

DISTRIBUTION AND ENRICHMENT OF HEAVY METALS IN SEDIMENTS AT THE TAPACURÁ RIVER BASIN, NORTHEASTERN BRAZIL

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ABSTRACT

Aprile, F.M. & Bouvy, M. 2008. Distribution and enrichment of heavy metals in sediments at the Tapacurá River Basin, Northeastern Brazil. *Braz. J. Aquat. Sci. Technol.* 12(1):1-8. ISSN 1808-7035. Distribution and enrichment of heavy metals in the sediments at the Tapacurá River basin (Northeastern Brazil) were examined. Sediment samples from eight sites in the basin were collected each three months in the period from April/1997 to January/1999 and between June/2005 and March/2006. Metal levels in sediments varied from 550 to 32,606 Fe, 13.46 to 157.62 Mn, 0.96 to 57.32 Cu, <0.01 to 1.31 Pb, <0.0005 to 3.30 Cd, 4.03 to 55.16 Zn, 0.06 to 6.53 Ni and 0.04 to 5.90 Cr mg g⁻¹ dw. The concentrations of metals in the industrial and agricultural areas were higher than those in the urban areas. The results demonstrated that terrigenous sediments from the industrial and agricultural areas are dominating factor controlling the spatial variations of heavy metals on the Tapacurá River. Grain size and anthropogenic influences are also major factors modifying the spatial variations of heavy metals. Pb and Cd had higher enrichment factors. The maximum potential contamination indices for the basin were 218 to Pb and 660 to Cd. The correlation analysis showed that the Fe and OM varied independently from one another, implies that the concentration of metals in sediments can not be interpreted simply by a change in grain size. The first step to apply a remedial measure is the inspection of the agricultural areas and the use controlled of fertilizers and herbicides. Information of this nature on heavy metals can provide valuable contribution to the program of sanitation at the Companhia Pernambucana de Meio Ambiente - CPRH.

Keywords: trace metal; grain size; Enrichment factor; Index of Contamination; Tropical River

INTRODUCTION

The toxicity of heavy metals on aquatic organisms and its equilibrium is influenced by some limnological factors, such as pH, alkalinity, hardness, salinity, organic matter, total solids, and sedimentation load (Golterman, 2004; Aprile *et al.*, 2005). Human activities can modify the geochemical cycle of heavy metals, resulting in an environmental contamination. Although heavy metals enter rivers and estuaries from many natural sources, one of the most important sources is municipal sewage. The absence of sewage treatment in cities and agricultural runoff in the Tapacurá river basin is responsible for the anthropogenic sources of metallic elements. Researches on the geochemistry of heavy metals in the sediments between the river basin and the surrounding areas are limited. This study examined the temporal and spatial distributions of heavy metals in the Tapacurá River basin sediments, and analyzed the major factors controlling the variations of sedimentary heavy metals. The present paper aims also (1) to establish the heavy metal levels in sediments to evaluate managing strategies of the river basin; (2) to identify sampling sites that had similar or different contamination source zones, and (3) to provide data-base necessary

for developing strategies for pollution control and sediment remediation of the basin. Information on the distribution and enrichment of heavy metals at the Tapacurá River can provide valuable contribution to the program of sanitation at the Companhia Pernambucana de Meio Ambiente.

MATERIAL AND METHODS

Study area

The Tapacurá River basin (Figure 1) is located in the Zona da Mata region in the state of Pernambuco – Northeastern Brazil. It has an average flow of 2.10 m³.s⁻¹ and covers an area of about 360 km². It receives water flows from four tributaries namely Água Azul River, Itapessirica River, Várzea Grande River and Natuba River which run through the cities of Pombos and Vitória de Santo Antão, and through the agricultural areas (Figure 1). There is not efficiently sewage system in the cities until today, and over 80% of domestic wastewaters are directly discharged into the tributaries without any treatment. The result is a high concentration of organic sewages in the aquatic resources. Moreover, there are agricultural and industrial areas located in or around

Tapacurá River basin that contribute a significant amount of untreated and/or minimally treated wastewater to the tributaries. Other pollution source in river basin is the “manipueira,” a solid/liquid waste from the improvement of cassava starches that have created great threat to the public health in Pombos city, and enormous impact to the biota due to high toxicity by heavy metals and cyanide acid (Aprile *et al.*, 2004).

