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Série Tecnologia Ambiental

Heavy Metals in Estuarine Sediments Mangrove Swamps of the Subaé and Paraguaçu Tributary Rivers of Todos os Santos Bay, Bahia, Brazil

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PRESENTATION

This present work studies the dispersion of the heavy metals (Zn, Cu, Pb, Cd, Hg and Cr) and suporting elements (Fe and Mn) in the estuarines sediments of the Paraguaçu and Subaé Rivers.

The result thus obtained between 1991 and 1992 are compared to the results that were obtained ten years earlier on the same estuaries.

This work performed by Paredes, Queiroz, Carvalho, Ramos, Santos and Mosser is of great interest to the readers of this Series.

Rio de Janeiro, August, 1995.

Roberto C. Villas Boas
Director

CONTENTS

ABSTRACT

Different areas from Todos os Santos Bay were monitored and the fate of heavy metals in these environments determined. It was observed, from 1982 to 1992, a significant aggravation in the availability of heavy metals in the different sites of the Bay. However, it must be emphasized that the comparison between the present results and those obtained from other works is based in a gap of, at least, three years.

The determinations of heavy metals concentrations were based on analysis of the surface sediments of the different stations selected and the observed increase is probably to the transport of the elements by tidal dynamic and upstream riverine transport from industrial effluents.

Key words: *heavy metals, estuarine sediments*

RESUMO

Procurando examinar a dispersão de metais pesados em sedimentos de manguezais e de fundo de drenagem, os primeiros 25 centímetros desses sedimentos, retirados de testemunhos de sondagem, obtidos junto a 15 estações de estudo, foram analisados para Zn, Cu, Pb, Cd, Hg e Cr, além dos "elementos suportes" Fe e Mn. Os trechos estuarinos estudados foram os das duas principais bacias hidrográficas da região ocidental do Recôncavo da Bahia, correspondentes ao complexo estuarino do Rio Paraguaçu e ao estuário do Rio Subaé.

Os resultados das análises, obtidos entre 1991 e 1992, são comparados com resultados obtidos dez anos antes na região, em sedimentos semelhantes, através de trabalhos de monitoramento do governo estadual (Bahia-CEI, 1987). Nessa comparação, utilizou-se como padrão de referência os teores desses elementos indicados para folhelhos padrão por TUREKIAN & WEDEPOHL (1961). Também foram utilizados como referência os valores obtidos por um dos autores

(QUEIROZ, 1989) para sedimentos de manguezais do estuário do Rio Jacuípe, localizado ao norte da região do Recôncavo.

Mineralogicamente, os sedimentos estudados são constituídos de quartzo, caolinita, goethita e, subordinadamente, de clorita e ilita, sugerindo uma derivação a partir das coberturas dos granulitos e anfibolitos constituintes do embasamento cristalino arqueano, das rochas sedimentares mesozóicas do Grupo Brotas e da cobertura sedimentar cenozóica correspondente à Formação Barreiras.

As pesquisas efetuadas permitiram dignosticar uma situação crítica em relação à região estuarina do Rio Subaé. Nesta região, os teores mais recentes de Zn, Cu, Pb e Cd nos sedimentos estudados estão acima daqueles para o folhelho padrão, e, no decurso de uma década, sofreram um incremento cujos fatores, respectivamente, são da ordem de 2,6; 2,6; 13,0 e 4,2. Em relação ao complexo estuarino do Rio Paraguaçu, os valores estão abaixo, ou próximos dos correspondentes valores para o folhelho padrão, sendo a única exceção feita na zona de defluxo da Baía do Iguape com o Canal de São Roque, onde o Pb encontra-se 2,6 vezes mais enriquecido que o referido padrão.

Sugere-se o transporte fluvial, e a influência da dinâmica das marés, bem como das fumaças da refinaria de Mataripe, como os principais mecanismos da dispersão desses elementos. Entretanto, esses mecanismos, conjuntamente a outros fatores que podem contribuir com essa dispersão, carecem de estudos mais detalhados.

Palavras-chave: *metais pesados, sedimentos*

1. INTRODUCTION

The Todos os Santos Bay, Brazil's largest, lies in the State of Bahia and extends over 750 km². This bay belongs to the Reconcavo physiographic region, has a relatively high population density and also sustains a traditional variety of industrial, agriculture and pasture activities. Moreover, this region has exhibited for the last 20 years large urban and industrial development, including the industrial complexes of Subaé, near the City of Feira de Santana, and Aratu and Camaçari, near the City of Salvador.

