# TRACE ELEMENTS IN THE WATER AND FISH OF TROPICAL WATERCOURSES IN CENTRAL BRAZIL

Roseni da Silva SOUZA<sup>1</sup>; Francisco Leonardo TEJERINA-GARRO<sup>2,3</sup>; Cleonice ROCHA<sup>4</sup>; Luiz Fabrício ZARA<sup>5</sup>; Affonso Celso GONÇALVES-JUNIOR<sup>6</sup>

## ABSTRACT

The aim was to compare the trace element concentrations found in samples of water (cadmium, copper, manganese, lead and zinc) from ten water catchments and muscle tissues (aluminum, iron, manganese, lead and zinc) from six fish trophic guilds, both samples collected in watercourses of the Upper Tocantins River, Goiás, Central Brazil. Trace element concentrations did not differ among the water catchments, except for Cu and Mn that exceeded the concentrations allowed by the environmental Brazilian legislation. The highest concentrations (Al, Fe, Mn, Pb e Zn) were found in fish of the guild detritivores, omnivores and terrestrial insectivores, while the aquatic invertivores showed the lowest ones; no correlation was observed between the concentrations of Mn, Pb and Zn of the water samples and fish muscle tissues. It suggests that the hydrological and chemical characteristics of watercourses sampled influence on a similar way the availability of trace elements in the water column. The differences of trace element concentrations observed among the trophic guilds do not display a trend based on fish feed strategy, but on the availability of the trace element in the environment, finding reinforced by the absence of relationship between trace elements concentrations of water and fish muscle tissue.

Keywords: Trophic guild; bioaccumulation; bioconcentration; detritivorous; omnivorous

## ELEMENTOS-TRAÇO NA ÁGUA E EM PEIXES DE CURSOS DE ÁGUA TROPICAIS NO BRASIL CENTRAL

### RESUMO

Objetivou-se comparar as concentrações dos elementos-traço encontrados em amostras de água (cádmio, cobre, manganês, chumbo e zinco) de dez sub-bacias e tecido muscular (alumínio, ferro, manganês, chumbo e zinco) de peixes pertencentes a seis guildas tróficas, ambas as amostras coletadas em cursos de água do alto rio Tocantins, Goiás, Brasil Central. As concentrações dos metais traços da água não diferiram entre sub-bacias, exceto para Cu e Mn que ultrapassaram estas indicadas pela legislação ambiental brasileira. As maiores concentrações (Al, Fe, Mn, Pb e Zn) foram encontradas nos peixes detritívoros, onívoros e insetívoros terrestres, enquanto que os invertívoros aquáticos apresentaram as menores concentrações, não se observou correlação entre as concentrações de Mn, Pb e Zn na água e nos peixes. Isto sugere que as características hidrológicas e químicas dos cursos de água amostrados influenciam de maneira semelhante a disponibilidade de elementos-traço na coluna de água. As diferenças de concentrações dos elementos-traço observadas entre as guildas tróficas não apresentam uma tendência com base na estratégia de alimentação dos peixes, mas relacionada à disponibilidade do elemento-traço no ambiente, resultado reforçado pela ausência de relação entre a concentração dos elementos-traço da água e do tecido muscular dos peixes.

Bol. Inst. Pesca, São Paulo, 42(3): 500-513, 2016

Doi 10.20950/1678-2305.2016v42n3p500

Artigo Científico: Recebido em 01/12/2015 - Aprovado em 07/07/2016

<sup>&</sup>lt;sup>1</sup> Programa de Mestrado em Ecologia e produção sustentável, Campus II - PUC Goiás. GO, Brazil.

<sup>&</sup>lt;sup>2</sup> Centro de Biologia Campus II - PUC Goiás. GO, Brazil. garro@pucgoias.edu.br (corresponding author)

<sup>&</sup>lt;sup>3</sup> Programa de Mestrado em Sociedade, Tecnologia e Meio Ambiente, UniEVANGÉLICA. Anápolis, GO, Brazil.

<sup>&</sup>lt;sup>4</sup> Laboratório de Química, Departamento de Matemática e Física, Campus I - PUC Goiás, Brazil.

<sup>&</sup>lt;sup>5</sup> Universidade de Brasília, Faculdade de Planaltina. GO, Brazil.

<sup>&</sup>lt;sup>6</sup> Laboratório de Química Ambiental e Instrumental, Universidade Estadual do Oeste do Paraná, PR, Brazil.

Palavras-chave: guildas tróficas; bioacumulação; bioconcentração; detritívoros; omnívoros

## **INTRODUCTION**

The Tocantins River is located within the Tocantins-Araguaia basin and drains an area of 767,000 km<sup>2</sup> in northern Goiás (COSTA et al., 2003). It has ancient deep well-drained soils, with acidic nutrition, poor fertility and considerable iron and aluminum content (RIBEIRO and WALTER, 1998). In terms of climate, there is a dry season from April to September and a rainy season from October to March (NOVAES et al., 2004). The predominant vegetation is the natural savanna known as Cerrado and according to the 2000 census; the basin encompasses 71 municipalities (TEJERINA-GARRO et al., 2008) whose predominant anthropogenic activities are agriculture, livestock rearing and mining. The natural concentrations of trace elements in the aquatic environment may increase due to human activities such as agriculture (LEWIS et al., 1997; MATOS, 2010), livestock rearing (DORES and FREIRE, 2001), mining (KLAUBERG-FILHO et al., 2002; VEADO et al., 2006) and chemical pollution caused by household and industrial waste (ALONSO et al., 2002; BARBIERI et al., 2010; FRERET-MEURER et al., 2010). Given that human populations depend strongly on river resources either as source of drinking water or as source of food, there is an urgent need to study the amount of trace elements found in this habitat (THORNTON, 1995; BIZERRIL and PRIMO, 2001).

The availability of trace elements in the aquatic environment is influenced by the physicochemical properties of the water (NÚNEZ *et al.*, 1999; MORAES *et al.*, 2003; BARROS and BARBIERI, 2012), namely ionic strength, redox potential and pH. The last two exert a considerable influence on changes in the solubility of trace elements, which may be hazardous for the aquatic environment (NÚNEZ *et al.*, 1999). Certain hydrological factors, such as water flow, do not allow trace elements to concentrate in the water column (SANTOS *et al.*, 2008) or to be adsorbed into the sediment (SALVADÓ *et al.*, 2006). Fish are involved in numerous trophic (ARNOT and GOBAS, 2004) and habitat interrelationships, which may lead to an accumulation of trace elements absorbed from the ingestion of water, sediment or food (BORDAJANDI et al., 2003) in muscle, liver, and kidney tissues (BARBIERI et al., 2010). This phenomenon causes a bioconcentration of these trace elements, which, in turn, may lead to distribution/transference through the trophic network, i. e., bioaccumulation (MACKAY and FRASER, 2000; MARENGONI et al., 2008). Usually, bioconcentration of trace elements causes several reactions in fish, such as stress (VINODHINI and NARAYANAN, 2008), physiological dysfunction, structural changes in organs and tissues which affect their growth, reproduction (WINKALER et al., 2008) and behavior (CONNELL and MILLER, 1984).

