrations in estuarine sediments and observed values of 9.1, 0.7, and 15.3 $mg \cdot kg^{-1}$ in the Jaguaribe, Curimataú, and Açu River estuaries, respectively.

The Pb and Zn values in T-2 (Zn: 22 to 72 $mg \cdot kg^{-1}$; Pb: 3 to 14 $mg \cdot kg^{-1}$) were higher than T-1 (Zn: 6 to 40 $mg \cdot kg^{-1}$; Pb: 2 to 19 $mg \cdot kg^{-1}$). Zn concentrations reported by Aguiar (2005) were 0.40 to 7.0 $mg \cdot kg^{-1}$ and 1.8 to 12.64 $mg \cdot kg^{-1}$ in the mangroves of the Ceará and Pacoti Rivers, respectively. These values were less than the values obtained in this study, but similar values (9.4 to 50.1 $mg \cdot kg^{-1}$) were found in the Jaguaribe River estuary by Lacerda et al. (2004).

Torres (2009) found similar values of Pb (1.7 to 17.8 $mg \cdot kg^{-1}$) in sediments of the Jaguaribe River estuary but lower values in the Pacoti River estuary (1.7 to 6.4 mg estuary kg^{-1}).

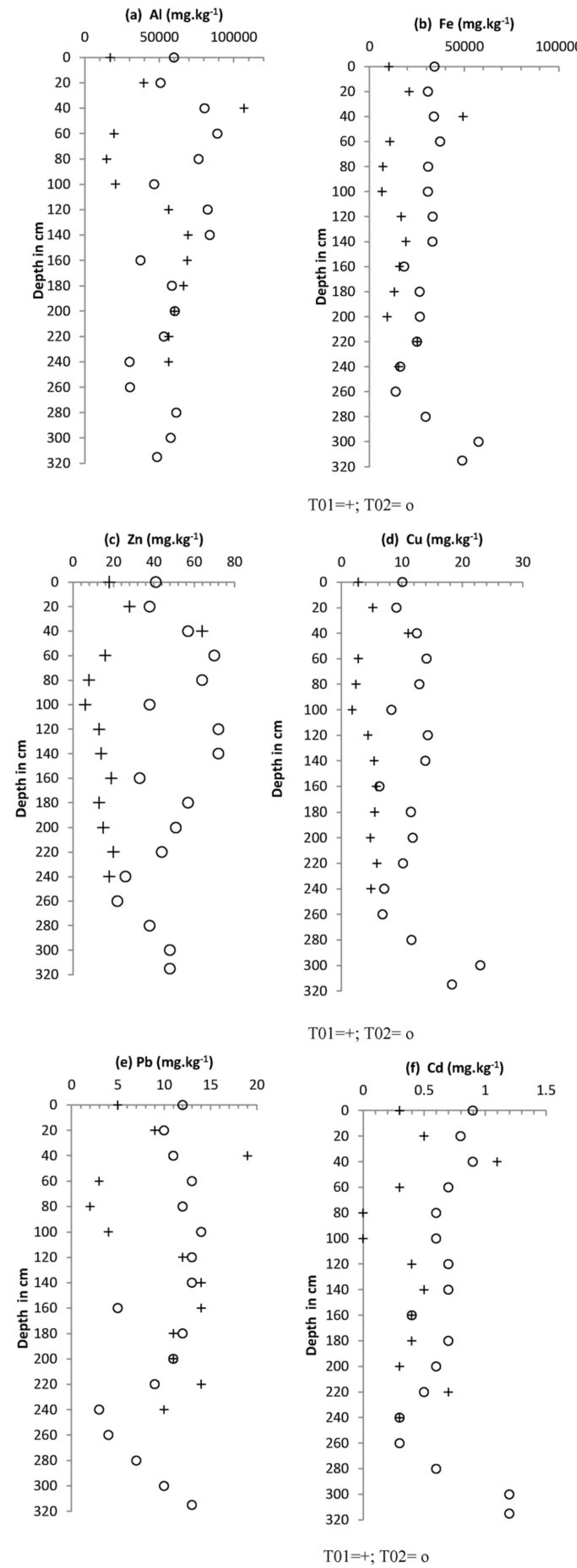

Fig. 3. Vertical profiles of trace metals (Al, Fe, Zn, Cu, Pb, and Cd) in sediment cores (T-1 and T-2) of the Coreaú River estuary, NE coast of Brazil.

Table 2
Correlation coefficient matrix of trace metals in sediment cores (T-1 and T-2) of the Coreaú river estuary, NE coast of Brazil.

