Heavy metal distribution in the sediment profiles of the Sauípe River Estuary, north seashore of the Bahia State, Brazil

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ABSTRACT

The distribution of the elements Al, Fe and selected heavy metals (Pb, Zn, Cd, Cu and Cr) plus the organic matter in the sedimentary substratum of the mangrove ecosystem that surrounds the estuary of the Sauípe River (Bahia, Brazil) is presented. Mangrove sediments were collected from six stations from where each sample was collected from the interface water-sediment till the depth of 50 cm and its location was in accordance to the inter-tidal transection in order to characterize the three mangrove stands (proximal, intermediate and distal spatial position in relation to the main river channel). The results are important to subsidize any further studies in this region that require local geochemical references. The substratum of the Sauípe River's mangrove is in accordance with the other mangroves that occur in the Bahia State where there is no evidence of anthropic source of pollution.

1. Introduction

Heavy metal cycling is a serious problem addressed in the mangrove environment. Many studies have revealed that mangrove environs act as a trap for heavy metals [1–4]. However, few studies have been made on nearly pristine areas [5–7], especially mangroves.

Incorporation of metals from the weathering of rocks within the catchment of the estuary; materials carried in by the tide; and anthropogenic sources into sedimentary landforms, such as salt marshes or mudflats, at any point within an estuary is further influenced by the interplay of water chemistry (salinity, pH and dissolved oxygen) and hydrological regime [8,9]. Diagenetic processes, determined by pH, redox conditions, organic matter content and soil texture, may further influence metal concentrations and distributions once incorporation in a sedimentary landform has occurred [10–12].

The Sauípe basin is a typical small coastal fluviatile basin located north from the city of Salvador (Fig. 1a, b) whose the main drainage, the Sauípe River, has about 80 km in length, and the lower course is typified by an extensive growth of mangrove. This ecosystem has a local economical importance because it supports the main resource disponible for the inhabitants, which have a secular fishery tradition. The present study was carried out in order to search geochemical background in the bottom sediments and to verify the possible existence

of contamination and the pollution level mainly accrued from the discharges of commercial and domestic sewages into this ecosystem.

2. Materials and methods

Eighteen (18) samples points were established in the mangrove estuarine area and from 6 sampling stations (Fig. 1c) that were located as follow: stations 1 and 2 were set in the lower portion; stations 3 and 4 in the intermediate portion, and stations 5 and 6 in the upper estuarine portion. Each station comprised three sampling points which were placed on an imaginary stand line being the stand I proximal to the river margins and the stand III the most distal and it was set where the mangrove vegetation gives place to the bushes of sand bar, shore sand dunes bushes and tropical wood. The samples were obtained using a cylindric boring-tool that penetrates the sedimentary bottom to the depth of 50 cm. The collected log-core was split into two portions, one from the surface to 25 cm and the other from 25 to 50 cm. From this procedure 36 samples were collected with plastic spatulae, homogenized, transferred to plastic zip-lock bags, and stored at 4 °C. These analyses were carried out in the Laboratory of Study on Biogeochemistry of Mangrove of the Geochemistry Department of Federal University of Bahia. The samples were divided into two parts, the first being used to characterize particle size fractions (percentage of sand, silt and clay) and the second for analysis of organic matter (OM) and total nitrogen by the method of Kjeldahl [13]. Results were expressed as a percentage (%) for particle size fractions and organic matter, and for total nitrogen as mg/kg, in dry weight.

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Another part of the sediment sample was used for chemical analysis, where were acidified for 30 min with a 1 M HCl solution to form H_2S that was collected in a 0.5 M NaOH solution. The metal contents were obtained by atomic absorption spectroscopy with flame atomization (AAS-F) for Al, Fe, plus the traces metals Pb, Zn, Cu, and Cr (ASTM 5258-02), and finally a fraction was destined for storage. Blanks were included in each batch of analysis. The precision and accuracy of the analytical technique were assessed by the analysis of a Certified Reference Material, MESS-2 (National Research Council of Canada) with each batch of samples. Results indicated good analytical precision, but incomplete digestion (4.6–62%). These results were not unexpected since the extraction procedure did not include HF. Results were expressed as mg/kg, in dry weight. Each sample was analyzed in duplicate.

Data were summarised by calculating means and standard errors, and by noting minimum and maximum values, for comparison with order data reported in the literature. The spatial variability in the data was assessed by calculating two-factor analyses of variance with replication, where the factors used were the broad-scale variation between compartments, the smaller-scale variation between plots within the same compartment, and the interaction between these two sources of variation.