Sampling stations

Overall, 92 sediment samples were collected each three months in the period from April/1997 to January/1999 and from June/2005 to March/2006 in the Tapacurá River and tributaries (Figure 1). Given that there was almost no previous data on heavy metal levels in the Tapacurá basin, a priori evaluation of possible pollution sources, anthropic activities, and river morphology was performed to select suitable stations for sample collection. This evaluation indicated that the ecological system of the Tapacurá River is strongly influenced by (I) human activities or domestic sewage, (II) agricultural runoff and (III) industrial plants. Eight sampling stations were selected along the river (Fig. 1 and Table 1).

Sample collection and grain-size analysis

About 3 kg sediment samples were obtained using 6” x 6” x 6” Ekman Dredge grab sampler, and the superficial 10 cm sample was retained for analysis. Samples were stored wet in sealed Zip-lock bags at -4 °C, and then transported to the laboratory for analysis. The chemical analysis was performed at the Laboratory

of Analytical Chemistry of the Companhia Pernambucana de Meio Ambiente and at the Laboratory of Water Chemistry of the Instituto Nacional de Pesquisas da Amazônia. Wet sediment samples were placed in an oven at 105 °C and heated to a constant weight (Bighman & Bartels, 1996). The sediment fractions were homogenized and passed through 2.0, 1.0, 0.5, 0.25, 0.125, 0.062, and 0.031 mm sieves for grain-size analysis (sand, silt, and clay). To remove large pebbles in the sediments they were passed through a 60-mesh sieve and subsequently the sub-samples were passed through 270-mesh (0.062 mm) sieve before being used in the adsorption trials (for details see 2.4 Sediment analysis).

Sediment analysis

In brief, analysis of total organic matter content (OM) in the dry sediments was performed using the wet oxidation method with a hydrogen peroxide solution at 100 °C for four hours (Bighman & Bartels, 1996). Organic carbon (C_{org}) following carbonate removal with 1M HCl was determined on freeze-dried sediment using an elemental analyzer (LECO SC-1440H). The total metals (Fe, Mn, Cu, Pb, Cd, Zn, Ni and Cr) were digested using mixture (HNO₃ + HCl)-HClO₄-HF (Merck 2:1:1) in an open system as described in APHA (1998) and Hyacinthe & Van Cappellen (2004). Samples (10 g) were treated with 40 ml of the acid mixture, heated at 200 °C to insipid dryness, re-digested in 5 ml of HClO₄ and made up to 50 ml in a volumetric tube (Loring & Rantala, 1992). Metal concentrations were determined by flame

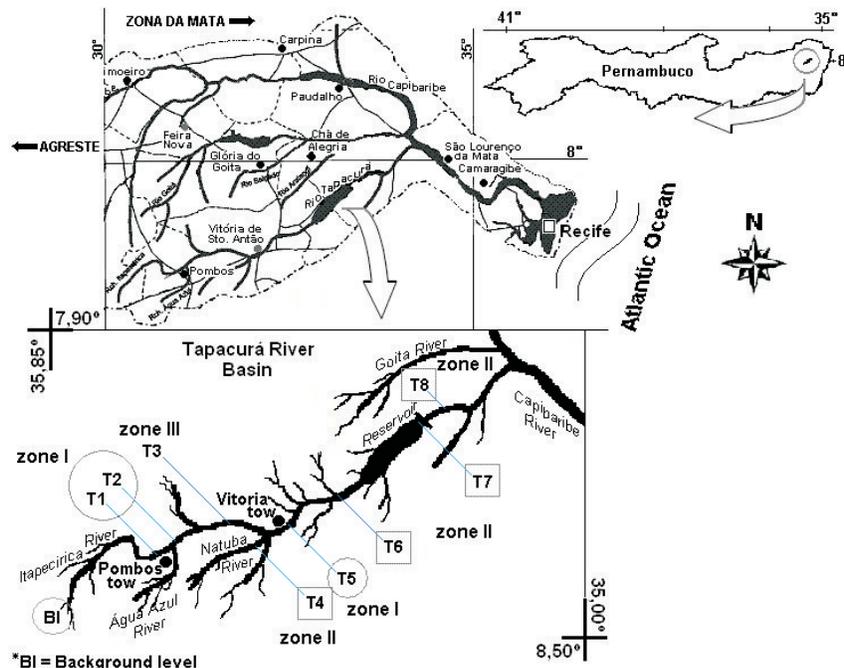


Figure 1 - Location of sampling sites in the Tapacurá River basin, Pernambuco State, Northeastern Brazil.

Table 1 - Locations of the eight sampling stations along the Tapacurá River basin.

