

# Heavy metal levels in surface waters from a tropical river basin, Pernambuco State, northeastern Brazil

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**ABSTRACT.** Monthly, the distribution and enrichment of heavy metals (Fe, Mn, Cu, Pb and Zn) in surface waters were examined at eight sampling sites, in Tapacurá river (Pernambuco State, Brazil), from March 1997 to December 1998 and from June 2005 to March 2006. On average, metal levels ranged from 0.30 to 4.22 for Fe; 0.02 to 1.09 for Mn; 0.001 to 0.014 for Cu;  $\leq 0.006$  to 0.029 for Pb and 0.003 to 0.020 for Zn, all in mg L<sup>-1</sup>. Heavy metals presented a great heterogeneous horizontal distribution, with hotspots in municipal and agricultural areas. The enrichment factor (EF) and the potential contamination index (C<sub>p</sub>) indicated moderate to severe contamination by Cu and Zn. The results pointed the potential pathways of trace metals via the transport of soil for the river basin, mainly from agricultural areas, and inefficient sewage treatment at the cities. The first step to apply a remedial measure is the inspection of the agricultural areas, the controlled use of fertilizers and herbicides, as well as the development of an efficient sewage treatment to urban areas.

**Key words:** trace metal distribution, water quality, enrichment factor, index of contamination, anthropogenic sources.

**RESUMO.** Níveis de metais pesados em águas superficiais de um rio tropical, Estado de Pernambuco, Brasil. Mensalmente, a distribuição e o enriquecimento de metais pesados (Fe, Mn, Cu, Pb e Zn) em águas superficiais foram analisados em oito pontos de amostragem no rio Tapacurá, Estado do Pernambuco, Brasil. O estudo foi realizado entre março/1997 e dezembro/1998 e entre junho/2005 e março/2006. Em média, o nível de metais pesados variou em mg L<sup>-1</sup> entre 0,30 e 4,22 Fe; 0,02 e 1,09 Mn; 0,001 e 0,014 Cu;  $\leq 0,006$  e 0,029 Pb e 0,003 e 0,020 Zn. Os metais mostraram distribuição horizontal heterogênea grande com ênfase nas áreas municipais e agrícolas. O fator de enriquecimento (EF) e o índice de contaminação potencial (C<sub>p</sub>) indicaram moderada a severa contaminação por Cu e Zn. Os resultados indicaram um caminho preferencial de metais pelo transporte de solo para bacia, principalmente de áreas agrícolas e pelo tratamento ineficiente de esgotos urbanos. O primeiro passo para uma medida corretiva é a inspeção das áreas agrícolas e o controle do uso de fertilizantes e herbicidas, bem como desenvolver um sistema de tratamento de esgotos eficiente nas áreas urbanas.

**Palavras-chave:** distribuição de metais, qualidade da água, fator de enriquecimento, índice de contaminação, fonte antropogênica.

## Introduction

The gathering of data related to the levels of toxic metals in the environment is not satisfying, especially in view of the setting of future permissible concentrations. However, research on heavy metals has met with strong growing interest in recent years. This is partly a consequence from the concern for environmental protection, and is due to increasing knowledge about the role and effect of metallic elements on living organisms. In Brazilian rivers are decrypted studies on concentration, distribution and transport of heavy metals in Paraíba do Sul, Mogi-Guaçu, Pardo, Ribeira de Iguape and das

Pedras rivers in São Paulo State (CETESB, 1978a, b, c; BOLDRINI et al., 1983; EYSINK et al., 1985, 1988; 2000; PFEIFFER et al., 1986; SALOMÃO et al., 2001), in Irajá and São João do Meriti rivers, in Rio de Janeiro State (PFEIFFER et al., 1982; REGO et al., 1993) and in Amazonian rivers (HACON et al., 1995; LECHLER et al., 2000; PEREIRA FILHO, 1995). Specifically in Tapacurá and Capibaribe river basins, Aprile et al. (2003, 2004) and Aprile and Bouvy (2008) conducted preliminary studies on content and distribution of trace metals in water and sediments.