3. Results and discussions

Table 1 brings the analytical results for O.M., Al, Fe, Pb, Zn, Cu and Cr. To make easier the valuation of these data, in Fig. 2 is illustrated the spatial distribution of these contents, which is in relation to each station
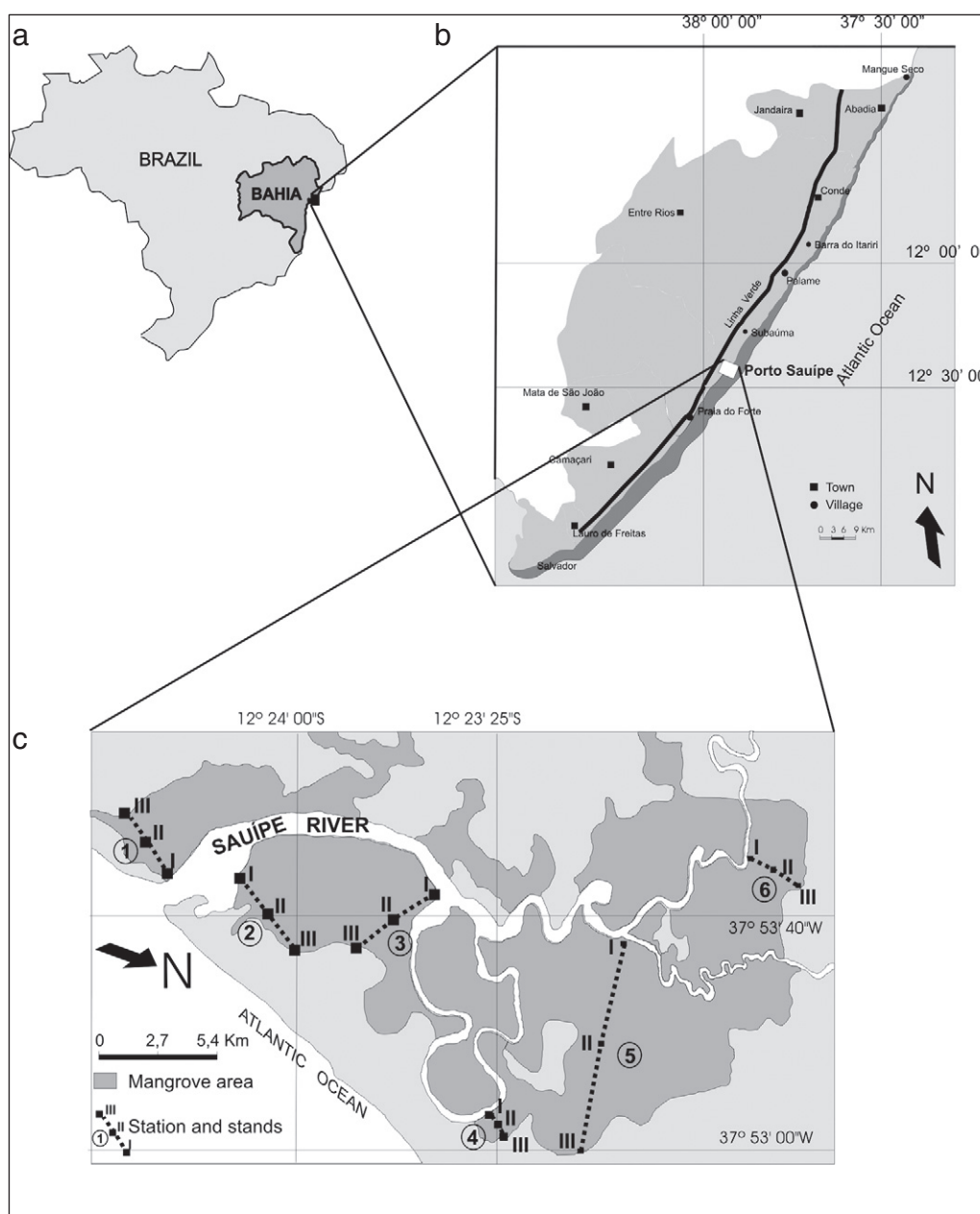

Fig. 1. (a) Situation map; (b) location map and (c) a sketch map of sampling sites in the Sauípe Basin, Bahia, Brazil.

Table 1
Contents (in mg/kg) of Al and Fe, heavy metal concentration and organic matter – O.M. (%) in different sections of the profile.

