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Evaluation of pseudo-total and labile metals (Cu^{2+} , Cr^{3+} , Ni^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+}) in surface sediments at the mouth of tributaries of the Itaipu Reservoir, Brazil

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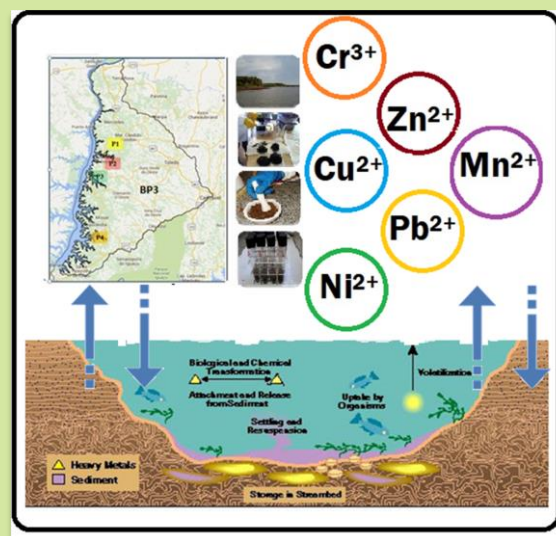
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ABSTRACT: Sediments are reservoirs for a variety of substances widely used as indicators of pollution in aquatic environments. In this research it was carried out the evaluation of the concentration of metals in the pseudo-total and labile fractions in surface sediments at the mouth of four main tributaries of the Itaipu Reservoir. Three samplings were performed between February 2014 and March 2015 using Petersen type dredger. The determination of metals occurred by atomic absorption spectrometry and physicochemical parameters by gravimetric and potentiometric techniques. The samples presented neutral to slightly alkaline character and homogeneous pH values. It was observed the predominance of the clay fraction and the occurrence of variable organic matter between the points. In the labile fraction, only the copper content reached concentrations higher than the thresholds effects levels (TEL) at all sampling points. In the pseudo-total fraction, some sites presented for Cr^{3+} , Pb^{2+} and Zn^{2+} TEL level. For Ni^{2+} , values of probable effects level (PEL) were verified and for Cu^{2+} , concentrations in severe effect level (SEL) were reported according to the international sediment classification criteria adopted by the National Oceanic and Atmospheric Administration (NOAA).



1. Introduction

The technological advancement resulting from population and industrial growth contributes to increasing the use and deterioration of ecosystems. Water is one of the main natural resources and after being used in various purposes, it returns to the environment with different quality from the original. Several contaminants, such as metals, are incorporated, thus favoring the pollution of water bodies and consequent

accumulation of these substances in sediments and biota.

Artificial reservoirs and natural lakes are important surface water resources with great relevance for water supply, flood control, irrigation, aquaculture, climate regulation and maintenance of the ecological balance¹. In this context, the Itaipu Reservoir is one of the largest artificial lakes in the world, whose main purpose is the generation of electricity, in addition to aquaculture and navigation. By its location and

extension, it exerts a direct influence on the local ecosystem².

The sediments comprise the unbound material, formed by particles of different sizes, shapes and chemical composition, carried by water, air or ice, distributed along the valleys of the drainage system and oriented from the processes of weathering and erosion³.

Increased concentrations of metals in sediments are related to anthropogenic activities, such as industrial effluent discharges, agriculture, land transport, lack of adequate sewage treatment and solid waste, which can result in contamination of the food chain and biological diversity^{4,5}.

The high capacity in the retention of sediment contaminants is a factor that highlights the importance of this matrix for the evaluation of pollution levels. Its composition reflects the environmental characteristics of both the sampling moment and the remote memory of the aquatic environment⁶. With this, it can be considered a key

compartment that reports the environmental history, through the permanent record of the effects of contamination⁷.

The objective of this study was to evaluate the pseudo-total and labile metal fractions extracted from sediments sampled at the mouth of tributaries of the Itaipu Reservoir and to compare the results with the National Oceanic and Atmospheric Administration (NOAA)⁸.

2. Experimental

2.1 Location of Collection Points

The study was carried out in the Paraná Basin 3 (BP3). BP3 has an area of approximately 8,000 km², involving 28 municipalities in the State of Paraná and one in Mato Grosso do Sul⁹ (Figure 1).