It is difficult to compare the trace elements concentrations between the same tissues of two different fish species or considering the trophic guilds omnivorous and carnivorous because of their different feeding habits (BARBIERI et al., 2010). However, the use of trophic guilds, defined as a group of species that uses similar environmental resources in the same way (NOBLE et al., 2007), show more efficiently the characteristics of ecosystem's functioning, which are difficult to see in individual species (VALE et al., 2010). In this way, the trophic guild of detritivores fish have a greater tendency to accumulate large amounts of trace elements in their bodies due to a rich diet of sediments, which are considered trace element deposits (WERNECK LIMA et al., 2003; SALVADÓ et al., 2006). Aquatic invertivores fish feed on macroinvertebrates associated with the substrate (BOLLMANN et al., 2001), whereas terrestrial insectivores bioaccumulate trace elements when they swallow terrestrial insects feeding on the aerial parts of plants containing, for example, considerable concentrations of lead (Pb) due to the use of pesticides (CORBI et al., 2006) or manganese (Mn) which is found in acidified soils (CAMARGO and FERREIRA, 1992). Piscivores fish are top predators of the food web, thus they have a tendency towards an elevated trace element bioaccumulation (TERRA et al., 2007; TELES et al., 2008).

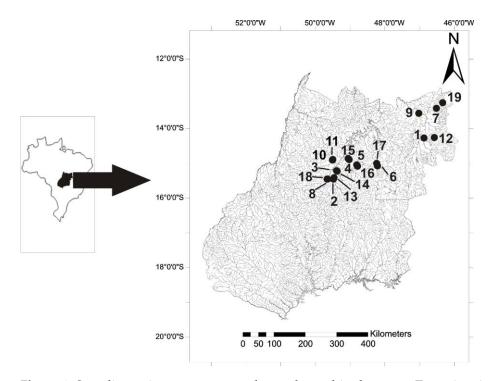
The aim of this study was to i) compare the trace element concentrations found in samples of water (cadmium, copper, manganese, lead and zinc) from ten water catchments and muscle tissue (aluminum, iron, manganese, lead and zinc) from six fish trophic guilds, and ii) determine the relationship between trace elements concentrations (manganese, lead, zinc) of both samples collected in watercourses of the Upper Tocantins River, Goiás, Central Brazil.

It is expected that the concentrations of trace elements will differ among the water catchments due to their hydrological and chemical local characteristics and among the fish trophic guilds, because of their different use of the environment resources. It is also expected a positive relationship between the trace elements concentrations of water and fish muscle tissue.

## MATERIAL AND METHODS

#### Study area

From July to August 2008, ten rivers and one tributary of each of them were sampled in the Tocantins River basin between the geographic coordinates 13° 0' 0" S; 46° 0' 00" W and 16° 0' 0" S; 50° 0' 0" W. Each pair (river and tributary) was named water catchment (Figure 1) and the tributaries were either a river or a stream. The Pedras River was an exception as none of its tributaries was sampled (Table 1). Each watercourse was georeferenced with a GPS (Garmin) and stretches of 50 m (for streams) and 1000 m (for rivers) were demarcated, where the fishes and water samples were collected. A synthetic characterization of the rivers and tributaries considering riparian channel vegetation, substrate and main anthropogenic activities is presented in Table 1.



**Figure 1**. Sampling points per water catchment located in the upper Tocantins river basin, Central Brazil. 1 = Corrente River, 2 = Almas River, 3 = Peixe River, 4 = Bois River, 5 = Patos River, 6 = Maranhão River, 7 = São Domingos River, 8 = Uru River, 9 = Pedras River, 10 = São Patricinho stream, 11 = Bandido stream, 12 = Prata

Bol. Inst. Pesca, São Paulo, 42(3): 499-513, 2016

stream, 13 = São Pedro stream, 14 = Palmital stream, 15 = Vereda stream, 16 = Pouso Alegre stream, 17 = Bom Jesus stream, 18 = Leão stream and 19 = Galheiros stream.

## Water sampling and determination of trace elements

Water samples (1 L) were manually collected at a depth of 50 cm from the surface, using a plastic

bottle, previously washed with 10% HCl, at both the beginning and the end of each predefined stretch. One mL of HCl was added to each sample and immediately afterwards the bottle was duly labeled with the place and date of collection and stored in a Styrofoam box with ice.

**Table 1.** Rivers and tributaries by water catchments of the Tocantins River sampled in July and August 2008. The substrate type, predominant vegetation in riparian forest and predominant human activity are indicated.

Water catchment	River	Tributary	Substrate type	Predominant	Predominant
	0- D - 1 - 1	<b>D</b> 111	0.1	type vegetation	human activity
São Patricinho	São Patricinho	Bandido	Gravel	Trees, shrubs	Urban area,
					agriculture, livestock rearing
Corrente	Corrente	Prata	_	Trees, shrubs	Agriculture,
corrente	contente	Tiutu		11003, 511 005	livestock rearing
Almas	Almas River	São Pedro	Sand	Trees, shrubs	Agriculture,
					livestock rearing
Pedras	Pedras	-	Sand	Trees, shrubs,	Agriculture,
				pasture	livestock rearing
				-	
Peixe	Peixe	Palmital	Rock and sand	Trees, shrubs,	Agriculture,
				pasture	livestock rearing
Bois	Bois	Vereda	Sand	No vegetation	Agriculture,
				cover	livestock rearing
Patos	Patos	Pouso Alegre	Rock	Trees, shrubs,	Mining,
				pasture	agriculture,
					livestock rearing
Maranhão	Maranhão	Bom Jesus	Rock and sand	Trees, shrubs	Agriculture,
					livestock rearing
São Domingos	São Domingos	Galheiros	Sand and gravel	Shrubs, pasture	Urban area,
Suo Donnigos	Sao Doninigos	Gamenos	Sand and graver	Sinus, pasture	agriculture,
					livestock rearing
Uru	Uru	Leão	Rock and sand	Shrubs, pasture	Urban area,
	-			· · · · · ·	agriculture,
					livestock rearing

In the laboratory, the samples were filtered through a  $0.45\mu m$  Millipore filter, then put into clean plastic bottles and stored at 4°C until analysis. Just before the analysis procedures, the samples were left to stand until they reach room

temperature. The cadmium (Cd), copper (Cu), manganese (Mn), lead (Pb) and zinc (Zn) concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP - OES) at the Spectroscopy Laboratory of the Catholic University of Brasilia, with the following detection limits: Cd =  $0.00948263 \mu g/L$ , Cu =  $0.019293 \mu g/L$ , Mn =  $0.004933 \mu g/L$ , Pb = 0.0555609

 $\mu$ g/L and Zn = 0.0316477  $\mu$ g/L.