	Mud	O.M.	$CaCO_3$	Al	Cd	Pb	Cu	Fe	Zn
T-1 (number of samples = 13)									
Mud	1								
O.M.	0.41	1							
$CaCO_3$	0.03	−0.08	1						
Al	**0.54**	**0.59**	**0.68**	1					
Cd	**0.55**	**0.52**	0.49	**0.80**	1				
Pb	**0.50**	**0.58**	**−0.68**	**0.96**	**0.84**	1			
Cu	**0.63**	**0.67**	**−0.55**	**0.93**	**0.93**	**0.90**	1		
Fe	**0.59**	**0.67**	−0.39	**0.77**	**0.95**	**0.78**	**0.93**	1	
Zn	**0.66**	**0.66**	−0.25	**0.66**	**0.87**	**0.62**	**0.88**	**0.93**	1
T02 (number of samples = 17)									
Mud	**1**								
O.M.	**0.50**	1							
$CaCO_3$	**0.56**	0.40	1						
Al	**0.69**	0.48	0.31	1					
Cd	−0.01	−0.45	−0.09	0.50	1				
Pb	**0.69**	0.07	0.21	**0.69**	**0.61**	1			
Cu	−0.03	0.005	0.08	0.48	**0.80**	**0.50**	1		
Fe	0.01	−0.25	0.01	0.43	**0.92**	**0.62**	**0.93**	1	
Zn	**0.69**	**0.51**	0.31	**0.93**	0.36	**0.75**	**0.55**	0.45	1

Note: Significant values are marked in bold ($p < 0.05$).

Cd concentrations in the sediments of the Coreaú River estuary were below the detection limit (DL) of the apparatus ($1.2\ mg \cdot kg^{-1}$). Cd concentrations in T-2 (0.3 to $1.2\ mg \cdot kg^{-1}$) were higher than T-1 (<DL to $1.1\ mg \cdot kg^{-1}$).

In T-2, Zn, Cu, Pb, and Cd concentrations increased at the bottom of the sediment core, as did the Fe concentration. This fact is probably due to the strong association of these metals with the Fe oxy-hydroxides (Machado et al. 2002). This indicates digenetic enrichment controlled by the redox cycle of Fe, which is related to anthropogenic input.

Statistical correlation analyses were performed in order to understand the behavior of and identify the main sources of Cu, Pb, Zn, and Cd in mangrove forests in the Camocim area (Table 2).

In T-1, metal levels indicated significant correlation to geochemical carriers except $CaCO_3$. The correlation matrix for T-1 demonstrated a positive correlation between OM and trace metals, suggesting possible organometallic complexation reactions. Significant positive correlations of Al and mud with the trace metals in T-1 also suggest an association with the sedimentary matrix.

The results of geochemical correlation for T-2 (Table 2) show that only Pb ($r = 0.70$) and Zn ($r = 0.93$) had significant correlation with Al. Positive correlations between Zn and Pb ($r = 0.75$), suggested that they had the same origin and were mostly from natural sources.

There was a positive correlation between Fe and Cd ($r = 0.94$), Pb ($r = 0.62$), and Cu ($r = 0.92$). Cd had a significant positive correlation with Cu ($r = 0.82$) and Pb ($r = 0.61$), suggesting that these metals have the same origin. Both Cu and Cd had no significant correlation with Al (Cu: $r = 0.48$; Cd: $r = 0.35$) and had negative correlations with mud (Cu: $r = -0.03$; Cd: $r = -0.01$) suggesting that these metals had an anthropogenic source.

The overall analysis of sedimentary profiles led to the conclusion that the contributions of Cd, Cu, Pb, and Zn were higher in T-2 than T-1, mainly in the surface layers. This indicates a greater input of metals in T-2, possibly due to anthropogenic activities in Coreaú River estuary.

The geochemical correlations in T-2 indicated that Zn and Pb were from lithogenic origin and that Cd and Cu may have originated from anthropogenic sources to the estuary. In T-1, trace metals had source associated with the sedimentary matrix in the area.

The grain size analysis also indicated the influence of shrimp farms located in the estuary. The highest levels of mud were measured in T-2. The data presented here justifies the need for detailed research and suggests that it is necessary to have authorities monitor metal accumulation in sediments of the Coreaú River estuary in Camocim.

Acknowledgments

The authors thank the Capes for financial support (Projeto Ciências do Mar 876/2010) and Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico (Funcap). Special thanks to Prof. Dr. Georg Irion for his valuable contributions to the fieldwork.