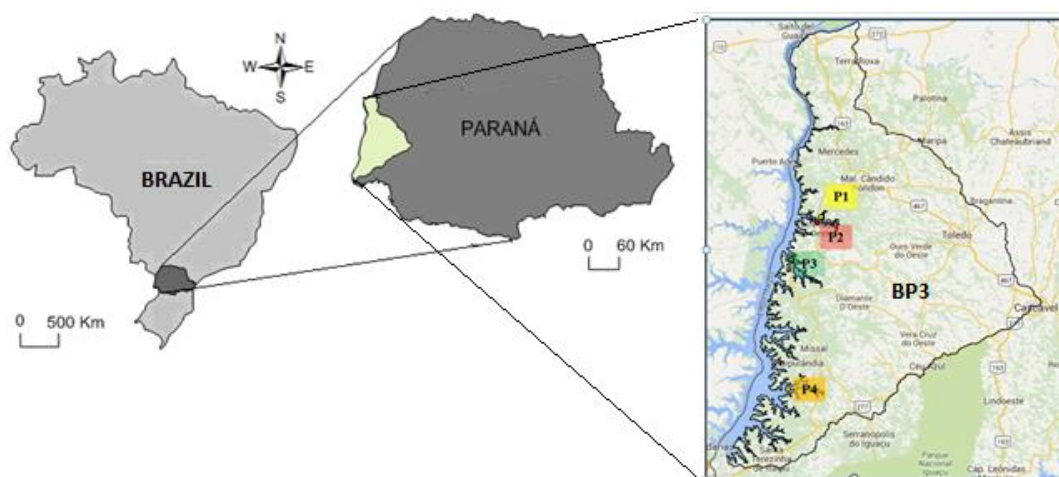




Figure 1. Delimitation of the Paraná River Basin 3 (BP3) and Sampling Points.

Sampling points were chosen at the mouth of the Arroio Fundo River, São Francisco Verdadeiro River, São Francisco Falso River and Ocoí River to characterize the tendency of contamination

through the concentration levels of metals in the recently deposited sediments (Table 1).

Table 1. Location of sediment sampling points.

Point	Location	River	Figure
P1	24° 39' 55" S 54° 13' 01" W	Arroio Fundo	
P2	24° 41' 00" S 54° 14' 10" W	São Francisco Verdadeiro	

P3	24°50'52"S 54°19'25"W	São Francisco Falso	
P4	25°13'56"S 54°13'24.4"W	Ocoí	

2.2 Sample Collection, Preparation and Physicochemical Characterization

Three samples were taken between February 2014 and March 2015. The sediments were collected between 0-10 cm depth with the use of a Pettersen type dredger. All glassware and polypropylene material were soaked in 10 % (v/v) HNO_3 for 24 h and rinsed thoroughly with ultrapure water before use. Ultrapure water was obtained from a Human UP 900 purification system, which was also used to prepare all of the solutions. After collection, samples were refrigerated for transport. The physical and chemical determinations were performed with the moist sediments. For the determination of metals, some of the material was being air-dried at room temperature ($25 \pm 1^\circ\text{C}$) for 2 weeks and then disaggregated with the use of mortar and pestle, sieved in a mesh of 500 μm , stored in glass flask.

Determination of the texture of sediment samples (e.g., silt, sand, clay) was performed using densitometry². The pH was determined in potentiometer with suspension of 1.0 g of sediment in KCl 1 mol L^{-1} ¹⁰. Total solids (TS), Total Fixed Solids (FTS) and total volatile solids (VTS) were determined by gravimetry, by drying 5.0 g of sample in an oven at 105°C until constant weight and then ignition in furnace at 500°C for 4 h¹⁰. Total organic carbon (TOC) content was calculated by the empirical formula Van Bemmelen factor: $\text{TOC} = \text{VTS}/1.724^{2,11}$.

2.3 Metals Determination

The analysis of labile metals in sediments is defined as the fraction extracted by diluted acid attack. Approximately 1.0 g dry sediment was added in Erlenmeyer flask, together with 25.0 mL of HCl (Biotec Ltda., São Paulo, SP, Brazil) 0.10 mol L^{-1} and kept under vigorous agitation using a rotary table (Orbital®) at 200 rpm for 2 h at room temperature ($25 \pm 1^\circ\text{C}$)¹².

The pseudo-total metals were extracted by acid digestion according to Environmental Protection Agency (EPA) method 3050B: 0.50 g dry sediment were added in Erlenmeyer flask containing 15.0 mL HNO_3 (Neon, Suzano, SP, Brazil) and heated for 4 h at 60°C . Subsequently, 8.0 mL of H_2O_2 (Neon, Suzano, SP, Brazil) were added and heated for 30 min. After extraction, samples for pseudo-total and available metals were gravity filtered by washing the filter paper with ultrapure water and completed to 50 mL and stored at 4°C ^{2,13}.

Metallic-ion quantification was performed using flame atomic absorption spectrometry (FAAS; model SpectraAA-220, equipped with hollow cathode lamps and deuterium lamp for background correction (Varian, Palo Alto, CA). All absorbance measurements were determined by integration area; the samples were prepared in triplicate; and the signal of the blank experiment was discounted. Table 2 lists the FAAS operating conditions for the determination of metallic ion.

Table 2. FAAS operating conditions for determination of metallic ions.