Station	Zone	Description	GPS position
T1	I	Itapecirica River near the Pombos district	08°07'53"S;35°24'58"W
T2	I	Tapacurá River upstream Vitória de Santo Antão district	08°07'26"S;35°22'29"W
T3	III	Tapacurá River at the spirit company Pitú	08°07'11"S;35°19'15"W
T4	II	Natuba River in an agricultural area	08°10'56"S;35°20'22"W
T5	I	Tapacurá River downstream Vitória de Santo Antão district	08°05'55"S;35°15'37"W
T6	II	Tapacurá River at the Manain farm	08°05'57"S;35°14'39"W
T7	II	Tapacurá Reservoir	08°02'12"S;35°09'44"W
T8	II	Supply line located about 300 meters downstream of the dam	08°02'06"S;35°09'39"W

atomic absorption spectrometry using Perkin-Elmer AAS 3300 using air-acetylene flame. Blanks and standard reference materials (SRMs) were included in the analysis to verify the accuracy of the extraction method. Quantification of trace metal concentrations was based upon calibration curves involving standard solutions prepared from a commercial stock solution (trace metals 1 ICM-411H in 5% HNO₃, Radian International LLC) and use of standard seawater reference materials (CASS 1-4 and SLEW 1) from the National Research Council of Canada. These calibration curves were determined several times during the period of analysis. The detection limits were 0.05 Fe; 0.02 Mn; 0.001 Cu; 0.01 Ni, Cr, Pb and Cd, and 0.003 Zn mg g⁻¹.

Data analysis

The extent of metal contamination compared to the background area (see "Ba" Figure 1) was assessed using the enrichment factor (EF, *Woitke et al., 2003; Selvaraj et al., 2004*). Metal concentrations were normalized to the textural characteristic of sediments with respect to Fe. Iron was selected because it is a major sorbent phase for trace metals, and is a quasi-conservative tracer of the natural metal-bearing phases in fluvial and coastal sediments (*Schiff & Weisberg, 1999; Turner & Millward, 2000*). Therefore, EF was defined as:

$$EF = \left\{ \frac{[Metal]_{\text{sediment}}}{[Fe]_{\text{sediment}}} \right\} / \left\{ \frac{[Metal]_{Ba}}{[Fe]_{Ba}} \right\}$$

An estimate of the amount of metallic elements detectable from sediment analysis was obtained using the potential contamination index (C_p) demonstrated by *Davault & Rognerud (2001)*. Therefore, $[Metal]_{\text{max}}$ is the maximum concentration of a metal in sediment, and $[Metal]_{Ba}$ is average value of the same metal in a background level (see "Ba" Figure 1).

$$C_p = [Metal]_{\text{max}} / [Metal]_{Ba}$$

A Pearson Correlation coefficient matrix was determined to heavy metals, OM, C_{org} and to the categories of sediment (sand, silt, and clay). The data were analyzed by hierarchical cluster analysis using the complete linkage method as an amalgamation rule.

RESULTS AND DISCUSSION

Textural characteristics of the sediments are showed according to the classification of Shepard (*Shepard & Moore, 1954*). Grain sizes display medium to large variations in the Tapacurá River basin surface sediments. Results showed that course sand (CS 1.0-0.5 mm) and medium sand (MS 0.50-0.25 mm) were the dominant fractions of all sediment samples, with range from 12.5 to 29.7% and 12.7 to 43.2%, respectively. Total means for all study area were $19.7 \pm 4.2\%$ course sand and $23.9 \pm 8.4\%$ medium sand. Other results were pebbles with $16.2 \pm 6.6\%$; very coarse sand (2.0-1.0 mm) $15.7 \pm 6.7\%$; fine sand (0.250-0.125 mm) $11 \pm 5.2\%$; very fine sand (0.125-0.062 mm) $7.4 \pm 5.4\%$, and silty more clay (< 0.031 mm) with $0.15 \pm 0.21\%$ (Table 2). Stations T1, T3 and T8 had the highest sand contents (99.1-99.6%) and the lowest silt and clay contents (0.01-0.02%), while stations T6 and T7, located at the agricultural area (zone II), had the lowest sand content (93.7-93.8%) and the highest silt and clay contents (0.19-0.70%, Table 2 and Figure 2). The more effective contribution in the stations was the fluvial deposition with high values of course sand. This dominance of sand (Figure 2) was related to the high sandy content of natural soils in the area bordered with Agreste region. In general, sediments displayed a normal grain size distribution (symmetrical distribution), with the exception of station T6, located in agricultural area. In that station, sediments displayed a bimodal size distribution. The bimodality indicated that the samples were not homogeneous. In fact, the bimodal appearances of sediment grain sizes indicated that sediments in the station T6 were composed of a mixture between the fine-grained Natuba River sediment and the coarse-grained Tapacurá River sediment.