*Fish collection and determination of trace elements in fish muscle tissues* 

Twenty-one fish species (Table 2) were collected using trawls or gillnet and then sorted according to the size.

**Table 2**. Number of samples per fish species and water catchment of the upper Tocantins River, Central Brazil and trophic guild determined according to literature.

ORDER	Trophic	Literature	Water catchment									
Family	Guild											
Genus and species			SP	CO	AL	PE	PI	BO	PA	MA	SD	UR
CHARACIFORMES												
Characidae												
Astyanax fasciatus	ON	Ι	-	-	-	1	3	-	-	1	-	1
Astyanax sp. 2	ON	Ι	-	1	-	-	-	-	-	-	-	-
Creagrutus sp.	IV	Ι	-	1	-	-	1	-	-	-	-	-
Hyphessobrycon sp.	IV	Ι	3	1	-	-	-	-	1	1	1	-
Knodus sp.	ON	Ι	1	-	-	-	-	-	-	-	-	-
Myleus torquatus	HB	Ι	-	-	-	-	-	-	2	-	-	-
Moenkhausia sp. 2	IN	Ι	-	-	-	-	-	-	1	2	-	-
Moenkhausia sp. 3	IN	Ι	-	-	-	-	1	-	1	-	-	-
Moenkhausia sp. 4	IN	Ι	-	-	1	-	-	-	1	-	1	-
Triportheus trifurcatus	IV	Ι	-	-	1	-	-	-	-	-	1	1
Crenuchidae												
Characidium zebra	IV	Ι	1	-	-	-	-	-	1	-	-	-
Hemiodontidae												
Hemiodus unimaculatus	DT	III	-	-	1	1	-	-	1	-	-	3
Cynodontidae												
Hydrolycus tatauaia	PC	Ι	-	-	-	-	-	-	-	-	-	3
Anostomidae												
Leporinus friderici	ON	II; IV	-	-	3	1	1	1	2	1	-	-
<i>Leporinus</i> sp.	ON	Ι	-	1	1	-	1	-	-	-	-	1
Prochilodontidae												
Prochilodus nigricans	DT	Ι	-	1	-	-	-	1	1	-	-	-
SILURIFORMES												
Auchenipteridae												
Auchenipterus nuchalis	IV	Ι	-	-	-	-	-	-	3	-	-	-
Loricariidae												
Hypostomus plecostomus	DT	Ι	-	-	-	-	2	-	1	-	3	-
Squaliforma emarginata	DT	Ι	-	-	2	1	-	-	-	-	-	-
Pimelodidae												
Pimelodus blochii	ON	Ι	-	-	-	-	-	1	2	-	-	-
PERCIFORMES												
Cichlidae												
Satanoperca pappaterra	ON	Ι	-	1	_	-		-	_			-
SP=São Patricinho: CO=Corr	ente AI=Alm	as• PF=Pedras	• <i>PI</i> =	Poiro	$B \cap = F$	Soie	PA = I	Patos	MA = I	Maranh	ão: SI	$D = S\tilde{a}o$

SP=São Patricinho; CO=Corrente; AL=Almas; PE=Pedras; PI=Peixe; BO=Bois; PA=Patos; MA=Maranhão; SD=São Domingos; UR=Uru. DT=Detritivore; HB=Herbivore; IN=Terrestrial insectivore; IV=Aquatic invertivore; ON=Omnivore; PC=Piscivore. I=De Carvalho and Tejerina-Garro (2015); II=Durães et al. (2001); III=Froese and Pauly (2015); IV=Hahn et al. (2004).

Bol. Inst. Pesca, São Paulo, 42(3): 499-513, 2016

Due to the available muscle tissue sample for further analysis, fish <10 cm were preserved entire, while a piece of muscle tissue from above the lateral line of the back was removed from the larger specimens (>10 cm). In both cases, samples were placed in plastic bags, labeled with the date and place of capture and stored in a box with ice.

In the laboratory, at the Aquatic Biology Centre of the Pontifícia Universidade Católica de Goiás, they were taxonomically identified, measured, weighed and stored in a freezer at a temperature of -10° C until analysis. Duplicates of each species were sent to the Ichthyology Laboratory at the Museum of Science and Technology, Pontifícia Universidade Católica de Rio Grande do Sul to confirm taxonomic identification. In this study, the trophic guild adopted for each species of fish (detritivore; herbivore; terrestrial insectivore; aquatic invertivore; omnivore; piscivore) was taken from DE CARVALHO and TEJERINA-GARRO (2015) who used the same fish samples from which the specimens in this study were selected. DURÃES et al. (2001), HAHN et al. (2004) and FROESE and PAULY (2015) were also consulted. Thus, seven species were classified as omnivores, five as aquatic invertivores, four as detritivores, three as terrestrial insectivore, one as piscivore and one as herbivore (Table 2).

To determine trace elements concentrations, the whole fish or pieces of muscle tissues were thawed and allowed to stand to reach room temperature. They were then lyophilized (Labconco Freeze Dryer Freezone) after which 1.0 g of the material was digested in triplicate with nitric acid and hydrogen peroxide following the wet oxidation process (JAFFAR et al., 1988). The digested material was stored in a polyethylene bottle and sent to the Environmental and Instrumental Chemical Laboratory at the University of Paraná, where the concentrations of aluminum (Al), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn) were determined flame atomic absorption by spectrometry (flame - AAS), considering the detection limits: Al =  $0.8 \mu g/g$ , Fe =  $1.2 \mu g/g$ , Mn =  $0.004 \ \mu g/g$ , Pb =  $0.01 \ \mu g/g$  and Zn =  $0.001 \ \mu g/g$ .