The necessary presence of metals in trace amounts, in all living organisms seems to obey to equilibrium

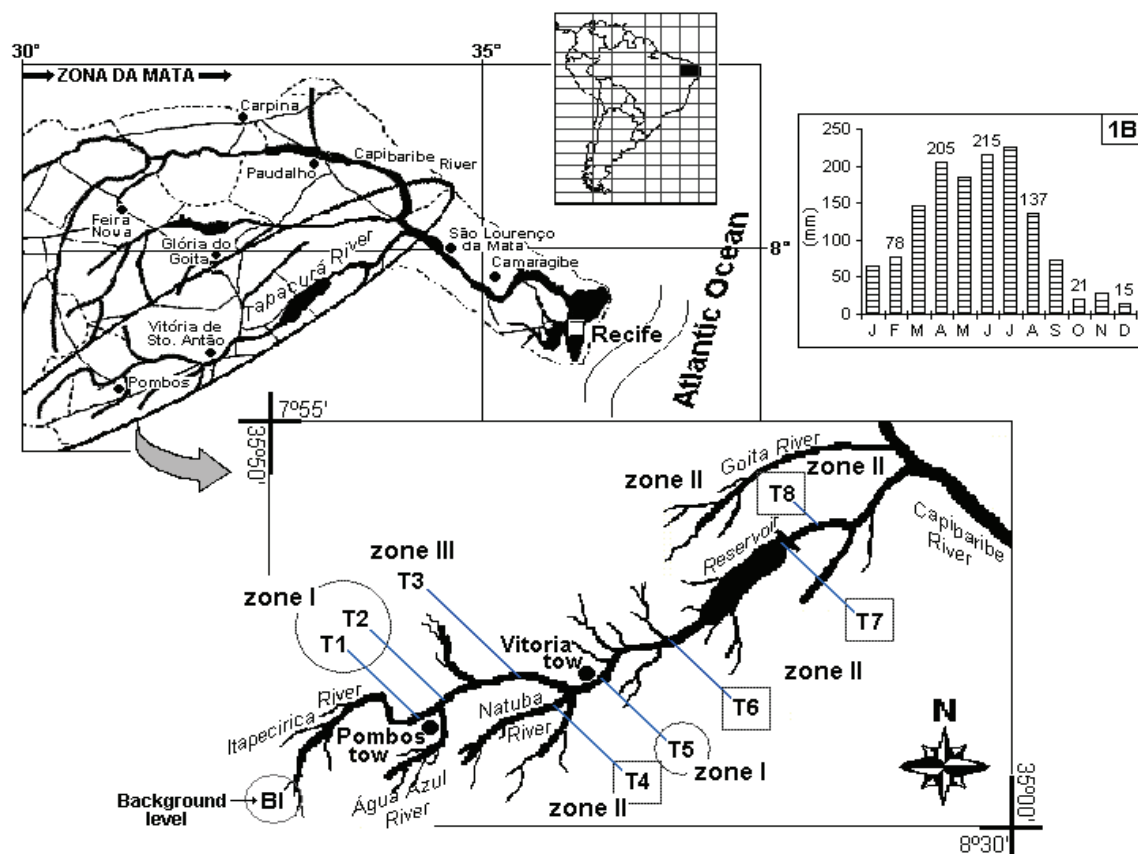
laws among the different metals. In order to understand the behavior of heavy metals in an aquatic ecosystem, we need to identify the major reservoirs of these elements, as well determine the rates of elemental turnover, among reservoirs. The purpose of this research was: (1) to establish the dissolved heavy metal (Fe, Mn, Cu, Pb and Zn) concentrations in natural waters, to evaluate managing strategies of the Tapacurá river basin, used to supply urban and rural areas; (2) to estimate significant relationships between trace metals; and (3) to provide a database necessary for developing strategies for pollution control of the basin. These reports on the distribution of heavy metals at the Tapacurá river can provide valuable contribution to the program of sanitation from the Company of Environment.