Among the factors influencing the accumulation of nutrients, particle size played a significant role. Fine-grained sediments often show higher concentrations of nutrients due to their greater surface-to-volume ratio and enrichment of OM (*Wang et al., 2004*). Mean organic matter contents in sediments at the Tapacurá River basin were in the range of 0.4–6.1% dw (Figure 2). The results showed that the anthropogenic contribution from discharge of domestic sewage at the Vitória de Santo Antão city was an important source of OM to the station

Table 2 - Mean values (%) of the grain-size analysis at the Tapacurá River basin stations (n=48).

Station	Pb	VCS	CS	MS	FS	VFS	St+Cy
T1	14.7	15.4	29.7	32.5	5.2	2.1	0.02
T2	10.4	6.6	14.6	43.2	15.0	7.7	0.07
T3	30.7	19.6	19.3	18.6	6.0	5.1	0.02
T4	8.0	16.0	19.7	24.6	21.5	8.6	0.12
T5	23.3	25.4	23.6	15.5	4.7	3.2	0.11
T6	8.6	4.8	12.5	26.9	17.3	23.7	0.19
T7	15.6	13.4	18.3	21.5	15.9	9.0	0.70
T8	22.9	28.7	24.0	12.7	6.5	4.3	0.01
mean	16.2	15.7	19.7	23.9	11.0	7.4	0.15
SD	6.6	6.7	4.2	8.4	5.2	5.4	0.21

Pb= pebbles; VCS= very course sand; CS= course sand; MS= medium sand; FS= fine sand; VFS= very fine sand; St+Cy= silte more clay.

T5. High values of organic content at the stations T6 and T7 were due to agricultural activities around Tapacurá reservoir (zone II). The level of OM in the Tapacurá basin was not high in contrasts the others Brazilian rivers. Brigante *et al.* (2003a) found levels of OM ranged from 0.9 to 48% in the rivers Peixe, Espirado, and Mogi-Guaçu. The organic carbon content ranged from 0.2% dw (T1) to 3.3% dw (T7) with total average $1.6 \pm 0.9\%$. Organic carbon concentrations increased reservoir ward, reflecting a corresponding decrease of the sediment grain size. The highest C_{org} contents occurred at the stations that had the lowest sand contents and the highest silt and clay contents (Figure 2).

Table 3 presents the mean \pm SD, minimum, and maximum concentrations of heavy metal in the surface sediments of all stations studied in the Tapacurá River basin. The concentrations of heavy metals in the sediments were higher at stations T3, T4 and T7 that were identified as hotspots. Heavy metal concentrations in sediments are strongly determined by local geology or anthropogenic influences. The weathering of minerals is one of the major natural sources, while anthropogenic sources include use of fertilizers and herbicides, irrigation, industrial effluent, and leakage from service pipes. In the industrial area (T3) and agricultural activities (stations T4, T6-T8) are likely to be the major contamination sources because of the presence of these actions.

Trace metal concentrations varied substantially in the period of study. The coefficients of variation ranged from 7.77% for Mn to 200% for Pb both at site T8. Iron levels were highest at station T3 ($19.83 \pm 12.57 \times 10^3 \mu\text{g g}^{-1}$). High values were also found at station T4 ($8.28 \pm 1.31 \times 10^3 \mu\text{g g}^{-1}$) and T7 ($9.79 \pm 2.19 \times 10^3 \mu\text{g g}^{-1}$). Total Fe ranged from 0.55 to $32.61 \times 10^3 \mu\text{g g}^{-1}$. The metal Fe is to consider the main factor that determines adsorption capacity, because of the high specific surface of the Fe^{3+} and Al^{3+} . Moderately high iron levels are also noted

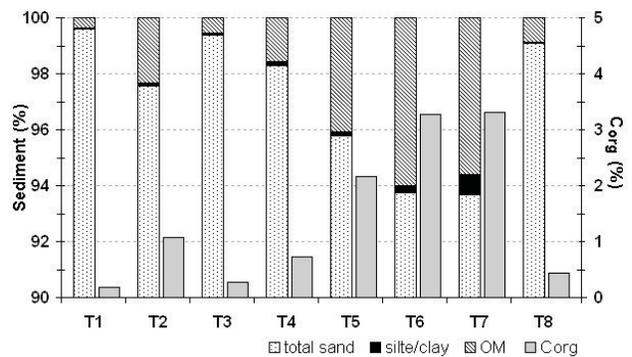


Figure 2 - Characteristics of the sediments at the Tapacurá River basin.