### Data analysis

To compare the trace element concentrations in the water samples among water catchments and in fish muscle tissues among trophic guilds, the nonparametric Kruskal-Wallis statistical analysis test was used, since the assumptions of normality and homogeneity were not reached (SOKAL and ROHLF, 1995). This test allows for comparisons among various independent groups (KATZ and McSWEENEY, 1980) and is usually followed by a multiple comparison *post hoc* analysis.

Additionally, data recommended by the CONAMA Resolution No. 357 for Class 3 waters (CONAMA, 2005) were used as a reference for the maximum permissible values of trace element for water.

To determine the relationship among the trace element concentrations of Mn, Pb and Zn found in the water samples and in the fish muscle tissues a Spearman rank correlation analysis was conducted. All statistical analyzes were performed using the *Statistica*© 8 software.

### RESULTS

There were no significant differences among concentrations of trace elements analyzed in the water among water catchments (Table 3). Comparing the median values found with the maximum values allowed by CONAMA (2005), it was observed that the concentrations of Cd in the water catchment of Pedras, Patos and São Domingos were equal to those allowed, while the levels of Cu at São Patricinho, Corrente, Peixe, Bois, and São Domingos were above the permitted levels, as well as Pb levels at São Patricinho, Almas, Peixe, Bois, Maranhão and São Domingos. It is detected a low oscillation of pH values (6.1 to 6.4) in all the water catchments sampled (Table 3).

Significant differences were observed among the trophic guilds for Al (p=0.01), Fe (p=0.00), Mn (p=0.00), Pb (p=0.01) and Zn (p=0.01; Figure 1a-e) trace element. The detritivore guild stands out for presenting higher concentration of: Al, Fe, Mn, Pb and Zn than the aquatic invertivores (p=0.00; p=0.00; p=0.00; p=0.00; p=0.00, respectively; Figure 1a-e), Fe and Mn than piscivores (p=0.02 in both cases; Figure 1b-c), and Pb than terrestrial insectivores (p=0.04; Figure 1d).

A second prominent guild is omnivorous that displays more elevated concentration values of Mn, Pb and Zn than aquatic invertivores fish (p=0.00; p=0.03; p=0.00, respectively; Figure 1c-e). Finally, terrestrial insectivores show higher concentrations of Mn in relation to aquatic invertivores (p=0.04; Figure 1c). The analysis of correlation showed no relationship among the concentrations of the three common base trace elements (Mn, Pb, Zn) in the water samples versus fish muscle tissues (Table 4).

**Table 3.** Median (Md), minimum (Min.) and maximum (Max.) concentration levels of trace elements ( $\mu$ g/L) and median pH in the water samples per water catchment of the Upper Tocantins River basin, Central Brazil. The statistics of the Kruskal-Wallis test (p<0.05) and the maximum levels ( $\mu$ g/L) allowed by CONAMA (2005), for water class 3 are indicated.

Trace	e element	Water catchment									Р	CONAMA	
		SP	СО	AL	PE	PI	ВО	PA	MA	SD	UR		
Cd	Md	9.1	7.5	9.1	10.2	9.0	7.8	10.2	8.9	10.6	9.3	0.86	10
	Min.	8.6	4.6	8.6	6.6	6.3	6.6	7.1	5.6	7.6	4.7		
	Max.	16.9	10.6	11.5	13.8	12.2	12.3	13.3	11.0	13.6	10.5		
Cu	Md	15.0	31.1	11.0	6.9	19.3	19.3	2.4	12.9	19.3	10.1	0.23	13
	Min.	6.2	2.8	0.1	5.0	2.8	6.3	2.2	1.1	19.3	0.9		
	Max.	19.3	94.8	19.3	8.7	51.2	153.0	2.6	19.3	151.6	75.1		
Mn	Md	53.4	21.1	47.2	4.3	28.3	48.5	13.3	14.3	21.1	24.2	0.19	500
	Min.	12.3	11.0	30.9	4.2	11.7	8.6	7.9	12.3	8.6	13.4		
	Max.	72.2	27.4	53.0	4.4	168.5	105.6	18.7	32.4	116.6	404.2		
Pb	Md	32.1	28.7	37.7	5.4	37.7	53.5	15.8	36.7	39.0	25.0	0.74	33
	Min.	0.7	25.8	1.0	4.5	15.3	3.2	9.0	15.1	20.4	0.7		
	Max.	55.6	55.6	55.6	6.3	55.6	82.4	22.6	55.6	55.6	55.6		
Zn	Md	418.1	462.3	431.8	492.9	448.1	434.7	308.3	480.5	346.0	529.0	0.54	5000
	Min.	143.9	379.7	31.6	453.6	282.0	334.4	210.8	343.5	190.0	294.4		
	Max.	449.4	690.8	475.5	532.2	620.3	537.0	405.7	492.6	524.9	648.1		
pН		6.2	6.3	6.2	6.1	6.2	6.2	6.3	6.4	6.2	6.3		

SP=São Patricinho; CO=Corrente; AL=Almas; PE=Pedras; PI=Peixe; BO=Bois; PA=Patos; MA=Maranhão; SD=São Domingos; UR=Urus.

Comparing the median values found with the maximum values allowed by CONAMA (2005), it was observed that the concentrations of Cd in the water catchment of Pedras, Patos and São Domingos were equal to those allowed, while the levels of Cu at São Patricinho, Corrente, Peixe, Bois, and São Domingos were above the permitted levels, as well as Pb levels at São Patricinho, Almas, Peixe, Bois, Maranhão and São Domingos. It is detected a low oscillation of pH values (6.1 to 6.4) in all the water catchments sampled (Table 3).

Significant differences were observed among the trophic guilds for Al (p=0.01), Fe (p=0.00), Mn (p=0.00), Pb (p=0.01) and Zn (p=0.01; Figure 1a-e) trace element. The detritivore guild stands out for presenting higher concentration of: Al, Fe, Mn, Pb and Zn than the aquatic invertivores (p=0.00; p=0.00; p=0.00; p=0.00; p=0.00, respectively; Figure 1a-e), Fe and Mn than piscivores (p=0.02 in both cases; Figure 1b-c), and Pb than terrestrial insectivores (p=0.04; Figure 1d).

