Distribution of metals in the sediment of the Itá Reservoir, Brazil

Distribuição de metais no sedimento do Reservatório de Itá, Brasil

Bonai, NC., Souza-Franco, GM., Fogolari, O, Mocelin, DJC. and Dal Magro, J.

[1]Programa de Pós-Graduação em Ciências Ambientais,
Universidade Comunitária Regional de Chapecó – UNOCHAPECÓ,
Av. Senador Attílio Fontana, 591-E, Efapi, CP 1141, CEP 89809-000, Chapecó, SC, Brazil
e-mail: nadiab@unoescxxe.edu.br; gfranco@unochapeco.edu.br;
fogolari@gmail.com; douglasmocellin@gmail.com; jacir@unochapeco.edu.br

Abstract: Aim: Nowadays, one of the major concerns of the ecology studies relating to aquatic ecosystems refers to the impact caused by the releasing of heavy metals in several natural environments, mainly in the ones that have a greater interaction with anthropic activities. In relation of reservoirs, sediments are considered to be compartments of accumulation of pollutants, brought by the water column, that have their origin in the different uses of soil of the drainage areas' basin. The objective of this research was to evaluate the concentration of heavy metals in several sites distributed along the Itá Reservoir in Santa Catarina state, Brazil. **Methods:** Samples were collected in five sites: in the reservoir (deep zone) and in two tributaries (Fragosos and Rancho Grande rivers) between November/04 and August/05 (three sampling occasions). **Results:** High concentrations of Fe were found in all the sites; the concentration of Zn and Cu was higher in Fragosos River compared to the other sites. **Conclusions:** High levels of organic matter and the concentration of heavy metals are both related to the use and occupation of soil, specifically due to intensive agriculture/cattle activities and urbanization.

Keywords: reservoirs, trace-elements, contaminators, sediments.

Resumo: Objetivo: Atualmente uma das grandes preocupações na área da ecologia de ecossistemas aquáticos refere-se ao impacto causado pela liberação de metais pesados nos diversos ambientes naturais, principalmente, naqueles de maior interação com atividades antrópicas. No que se refere os reservatórios, os sedimentos são considerados como um compartimento de acumulação de poluentes, a partir da coluna d'água originados dos diferentes usos do solo da bacia de drenagem. Este estudo teve por objetivo avaliar a concentração de metais pesados no sedimento do reservatório da usina Hidrelétrica de Itá. **Métodos:** As coletas do sedimento foram feitas em 5 pontos amostrais, no corpo do reservatório (zona profunda) e em dois tributários (Rio Fragosos e Rio Rancho Grande) entre os meses de novembro/04 e agosto/05 (3 campanhas). **Resultados:** Altas concentrações de Fe foram registrados em todos os pontos; no rio Fragosos a concentração de Zn e Cu foi significativamente superior aos demais locais. **Conclusões:** Os elevados teores de matéria orgânica bem como as concentrações de metais pesados estão relacionados com o uso e ocupação do solo, como a intensa atividade agropecuária e a urbanização.

Palavras-chave: reservatórios, elementos-traço, contaminantes, sedimento.

1. Introduction

The construction of dams constitutes one of the oldest natural human interventions and it has been a very important activity in Brazil throughout the last decades, due to its several uses. From the biological point of view, the reservoirs constitute an interactive and complex net between the organisms and their physical and chemical environments, which is the result of the permanent processes of dealing with the functions of climatic forces and with the effects produced by the system's manipulation (Tundisi, 1999).

Thornton (1990) emphasizes that sedimentation constitute the main way through where the allochthonous material that lands in the reservoir is removed, exerting influence in the distribution of particles and in the zoning of the reservoirs. According to Almeida and Weber (1999), sediments are not just stocks of substances generated in the water column or brought by rivers, winds and rain, but they also function as a compartment that reprocesses these materials, and in the long term they can supply toxic substances in the biota and consequently risk the lives along the trophic chain.

Considering the dynamics of aquatic ecosystems and the accumulative characteristic of the reservoirs, it is expected that most trace-elements which enter into the system are deposited onto the sediment. Thus, throughout the years, sediments tend to be potentially more and more toxic in the environment, causing adverse effects to the biota (Espíndola et al., 1998; Tonissi, 1999).

The toxicity of the trace-elements comes mainly from their capacity of interfering in the enzymatic processes and from their small mobility in the organism, due to their small sizes and to the charges they possess. Thus, sediments constitute an important chemical indicator of the contamination of the aquatic ecosystems, due both to their capacity of accumulating trace-elements and to the role in the transport and, as a possible source of contamination.