## Material and methods

### Study area

Tapacurá river basin is located in Zona da Mata at Pernambuco State, Northeast of Brazil (Figure 1). This basin is responsible for 9.5% from the water supply to Recife Metropolitan Region. The rainfall

is about 2,000 mm year<sup>-1</sup>, in the Zona da Mata Region, with maximum concentration between April and July (see Figure 1B), and 700 mm year<sup>-1</sup>, at the Agreste. Nevertheless, many people in Agreste and Zona da Mata have no access to potable water. In general, the water depths are less than eight meters, with lower spring tides (exception of the reservoir), resulting in environments not well-mixed vertically and with lowly dynamic. There is not efficient sewage treatment system in the municipalities until today, and over 80% from domestic wastewaters are directly released into the tributaries without treatment. Furthermore, there are agricultural and industrial areas located within or around the basin, which contribute with significant amount of untreated effluents for the tributaries, in the Pombos and Vitória de Santo Antão cities. Agriculture is the most important economic sector in semi-arid and Zona da Mata from the Pernambuco State. In Pombos city, we observed the improvement of cassava starch, whose result is the production of manipueira, a solid/liquid waste that creates a huge impact on the biota, due to high toxicity caused by heavy metals and cyanide acid (APRILE et al., 2004).



**Figure 1.** Tapacurá river basin with location of sampling sites, and average monthly rainfall (1B) in the basin, between 1996 and 2000.

### Proceedings

Eight sampling sites were established along the river, considering the area influenced by municipal sewage (zone I), agricultural runoff (zone II) and industrial plant (zone III, Figure 1). Coordinates for sampling sites were determined with Garmin brand GPS-12XL and the locations were: T1 (08°07'53"S-35°24'58"W) at Itapecirica river, upstream from Pombos city, receiving solid/liquid wastes from the improvement of cassava starch; T2 (08°07'26"S-35°22'29"W) in Tapacurá river, downstream from the confluence between Água Azul and Itapecirica rivulets, and upstream from Vitória de Santo Antão city; T3 (08°07'11"S-35°19'15"W) at Tapacurá river, downstream from the wastewater at the spirit company Pitú; T4 (08°10'56"S-35°20'22"W) in Natuba river, affluent of Tapacurá river, in an agricultural area near at the Mocotó Sugar Mill, where the uncontrolled use of fertilizers and herbicides was observed; T5 (08°05'55"S-35°15'37"W) in Tapacurá river, downstream from Vitória city, and receiving part of the municipal sewage; T6 (08°05'57"S-35°14'39"W) at Tapacurá river, in an agricultural area near to Manaín farm, with uncontrolled use of fertilizers and herbicides; T7 (08°02'12"S-35°09'44"W) in Tapacurá reservoir, and T8 (08°02'06"S-35°09'39"W) in Tapacurá river, located 300 m downstream from the dam, before the supply line.

Temperature ( $\pm 0.1^\circ\text{C}$ ) and pH ( $\pm 0.1$ ) of the surface waters were measured with a termistor and ohmmeter WTW, respectively. At each site, surface water samples (0 - 20 cm) were taken monthly, from March 1997 to December 1998, and from June 2005 to March 2006, using a Van-Dorn bottle and stored in one liter polystyrene bottles, refrigerated at  $4^\circ\text{C}$ . Water samples for chemical analysis were acidified to pH 2, using HCl (0.1 N), and filtered through a GF/C filter to remove the suspended material. All the manipulations were conducted inside a clean room. Heavy metals (Fe, Mn, Cu, Pb and Zn) in the 1 liter filtered samples were digested with 5 mL each of aqua-regia ( $\text{HNO}_3 + \text{HCl}$ ) +  $\text{HClO}_4$  (Merck) at  $200^\circ\text{C}$ , made up to 50 mL in a volumetric tube, and measured using a Perkin-Elmer AAS Model 3300 equipped with an air-acetylene flame. All the samplings and analytical determinations followed the suggestions from Loring and Rantala (1992) and APHA (1998). Quantification of metals was based on calibration curves of standard solutions of respective metals, prepared from a commercial stock solution (trace metals 1 ICM-411 H in 5%  $\text{HNO}_3$ ,