The purpose of this paper is to examine the dispersion of Cr, Zn, Cu, Pb, Cd and Hg in the bed sediments and mangrove swamps located in two main estuaries: one of the Paraguaçu River, Maragogipe Region and the other of the Subaé River, Santo Amaro Region (Figure 1 and Figure 2), with the objective to study the behavior of these metals and their influences on that region. With this in mind, a comparison of these data with earlier data collected at the Paraguaçu and Subaé estuaries by the governmental agency Bahia-CEI (1987) will be discussed.

Both Paraguaçu and Subaé estuarine areas are characterized by marine influences. In the case of the Paraguaçu estuary, these influences are mainly observed during the low discharge period of the riverine flow which is controlled by the Pedra do Cavalo Dam, 20 km upstream the estuary. RAMOS (1993) emphasized that the flood-tide exhibited a larger influence in the Paraguaçu estuary, than the ebb-tide which ran only during more or less two hours, at least in the low discharge period. The flood-tide peaks occurred usually at the second and third hour of the flood. However, the faster currents observed were at the surface, in the beginning of neap-tide (August/1992), as it is shown in Figure 3. All this estuarine complex (Iguape Bay plus São Roque Channel) is characterized by an intense biological activity and a conspicuous organic matter corresponding to the eutrophication

of natural conditions. Indeed the Iguape Bay is bordered by a luxuriant mangrove vegetation responsible for the great amount of organic matter.

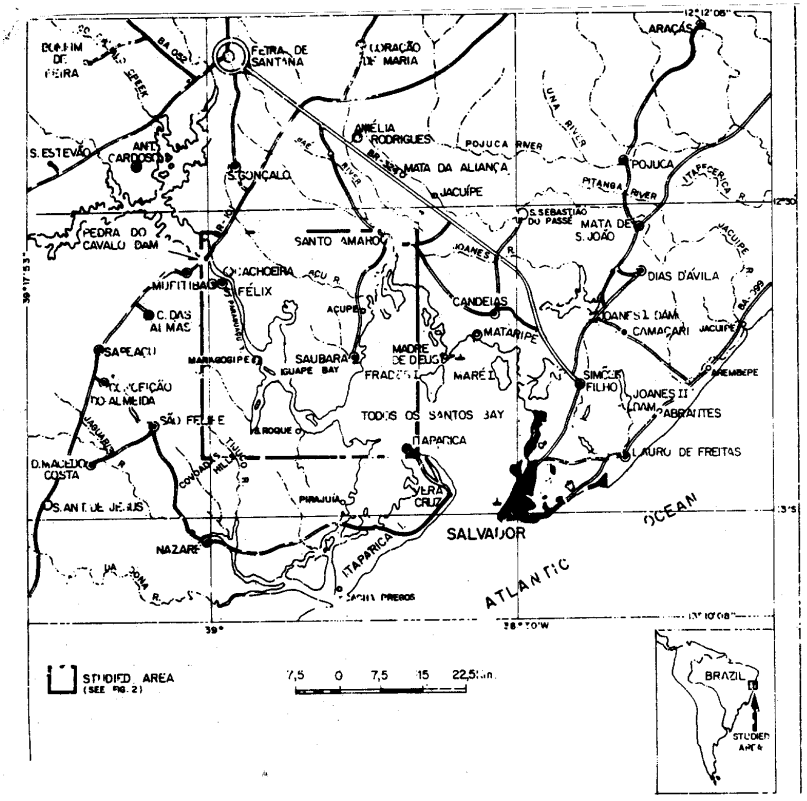

Figure 1 - General location of the study area.