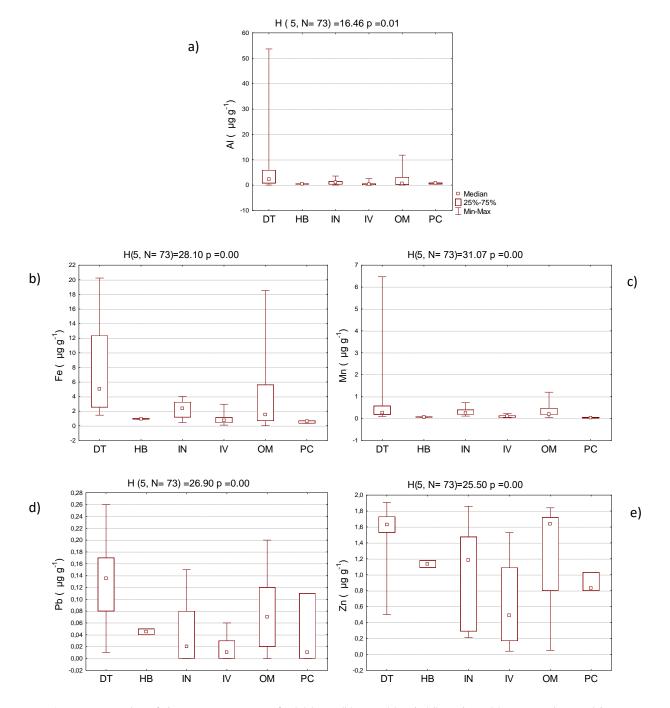
A second prominent guild is omnivorous that displays more elevated concentration values of Mn, Pb and Zn than aquatic invertivores fish (p=0.00; p=0.03; p=0.00, respectively; Figure 1c-e). Finally, terrestrial insectivores show higher concentrations of Mn in relation to aquatic invertivores (p=0.04; Figure 1c).

The analysis of correlation showed no relationship among the concentrations of the three common base trace elements (Mn, Pb, Zn) in the water samples *versus* fish muscle tissues (Table 4).

## DISCUSSION

In terms of trace element concentrations in the water samples, the results were contrary to expected, showing that there were not significant differences among the water catchments considered in this study. This result seems related to the influence of the water flow on trace elements concentration. Water flow does not allow trace elements to concentrate in water column (SANTOS et al., 2008). Additionally, the adsorption of trace elements by sediments also reduces the concentration of these chemicals in water column. This can be favored by the high water pH values observed in all water catchments sampled, that is, a reduction of dissolved forms of trace elements in the water column and an increasing of precipitated and adsorbed ones (GUILHERME et al., 2005). However, the absence of significant differences among the trace element concentrations in the water samples of the water catchments analyzed in this study does not mean that the environments are not polluted, because some concentrations were similar (Cd) to or higher (Cu and Pb) than those allowed by CONAMA (2005). In contrast to previous studies examining the positive relationship among trace concentration of water and aquatic element organism (BORDAJANDI et al., 2003; TELES et al.,

2008; BARBIERI et al., 2010), the current study indicated that there was no correlation between the Mn, Pb and Zn trace element concentrations found in the water and muscle tissues of the fish analyzed. Relationships results from the fact that watercourses are responsible for the dissolution and transport of trace elements in the aquatic environment. This increases their concentration in the water leaving fish further exposed and, consequently, absorbing trace elements through the gills (BORDAJANDI et al., 2003), because of the chemical changes that these trace elements undergo in the aquatic environment (ESTEVES, 1998). However, in this study this was not the case even with Mn, which showed levels higher than those allowed by law in water column. This suggests that the Mn available in the water did not lead to the contamination of the fish via absorption of this trace element through gill, but rather through contaminated organic food (BORDAJANDI et al., 2003; TELES et al., 2008) since other investigations also found this trace element in other vertebrates (LOUREIRO et al., 2007) and sediments (CUNHA and CALIJURI, 2008). Accordingly to expected, there were significant differences in the trace element concentrations among fish samples from different trophic guilds for Al, Fe, Mn, Pb and Zn. Variety in the diet and different feeding habitat of the fish species influence on trace element concentration levels in their bodies (BARBIERI et al., 2010; MAZZONI et al., 2010), this is especially true for Cu and Zn (BORDAJANDI et al., 2003). In this study, the detritivores (muscle tissue concentrations of Al, Fe, Mn, PB, Zn), omnivores (Mn, Pb, Zn) and terrestrial insectivores (Mn) display higher concentrations mainly in relation to aquatic invertivores. This result suggests that trace element concentration level by trophic guild considered not display a trend based on fish feed strategy, that is carnivorous species displays higher trace element concentrations than herbivorous, omnivorous or planktivorous species (BARBOSA et al., 2003; TERRA et al., 2007), but on the availability of the trace element in the environment.



**Figure 1**. Boxplot of the concentrations of Al (a), Fe (b), Mn (c), Pb (d) and Zn (e) per trophic guild. Statistics of the Kruskal-Wallis test (H) and the p values (p<0.05) are indicated. DT=Detritivore; HB=Herbivore; IN=Terrestrial insectivore; IV=Aquatic invertivore; OM=Omnivore; PC=Piscivore.

Bol. Inst. Pesca, São Paulo, 42(3): 499-513, 2016

Relationship	Correlation							
Water vs. Fish		Mn	Pb	Zn				
	Mn	-0.04	-0.11	0.11				
	Pb	0.26	-0.04	0.08				
	Zn	0.13	0.01	-0.01				

**Table 4**. Matrix of correlation (Spearman) among trace elements (Mn, Pb and Zn) in water ( $\mu$ g/L) and in fish muscle tissue ( $\mu$ g/g) in the Upper Tocantins River basin, Central Brazil.

An example of the absence of the trend based on feed strategy is the case of the piscivorous guild, represented in this study by the dogtooth characin Hydrolycus tatauaia, which the concentration levels of Fe and Mn in the muscle tissue were lower than in the detritivores. This trophic guild has a tendency to accumulate trace elements both in freshwater (TERRA et al., 2007; TELES et al., 2008) and marine environments (KEHRIG et al., 2007) as they are considered top-of-the-chain. Certain trace element not found in piscivores of this study, have been reported in fish from other environments. This was the case of Al, which showed negligible levels in this study, but has been found in high concentration in the muscle of the Serrasalmus spp. species (piranha) in the Gelado River in Pará State (BARROS et al., 2010). Like Al, Zn did not stand out as a contaminant of the piscivorous species in this study, but it was assessed and found in the viscera of a piscivore, the traíra Hoplias malabaricus in the Billings reservoir, São Paulo (ROCHA et al., 1985).