Radian International LLC) and standard seawater reference materials (CASS 1-4) from the National Research Council of Canada. Blanks and standard reference materials (SRMs) were included in the analysis, and the calibration curves were determined several times during the analysis, to check the efficiency of the extraction technique. The detection limits (DL) obtained in the analysis for the metallic ions were 0.05 Fe, 0.02 Mn, 0.001 Cu, 0.006 Pb and 0.003  $\text{mg L}^{-1}$  Zn. Values were always within the certified range. The heavy metal contamination levels were compared to the background level in a close area (see B1 in Figure 1), using the enrichment factor (EF), (ALOUPI; ANGELIDIS, 2001; SELVARAJ et al., 2004; WOITKE et al., 2003), and the potential contamination index ( $C_p$ ) (DAVAULTER; ROGNERUD, 2001). The metal levels were normalized to the surface water characteristics, with respect to iron. Therefore, EF and  $C_p$  were defined as:

$$\text{EF} = [\text{Metal}]_{\text{surface water}} / [\text{Fe}]_{\text{surface water}} / [\text{Metal}]_{\text{background}} / [\text{Fe}]_{\text{background}} \quad (\text{eq. 1})$$

$$C_p = [\text{Metal}]_{\text{maximum}} / [\text{Metal}]_{\text{background}} \quad (\text{eq. 2})$$

Where  $[\text{Metal}]_{\text{surface water}}$  and  $[\text{Metal}]_{\text{background}}$  are the levels of targeted metals (Mn, Cu, Pb and Zn) in the water samples, and uncontaminated local, respectively. Baseline values for  $[\text{Metal}]_{\text{background}}$  were as follows: 0.65 for Fe, 0.12 for Mn, 0.002 for Cu, 0.006 for Pb, and 0.004 for Zn, all these values in  $\text{mg L}^{-1}$ . Martin and Meybeck (1979) recommend 3.6% for Fe, 32.0  $\text{mg L}^{-1}$  for Cu, 16.0  $\text{mg L}^{-1}$  for Pb, and 127.0  $\text{mg L}^{-1}$  for Zn, as baseline values for  $[\text{Metal}]_{\text{background}}$ . Ratios between dissolved metals were determined for the waters of Tapacurá river. For the chemical interpretation, the dates were analyzed using simple statistical tests and multivariate statistical analyses. Linear regressions with respective standardized residual plot were performed to estimate significant relationships between dissolved metals.

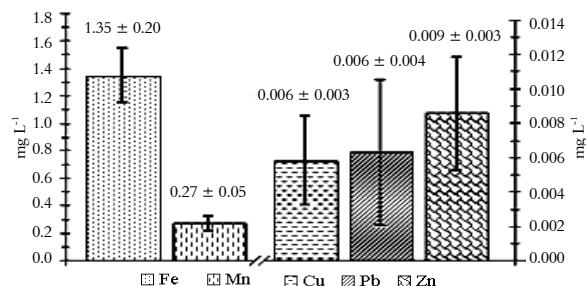
### Results and discussion

Dissolved trace metals concentrations at surface waters are summarized in Table 1 (levels per sites) and Figure 2 (total averages). The concentrations of dissolved trace metals in Tapacurá river basin indicate contamination with regard to anthropogenic metals. The lower distribution of dissolved metals in surface water can indicate that sedimentation process affects the suspended particle composition. The total level of dissolved Fe was high; the results were characterized by Fe concentrations ranging

from 0.30 to 4.22 mg L<sup>-1</sup>, and with average 1.35 mg L<sup>-1</sup>, exceeding those elements in the respective river by an order of magnitude. A strong link between high soil surface and water iron levels is consistent with major erosion observed along the riverbanks. However, in the Tapacurá river basin we did not verify indications of this process. Dissolved manganese presented concentrations ranging from 0.02 to 1.09 mg L<sup>-1</sup> (average 0.27 mg L<sup>-1</sup>). The highest levels of Fe and Mn were found at sites T4, T5 and T6. Copper values ranged from 0.001 to 0.014 mg L<sup>-1</sup>, with average concentration of 0.0058 ± 0.03 mg L<sup>-1</sup>, and lowest concentration at site T1 (average 0.002 mg L<sup>-1</sup>). Lead concentrations were low, and varied between ≤ 0.006 (detection limit) and 0.029 mg L<sup>-1</sup> in site T4. This metal was below the detection limit at sites T1, T5, T6, and T8. The highest concentrations were found at sites T2, downstream from Pombos city; T3, downstream from the spirit company Pitú Ltd, and T4, in an agricultural region. Dissolved zinc ranged from ≤ 0.003 to 0.020 mg L<sup>-1</sup> (average 0.009 ± 0.003 mg L<sup>-1</sup>, see Table 1 and Figure 2).