References

Aguiar, E., 2005. Geoquímica de metais-traço em sedimentos superficiais nos estuários dos rios Ceará e Pacoti. CE. Trabalho de Conclusão de Curso. Graduação em Geologia – UFC (64p).
Alongi, D.M., Wattayakorn, G., Boyle, S., Tirendi, F., Payn, C., Dixon, P., 2004. Influence of roots and climate on mineral and trace element storage and flux in tropical mangroves soils. Biogeochem. Biogeochem. 69, 105–123. http://dx.doi.org/10.1023/B:BIOG.0000031043.06245.af.
Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43, 1075–1090. http://dx.doi.org/10.1016/0016-7037(79)90095-4.
Godoy, M.D.P., 2011. Mudanças na sedimentação no estuário no Rio Jaguaribe (CE) devido a mudanças nos usos do solo. Dissertação de Mestrado. Pós-graduação em Ciências Marinhas Tropicais (79p).
Harbison, P., 1986. Mangrove muds — a sink and a source for trace metals. Mar. Pollut. Bull. 17, 246–250. http://dx.doi.org/10.1016/0025-326X(86)90057-3.
Lacerda, D.L., Solomons, W., 1998. Mercury from Gold and Silver Mining: A Chemical Time Bomb? Springer-Verlag, Berlim http://dx.doi.org/10.1007/978-3-642-58793-1
Lacerda, L.D., Rezende, C.E., Aragon, G.T., Ovalle, A.R.C., 1991. Iron and Chromium transport and accumulation in a mangrove ecosystem. Water Air Soil Pollut. 57/58, 513–520. http://dx.doi.org/10.1007/BF00282915.
Lacerda, L.D., Marins, R.V., Vaisman, A.G., Maia, S.R.R., Aguiar, J.E., Dias, F.J.S., 2004. Contaminação por metais pesados nas bacias inferiores dos Rios Curimataú e Açú (RN) e Rio Jaguaribe (CE). Sociedade Internacional par Ecossistemas de manguezal do Brasil. Instituto de Ciências do Mar, Associação Brasileira de Criadores de Camarão, Fortaleza (63 p).
Lamas, F., Irigaray, C., Oteo, C., Chacon, J., 2005. Selection of the most appropriate method to determine the carbonate content for engineering purposes with particular regard to marls. Eng. Geol. 81, 32–41. http://dx.doi.org/10.1016/j.enggeo.2005.07.005.
Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth-Science Reviews 32. Elsevier Science Publishers B.V., pp. 235–283. http://dx.doi.org/10.1016/0012-8252(92)90001-A.
Machado, W., Moscatelli, M., Rezende, L.G., Lacerda, L.D., 2002. Mercury, zinc, and copper accumulation in mangrove sediments surrounding a large landfill in southeast Brazil. Environ. Pollut. 120, 455–461. http://dx.doi.org/10.1016/S0269-7491(02)00108-2.
Merkt, J.U., Streif, H., 1970. Stechrohr-Bohrgerate fur limnische und marine Lockersedimente. Geol. Jahrb. 88, 137–148.
Rodrigues, S.W.P., Souza Filho, P.W.M., 2011. Detecção de mudança no manguezal ao longo do estuário do rio Coreaú-CE, através da análise multitemporal em imagens TM/Landsat-5 no período de 1985 a 2008. XIII Congresso da Associação Brasileira de Estudos do Quaternário – ABEQUA.
Salomão, M.S.M.B., Molisani, M.M., Ovalle, A.R.C., Rezende, C.E., Lacerda, L.D., Carvalho, C.E.V., 2001. Particulate heavy metal transport in the lower Paraíba do Sul River basin, southeastern, Brazil. Hydrol. Process. 15, 587–593. http://dx.doi.org/10.1002/hyp.168.
Sageman, B.B., 2005. In: Mackenzie, F.T. (Ed.), Sediments, Diagenesis, and Rocks. Elsevier-Pergamon, Oxford. ISBN: 978-0-08-044849-7, pp. 115–158.
Santschi, P.H., Hohener, P., Benoit, G., Bucholtz-ten Brink, M., 1990. Chemical processes at the sediment water interface. Mar. Chem. 30, 269–315. http://dx.doi.org/10.1016/0304-4203(90)90076-O.
Shaw, T.J., Gieskes, J.M., Jahnke, R.A., 1990. Early diagenesis in differing depositional environments. The responses of transition metals in pore water. Geochim. Cosmochim. Acta 54, 1233–1246. http://dx.doi.org/10.1016/0016-7037(90)90149-F.
Silva, L.F.F., Machado, W., Lisboa Filho, S.D., Lacerda, L.D., 2003. Mercury accumulation in sediments of a mangrove ecosystem in SE Brazil. Water Air Soil Pollut. 145, 67–77. http://dx.doi.org/10.1023/A:1023610623280.
Skei, J., Paus, P.E., 1979. Surface metal enrichment and partitioning of metals in a dated sediment core from a Norwegian fjord. Geochim. Cosmochim. Acta 43, 239–246. http://dx.doi.org/10.1016/0016-7037(79)90242-4.
Suguio, K., 1973. In: Paulo, S. (Ed.), Introdução à sedimentologia. Edgard Blucher. EDUSP, p. 317.
Szefer, P., Skwarzec, B., 1988. Distribution and possible sources of some elements in the sediment cores of the southern Baltic. Mar. Chem. 23, 109–129. http://dx.doi.org/10.1016/0304-4203(88)90026-6.
Tam, N.F., Wong, Y.S., 1995. Spatial and temporal variations of heavy metal contamination in sediments of a mangrove swamp in Hong Kong. Mar. Pollut. Bull. 31, 254–261. http://dx.doi.org/10.1016/0025-326X(95)00141-9.
Torres, R.F., 2009. Disponibilidade dos metais cobre e chumbo em um canal de maré receptor de efluentes de carcinicultura. Dissertação de Mestrado, Pós-graduação em Ciências Marinhas Tropicais – UFC (134p).