Metals	λ (nm)	i (mA)	Slit (nm)	Flame	Range (mg L^{-1})
Cu^{2+}	324.7	4	0.5	$\text{Ar}/\text{C}_2\text{H}_2$	0.03–8.0
Cr^{3+}	357.9	7	0.2	$\text{Ar}/\text{C}_2\text{H}_2$	0.06–20.0
Mn^{2+}	279.5	5	0.2	$\text{Ar}/\text{C}_2\text{H}_2$	0.02–6.0
Pb^{2+}	217.0	5	1.0	$\text{Ar}/\text{C}_2\text{H}_2$	0.1–20.0
Zn^{2+}	213.9	5	1.0	$\text{Ar}/\text{C}_2\text{H}_2$	0.01–2.0
Ni^{2+}	232.0	4	0.2	$\text{Ar}/\text{C}_2\text{H}_2$	0.1–8.0

The FAAS was calibrated with analytical curves prepared with aliquots of standard solutions of 1000 mg L⁻¹ of the Cu²⁺, Cr³⁺, Mn²⁺, Pb²⁺, Zn²⁺ and Ni²⁺ metal ions. The method was validated by means of linearity, with regression analysis of the calibration curves for each metal, by determination of the limits of quantification (LOQ) and detection (LOD) and by a comparative recovery test to the certified reference material (MRC-PACs-2, National Research Council of Canada). For the linearity, the coefficient of determination (R²) was considered being adequate when close to 100 %. Limits of detection (LODs) and quantification (LOQs) were calculated using signal-to-noise ratios of 3 and 10, respectively, as well as parameters from the linear equation¹⁴. The accuracy of the method was verified considering the recovery in relation to the values measured for the MRC: Accuracy (%) = 100×C_{med}/C_{MRC}, where C_{med} is the concentration obtained experimentally and C_{MRC} is the concentration declared in the certificate.

2.4 Analyses of Correlations Among the Parameters Evaluated

The statistical tool used was principal component analysis (PCA). PCA permits evaluation of the data set by decreasing the dimension of the data and conserving the most useful statistical information present in the original data. PCA is performed through the determination of distances among the sample data, which can be calculated considering the closest K-neighbor or

mean of the samples. The data can be either the original (scaled or centered on the mean) data or the scores generated by the PCA^{15,16}. The statistical operations were performed using the Statistica 10.0 software¹⁷. Statistical analysis was performed using analysis of variance (ANOVA).

3. Results and Discussion

3.1 Physical-Chemical Characteristics of the Sediment

The pH values of the sediments indicated a neutral to slightly acid character. The greatest difference between the values occurred between points 2 and 3 (0.53 pH units). This indicates that the studied sediments have relatively homogeneous pH. This characteristic can favor the accumulation of metals in sediments because, the increase of the pH favors the precipitation of the dissolved metals⁶.

The largest fraction of FTS occurred in P3 and the lowest was observed in P4. The concentrations of VTS and total carbon were higher in P4, followed by P1 and P2. This higher VTS concentration indicates a higher occurrence of organic matter at these sampling points, which may favor the retention of metals in this matrix (Table 3). Sediments of fine granulometry, clayey, rich in nutrients and organic matter constitute one of the main adsorbents of several metals that may be present in the aquatic environment.

Table 3. Results of the analysis of physicochemical parameters of sediment samples.

Sample	pH	TS (%)	FTS (%)	VTS (%)	TOC (%)	Clay (%)	Silt (%)	Sand (%)
P1	6.83±0.04	52±2	88±1	12±2	6±1	44	14	42
P2	7.19±.02	59±3	89.8±0.3	10.2±0.3	5.7±0.2	44	14	42
P3	6.66±0.04	68±1	91.0±0.2	9.0± 0.2	5.0±0.1	22	8	70
P4	7.10±0.05	28±1	3.8± 0.6	16.2±0.6	9.0±0.3	42	8	50

P1 - Arroio Fundo River; P2 – São Francisco Verdadeiro River; P3 – São Francisco Falso River; P4 – Ocoí River.

The samples of P1, P2 and P4 presented equivalent results, with the predominance of the clay fraction. Sediments with predominance of this fraction provide a higher concentration of metals due to the high tendency of adsorption in groups of fine granulometry. Sediments with smaller particles have higher adsorption capacity. Consequently, they have a greater potential of environmental contamination, because the metals retained in these sites are more labile^{18,19}.

The lowest fraction of clay occurred in P3, with only 22 %, at this point the predominance of the sand fraction can be justified by the proximity of the artificial beach of Santa Helena, which is periodically coated with this material and which is transported to the bed of the reservoir. When the sediments present values of organic matter above 10 % are considered organic, and below 10 % are considered inorganic or mineral sediments. In this study all sediments were classified as primarily

mineral^{20, 21}.