The heavy metals are environmental contaminants, very common from metal mining and processing, as well as from many other industrial, municipal and agricultural activities. According to IPCS (2001), local geological and anthropogenic influences determine the concentrations of heavy metals in aquatic systems. In general, the concentration of dissolved metals increased between the sampling sites T2 and T5. The absence of efficient sewage treatment in Pombos and Vitória cities may be contributing to increase the levels of trace metals in part of the basin. According to National Recommended Water Quality Criteria Correction by U.S. Office of Water Drinking Water and Health (EPA, 1999); the safe limits established by Cetesb (2001), and Brazilian Health Ministry

(BRASIL, 2004) to drinking water directive, in Tapacurá river basin was not observed high levels of contamination by heavy metals in the water. However, in some sampling sites, the levels of Fe, Mn and Pb exceeded the recommended limits, suggesting more caution in the monitoring process of these sites.



**Figure 2.** Total average ± SD of trace metals in surface waters from the Tapacurá river basin.

The degree of anthropogenic impact, estimated through enrichment factor (EF) and potential contamination indices (C<sub>p</sub>), is listed in the Table 2. Based on the classification from Taylor (1964), Mn and Pb presented the lower enrichments with EF ranging from 0 to 4 (average 1.3) for Mn, and 0 to 1.8 (average 0.5) for Pb. Enrichment factor is a good tool to distinguish the natural and anthropogenic sources (SELVARAJ et al., 2004). Five sampling sites with EF < 1 for Mn, and six sites with EF < 1 for Pb, indicated that there is no enrichment by these metals in the water column. In other words, these metals are close to background levels. On the other hand, copper and zinc presented, according to the same Taylor's classification, enrichment from moderate to severe at sampling sites T2, T7, and T8. Probably, this result means a heavy metal release, from moderate to high amount from urban area/municipal sewage (zone I) and agricultural runoff (zone II). According to the classification from

**Table 1.** Concentrations (average ± SD) and range of dissolved trace metals (mg L<sup>-1</sup>).

Site	Fe	Mn	Cu	Pb	Zn
T1	1.30 ± 0.143 1.16 - 1.44	0.21 ± 0.052 0.14 - 0.27	0.002 ± 0.003 0.001 - 0.005	- < 0.006	0.010 ± 0.001 0.009 - 0.011
T2	0.77 ± 0.066 0.71 - 0.84	0.34 ± 0.061 0.26 - 0.41	0.011 ± 0.002 0.009 - 0.014	0.008 ± 0.006 < 0.006 - 0.014	0.004 ± 0.003 0.003 - 0.008
T3	1.22 ± 0.202 1.02 - 1.42	0.24 ± 0.072 0.15 - 0.33	0.004 ± 0.003 0.001 - 0.007	0.011 ± 0.008 < 0.006 - 0.018	0.009 ± 0.008 0.003 - 0.019
T4	3.66 ± 0.553 3.11 - 4.22	0.03 ± 0.001 0.02 - 0.03	0.007 ± 0.001 0.006 - 0.008	0.019 ± 0.013 < 0.006 - 0.029	0.010 ± 0.001 0.010 - 0.011
T5	2.09 ± 0.336 1.75 - 2.42	0.30 ± 0.090 0.19 - 0.41	0.006 ± 0.004 0.001 - 0.011	- < 0.006	0.008 ± 0.000 0.008 - 0.008
T6	1.35 ± 0.232 1.10 - 1.56	1.00 ± 0.091 0.87 - 1.09	0.005 ± 0.004 0.001 - 0.008	- < 0.006	- < 0.003
T7	0.50 ± 0.016 0.49 - 0.52	0.06 ± 0.017 0.04 - 0.08	0.008 ± 0.001 0.007 - 0.009	0.008 ± 0.007 < 0.006 - 0.016	0.013 ± 0.006 0.010 - 0.020
T8	0.33 ± 0.033 0.30 - 0.36	0.05 ± 0.021 0.03 - 0.08	0.004 ± 0.003 0.001 - 0.008	- < 0.006	0.009 ± 0.004 0.006 - 0.013
N=	132	176	176	154	132

Davault and Rognerud (2001), 30% of the samples present potential contamination indices ranging from severe to very severe contamination by heavy metals in the water column. The heavy metals showing the most extensive contamination were Mn that ranged from 0.2 to 9.1 and Cu, ranging from 1.7 to 4.6. The metal that presented the narrowest contamination was Pb, with  $C_p$  varying between 0 and 4.8 (average 1.6).