in the sediments that are consistent with high levels of iron in local surface soils (Bighman & Bartels, 1996). Total Mn showed higher concentrations at stations T4 ($88.57 \pm 44.19 \mu\text{g g}^{-1}$); T7 ($77.92 \pm 9.31 \mu\text{g g}^{-1}$) and T8 ($69.12 \pm 5.37 \mu\text{g g}^{-1}$). The lowest levels of Mn were found at station T2 ($28.81 \pm 14.84 \mu\text{g g}^{-1}$) in the Tapacurá River upstream from Vitória de Santo Antão city and at station T6 ($20.80 \pm 4.83 \mu\text{g g}^{-1}$). Copper is widely distributed in aquatic ecosystems because it is a naturally occurring element. However, Cu and Zn concentrations are greatly influenced by anthropogenic sources (IPCS, 1998). Total Cu showed higher concentrations at stations T3 and T4 with $24.87 \pm 20.12 \mu\text{g g}^{-1}$ and $36.13 \pm 9.97 \mu\text{g g}^{-1}$, respectively. Total Zn also showed similar trends with highest level at stations T2-T4 and T7. The results showed an increasing of zinc in the sediments by domestic and industrial wastewaters, and agricultural runoff. The exception was the site T1 that showed lower concentrations for this element. The total lead load does not show any significant spatial or temporal variation when as compared to the others tropical rivers (Eysink *et al.*, 1988; Brigante *et al.*, 2003b; Siqueira, 2003; Jain, 2004; Muniz *et al.*, 2004; Olivares-Rieumont *et al.*, 2005), suggesting that this element was preferentially deposited there by natural occurrence. Total lead ranged from ≤ 0.01 (detection limit) to $1.31 \mu\text{g g}^{-1}$. Cadmium and chromium average levels not exceeded world average levels for surface rock exposed to weathering (Turekian & Wedepohl, 1961), except to Cd at site T7 ($2.22 \pm 1.14 \mu\text{g g}^{-1}$). Likewise, their concentrations were lower than others tropical rivers (Eysink *et al.*, 1988; Brigante *et al.*, 2003b; Siqueira, 2003; Jain, 2004; Olivares-Rieumont *et al.*, 2005). Total Cr ranged from 0.04 to $5.90 \mu\text{g g}^{-1}$, and the higher concentration was observed at site T3 ($4.25 \pm 1.08 \mu\text{g g}^{-1}$). Total Ni levels remains more or less constant along the river basin with variation from 0.06 to $6.53 \mu\text{g g}^{-1}$ (Table 3).

The enrichment factor (EF) values (Table 4) were interpreted with support of the classification of Taylor (1964) to abundance of heavy metals in the continental

Table 3 - Concentrations (mean \pm SD) and range of trace metals (mg g⁻¹ dry weight) in the surface sediments of the Tapacurá River basin.