On the other hand, it is supposed the existence of a high concentration of these chemical elements in the sediments of the watercourses sampled due to the natural presence of them in the Cerrado soil such as the case for Pb or Zn (FAGERIA, 2000). However, in the terrestrial environment, soils have a striking capacity to retain trace elements due to atmospheric deposition or industrial and agricultural sources (PIERANGELI *et al.*, 2001),

which can be transported to the aquatic environment by severe wet weather conditions. In this circumstance, the fact that detritivores presented a higher trace element concentration than most other trophic groups considered can be related to the certainty that detritivores feed on sediments (BORDAJANDI et al., 2003) and to morphophysiological characteristics that facilitate the ingestion and absorption of nutrients present in these foods (DE MORAES et al., 1997; BORDAJANDI et al., 2003).

The fact that aquatic invertivores displayed low muscle tissues element trace concentration reinforce the role of the sediments in this study at the expenses of other components of the aquatic systems sampled such as the organic one represented by the macroinvertebrates. Aquatic invertivores, represented in this study by the catfish *Auchenipterus nuchalis* and the characins *Characidium zebra*, *Creagrutus* sp., *Hyphessobrycon* sp. and *Triportheus trifurcatus* are the most dominant trophic guild in many rivers (OLIVEIRA and FERREIRA, 2002) and feed on macroinvertebrates associated with the substrate (BOLLMANN *et al.*, 2001).

There was a higher concentration of Mn in the terrestrial insectivores characins *Moenkhausia* sp. 2; *Moenkhausia* sp. 3 and *Moenkhausia* sp. 4 than in the aquatic invertivores. This result seem related to the fact that the species representing this trophic guild feed mainly on terrestrial insects, which could be

contaminated by ingesting the aerial parts of plants in acidic soils with high concentration levels of Mn (FOY, 1984; VELOSO *et al.*, 1995; SALVADOR *et al.*, 2003; TELES *et al.*, 2008). The combination of contaminated terrestrial insects and plants could explain partially the case of omnivorous species that is, the fact that omnivorous feed on vegetal and animal matter potentially the bioaccumulation.

### CONCLUSION

Contrary to expected, concentrations of the trace elements investigated in this study did not differ in the waters among the ten water catchments analyzed, but significant differences were observed among the six trophic guilds of fish analyzed. No relationship was found among trace elements concentrations of water and fish muscle tissue. These results suggest that the hydrological and chemical characteristics of watercourses sampled influence on a similar way the availability of trace elements in the water column. The differences of trace element concentrations observed among the trophic guilds considered do not display a trend based on fish feed strategy, but on the availability of the trace element in the environment, finding reinforced by the absence of relationship between the trace elements concentration of water and fish muscle tissue.

These results add further evidence that the examination of two compartments (water and fish, in this case) is not enough for the assessment of trace element pollution in the ecosystem, requiring the incorporation of the sediment compartment. Additionally, the determination of Cd and Cu in fish, not measured in this study, must be considered in future studies once both trace elements displayed elevated values in the water when compared to those allowed by CONAMA (2005).

### ACKNOWLEDGEMENTS

The authors thank the National Council for Scientific and Technological Development (CNPq) for funding the project of which this study is part (Process 471283/2006-1), the entire staff at the

Bol. Inst. Pesca, São Paulo, 42(3): 499-513, 2016

Center for Aquatic Biology PUC Goiás for the data collection in the field specially Waldeir Francisco de Menezes, and Rodrigo Assis de Carvalho for his valuables suggestions.

### REFERENCES

- ALONSO, M.L.; BENEDITO, J.L.; MIRANDA, M.; CASTILLO, C.; HERNÁNDEZ, J.; SHORE, R.F. 2002 Interactions Between Toxic and Essential Trace Metals in Cattle from a Region with Low Levels of Pollution. *Archives of Environmental Contamination and Toxicology*, 42: 165-172.
- ARNOT, J.A.E. and GOBAS, F.A.P.C. 2004 A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environmental Toxicology and Chemistry*, 23(10): 2343-2355.
- BARBIERI, E.; PASSOS, E..A.; ARAGÃO, K.A.S.; SANTOS, D.B.; GARCIA, C.A.B. 2010 Assessment of trace metal levels in catfish (*Cathorops spixii*) from Sal river estuary, Aracaju, State of Sergipe, northeastern Brazil. *Water Environment Research*, 82(12): 2301-2305.
- BARBOSA, A.C.; SOUZA, J.D.; DÓREA, J.G.; JARDIM, W.F.; FADINI, P.S. 2003 Mercury Biomagnification in a Tropical Black Water, Rio Negro, Brazil. Archives of Environmental Contamination and Toxicology, 45: 235-246.
- BARROS, B.C.V.; PINHEIRO, S.F.; PEREIRA, D.C.P.; SILVA, C.S. 2010 Determinação de Cd, Cr, e Al em tecido de peixes provenientes do rio Gelado/APA, floresta de Carajás-PA. *Holos Environment*, 10(2): 195-208.
- BARROS, D. and BARBIERI, E. 2012 Análise da ocorrência de metais: Ni, Zn, Cu, Pb e Cd em ostras (Crassostrea brasiliana) e sedimentos coletados no Estuário de Cananéia, SP (Brasil). O Mundo da Saúde, 36(4): 635-642.
- BIZERRIL, C.R.S.F. and PRIMO, P.B. 2001 Peixes de águas Interiores do Estado do Rio de Janeiro. FEMAR, Rio de Janeiro. 417 p.

- BOLLMANN, H.A.; MAIA, N.B.; MARTOS, H.L.; BARRELLA, W. 2001 Indicadores ambientais: conceitos e aplicações. EDUC/COMPED/INEP, São Paulo. 285 p.
- BORDAJANDI, L.R.; FERNANDEZ, M.A.; ABAD, E.; RIVERA, J.; GONZALEZ, M.J. 2003 Study on PCBs, PCDD/Fs, organochlorine pesticides, heavy metals and arsenic content in freshwater fish species from the River Turia (Spain). *Chemosphere*, 53(2): 163-171.
- CAMARGO, C.E.O. and FERREIRA, A.W.P. 1992 Tolerância de cultivares de trigo a diferentes níveis de manganês em solução nutritiva. *Pesquisa Agropecuária Brasileira*, 27(3): 417-422.
- CONAMA Conselho Nacional do Meio Ambiente.
  2005 RESOLUÇÃO nº 357, de 17 de março de 2005.
  Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências. *Diário Oficial da União*, Brasília, 18 de março de 2005, nº 053, p. 58-63.
- CONNELL, D.W. and MILLER, G.J. 1984 *Chemistry and Ecotoxicology of Pollution*. John Wiley & Sons, New York. 444 p.
- CORBI, J.J.; STRIXINO, S.T.; SANTOS, A.; DEL GRANDE, M. 2006 Diagnóstico ambiental de metais e organoclorados em córregos adjacentes a áreas de cultivo de cana-de-açúcar (Estado de São Paulo, Brasil). Química Nova, 29(1): 61-65.
- COSTA, M.H.; BOTTA, A.; CARDILLE, J.A. 2003 Effects of large-scale changes in land cover on the discharge of the Tocantins River, Southeastern Amazonia. *Journal of Hydrology*, 283: 206-217.
- CUNHA, D.G.F. and CALIJURI, M.C. 2008 Comparação entre os teores de matéria orgânica e as concentrações de nutrientes e metais pesados no sedimento de dois sistemas lóticos do Vale do Ribeira de Iguape, SP. *Revista de Engenharia Ambiental*, 5(2): 24-40.
- DE CARVALHO, R.A. and TEJERINA-GARRO, F.L. 2015. Relationships between taxonomic and functional components of diversity: implications