According to Lamberson et al. (1992), the toxicity of heavy metals in the sediment can be affected by the connections between the ions of the metals and the constituents of the sediment. Thus, the availability of the contaminators in the sediment is associated to parting behavior with the organic matter, in addition to the adsorbing processes that occur between heavy metals and fine particles size. Metals that have a weak association, commonly linked to the sediments, can be easily broken by the biota, becoming bio-available (Försten and Wittmann, 1981; Wetzel, 1983; Gatti, 1997).

The organic matter is closely linked to the elements Cu, Zn and Fe, in the lakes' sediments, and to the Cu in the rivers'. The organic matter has a good capacity of absorption of heavy metals; this affinity can both concentrate metals in the environment, having an impact on it, or it can be used in the removing of metals in affected environments. An important physical property of the organic matter is associated with the fine texture of the sediments, generally containing a natural percentage of humic material derived from the biological transformations of plants and animal waste. The humic material can be there as a discrete particle or as a layer of clay particles, because the humic material increases the affinity between the sediment and the metals (Förstner and Wittmann, 1981; Wetzel, 1983; EPA, 1991).

Heavy metals are part of the environment and the living matter, occurring naturally in small concentrations, ranging from parts per billion to parts per million. Among them, elements such as Zn, Fe, Mn, Cu, Co and Mo are essential to organisms, even in minimum quantities, because they take part in the physiologic processes; other trace elements, such as the Hg, Pb and Cd, don't have any known biological function, and they are responsible for adverse effects on the biotic community. Even the ones which hold a biological function, in high concentrations, can cause toxicity to organisms (Esteves, 1998).

The main purpose of this research was to characterize the chemical composition of the sediment, and to evaluate the concentration of the heavy metals Cr, Cu, Pb, Zn, Mn, Fe and Cd as an indicator of contamination, in the Itá Reservoir (south of Brazil).

2. Material and Methods

2.1. Study area

The Itá reservoir forms a lake that has a surface of 141 km^2; it is located in the Uruguai River, between the states of Santa Catarina and Rio Grande do Sul. Its closing occurred in 2000, holding a 1450 MW capacity. The two main rivers that flow down towards the reservoir are Peixe River in Santa Catarina and Apuaê River in Rio Grande do Sul.

The region object of this study contains the largest density of pigs of the Santa Catarina State, which causes a large concentration of waste by unit of area, originating serious pollution problems that affect the region's hydro resources, mainly by the launching of wastes into the rivers and streams that flow down to the Uruguai River, causing ecological unbalances and the increase of organic matter along the water courses, among other problems.

The samplings were collected in five sites (Figure 1): in the body of the reservoir (deep zone) and in two branches, in November/04, April/05 and August/05 .

2.2. Sampling and chemical analysis

Sediment samples were collected with a Petersen grab dredge (stainless steel), packed in plastic bags, and stored into freezers till they were processed by drying (at 80 °C during 24 hours), grinding and sieving (62 µm).

The determination of concentrations of heavy metals was based on Alagarsamy (2006) where, three 250 mg portions (triplicate) of each sample of grinded and dried sediment (digested in an acid environment for later analysis) were prepared. Each sample was digested in teflon becker, with 10 mL of concentrated HNO_3 and 10 mL of HF (48%), on an electric heating plate, and left reacting for 12 hours. Later, 3 mL of $HCLO_4$ (70%) were added, and warmed till 120 °C, becoming almost dry. After that, 1 mL of HNO_3 was added to the sample, waiting again to become almost dry. This procedure was repeated more than once. When the digestion was over, 2 mL of HNO_3 10% and about 10 mL of deionized water were added, the solution was transferred to a volumetric balloon, making a volume of 25 mL; afterwards, it was used a spectrophotometer (Varian, model Spectra 220 FS) of atomic absorption to analyze the metals. The concentration of organic matter (%) in the sediments was obtained by incinerating 10 g of sediment at 500 °C during 4 hours.

The statistical analysis of the data was made using the one-way analysis of variance (ANOVA), followed by a Tukey test; p-values less than 0.05 were considered significant. The statistical program Statistica 5.0 (Statsoft, 2001) was used for analyses.

3. Results

The sediment of the Itá reservoir can be characterized as organic in most of the sites, demonstrated by the sites 1, 3, 4 e 5, because it contains more than 10% of organic matter in its dry weigh, according to Esteves (1998).