Site	Fe/10 ³	Mn	Cu	Pb	Cd	Zn	Ni	Cr
T1	4.15 \pm 0.55	32.53 \pm 8.24	5.63 \pm 0.68	0.08 \pm 0.08	-	7.82 \pm 1.85	0.39 \pm 0.03	0.81 \pm 0.26
(n= 10)	3.38 – 4.83	22.52 – 40.18	4.94 – 6.45	<0.01 – 0.17	<0.01	5.70 – 10.38	0.33 – 0.41	0.54 – 1.20
T2	5.51 \pm 4.33	28.81 \pm 14.84	7.31 \pm 6.57	0.16 \pm 0.18	-	20.58 \pm 5.60	0.53 \pm 0.42	0.45 \pm 0.55
(n= 11)	1.30 – 9.59	13.46 – 42.80	1.05 – 13.52	<0.01 – 0.36	<0.01	14.30 – 28.18	0.12 – 0.93	0.04 – 1.33
T3	19.83 \pm 12.57	51.58 \pm 35	24.87 \pm 20.12	0.35 \pm 0.35	0.22 \pm 0.03	36.28 \pm 14.82	3.93 \pm 2.30	4.25 \pm 1.08
(n= 12)	6.78 – 32.61	19.14 – 92.18	11.82 – 57.32	0.03 – 0.74	0.19 – 0.25	20.80 – 55.16	1.63 – 6.53	3.16 – 5.90
T4	8.28 \pm 1.31	88.57 \pm 44.19	36.13 \pm 9.97	0.67 \pm 0.56	0.23 \pm 0.04	25.64 \pm 4.74	0.80 \pm 0.52	3.32 \pm 0.52
(n= 12)	6.87 – 10.07	48.42 – 157.6	23.91 – 45.78	0.01 – 1.31	0.18 – 0.27	21.42 – 33.09	0.27 – 1.47	2.66 – 3.78
T5	1.25 \pm 0.48	61.24 \pm 23.36	3.65 \pm 1.80	0.01 \pm 0.01	-	11.46 \pm 1.64	0.40 \pm 0.18	0.55 \pm 0.53
(n= 12)	0.55 – 1.79	40.03 – 90.57	0.96 – 5.45	<0.01 – 0.02	<0.01	8.95 – 12.99	0.14 – 0.58	0.12 – 1.38
T6	4.44 \pm 2.52	20.80 \pm 4.83	6.96 \pm 5.06	0.09 \pm 0.09	-	14.17 \pm 10.59	0.18 \pm 0.11	1.26 \pm 0.44
(n= 11)	1.86 – 7.21	15.46 – 25.30	3.20 – 15.05	<0.01 – 0.19	<0.01	4.03 – 24.18	0.06 – 0.32	0.62 – 1.77
T7	9.79 \pm 2.19	77.92 \pm 9.31	8.24 \pm 1.46	0.20 \pm 0.22	2.22 \pm 1.14	23.72 \pm 4.01	0.66 \pm 0.27	0.99 \pm 0.49
(n= 12)	7.94 – 12.86	63.77 – 85.86	6.82 – 10.24	<0.01 – 0.45	1.11 – 3.30	19.98 – 27.74	0.33 – 1.00	0.48 – 1.45
T8	6.51 \pm 1.94	69.12 \pm 5.37	7.61 \pm 3.89	0.01 \pm 0.02	-	12.01 \pm 5.07	1.29 \pm 0.33	2.05 \pm 0.53
(n= 12)	5.05 – 9.57	60.73 – 74.08	3.58 – 11.28	<0.01 – 0.04	<0.01	7.47 – 19.87	0.83 – 1.70	1.51 – 2.86

crust, and based in the values of a background area near to the basin (see “Ba” Figure 1). The EF of some heavy metals as chromium (eight stations EF <1), zinc and nickel (seven stations EF <1) indicated there is not enrichment by these metals in the sediments of the basin. This result means that these metals in the sediments of the river basin are close to background levels. High EF values as 20.5 for Pb in T4 and 68.4 for Cd in T7 both in zone II (Fig. 1) can mean a high amount of metallic discharge from agricultural runoff. Enrichment factor is a good tool to differentiate the metal source between anthropogenic and naturally occurring (Woitke *et al.*, 2003; Selvaraj *et al.*, 2004; Adamo *et al.*, 2005).

Potential contamination indices (C_p , Table 4) showed that 54.7% of the samples were higher than three indicated severe or very severe contamination by heavy metals in the sediments. The metals that showed the most extensive contamination were Fe (ranged from 1.2 – 21.4) and Pb (ranged from 3.3 - 218.3). The highest contamination index, however, was determined to the Cd ($C_p = 660$) in the site T7. The heavy metals that showed the narrowest contamination were Cr and Ni. The sampling sites T3, T4, and T7 showed the highest degree of anthropogenic impact estimated based in the C_p to the sediments of the Tapacurá basin. According to National Recommended Water Quality Criteria Correction by U.S. Office of Water Drinking Water and Health (US-EPA, 1999), and reports on the establishing of safe values to heavy metals in soil, water and human health (WHO, 1996; CETESB, 2001), in the Tapacurá

River basin was not observed high levels of contamination by heavy metals in the sediments.