for conservation of tropical freshwater fishes. *Freshwater Biology* 60(9): 1854-1862.

- DE MORAES, M.F.; BARBOLA, I.F.; GUEDES, É.A. 1997. Alimentação e relações morfológicas com o aparelho digestivo do "curimbatá", *Prochilodus lineatus* (Valenciennes) (Osteichthyes, Prochilodontidae), de uma lagoa do Sul do Brasil. *Revista Brasileira de Zoologia*, 14(1): 169-180.
- DORES, E.F.G.C. and FREIRE, E.M.L. 2001 Contaminação do ambiente aquático por pesticidas. Estudo de caso: águas usadas para consumo humano em Primavera do Leste, Mato Grosso. *Química Nova*, 24(1): 27-36.
- DURÃES, R.; POMPEU, P.S.; GODINHO, A.L. 2001 Alimentação de quatro espécies de *Leporinus* (Characiformes, Anostomidae) durante a formação de um reservatório no Sudeste do Brasil. *Iheringia*. *Série Zoologia*, 90: 183-191.
- ESTEVES, F.A. 1998 *Fundamentos de limnologia*. Rio de Janeiro: Interciência, Finep. p. 574.
- FAGERIA, N.K. 2000 Níveis adequados e tóxicos de zinco na produção de arroz, feijão, milho, soja e trigo em solo de cerrado. *Revista Brasileira de Engenharia Agrícola e Ambiental*, 4(3): 390-395.
- FOY, C. D. 1984 Physiological effects of hydrogen, aluminum, and manganese toxicities in acid soil. In: ADAMS, F. Soil acid and liming. American Society of Agronomy, Madison. p. 57-98.
- FRERET-MEURER, N.V.; ANDREATA, J.V.; MEURER, B. C.; MANZANO, F.V.; BAPTISTA, M.G.S.; TEIXEIRA, D.E.; LONGO, M.M. 2010 Spatial distribution of metals in sediments of the Ribeira Bay, Angra dos Reis, Rio de Janeiro, Brazil. *Marine pollution bulletin*, 60(4): 627-629.
- FROESE, R. and PAULY, D. 2015 FishBase, World Wide Web electronic publication. <http://www.fishbase.org.> Accessed in: 27 Nov. 2015.
- GUILHERME, L.R.G.; MARQUES, J.J.; PIERANGELI, M.A.P.; ZULIANI, D.Q.; CAMPOS, M.L.; MARCHI, G. 2005 Elementos-traço em solos e sistemas aquáticos. In: TORRADO-VIDAL, P.;

Bol. Inst. Pesca, São Paulo, 42(3): 500-513, 2016

ALLEONI, L.R.F.; COOPER, M.; SILVA, A.P. *Tópicos em Ciências do Solo 4*. Sociedade Brasileira de Ciência do Solo, Viçosa. p. 345-90.

- HAHN, N.S.; FUGI, R; ANDRIAN, I. de F. 2004 Trophic ecology of the fish assemblages. In: THOMAZ, S.M.; AGOSTINHO, A.A.; HAHN, N.S. The Upper Paraná River and its floodplain: physical aspects, ecology and conservation. Backhuys Publishers, Leiden. p. 247-269.
- JAFFAR, M.; ASHRAF, M.; RASOLL, A. 1988 Heavy metal contents in some selected local freshwater fish and relevant waters. *Pakistan Journal of Science and Industrial Research*, 31: 189-193.
- KATZ, B.M. and McSWEENEY, M. 1980 A multivariate Kruskal-Wallis test with post hoc procedures. *Multivariate Behavioral Research*, 15(3): 281-297.
- KEHRIG, H.A.; COSTA, A.; MALM, O. 2007 Estudo da contaminação por metais pesados em peixes e mexilhão da baia de Guanabara - Rio de Janeiro. *Tropical Oceanography*, 35(1): 32-50.
- KLAUBERG-FILHO, O.; SIQUEIRA, J.O.; MOREIRA, F.M.S. 2002 Fungos micorrízicos arbusculares em solos de área poluída com metais pesados. *Revista Brasileira de Ciência do Solo*, 269(1): 125-134.
- LEWIS, W.J.; LENTEREN, J.C.V.; PHATAK, S.C.; TUMLINSON, J.H. 1997 A total system approach to sustainable pest management. *Proceedings of the National Academy of Sciences*, 94: 12243-12248.
- LOUREIRO, V.R.; SALEH, M.A.; MORAES, P.M.; NEVES, R.C.; SILVA. F.A.; PADILHA, C.C.; PADILHA, P.M. 2007 Manganese determination by GFAAS in feces and fish feed slurries. *Journal-Brazilian Chemical Society*, 18(6), 1235-1241.
- MACKAY, D. and FRASER, A. 2000 Bioaccumulation of persistent organic chemicals: mechanisms and models. *Environmental Pollution*, 110(3): 375-391.
- MARENGONI, N.G.; POSSAMAI, M.; GONÇALVES JÚNIOR, A.C.; OLIVEIRA, A.A.M.D.A. 2008 Performance e retenção de metais pesados em três linhagens de juvenis de tilápia-do-Nilo em hapas. *Acta Scientiarum. Animal Sciences*, 30(3): 351-358.
- Bol. Inst. Pesca, São Paulo, 42(3): 499-513, 2016