On Table 1 the results of the percentages of organic matter display minimum values of 8.57% for site 2, which corresponds to Rancho Grande River. The central region of the reservoir, site 3, has higher percentages of organic

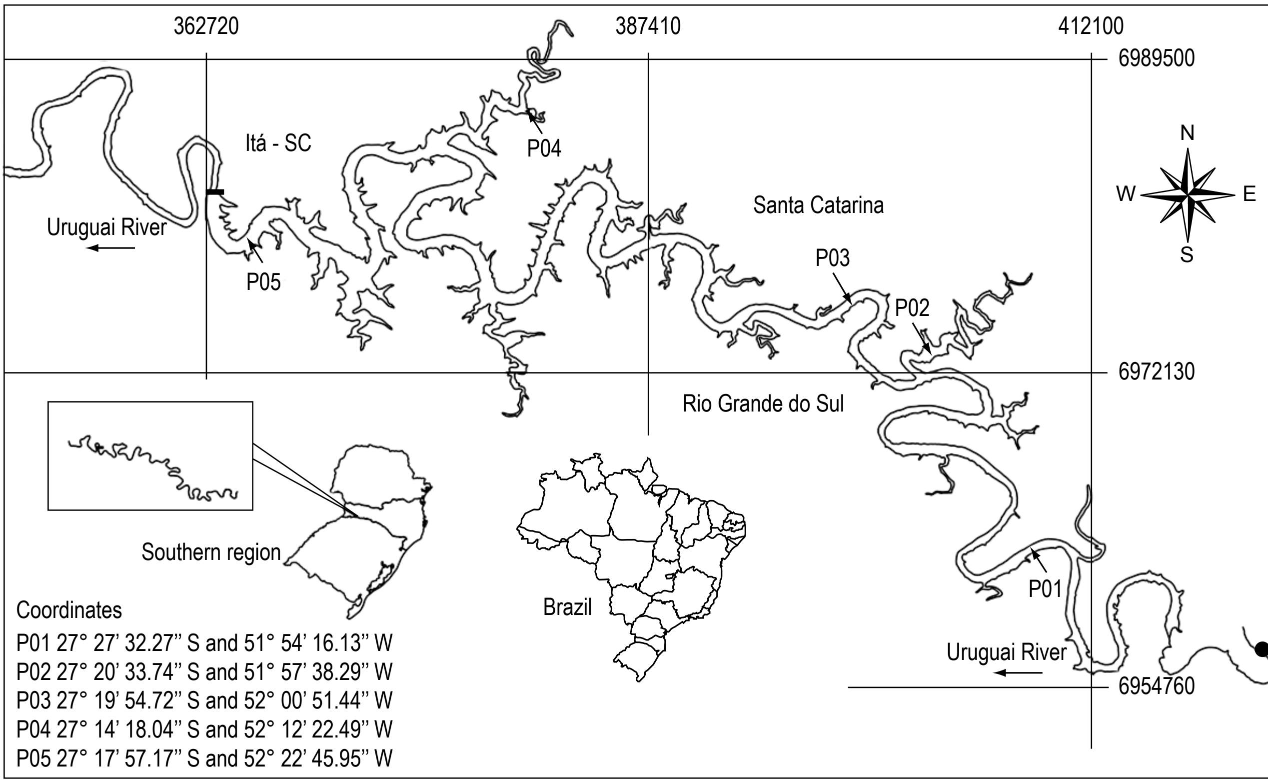

Figure 1. Location of the sites in the area of study.

matter than the margins, displaying maximum values of 17.29%.

Table 1 displays the averages of the concentrations of Cr, Cu, Mn, Fe, Cd, Pb and Zn from the stations sampled in the Itá Reservoir and the values of concentrations of organic matter (O.M). As a comparative for metals, we used the concentration limit established by the Conama Resolution 344/04 (Brasil, 2004), which is the only legal document in Brazil that refers to sediment contaminations.

Figures 2 and 3 display the mean values and standard deviation (SD) of concentration (mg.kg^{-1}) of metals and the analysis of variance of the sediments collected at the diverse sites of the reservoir. The metals which concentration displayed a statistically significant difference for the Tukey test ($p < 0.05$) between the different sites, were only the Cu and the Zn, in sites P2 and P4 (Figure 2c and 2d).

4. Discussion

When the results of this study are compared with other reservoirs such as Salto Grande (Americana-SP) studied by Dornfeld (2002), in what relates to organic matter, we notice that the average of its percentages is very similar to the maximum concentration evaluated in Salto Grande (1.0 to 17.47%). If we compare it with other studies such as Zanata (1999), with maximum values of 12.71%, it can be verified that the Itá reservoir contains high values of organic matter.