3.2 Metals determination validation parameters

The validation parameters for the metals determinations regarding linearity, limit of detection, limit of quantification and accuracy were considered satisfactory (Table 4). All linear regression equations, obtained by means of

solutions of known concentration of the studied metals and their respective absorbances, presented determination coefficients in the range of 99.1 % to 100 %, indicating a high relation between the concentrations and respective absorbances. The LOD and LOQ values ranged from 0.009 to 0.072 mg L⁻¹ and 0.029 to 0.23 mg L⁻¹ respectively. The lowest values are for Cu²⁺ and the highest values for Mn.

Table 4. Determination of metal ions in CRM by the method of pseudo-total digestion and validation parameters.

Metal	Equation	R ² (%)	LOD (mg L ⁻¹)	LOQ (mg L ⁻¹)	Certified (mg kg ⁻¹)	Measured (mg kg ⁻¹)	Extracted (%)
Cu ²⁺	ABS = 0.15×[Cu] + 0.03	100	0.009	0.029	310± 12	291 ± 5	93.9
Cr ³⁺	ABS = 0.02×[Cr] + 0.0005	99.6	0.022	0.074	91± 5	86 ± 6	94.4
Mn ²⁺	ABS = 0.17×[Mn] – 0.03	100	0.072	0.239	440 ± 19	381 ± 25	86.6
Pb ²⁺	ABS = 0.04×[Pb] + 0.003	99.9	0.025	0.082	183± 12	147 ± 15	80.5
Zn ²⁺	ABS = 0.08×[Zn] + 0.19	100	0.039	0.061	364 ± 23	336 ± 13	92.2
Ni ²⁺	ABS = 0.13×[Ni] – 0.0003	99.9	0.005	0.016	40 ± 2	36 ± 2	91.1

For the recovery study, the methodology used in the pseudo-total extraction of the metals ions in sediment samples was compared with the MRC (PACs 2). Certified values and percent recovery after application of the metal extraction procedure in the pseudo-total sediment fraction were satisfactory (Table 4), indicating which method used provided the analytes to be quantified by FAAS and that the determined concentrations are

consistent with that certified in the reference material.

3.3 Monitoring Study

Higher concentrations were found in the three samples at Cu²⁺, Mn²⁺, Pb²⁺ and Zn²⁺ at points 2 and 4 (Table 5).

Table 5. Metal concentrations metals in sediment samples.

Table 2: Metal Concentrations (mg kg ⁻¹) in sediment samples.							
		Labile Fraction (mg kg ⁻¹)					
Sample		Cu ²⁺	Cr ³⁺	Mn ²⁺	Pb ²⁺	Zn ²⁺	Ni ²⁺
P1	Feb. 2014	31 ± 4	12.3 ± 0.2	400 ± 1	10.3 ± 0.7	25 ± 2	4.1 ± 0.2
	Aug. 2014	57 ± 2	14.9 ± 0.6	407 ± 3	13.8 ± 0.7	31 ± 2	5.3± 0.3
	Mar. 2015	71.9 ± 0.3	17 ± 1	391 ± 2	13.5 ± 0.4	24.5 ± 0.7	4.6 ± 1.2
P2	Feb. 2014	79.9 ± 9.3	12.8 ± 0.2	406.8 ± 0.7	14 ± 2	32 ± 3	3.2 ± 0.3
	Aug. 2014	73 ± 3	15.0 ± 0.4	407.7 ± 0.2	14.9 ± 0.5	42 ± 2	5.5 ± 0.5
	Mar. 2015	66 ± 3	17.1 ± 0.7	401.2 ± 0.9	14 ± 2	25 ± 2	3.6 ± 0.2
P3	Feb. 2014	18 ± 1	12.2 ± 0.4	403 ± 3	9.4 ± 0.7	4.0 ± 0.6	0.4 ± 0.2
	Aug. 2014	17.4 ± 0.9	15.3 ± 0.4	385 ± 6	18 ± 1	4 ± 2	0.4± 0.2
	Mar. 2015	67 ± 3	19.2 ± 0.7	330 ± 2	17.4 ± 0.7	39 ± 2	3.0 ± 0.6
P4	Feb. 2014	74 ± 6	16.2 ± 0.9	410.4 ± 0.4	13.0 ± 0.6	43 ± 4	3.3 ± 0.3
	Aug. 2014	55 ± 3	16.7 ± 0.2	405 ± 2	12 ± 1	35.2 ± 0.9	5.3 ± 0.6
	Mar. 2015	65 ± 3	3.0± 0.4	406 ± 3	15 ± 2	36 ± 2	3.2 ± 0.2
Pseudo-total Fraction (mg kg ⁻¹)							
Sample		Cu ²⁺	Cr ³⁺	Mn ²⁺	Pb ²⁺	Zn ²⁺	Ni ²⁺
P1	Feb. 2014	188 ± 2	77 ± 1	929 ± 6	45.4 ± 0.8	212 ± 3	57 ± 2
	Aug. 2014	159 ± 25	68 ± 2	945.1 ± 0.9	30 ± 3	167± 14	41 ± 3
	Mar. 2015	179 ± 3	81 ± 3	939 ± 9	41 ± 9	181 ± 4	43.1 ± 0.7
P2	Feb. 2014	163 ± 2	104 ± 2	947.5 ± 0.4	64 ± 2	178 ±13	72 ± 8
	Aug. 2014	238±14	88±2	944 ± 4	62 ± 2	249 ± 9	58 ± 5