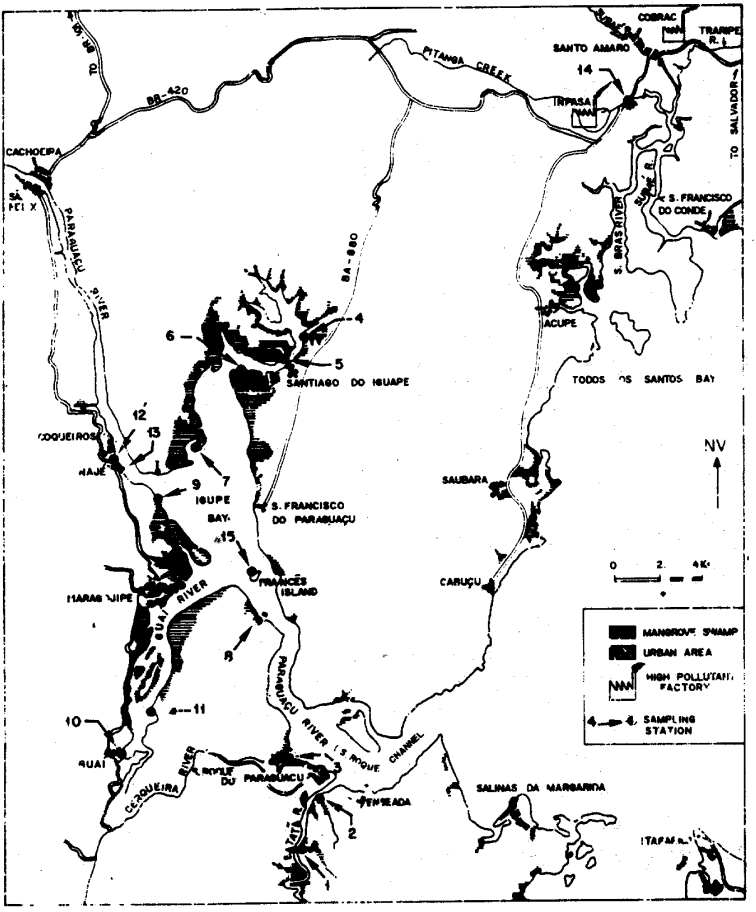

Figure 2 - Specific location of the sample stations in Todos os Santos Bay.

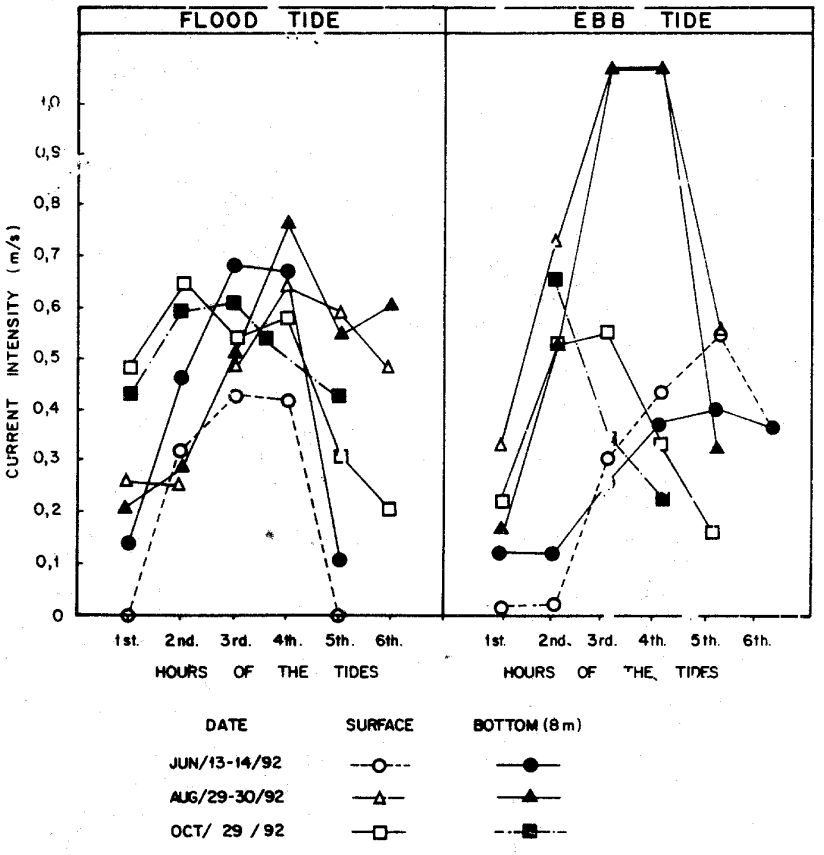

Figure 3 - Diagrams of current intensity during tides cycles monitored in the estuary of the Paraguaçu River.

2. METHODOLOGY

Fourteen sounding carrots of about 1 meter length and diameter of approximately 70 mm were collected from mangrove sediments at the Maragogipe lagoonal estuary, the São Roque Channel and at the narrow Subaé estuary, according to sampling points plotted in Figure 2 (stations 1 to 14).

The sediments carrots were then sectioned in 25 centimeter thick slices to model or pattern the heavy metals in question, according to the sediments depth (QUEIROZ, 1992). However, for the present study, only the uppermost slice (first 25cm) was considered.

Cr, Zn, Cu, Fe and Mn levels were measured at the Spectrochemical Analysis Laboratory of the Surface Geochemistry Center, Strasbourg, France, using the method described by SAMUEL et al. (1983). Hg, Cd and Pb were analyzed in the Atomic Absorption Spectrochemistry Laboratory of the ORSTOM Center, Bondy, France, using the method described by PINTA (1985).