The organic matter is closely linked to some heavy metals, mainly Cu, Zn and Fe, in the sediments of lakes. According to Forstner and Wittmann (1981), the organic matter has, for heavy metals, a great capacity of adsorption; this affinity can concentrate metals in the environment, causing an impact on it. According to the same authors (Canellas et al., 1999; Jordão et al., 1993) the organic matter can adsorb the metals, after they are complexed (Sargentini Jr. et al., 2001), heavy metals are dragged towards the sediment; as time goes by, and due to their bio-accumulative traits that sediment tends to become effectively toxic for the ecosystem.

The high concentrations of Fe and Mn in the sediment of the Itá reservoir are higher than those reported for other reservoirs, such as the Salto Grande Reservoir, studied by Dornfeld et al. (2004). High concentrations of these elements are related mainly with the geochemical characteristics of the watershed drainage and with an inadequate soil management. According to Ker (1997), the region's soil is classified as violet latosoil, which is rich in Fe_2O_3 and possesses higher concentrations of manganese compared with the other latosoils, and also, according to Moreira et al. (2004), the manganese is found in high concentrations in the micro-basins' soils where there is an intense application of pigs' dirt. Therefore, the natural conditions linked to the breeding of pigs result in high concentrations of Mn and Fe, found in the studied area. The highest concentration of Cu and Zn in site 4, with a

Table 1. Comparison between the concentrations of metals (mg.kg^{-1}) of the sediments collected in the Itá Reservoir's sites and the limit established by the Conama Reservoir 344/04 (Brazil, 2004), and the values of the concentration of organic matter (O.M) in the Itá Reservoir.

	P1	P2	P3	P4	P5	CONAMA
Cr (mg.kg^{-1})	80.98	89.55	74.63	86.70	119.50	37.3
± SD	18.45	7.28	11.26	20.93	14.39	-
Cu (mg.kg^{-1})	151.60	182.30	155.47	233.95	176.00	35.7
± SD	16.12	31.53	24.40	21.70	7.04	-
Mn (mg.kg^{-1})	2,611.38	1,937.65	2,217.35	2,663.60	1,895.60	-
± SD	792.30	429.85	348.49	843.29	617.32	-
Fe (mg.kg^{-1})	82,552.72	116,098.00	94,952.50	137,243.5	95,663.00	-
± SD	36,007.66	42,659.75	20,490.57	21,860.20	15,280.48	-
Cd (mg.kg^{-1})	5.33	5.40	7.87	6.45	6.60	0.6
± SD	2.43	0.56	2.02	1.62	1.50	-
Pb (mg.kg^{-1})	18.03	17.60	31.58	18.65	17.00	35
± SD	3.14	1.41	15.94	0.49	4.62	-
Zn (mg.kg^{-1})	177.52	240.65	188.80	307.65	245.60	123
± SD	28.67	4.73	41.87	11.80	61.89	-
O.M. (%)	16.57	8.57	17.29	15.76	16.36	-
± SD	0.25	0.30	0.54	0.11	0.27	-