Sample	Depth (cm)	Al ($\times 10^{-3}$)	Fe ($\times 10^{-3}$)	Pb	Zn	Cu	Cr	O.M. (%)
0–25								
1.I		2.45	8.64	8.77	1.14	11.54	13.36	6.96
1.II		4.81	12.13	6.58	1.36	20.00	20.79	9.16
1.III		2.45	2.76	8.77	0.68	36.92	12.47	2.02
2.I		4.14	11.40	15.35	1.29	12.31	17.22	6.55
2.II		1.86	6.25	10.97	0.91	6.92	9.80	4.4
2.III		2.11	6.18	21.93	0.83	7.69	10.69	4.06
3.I		4.65	15.99	10.97	1.82	13.85	15.14	15.03
3.II		5.49	16.91	4.39	1.29	17.69	24.35	24.52
3.III		2.37	6.80	4.39	0.68	10.00	12.17	3.28
4.I		4.98	18.38	10.97	1.82	17.69	26.72	21.44
4.II		5.32	16.54	8.77	1.29	15.39	19.60	28.28
4.III		3.38	11.58	10.97	1.29	17.69	15.14	4.81
5.I		4.90	14.89	6.58	1.29	11.54	19.89	17.08
5.II		0.68	2.94	2.19	0.23	4.62	4.75	2
5.III		1.69	3.86	4.39	1.29	13.85	8.31	0.73
6.I		2.53	10.85	2.19	0.91	10.00	11.28	8.48
6.II		1.77	7.35	2.19	0.76	9.23	10.10	15.13
6.III		2.97	8.82	4.39	0.76	13.85	15.74	7.47
25–50								
1.I		4.31	13.79	13.16	1.14	16.92	21.68	13.18
1.II		3.89	11.21	8.77	1.44	16.16	19.00	8.77
1.III		2.70	9.38	21.93	0.91	69.23	16.63	2.99
2.I		3.63	10.29	17.55	1.14	11.54	15.14	6.41
2.II		2.28	7.17	10.97	0.83	6.92	9.80	4.52
2.III		2.11	7.72	15.35	0.91	7.69	9.80	4.08
3.I		6.25	16.73	10.97	1.97	14.62	19.89	18.25
3.II		5.66	15.26	8.77	1.74	16.16	25.54	19.77
3.III		4.22	9.74	4.39	0.91	11.54	16.33	5.74
4.I		6.84	18.20	10.97	1.82	17.69	26.43	21.5
4.II		4.14	15.99	8.77	1.21	14.62	18.71	31.04
4.III		3.89	10.29	13.16	0.83	15.39	15.44	5.81
5.I		6.08	14.89	6.58	1.29	11.54	19.89	16.14
5.II		0.68	3.68	2.19	0.15	6.16	4.75	2.57
5.III		2.03	5.52	4.39	0.91	13.85	9.80	4.04
6.I		2.70	11.21	2.19	0.71	9.23	10.10	11.79
6.II		2.70	12.32	2.19	0.91	12.31	17.20	19.26
6.III		3.46	10.11	6.58	1.52	15.39	17.52	8.99

and the related depth. The following patterns of distribution exhibited by Pb, Zn, Cu and Cr in which for the 1, 3 and 6 stations the I-positioned samples have a higher content than those respective contents for the S-positioned ones, and for the 2, 4 and 5 stations there is no defined behavior in the distribution of these elements. Zn and Cu do not present any noticeable changes with depth (Table 2).

Table 3 shows the average contents related to the stands. In terms of the stands it can be seen that the highest contents for Al, Fe, Cr and O.M. are reported in the stand I, and the respective lowest values are reported in the stand II. The highest records for Cu, Pb, and Zn in stand III. The significance levels of distinction among the stands show that, the composition of O.M., Fe, Al and Zn become much more distinct going from stand I towards stand III. Also, the contents considered for stands II and III do not exhibit significative differences, with the exception made for the O.M. and Pb. Concentration of metals analysed varied considerably. This was evidenced by the ANOVA test, which there was significant variation in the metal concentration with respect to different sampling locations ($p < 0.05$). This reveals that different stands area capable of accumulating metals differently.

Clay minerals in the fine sediment fraction, such smectite and ilite, are rich in Al and Li and are major components of the sediments in the Saúpe Estuary.