	Mar. 2015	144 ± 5	57 ± 5	904 ± 12	40 ± 7	152 ± 8	36.3 ± 0.7
	Feb. 2014	70 ± 2	85 ± 4	959 ± 3	76 ± 8	90 ± 20	31.4 ± 0.8
P3	Aug. 2014	126 ± 14	124 ± 7	933 ± 8	79 ± 8	103 ± 4	46 ± 4
	Mar. 2015	130 ± 2	46 ± 4	612 ± 16	51.7 ± 0.2	94 ± 10	29 ± 2
P4	Feb. 2014	208.4 ± 0.5	71 ± 4	957 ± 8	57 ± 5	192 ± 2	43 ± 3
	Aug. 2014	264 ± 5	97.6 ± 0.8	955.4 ± 0.7	57 ± 2	240 ± 4	58 ± 2
	Mar. 2015	228 ± 6	78 ± 3	962 ± 3	66 ± 4	247 ± 23	50 ± 7
TEL^a		35.7	37.3	-	35.0	123.0	18.0
PEL^a		97.0	90.0	-	91.3	315.0	36.0
SEL^a		110.0	110.0	1100.0	250.0	820.0	75.0

P1 - Arroio Fundo River; P2 - São Francisco Verdadeiro River; P3 - São Francisco Falso River; P4 - Ocoí River.

^a Quality guidelines of segment trace metals in sediment adopted by NOAA (mg kg⁻¹ dry basis)

TEL - Thresholds Effects Level; PEL - Probable Effect Levels; SEL - Severe Effect Level

In the pseudo-total fraction, in February 2014, in the samples P1 and P2, the concentrations of Pb²⁺, Zn²⁺ and Ni²⁺ were higher when compared to the other samples. At the collected station there was a lower volume of rainfall. This may have contributed to the preconcentration of some metal ions at these two points. The analyte concentrations in the pseudo-total fraction were always higher than in the environmentally available fraction. The toxic potential of metals is related to their bioavailability. This shows the importance of determining the concentration of metals in the total and labile fractions in the sediment. However, these lower levels of labile fraction, compared to pseudo-total, do not exempt sediments from negative environmental impacts²².

The lowest copper content in the available fraction was observed in the sediments sampled in the year of 2014 in P3 and P1, only these samples had concentrations below the TEL level (values below which adverse effects are rarely expected) 35.7 mg kg⁻¹. In 2015, the concentrations of this element in the same fraction were higher than the TEL level at all sampling points. This indicates the increase of this analyte in the sediments during the period studied. The labile fraction represents the dynamics of exchange between the compartments and the organisms. This indicates potential risk due to higher TEL values. Although it is an essential element in lesser amounts, in larger doses it is toxic. Similar results were obtained in sediment samples from the Itaipu Reservoir in similar studies, where Cu²⁺ concentrations higher than the TEL were reported at some points⁷.

In the pseudo-total fraction, all sediment samples had concentrations higher than the TEL level. The sediment samples collected in August 2014 at point 2 and all samples at point 4 showed concentrations of Cu²⁺ that exceeded the PEL limit

(probable effects levels), 197.0 mg kg⁻¹.

The highest concentrations of Cu in P1, P2 and especially in the sediments of the mouth of the Ocoí River (P4) may be related to the intensive agriculture that are predominant in this region of study. In these activities are applied various compounds containing copper, as fungicides. In addition, the low solubility of the oxides of this metal increases the possibility of increment of this element in the sediments of the studied sites²³. Pork farming is another activity intensely performed in the region of study that may contribute to the increase of Cu²⁺ and Zn²⁺ in the environment. This is related to the supply of highly concentrated rations, which means that the manure from this activity presents elevated levels of these elements. The disposal of these residues as fertilizer can provide the contamination of the water bodies, through the lixiviation surface runoff²⁴.

Concentrations of Cu²⁺, both labile fraction and pseudo-total fraction, were higher at points 1, 2 and 4, as well as concentrations of VTS and TOC (Table 3). This indicates a higher occurrence of organic matter at these points, which may have provided greater retention of metals. Sediments of lower granulometry, rich in clay, nutrients and organic matter are one of the main adsorbents of several metals that may be present in the aquatic environment⁶. The concentrations of Cu²⁺ obtained were close to the values found in the surface sediment of the Cachoeira River in Bahia, where there was variation between 4.9 and 206.3 mg kg⁻¹²².