**Table 2.** Degree of anthropogenic impact estimated based on the enrichment factor (EF)\* and potential contamination index ( $C_p$ )\*\* for the waters of the basin.

Site	Temp. (°C)	pH	Fe		Mn		Cu		Pb		Zn	
			EF	$C_p$	EF	$C_p$	EF	$C_p$	EF	$C_p$	EF	$C_p$
T1	25.5	7.70	1.0	2.2	0.9	2.3	0.3	1.7	0.0	0.0	1.3	2.8
T2	29.6	8.04	1.0	1.3	2.4	3.4	4.8	4.6	1.1	2.3	1.2	2.1
T3	31.7	7.95	1.0	2.2	1.1	2.8	1.2	2.3	0.9	3.0	1.7	4.7
T4	29.0	7.26	1.0	6.5	0.0	0.2	0.6	2.6	0.6	4.8	0.5	2.8
T5	27.4	7.02	1.0	3.7	0.8	3.4	0.9	3.5	0.0	0.0	0.6	2.0
T6	27.4	7.33	1.0	2.4	4.0	9.1	1.3	2.8	0.0	0.0	0.0	0.0
T7	29.2	7.78	1.0	0.8	0.6	0.6	5.4	3.1	1.8	2.7	4.3	5.0
T8	28.5	7.32	1.0	0.6	0.8	0.6	4.4	2.5	0.0	0.0	4.3	3.2

\*EF < 1 no enrichment; EF ≥ 1 - < 3 minor enrichment; EF ≥ 3 - < 5 moderate enrichment; EF ≥ 5 - < 10 moderate - severe enrichment; EF ≥ 10 - < 25 severe enrichment; EF ≥ 25 - < 50 very severe enrichment and EF ≥ 50 extremely severe enrichment (Taylor, 1964). \*\* $C_p$  > 3 (**bold**) ⇒ severe contamination.

In water systems, estimates point that amorphous forms of Fe (FeOOH) and Mn (MnOOH) are predominant (LAKIND; STONE, 1989). The ratio between FeOOH and MnOOH (Fe/Mn) indicate the relative abundance of each sorbent phase. In natural conditions, there is a direct relationship between the Fe and Mn concentrations, within a confident interval. When any change in the water quality occurs (e.g. by industrial discharge), the equilibrium Fe/Mn is lost. A summary of the ratios between trace elements at each sampling site is given in Table 3. The average ratios of Fe/Mn for the Tapacurá river varied from 1:1 (T6) to over 145:1 (T4). Duff (1992) reported that exist ratios of 20:1, which represents the ratio in which Fe: Mn is found in aqueous solution due to the anthropogenic activities, such as mining. Inter-riverine variations in Fe and Mn at Tapacurá river may be associated to municipal sewage. Fe and Mn are diagenetically mobile in aqueous ecosystems. Reduced Fe and Mn can migrate to the marsh surface, via the pore fluids, to be re-oxidized and precipitated as (oxy) hydroxides. This process produces higher concentrations of Fe and Mn at sediments' surface (TURNER; MILLWARD, 2000), consequently reducing the levels at the water column. Other significant ratios obtained were: Fe:Cu, ranging from 60:1 (T7) to 1039:1 (T1); Fe:Zn, from 38:1 (T7 and T8) to 354:1 (T4); Mn:Cu, from 4:1 (T4) to 189:1 (T6). We also observed relationships quite close between Cu: Pb, ranging from 0.4:1 (T4) to