The particle size (Fig. 2) indicates a sandy composition. If one goes from Stand I to Stand III, the sand fraction tend to be proportionally higher if compared to the remainder silt plus clay fractions. However no particle size change is reported in relation to the depth. Also it can be seen that the clay content in these sediments is higher in the intermediate

portion of the Saúpe River estuary (stations 3 and 4) and that it becomes lower towards the upper estuarine portion (stations 5 and 6), being this behavior more noticeable in the stand I which is set in the margin of the river. For station 4 and from stand I to stand III the decreasing in the clay content followed by the increasing in the contents of sand are much more conspicuous. Although this station be set in the intermediate estuarine portion it is in a meandriform branch of the river that has a lower hydrodynamic and transportation energy to carry high amounts of non clayey fractions.

The Pearson's linear correlation indexes from the obtained data are in Table 3, from which it can be seen that good positive correlations ($\tau > 0.70$) are those exhibited (a) between Al and Cr (0.92), Fe (0.91), Zn (0.84), and the O.M. (0.71), (b) between Fe and Cr (0.88), O.M. (0.85), and Zn (0.79), (c) for the pairs of heavy metals Cr-Zn (0.79), and (d) between the O.M. and Cr (0.71). The correlations of metals with Fe suggest that Zn and Cr were strongly associated with Fe oxyhydroxides phase, and/or they have a common source.

Sediment grain size is a significant factor in influencing the concentration of heavy metals in estuarine and marine sediments. Among all the metals studied, Al, Fe, Zn and Cr showed significant positive correlation with clay. This indicates that these metals better bind with the finer particles than the larger sand particles. Incidentally, the mangrove stations which recorded more clay composition registered higher concentrations of these metals.

Table 4 brings the values of heavy metals for the standard shale [14] plus the respective average contents in the studied mangrove's sediments and in the sediments of mangrove of other areas of the
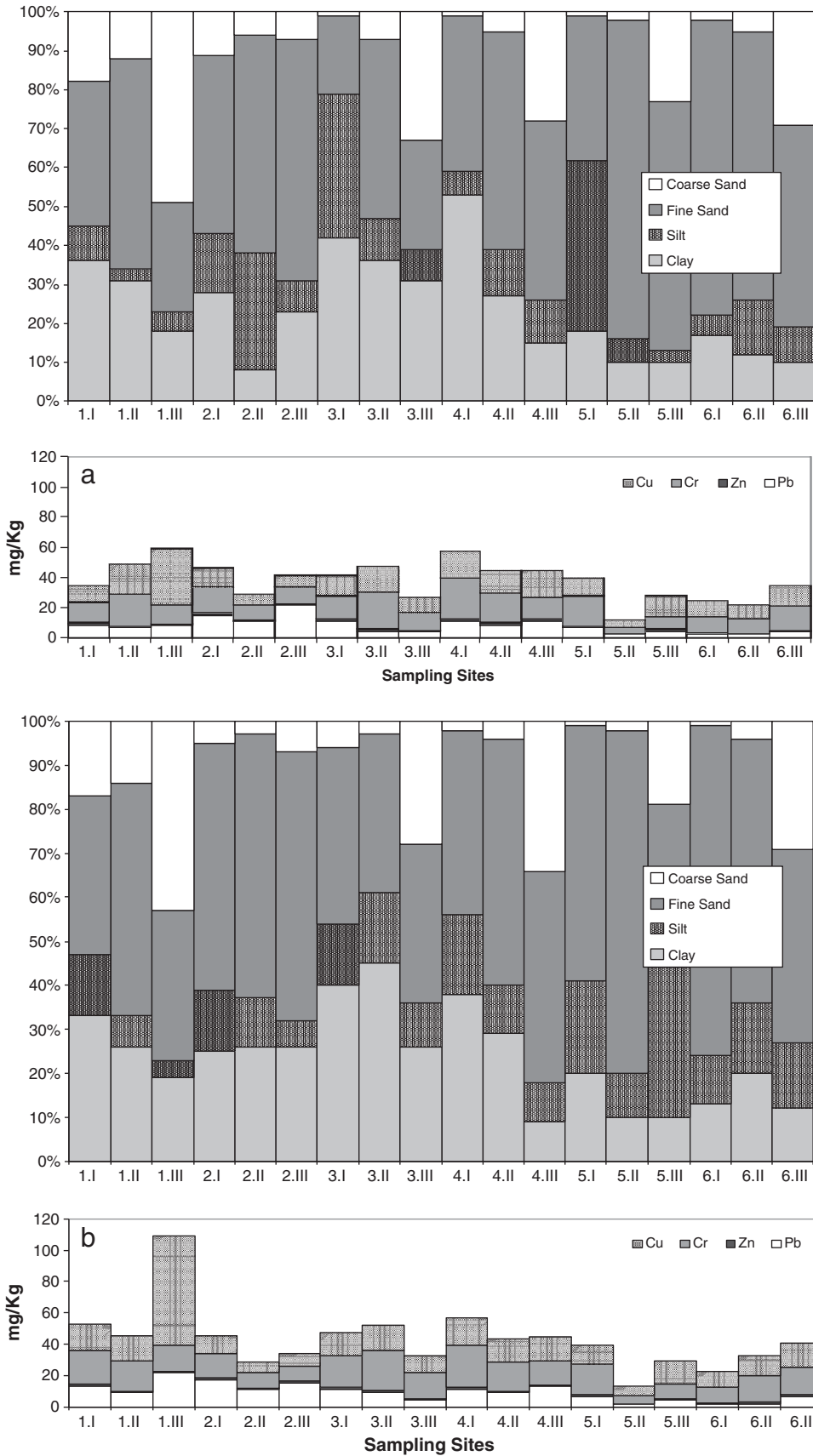
Fig. 2. a. Lateral and vertical variation of metal distribution and its correlation with particle size: samples collected from 0 to 25 cm of depth. Sites show in Fig. 1c. b (continued). Lateral and vertical variation of metal distribution and its correlation with particle size: samples collected from 25 to 50 cm of depth. Sites show in Fig. 1c.