The chromium concentration for the labile fraction presented a uniform distribution at all the points sampled. Concentrations below the threshold where adverse effects are rarely expected (TEL), 37.3 mg kg⁻¹ have been found. In the pseudo-total fraction, at all points Cr³⁺ concentrations were

higher than the TEL level, 37.3 mg kg^{-1} . The sediment samples collected in 2014, in February in point 2 and August in points 3 and 4, exceeded the limit of PEL, 90.0 mg kg^{-1} . In August 2014, concentrations in the pseudo-total fraction at point 3 were above the severe effects (SEL) levels, 110.0 mg kg^{-1} . These results are similar to concentrations already reported in sediments of the Itaipu Reservoir, in the Cr^{3+} concentrations of 6.4 to 71.9 mg kg^{-1} ⁷.

The concentrations of manganese presented similar concentrations between points and collections, both in the fraction labile and in the pseudo-total fraction, except for point 3, where a reduction in the concentration of Mn^{2+} occurred in the sample collected in March 2015. In all fractions Mn concentrations were lower than the SEL level of $1100.0 \text{ mg kg}^{-1}$. Mn concentrations in the pseudo-total fraction were close to and higher than those determined in sediment samples from the Itaipu Reservoir, Paraná, where concentrations of Mn^{2+} were reported between 182.0 and 543.0 mg kg^{-1} ⁷.

In general, the Pb^{2+} concentration was low for the fraction labile. The highest levels were verified in August 2014 and March 2015. In the pseudo-total fraction, all the collection points had Pb^{2+} concentrations higher than the TEL level, 35.0 mg kg^{-1} , except for point 1 in August 2014. Pb^{2+} is poorly soluble in water. This can certainly contribute to its increase in sediment. Lead can have several origins, such as old paint chips, ceramics, plastics, gasoline, lead salts used in hair dye preparations²⁵. The Pb^{2+} concentration in the pseudo-total fraction, when compared to another study in the same region (12.0 to 38.1 mg kg^{-1}), was higher than that reported⁷.

For the Zn^{2+} , in the labile fraction all collection points had concentrations lower than the TEL level, 123.0 mg kg^{-1} . In the pseudo-total fraction, they exceeded the limits of TEL, except in point 3. The high concentrations of Zn^{2+} , with emphasis on the pseudo-total fraction at points 1, 2 and 4, may be related to pork farming in region of study and that can certainly contribute with the increase of Zn^{2+} , similar to that observed for Cu^{2+} ²⁴.

All nickel concentrations of the labile fraction were lower than the TEL (18.0 mg kg^{-1}) level, the lowest concentrations occurred at point 3. In the pseudo-total fraction, Ni^{2+} levels exceeded the TEL level. At points 1, 2 and 4 the concentrations were higher than the PEL level, 36.0 mg kg^{-1} . The occurrence of Ni^{2+} in the study sites may contribute to agricultural activities, since fertilizers and correctives applied in soils usually have residual

impurities of their production and represent an important source of micronutrients, such as Zn^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} and Ni^{2+} ²⁶.

3.4 Multivariate Analysis and Correlation Study

Associations that reveal information about processes that influence the distribution of elements in the sediments were evaluated through a multivariate principal component analysis (PCA). It was verified that direct and positive correlations were higher than 0.6 for pseudo-total metals and physicochemical parameters Cu^{2+} -pH, Cu -VTS, Cu^{2+} -C total, Cu^{2+} -clay, Cr^{3+} -sand, Mn^{2+} -pH, Mn^{2+} -VTS, Mn^{2+} -TOC, Mn^{2+} -clay, Pb^{2+} -sand, Zn^{2+} -pH, Zn^{2+} -VTS, Zn^{2+} -TOC, Zn^{2+} -clay, Ni^{2+} -pH and Ni^{2+} -clay. Cu^{2+} -FTS, Cu^{2+} -sand, Cr^{3+} -clay, Cr^{3+} -silt, Mn^{2+} -ST, Mn^{2+} -FTS, Mn^{2+} -sand, Pb^{2+} -clay, Pb^{2+} -silt, Zn^{2+} -TS, Zn^{2+} -FST, Zn^{2+} -sand and Ni^{2+} -sand.

For the labile metals and physicochemical parameters, direct correlations were observed between Cu^{2+} -pH, Cu^{2+} -clay, Cr^{3+} -TS, Cr^{3+} -FTS, Mn^{2+} -pH, Mn^{2+} -VTS, Mn^{2+} -TOC, Mn^{2+} -clay, Pb^{2+} -TS, Pb^{2+} -FTS, Pb^{2+} -sand, Zn^{2+} -pH, Zn^{2+} -VTS, Zn^{2+} -TOC, Zn^{2+} -clay, Ni^{2+} -pH, Ni^{2+} -clay and Ni^{2+} -Silt. Mn^{2+} -TS, Mn^{2+} -FST, Mn^{2+} -sand, Pb^{2+} -VTS, Pb^{2+} -TOC, Pb^{2+} -clay, Zn^{2+} -TS, Zn^{2+} -FTS, Cr^{3+} -TOC, Cr^{3+} -TOC, Cr^{2+} -TOC, Zn^{2+} -sand, Ni-sand.