- MATOS, A.T. de 2010 Poluição ambiental Impactos no meio físico. Viçosa: Editora UFV. 260 p.
- MAZZONI, R.; MORAES, M.; REZENDE, C.F.; MIRANDA, J.C. 2010 Alimentação e padrões ecomorfológicos das espécies de peixes de riacho do alto rio Tocantins, Goiás, Brasil. *Iheringia. Série Zoologia*, 100(2): 162-168.
- MORAES, R.; GERHARD, P.; ANDERSSON, L.; STURVE, J.; RAUCH, S.; MOLANDER, S. 2003 Establishing causality between exposure to metals and effects on fish. *Human and Ecological Risk Assessment*, 9(1): 149-169.
- NOBLE, R.A.A.; COWX, I.G.; GOFFAUX, D.; KESTEMONT, P. 2007 Assessing the health of European rivers using functional ecological guilds of fish communities: standardising species classification and approaches to metric selection. *Fisheries Management and Ecology*, 14(6): 381-392.
- NOVAES, J.L.C.; CARAMASCHI, E.P.; WINEMILLER, K.O. 2004 Feeding of *Cichla monoculus* Spix, 1829 (Teleostei: Cichlidae) during and after reservoir formation in the Tocantins River, Central Brazil. *Acta Limnologica Brasiliensia*, 16(1): 41-49.
- NÚNEZ, J.E.V.; AMARAL SOBRINHO, N.M.B.; PALMIERI, F.; MESQUITA, A. 1999 As consequências de diferentes sistemas de preparo do solo sobre a contaminação do solo, sedimentos e água por metais pesados. *Revista Brasileira de Ciência do Solo*, 23(4): 981-990.
- OLIVEIRA, J.M. and FERREIRA, M.T. 2002 Desenvolvimento de um índice de integridade biótica para a avaliação da qualidade ambiental de rios ciprinícolas. *Revista de Ciências Agrárias*, 25: 198-210.
- PIERANGELI, M.A.P.; GUILHERME, L.R.G.; CURI, N.; SILVA, M.L.N.; OLIVEIRA, L.R.; LIMA, J.M. 2001. Teor total e capacidade máxima de adsorção de chumbo em Latossolos brasileiros. *Revista Brasileira de Ciência do Solo*, 25: 279-288.
- RIBEIRO, J.F. and WALTER, B.T. 1998 Fitofisionomias do Bioma Cerrado. In: SANO, S.M. and ALMEIDA, S.P. Cerrado - Ambiente e Flora. EMBRAPA-CPAC, Planaltina. p. 89-166.

- ROCHA, A.A.; PEREIRA, D.N.; PÁDUA, H.B. 1985 Fishing yield and chemical contamination of the water of the Billings Reservoir, S. Paulo (Brazil). *Revista de Saúde Pública*, 19(5): 401-410.
- SALVADÓ, V.; QUINTANA, X.D.; HIDALGO, M. 2006 Monitoring of nutrients, pesticides, and metals in waters, sediments, and fish of a wetland. *Archives* of *Environmental Contamination and Toxicology*, 51(3): 377-386.
- SALVADOR, J.O.; MOREIRA, A.; MALAVOLTA, E.; CABRAL, C.P. 2003 Influência do boro e do manganês no crescimento e na composição mineral de mudas de goiabeira. *Ciência e Agrotecnologia*, 27(2), 325-331.
- SANTOS, J.S.; SANTOS, M.L.P.; OLIVEIRA, E. 2008 Estudo da mobilização de metais e elementos traços em ambientes aquáticos do semi-árido brasileiro aplicando análises de componentes principais. *Química Nova*, *31*(5): 1107-1111.
- SOKAL, R.R. and ROHLF, F.J. 1995 *Biometry: the principles and practices of statistics in biological research.* Freeman and Company, New York. p. 776.
- TEJERINA-GARRO, F.L. 2008 Biodiversidade e impactos ambientais no estado de Goiás: o meio aquático. In: ROCHA, C.; TEJERINA-GARRO, F.L.; PIETRAFESA, J.P. Cerrado, sociedade e ambiente: desenvolvimento sustentável em Goiás. Editora da Universidade Católica de Goiás, Goiânia. p. 15-47.
- TELES, L.T.; ZARA, L.F.; FURLANETTO, U.L.R.; SILVA JR. N.J. 2008 Elementos traço em peixes de interesse comercial do rio Caiapó (Goiás, Brasil) em área sob impacto ambiental. *Estudos*, 35(11/12): 1055-1067.
- TERRA, B.F.; ARAÚJO, F.G.; CALZA, C.F.; LOPES, R.T.; TEIXEIRA, T.P. 2007. Heavy metal in tissues of three fish species from different trophic levels in a tropical Brazilian river. *Water, Air & Soil Pollution, 187*(1-4): 275-284.
- THORNTON, I. 1995 Metals in the global environment: facts and misconceptions. International Council on

Metals and the Environment – ICME, London. 103 p.

- VALE, V.S.; SCHIAVINI, I.; OLIVEIRA, A.P.; GUSSON, A.E. 2010 When ecological functions are more important than richness. *Journal of Ecology and the Natural Environment*, 2(12): 270-280.
- VEADO, M.A.R.V.; ARANTES, I.A.; OLIVEIRA, A.H.; ALMEIDA, M.R.M.G.; MIGUEL, R.A.; SEVERO, M.I.; CABALEIRO, H.L. 2006 Metal pollution in the environment of Minas Gerais State - Brazil. *Environmental Monitoring and Assessment*, 117(1-3): 157-172.
- VELOSO, C.A.C.; MURAOKA, T.; MALAVOLTA, E.; CARVALHO, J.G. 1995 Influência do manganês sobre a nutrição mineral e crescimento da pimenteira do reino (*Piper nigrum*, L.). Scientia Agricola, 52(2): 376-383.
- VINODHINI, R. and NARAYANAN, M. 2008 Bioaccumulation of heavy metals in organs of fresh water fish *Cyprinus carpio* (Common carp). *International Journal of Environmental Science and Technology*, 5(2): 179-182.
- WERNECK LIMA, J.E.F.; DOS SANTOS, P.M.C.; CARVALHO, N.O.; DA SILVA, E.M. 2003. Araguaia-Tocantins: Diagnóstico do fluxo de sedimentos em suspensão na bacia. Embrapa, ANEEL, ANA, Brasília. 116 p.
- WINKALER, E.U.; SILVA, A.D.G.; GALINDO, H.C.; MARTINEZ, C.B.D.R. 2008. Biomarcadores histológicos e fisiológicos para o monitoramento da saúde de peixes de ribeirões de Londrina, Estado do Paraná. Acta Scientiarum. Biological Sciences, 23(2): 507-514.