Table 2
Statistics comparisons between three stands of sampling. The significance levels of distinction are considered by comparisons between the average analytical values for each stands.

Analytical Item	Contents presented in the Stands		Significance level (p) between Stands		
	Higher values	Lower values	I × II	I × III	II × III
O.M.	I	II	ns	**	**
Al	I	II	ns	*	ns
Fe	I	II	ns	**	ns
Cr	I	III	*	***	ns
Cu	III	I and II	*	ns	ns
Pb	III	II and III	**	ns	*
Zn	III	II	ns	*	ns

n s = no significant difference, * = $p<0.05$; ** = $p<0.01$, and *** = $p<0.001$.

Table 3
Linear correlation indexes (τ) for the analysed elements plus O.M., clay and sand in the studied sediments of the Sauípe river mangrove.

Sample	Al	Fe	Zn	Cr	Pb	Cu	Clay	Sand	O.M.	N
Al										
Fe	**0.909**									
Zn	**0.839**	**0.788**								
Cr	**0.919**	**0.877**	**0.788**							
Pb	0.189	0.129	0.225	0.198						
Cu	0.144	0.077	0.117	0.276	0.401					
Clay	0.652	0.667	0.653	0.672	0.280	0.065				
Sand	−0.661	−0.687	−0.688	−0.602	−0.187	0.079	−0.772			
O.M.	**0.706**	**0.849**	0.559	**0.707**	−0.113	−0.040	0.532	−0.562		
N	−0.249	−0.201	−0.329	−0.260	−0.221	−0.123	−0.158	0.152	−0.100	

Significant correlation coefficients ($\tau>0.7$) are in bold.

Bahia State [15,16] which were considered without any record of pollution [17].

4. Conclusions

For all the stations there is a clear trend of increasing in the coarse grained fractions as one goes from the river margin, which is the place that corresponds to stand I, towards stand III. The coarse sand fraction is higher for those samples collected at stand III and that correspond to those samples placed far from the river channel. This is because the sand grains from the dunes and beaches may be transported by the wind to these places where they were deposited and they rest without removal, since in these places (stand III). The effects of the hydrodynamic fluxes of the tides and the fluvial course become negligible.

Since the Al, Fe and Zn have a good correlation with Cr, it is suggested that these elements are mostly present as component of clay minerals as well as in the composition of the O.M. in which they may occur as adsorbed ions or forming organic complexes.

In terms of the distribution of the studied chemical elements, the substratum of the Sauípe River's mangrove shows values that fall within the normal background presented by unpolluted mangrove areas previously studied in the State. Also it is concluded that the heavy metals contents are lower than those values for standard shale and target [18].

Table 4
Average contents (mg/kg) of heavy metals in the sediments of mangroves from the estuarine areas of the Sauípe River (A). Paraguaçu River-Iguape Bay (B) and the Jacuipe River (C) to compare with theses for the standard shales (D) and target value (E).

Mangrove area [reference]	Pb	Zn	Cu	Cr
A – (this study)	8.26	1.05	14.15	14.77
B – [15]	8.80	47.80	13.60	64.20
C – [16]	12.60	44.95	15.20	57.10
D – [14]	20.00	95.00	45.00	90.00
E – [18]	85.00	140.00	36.00	100.00

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