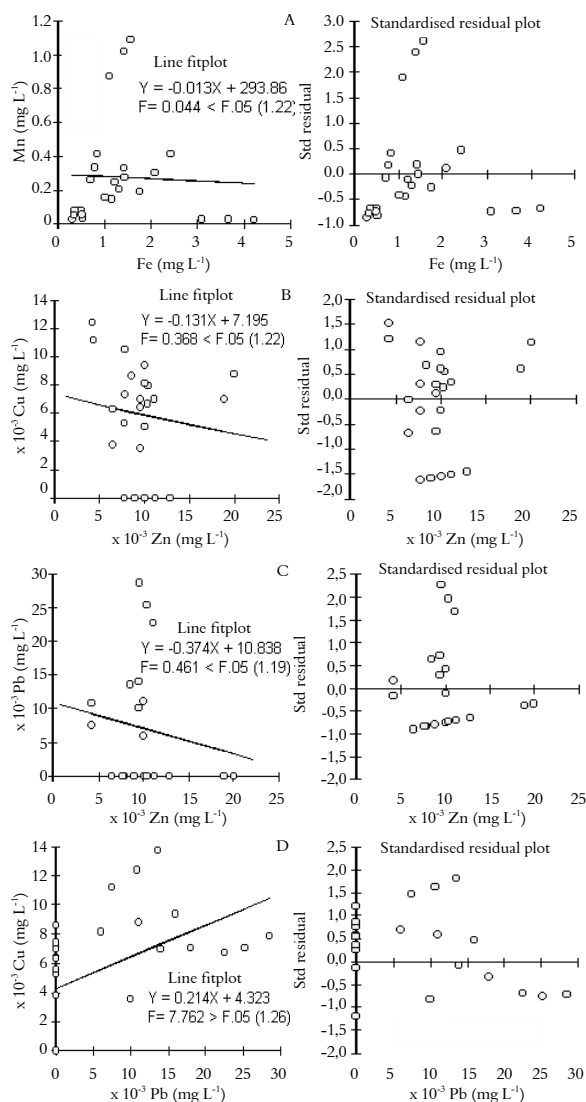
1.4:1 (T2), and Cu:Zn, from 0.1:1 (T1) to 2:1 (T2). Copper and zinc levels are strongly influenced by anthropogenic sources (IPCS, 1998) that may affect the two metals simultaneously.

**Table 3.** Ratios between trace metals in the fluvial waters.

Ratio	T1	T2	T3	T4	T5	T6	T7	T8
Fe:Mn	6:1	2:1	5:1	145:1	7:1	1:1	9:1	6:1
Fe:Cu	1039:1	67:1	278:1	524:1	362:1	257:1	60:1	74:1
Fe:Pb	-	97:1	116:1	192:1	-	-	61:1	-
Fe:Zn	129:1	137:1	96:1	354:1	269:1	-	38:1	38:1
Mn:Cu	166:1	29:1	55:1	4:1	52:1	189:1	7:1	12:1
Mn:Pb	-	42:1	23:1	1:1	-	-	7:1	-
Mn:Zn	21:1	59:1	19:1	2:1	38:1	-	4:1	6:1
Cu:Pb	-	1.4:1	0.4:1	0.4:1	-	-	1:1	-
Cu:Zn	0.1:1	2:1	0.3:1	0.7:1	0.7:1	-	0.6:1	0.5:1
Pb:Zn	< 0.01:1	1.4:1	0.8:1	1.8:1	< 0.01:1	-	0.6:1	< 0.01:1

Linear regression analysis was applied between dissolved trace metals at the sampling sites, and the significant results (at the 95% confidence interval) are reported in the Figure 3, including the residual plots. The residual analysis showed a heterogeneous trend of the 'y' axis (Mn, Cu, and Pb). The results evidenced that Fe and Mn are independent variables, that is, the presence of dissolved iron does not affect the concentrations of Mn, and vice versa (Figure 3A). We determined a factor F of 0.044, with  $p = 0.836$ , for Fe versus Mn. The results of the analysis for Zn versus Cu ( $F = 0.368$ ;  $p = 0.550$ , see Figure 3B), and Zn versus Pb ( $F = 0.461$ ;  $p = 0.505$ , see Figure 3C) indicated that the variables are also independent. Correlations were significant at the sites T3, T4 and T7, due to industrial and agricultural effluents. The results reflected a well-defined source of contamination, common for some trace metals. A plot composed by all samples indicates a general relationship between concentrations of Pb and Cu ( $F = 7.762$ ;  $p = 0.010$ , see Figure 3D), which is not driven by the abundance, and availability of oxide material, such as iron and manganese. The lead distribution at surface waters of the Tapacurá river is characterized by relative anthropogenic mobilization rates.