Five bottom sediment samples were collected in front of the Frances Island, between the lagoonal estuary of Paraguaçu (Iguape Bay) and the São Roque Channel which connects the estuary with Todos os Santos Bay (station 15, Figure 2). These samples were obtained during the low defluent discharges period (June through October, 1992). The samples were taken at a depth of 10 meters below surface water, either in syzygya tides or neap tides with a Van Lee sampler. These five samples were then subjected to mineralogical study and chemical analysis. Zn, Cd, Pb and Cu were analyzed at the Atomic Absorption Laboratory of the Geochemistry Department, Federal University of Bahia (UFBA), using the method described by FLETCHER (1981). Hg was measured in the Atomic Absorption Laboratory of

the Bahia State Research and Development Center (CEPED), according to the method described by the U.S.Environmental Protection Agency (U.S.EPA, 1974).

3. RESULTS AND DISCUSSION

The corresponding results concerning to this paper are presented in Table 1 and Table 2.

Table 1 - Heavy Metals Concentrations in Surface Sediments for Stations 1 to 14.

Station	Fe_2O_3 %	Mn ppm	Zn ppm	Cu ppm	Pb ppm	Cd ppm	Hg ppm	Cr ppm
01	.50	78.1	15.3	6.8	5.3	.01	<.05	23.3
02	6.84	400.0	83.5	21.5	16.5	.12	<.05	109.0
03	5.08	186.0	59.5	14.6	12.0	.06	<.05	74.5
04	2.92	173.0	21.1	8.2	2.5	<.01	.30	36.1
05	7.09	337.0	78.9	31.9	15.5	.13	<.05	108.0
06	6.88	376.0	67.0	25.0	19.0	.16	<.05	112.0
07	4.43	206.0	44.6	8.6	4.0	<.01	<.05	33.9
08	3.17	175.0	28.0	10.1	5.5	.05	<.05	34.3
09	5.28	487.0	45.6	9.4	5.0	.07	<.05	107.0
10	2.05	122.0	39.1	9.5	4.0	.08	<.05	22.0
11	4.84	228.0	52.2	20.5	7.0	.14	<.05	67.7
12	3.84	230.0	47.5	10.4	8.5	.04	<.05	57.4
13	4.18	220.0	40.3	8.6	10.0	.08	<.05	49.0
$\bar{X}(n = 13)$	4.39	250.6	47.8	36.6	8.8	.07	<.05(n=12)	64.2
14	5.72	207.0	102.0	51.0	156.0	11.40	<.05	73.4

Table 2 - Heavy Metals Concentrations in Surface Sediments for Station 15.

Sampling Date	Fe_2O_3 %	Mn ppm	Zn ppm	Cu ppm	Pb ppm	Cd ppm	Hg ppm
06.14.92	.22	355.79	48.73	38.80	62.58	<1.3	.173
08.30.92	.20	233.57	43.13	45.11	50.90	<1.3	.232
09.20.92	.22	289.03	44.83	37.87	52.90	<1.3	.200
10.20.92	.20	240.67	43.24	33.37	44.70	<1.3	.200
10.26.92	.22	221.62	43.55	45.56	44.40	<1.3	.208
$\bar{X}$	.21	268.13	44.70	40.14	51.10	<1.3	.203

The results of the study carried out in 1982 by Bahia-CEI are in Table 3. Although other areas of the Todos os Santos Bay were researched by that governmental agency, only the data from the sediments of the mouth of Paraguaçu River and from the estuarine area of the Subaé River will be here reported.

Table 3 - Average Contents of Heavy Metals in Surface Sediments from Mangroves (M) and Estuaries (E) of the Studied Area, to Compare with those ones from the Jacuipe River and the Standard Shales.

Source	Fe_2O_3 %	Mn mg/kg	Zn mg/kg	Cu mg/kg	Pb mg/kg	Cd mg/kg	Hg mg/kg	Cr mg/kg
1. This paper (1992-1993)	4.39	250.6	47.8	36.6	8.8	0.07	<0.05	64.2
1.1 Paraguaçu Estuary (Frances Isl.) (E) RAMOS (1993)	0.21	268.1	44.7	40.1	51.1	<1.3	.203	-
1.2 Paraguaçu Estuary (Iguape Bay) (M) QUEIROZ (1992)	4.39	250.6	47.8	13.6	8.8	.07	<.05	64.2
1.3 Subaé Estuary (Santo Amaro) (M & E) QUEIROZ (1992)	5.72	207.0	102.0	51.0	156.0	11.4	<.05	73.4
2. Former Studies								
2.1 Subaé Estuary (1982) (E) Bahia-CEI (1987)	-	-	38.7	20.0	12.6	2.7	.019	-
2.2 Paraguaçu Estuary (1982) (E) Bahia-CEI (1987)	-	-	37.0	17.3	12.0	.4	.029	-
3. Other Areas								
3.1 Jacuipe Estuary (1989) (M & E) QUEIROZ (1989)	2.35	104.6	44.95	15.2	12.6	.05	-	57.1
4. Standard Shales TUREKIAN & WEDEPOHL (1961)	4.7	850.0	95.0	45.0	20.0	.3	.4	90.0