Pearson Correlation was determined to the limnological parameters with base on eight sampling sites (n= 92), and significance at $p < 0.050$. Fe correlation was high for Mn and Cu (both $r^2 = 0.78$) and Cr ($r^2 = 0.73$), and stronger for Zn ($r^2 = 0.88$) and Ni ($r^2 = 0.92$). Sand concentrations displayed stronger negative correlations with OM ($r^2 = -0.99$) and C_{org} ($r^2 = -0.99$). The concentrations of Cu and Cr in sediments of the Tapacurá River were also strongly correlated ($r^2 = 0.81$), suggesting similar associations between that metals in the lake bottom. Sediment grain size is one of the main controlling factors for the distribution of heavy metals in an aquatic ecosystem, normally presented strong negative correlation with metals. The distribution of grain size and organic matter content are two critical factors that influencing the metal distribution in sediments (Aloupi & Angelidis, 2001; Liaghati *et al.*, 2003). Course sand particles with diameter ≥ 0.5 mm consist of geological minerals (e.g. quartz, feldspars), and the heavy metals in these fractions are principally in the crystalline solid form and are environmentally immobile. The fine particles as silt, clay, and colloidal materials yet are generally surface-active and contain OM and Fe/Mn oxide in association, which can contribute to the deposition of metals. In this research, the correlation of Pearson showed that the concentrations of Fe/Mn and OM in the sediment varied independently from one another. Other important fact observed the correlation

Table 4 - Degree of anthropogenic impact estimated based in the enrichment factor (EF)* and potential contamination index (C_p)** to the sediments of the Tapacurá River basin.

	Fe		Mn		Cu		Pb		Cd		Zn		Ni		Cr	
	EF	C _p	EF	C _p	EF	C _p	EF	C _p	EF	C _p	EF	C _p	EF	C _p	EF	C _p
T1	1.0	3.2	0.5	1.6	0.5	1.4	5.0	28.3	0.4	1.0	0.4	1.4	0.4	1.0	0.3	1.1
T2	1.0	6.3	0.3	1.7	0.4	3.0	7.5	60.0	0.3	1.0	0.8	3.8	0.4	2.3	0.1	1.2
T3	1.0	21.4	0.2	3.6	0.4	12.7	4.5	123.3	3.4	50.0	0.4	7.4	0.8	16.3	0.3	5.4
T4	1.0	6.6	0.6	6.2	1.5	10.2	20.5	218.3	8.3	54.0	0.6	4.4	0.4	3.7	0.6	3.4
T5	1.0	1.2	2.9	3.6	1.0	1.2	2.0	3.3	1.2	1.0	1.9	1.7	1.2	1.5	0.6	1.3
T6	1.0	4.7	0.3	1.0	0.5	3.3	5.0	31.7	0.3	1.0	0.6	3.2	0.2	0.8	0.4	1.6
T7	1.0	8.4	0.5	3.4	0.3	2.3	5.3	75.0	68.4	660.0	0.5	3.7	0.3	2.5	0.1	1.3
T8	1.0	6.3	0.6	2.9	0.4	2.5	0.4	6.7	0.2	1.0	0.4	2.6	0.8	4.3	0.4	2.6

* EF <1 no enrichment; EF ³¹-<3 minor enrichment; EF ³³-<5 moderate enrichment; EF = ³⁵-<10 moderately - severe enrichment; EF ³¹⁰-<25 severe enrichment; EF ³²⁵-<50 very severe enrichment and EF ³⁵⁰ extremely severe enrichment (Taylor, 1964). ** C_p >3 (**bold**) P severe contamination.

analysis was weaker between the metallic elements and the sedimentary fractions. This implies that the concentration of heavy metals in sediments cannot be interpreted simply by a change in grain size can be involved other physical-chemical processes.

Table 5 shows the average metal concentrations reported in sediments from different tropical regions of the world in comparison with this work. Trace metal concentrations showed a conservative behavior in sediments of the Tapacurá River. The exceptions were Fe with SD range from 0.48 to 12.57 x10³ µg g⁻¹ and Mn (moderate to high SD – range from 4.83 to 44.19 µg g⁻¹, see Table 3). A general increase in the sediment metallic fraction from river to site T7 was observed, due to the decrease of the water flux at the reservoir.

Cluster analysis (Fig. 3) was engaged to quantitatively identify areas with similar characteristics of metallic concentration. Heavy metal concentrations in sediments can very greatly depending on the source natural or anthropogenic such as, sewage, lixiviation including agricultural runoff, and erosion processes. A major cluster can be seen with zones I (domestic sewage) and II (agricultural activities). The station T3 was isolated owing to its typical pollution sources (zone III = industrial activities). A strong cluster includes stations T4, T6, T7 and T8 was observed which represents moderately to severe contamination by heavy metals in the sediments. Probably, one of the most important natural factors controlling the spatial variations of the heavy metals in the sediments included limnological processes, such as sorption and adsorption. Heavy metals in water-sediment interface can combine with different organic groups, such as amino acids, peptides, proteins, and carbohydrates. The association occurs between the metallic ion and the functional group

(e.g. carboxyl acid or amine) of the organic compound. The oxygen level in the water can influence in the velocity of this association. Its concentration can regulate metabolic rates of benthonic organisms and decomposition processes.