These relationships indicated that pH and TOC are related to the occurrence of some elements in the sediments. The relationship between pH increase and the concentration of some metal ions in sediments may be related to the fact that more alkaline pH favors the precipitation of the dissolved metals in the form of insoluble oxides and hydroxides, especially with Fe and Mn oxides⁶.

The low affinity of the sand in the retention of metallic species is one of the factors that explain its inverse effect for the majority of the metals studied. It was possible to observe among the metals of the pseudo-total fraction that Mn^{2+} - Cu^{2+} , Pb^{2+} - Cr^{3+} , Zn^{2+} - Cu^{2+} , Zn^{2+} - Mn^{2+} , Ni^{2+} - Cu^{2+} , Ni^{2+} - Mn^{2+} and Ni^{2+} - Zn^{2+} obtained direct correlations and higher than 0.6. The occurrence of inverse correlation was observed between Pb^{2+} - Mn^{2+} . In the available fraction Mn^{2+} - Cu^{2+} , Zn^{2+} - Cu^{2+} , Zn^{2+} - Mn^{2+} , Ni^{2+} - Cu^{2+} , Ni^{2+} - Zn^{2+} and Ni^{2+} - Mn^{2+} presented direct correlation.

The inverse correlation was observed between Mn^{2+} - Cr^{3+} , Pb^{2+} - Mn^{2+} , Zn^{2+} - Cr^{3+} and Ni^{2+} - Pb^{2+} . The good correlations of Mn^{2+} with trace metals indicate the presence of iron and manganese oxides associated with these metals. The precipitation of hydrated oxides of Fe and Mn is associated with the

transport and availability of trace metals, which influence the changes in the water-sediment interface²⁷. A similar study with samples collected in the same region also reported the occurrence of positive correlations between Cu^{2+} - Mn^{2+} , Fe^{2+} - Mn^{2+} and Cr^{3+} - Pb^{2+} in surface sediments⁷.

The concentration of Zn^{2+} in sediments of the Terengganu River basin in Malaysia also showed a relation with the Fe concentration, which can be explained by the adsorption of Zn^{2+} by secondary Fe oxides and hydroxides²⁸. The relationships between the collection points with the physical-chemical variables and metals studied can be better visualized in Figure 3, where the PCAs are plotted considering the pseudo-total and labile fraction.

For de labile fraction, in the PCA (Figure 3a and 3b) the first and second principal components captured 41.04 and 26.13 % of the variance of the

experimental data, respectively, together totaling 67.17 % of variance captured. The first and second principal components (Figure 3a) did not separate the samples by collections (years), but by points sampled. All samples of P3 and P4 were placed in the positive quadrant of the y-axis (PCA factor 2), indicating similarity of sediments sampled at these sites. The samples of P1 and P2 appeared in the negative quadrant of the y axis (PCA factor 2) also showing similarity between these points and indicating differences in relation to P3 and P4.

In Figure 3b (PCA factor 1), it can be seen that metallic ions show a strong correlation with pH, clay and silt, indicating a preference of adsorption by sediment of smaller particle sizes, which shows that the distribution of metals is controlled by the transport and sedimentation of fine particles^{2, 28, 29}.