Table 3 also brings the average values of heavy metals concentrations in surface sediments from mangroves of the Paraguaçu (stations 1 to 13) and the Subaé (station 14) estuaries and in bottom sediments from the Paraguaçu River (station 15), as well as the average values obtained by QUEIROZ (1989) for the mangrove sediments from the estuary of the Jacuipe River, and those values indicated by TUREKIAN & WEDEPOHL (1961) for standard shales.

All the observations in the Paraguaçu lagoonal estuary were performed in the mean salinity of 30% (28-34%). This high salinity accounts to the halite crystals in the sediments collected due to the natural water evaporation in laboratory. The mineralogical composition of these sediments (quartz, kaolinite, goethite and minor chlorite and illite) (QUEIROZ, 1992; RAMOS, 1993), reflects the dominant lithologies at the region, as they are represented by the Crystalline Basement, and the sedimentary Brotas Group and the Barreiras Formation (INDA & BARBOSA, 1978).

The concentrations of Cr, Zn, Cu, Pb and Cd exhibited in the studied sediments are lower than the respective values indicated by TUREKIAN & WEDEPOHL (1961) for standard shales (Table 3). The sole exception is observed in the sediments from the mangrove of Santo Amaro, in the Subaé estuary (station 14), and also for Pb in the sediments collected in the station 15 (Frances Island). Besides these anomalous values, may be included here that one registered for Hg in the sediments from the Frances Island. They reveal the worse critical situation in the estuarine ecosystem of the Subaé River. On the other hand it should be stood out a significant aggravation of the regional environmental quality from 1982 to 1992. Also, it must be emphasized the fact that the values found in this study, excluding that one for Fe, in the Frances Island, and those for Cu and Pb, in the Iguape Bay are higher than the average values found by QUEIROZ (1989) for the recent sediments collected in the estuarine area of the Jacuipe River, east of the Reconcavo region (Figure 1), the basin of which drains the main industrialized area of the Reconcavo.

The heavy metals concentrations found in the samples reported to the Frances Island, when compared with those ones obtained in the mangroves of the Iguape Bay, lead us to outstand the higher concentrations of the Cu, Pb and Hg than those ones relative to the swamps in the same estuary. If compared with those concentrations obtained in 1982 by Bahia-CEI in the São Roque Channel, we may conclude that there are causes in course which they are getting worse the environmental conditions in this area. This situation arises the question: what is the direction of this transport? We believe that the main transport of those elements is carried out by tidal dynamic, being related with the conditions of Todos os Santos Bay. There must be also considered the action of the atmospheric plume from the Mataripe Petrol-Refinery (Figure 1), indeed, the fossil fuels sustain the most of heavy metals included in this study, since it does take the direction of the estuaries here referred when under the action of regional winds which blow from SE and E.

4. CONCLUSIONS

Concerned to this paper critical conditions were identified in both areas.

It should be stood out a significant aggravation of the environmental quality between 1982 and 1992 (Table 3), particularly on the estuarine waters of Subaé River, where all concentrations in heavy metals sharply increased in the sediments in the way that all of them largely overtook the concentrations of the standard shales, with the single exception for the Hg. The mentioned conditions relatively to Maragogipe area must be related with transport of these elements by tidal dynamic, while the influence in Subaé estuary must be mainly concerned with the riverine transport from upstream industrial effluents.

Comparing the concentrations of heavy metals exhibited in sediments obtained in front of Frances Island (Iguape Bay), we may see that the Pb largely exceeds the corresponding shale pattern, while the Cu almost reaches it. As regard the Cd we may also conclude that the situation is becoming critical, since even in 1982, the Bahia-CEI data concerning to São Roque Channel, transcend not only the permissible concentrations for the Cd (0.01 - 0.005mg/kg) but also it is above the standard shales (0.3mg/kg).

Regarding to the lagoonal estuary of Paraguaçu River, remains incognito the transport directions which give rise to the heavy metals mentioned in this study, chiefly on the behavior of Pb, Cu, Cd and Hg. Therefore, studies are recommended on this area in order to find out the lay-out of these transports, the accumulation of these heavy metals, their effects on the environment and the prognostic of their evolution.

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