Results indicate that heavy metals are been accumulated in the sediments of the basin, and they are greatly influenced by anthropogenic sources that include use of fertilizers and herbicides, municipal sewage, and industrial effluents. Chemical adsorption between the metals, grain size, and organic matter contributed largely in the metal immobilization process. The colloidal complex OM-metal can be stable in the sediment. In the Tapacurá River basin, there is not a program to remediate the contaminated water or sediments by heavy metals. We believe that the first step to apply a remedial measure and management strategies is the inspection of the agricultural areas surrounding of the basin, and the use controlled of fertilizers and herbicides. Heavy metal reduction from sources such as municipal sewage and industrial effluents is a more practicable approach.

CONCLUSIONS

The heavy metals showed a heterogeneous horizontal distribution. In the Tapacurá River basin was not observed high levels of contamination by heavy metals in sediments according to criterions at the US-EPA (1999), WHO (1996) and CETESB (2001). However, data analyses by EF and C_p indicated contamination by Pb and Cd in the river basin. The metallic levels in the industrial and agricultural areas were higher than those in the urban areas, and consequently hotspots of

Table 5 - Concentration of heavy metals in sediments of different rivers of the world (mg g⁻¹).

Region	Fe	Mn	Cu	Pb	Cd	Zn	Ni	Cr	Source
World average	46 700	850	45	20	0.3	95	68	90	Turekian and Wedepohl (1961)
Almendares river, Cuba	-	-	158	93	2.5	262	-	138	Olivares-Rieumont <i>et al.</i> (2005)
Yamuna river, India	-	-	22	58	10.1	62	-	-	Jain (2004)
Montevideo harbor, Uruguay	-	-	58-135	44-128	<1-1.6	174-491	-	79-253	Muniz <i>et al.</i> (2004)
Ribeira river, SE Brazil	-	-	7-60	4-4000	0.2-5.5	15-4090	-	-	Eysink <i>et al.</i> (1988)
Mogi-Guaçu river, SE, Brazil	36 400	51-332	2.8-49	5.1-109	0.01-5	12-103	19.3-44	5.4-135	Brigante <i>et al.</i> (2003b)
Amazon River mouth, Brazil	38 300	600	37.5	83	-	110	26.7	65	Siqueira (2003)
Pará River mouth, NE Brazil	44 500	700	37.0	95.5	-	122	32.5	75	Siqueira (2003)
Tapacurá river, NE Brazil	7470	53.8	12.5	0.2	0.3	18.9	1.1	1.7	Present study

contamination were identified. The results indicated the potential pathways of heavy metals via the transport of sediment from the agricultural areas to the reservoir.

Statistical analysis indicated a conservative behavior by the trace metals in the Tapacurá River, exceptions to Fe and Mn. Results indicate also that heavy metals are been accumulated in the sediments of the basin, and they are deeply influenced by anthropogenic sources such as fertilizers and herbicides, municipal sewage, and industrial effluents. The accumulation of metal contaminants in sediments can pose serious environmental problems to the surrounding areas. Results can help develop management strategies for pollution control and sediment remediation mainly in the agricultural areas surrounding of the basin with severe contamination.

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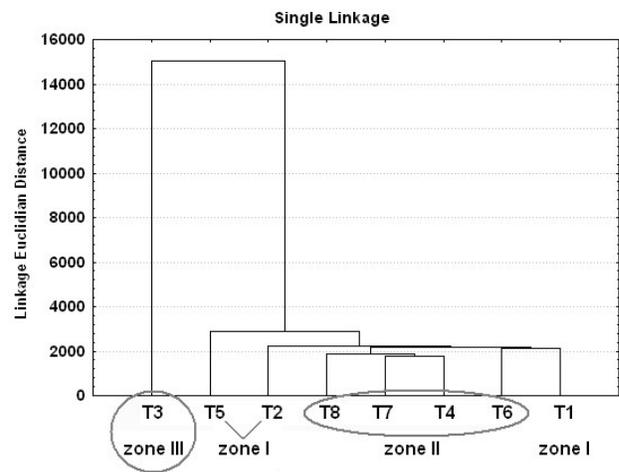


Figure 3 - Dendrogram indicating relatedness of sample sites with heavy metal concentration among the eight sampling stations.

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