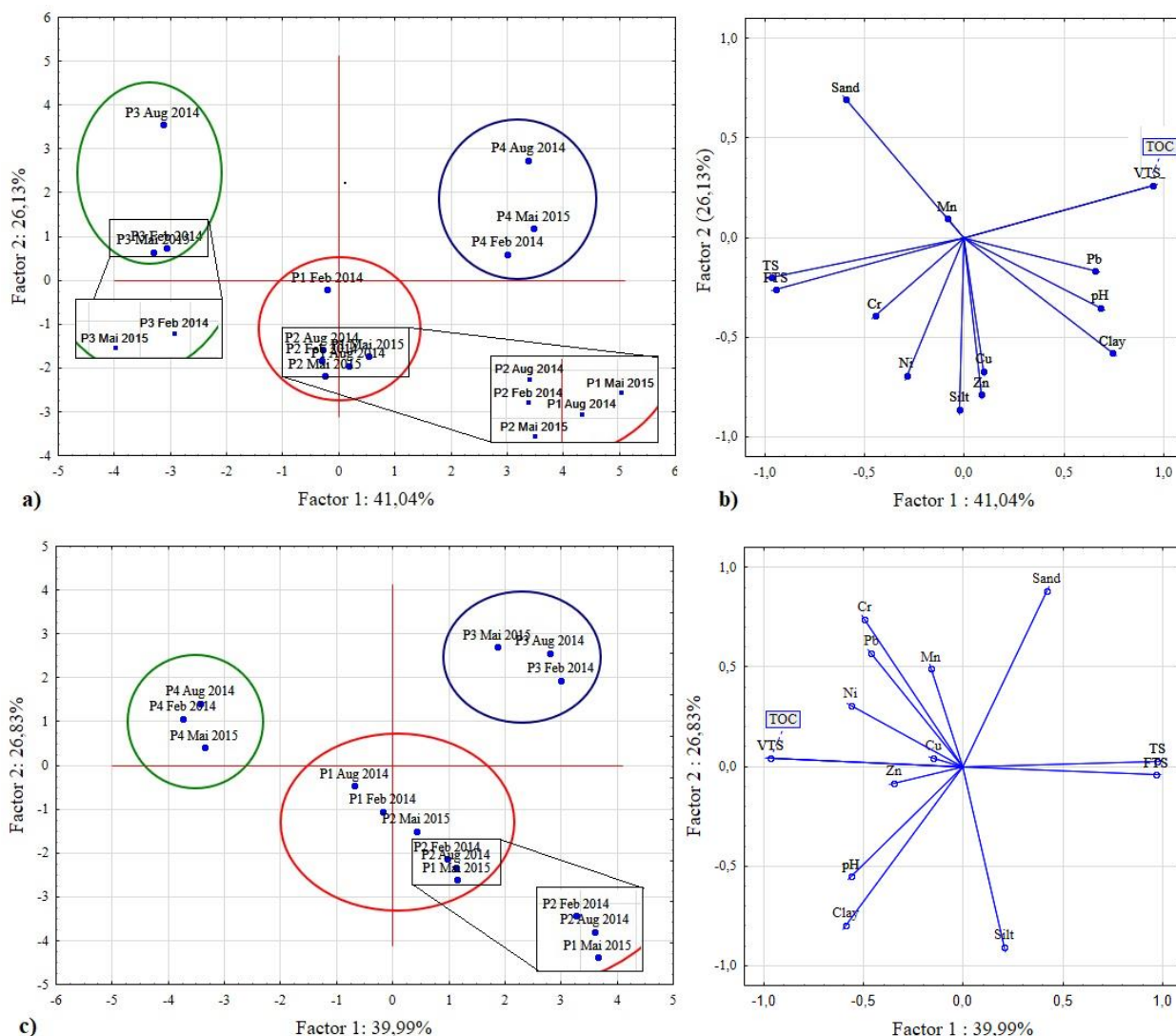


Figure 3. Scores of sampling sites (a) and (c) and loadings of variables (b) and (d) on the plane defined by the principal factor of PCA analysis for physical-chemical variables and metals.

For the pseudo-total fraction, in the PCA (Figure 3c and 3d) the first and second principal components captured 39.99 and 26.83 % of the variance of the experimental data, respectively, together totaling 66.83 % of variance captured. In this fraction, it was also observed behavior similar to labile metals, where the separation occurred because of the points sampled and not of the annual collections.

The grouped samples in the positive y-axis presented a high correlation with the variables Pb^{2+} , Mn^{2+} , Cu^{2+} , Ni^{2+} , Cr^{3+} , and TOC, whereas the sample located in the negative y-axis correlated with Zn^{2+} , pH and clay. In the positive quadrant of the x-axis, a group was formed by sampling of P3, these collection points showed lower concentrations of metal ions evaluated and a strong correlation with sand, FTS and TS.

Samples from the same point are more clustered in PCA for pseudo-total metals (Figure 3c), indicating variation between collection campaigns. For the bioavailable fraction (label) it was observed a greater dispersion of the data at each point (Figure 3a). This was confirmed at points P3 (Aug 2014), P4 (Aug 2015) and P1 (Feb 2014) which are further away from the others.

4. Conclusions

The sediments of the mouth of some of the main tributaries of the Itaipu Reservoir, in relation to the physicochemical parameters evaluated, presented neutral to slightly alkaline character. The concentrations of VTS and TOC were higher in P4, followed by P1 and P2. This higher concentration of VTS indicated the occurrence of organic matter, which may favor the retention of metals in the compartment. Regarding the granulometry, the predominance of the clay fraction was observed. Point 3 presented the smallest fraction of this mineral, only 22 %.

In the fraction labile, only Cu content reached concentrations higher than the TEL level at all sampling points. Regarding the pseudo-total fraction, some study sites reached concentrations for Cr^{3+} , Pb^{2+} and Zn^{2+} metals at the TEL level, below which adverse effects are rarely expected. For Ni^{2+} , PEL values were verified, being this the level of effects probable and for Cu^{2+} concentrations in SEL were reported where there is possibility of severe effects with rich in potentials on the quality of the environment, according to the international criteria of sediment

classification adopted NOAA.

The PCA was useful to evaluate the correlation between the sampling points, between collections and the interaction, with the physical-chemical variables and the fractions of metals studied, indicating that the anthropogenic activity exerts influence on the contents of metals in the sediment at the mouth of tributaries of the Itaipu Reservoir.

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6. References

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