A PCA was applied to discover and interpret relationships between trace metals at surface waters of the basin, and the results obtained through chemical analyses are supplied in Table 4 and Figure 4. All elements were well represented by three components. Based on initial component of matrix indicators, Mn and Zn with high value (> 0.89) were found within the first component. The first factor explained 37.34% of the total variability, with an eigenvalue of 1.867. This factor can be termed as anthropogenic factor from both urban/municipal sewage (zone I) and agricultural runoff (zone II). The second factor explained 25.94%



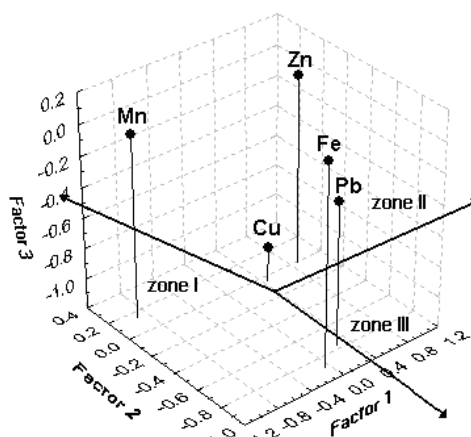
**Figure 3.** Plot of linear regression with standardized residual to A) Fe vs Mn; B) Zn vs Cu; C) Zn vs Pb, and D) Pb vs Cu.

of the total variability, with an eigenvalue of 1.297, and medium to high values of Fe and Pb. This factor can be termed as 'transition factor', with characteristics from zones I and II for Fe, and with characteristics from zones II and III (industrial plant) for Pb. Although erosion processes along the riverbanks had not been observed, the contribution of iron from geogenic origin is not refused. The third factor explained 19.13% of the total variability, with an eigenvalue of 0.956, and high Cu value ( $> 0.97$ ). Copper may have arisen from an anthropogenic source from agricultural runoff, although the highest levels of this element had been verified at site T2, downstream from Vitória city. As observed in linear regression analysis, Fe and Mn were independent variables; in fact, the PCA presented two distinct factor explanations for each one.

**Table 4.** Explanation of total variability from the water samples with rotated component matrix (for three factors) and initial eigenvalues.

	Component matrix		
	Factor 1	Factor 2	Factor 3
Fe	-0.0599	-0.8827	0.1119
Mn	-0.9096	0.1525	-0.0125
Cu	-0.0566	-0.0497	-0.9759
Pb	0.2628	-0.7619	-0.2653
Zn	0.8914	0.0020	0.0415
Initial Eigenvalues			
Eigenvalue	1.8669	1.2970	0.9564
Cumul. Eigenval	1.8669	3.1639	4.1203
% total Variance	37.34	25.94	19.13
Cumulative %	37.34	63.28	82.41

\*Bold values are similar sources in factors  $> 0.7000$ .



**Figure 4.** Principal Component Analysis (PCA) loading plot in rotated space (Varimax with Kaiser normalization).

The precision and accuracy were quite good, with most relative standard deviations and relative errors below 10% over the data tested through AAS method. In general, the industrial release of heavy metal was low, in comparison to those from municipal and agricultural areas. The metals presented a horizontal distribution very heterogeneous. In the Tapacurá river basin, there is no program to remediate the contaminated water by heavy metals. As a result, we believe that the first step to apply a remedial measure and management strategies is the inspection of the agricultural areas surrounding the basin, with appropriate control in the use of fertilizers and herbicides, as well as a significant financial support to develop an efficient sewage treatment in Pombos and Vitória cities.

## Conclusion

Heavy metals presented a horizontal distribution quite heterogeneous with hotspots in the municipal and agricultural areas. Data analyses through EF and  $C_p$  indicated moderate to severe contamination by Cu and Zn, at surface waters of the basin. The results indicated the potential pathways of trace

metals, via soil from the agricultural areas and from inefficient sewage treatment, at the cities of the river basin. According to recommended safe limits, in the Tapacurá river basin we did not observe high contamination levels by heavy metals, at surface waters, during this study. Nevertheless, the sampling sites from T2 to T4, and T7, require more attention in future researches. The results may assist the development of management strategies for pollution control, mainly in the agricultural areas surrounding the basin, with severe contamination.

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