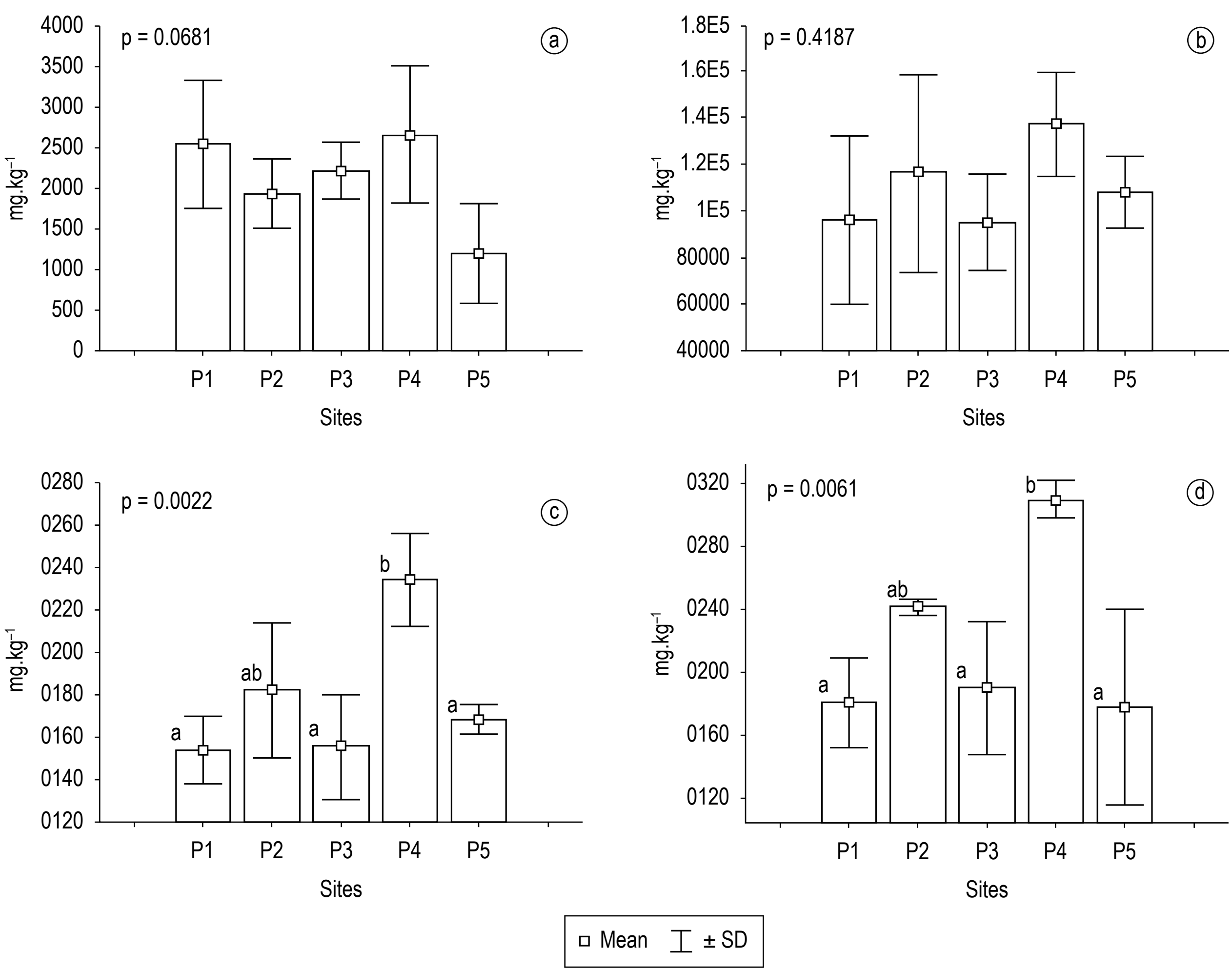

Figure 2. Mean values and standard deviation (SD) of the concentrations (mg.kg^{-1}) of Mn (a), Fe (b), Cu (c) and Zn (d) in the sediments' samples of the different sites of the reservoir. The means followed by the same letters in the columns, for each site, don't differ among them according to the Tukey test.

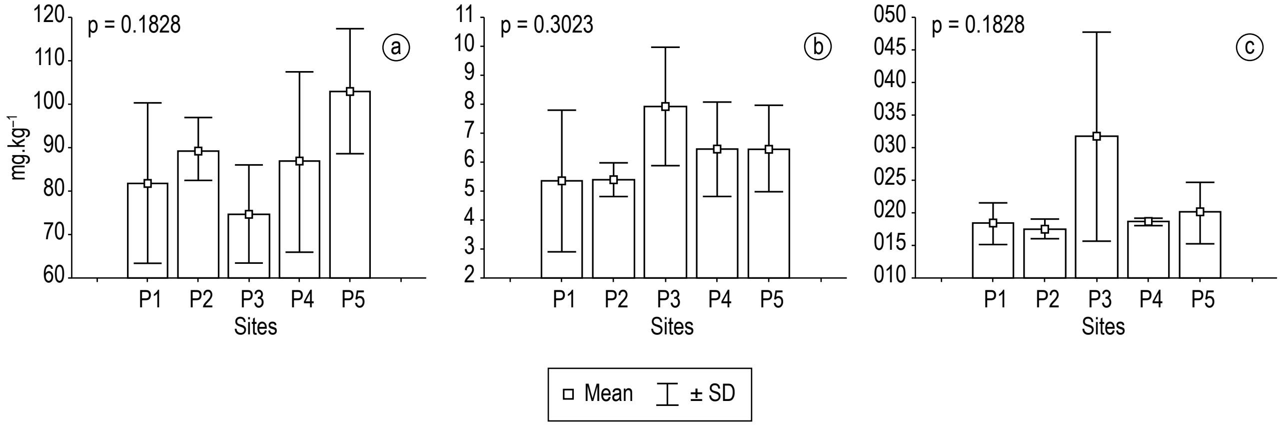

Figure 3. Mean values and standard deviation (SD) of the concentrations (mg.kg^{-1}) of Cr (a), Cd (b) and Pb (c) in the sediments' samples of the different sites of the reservoir.

significant difference in comparison with sites 1, 3 and 5, corroborates the hypothesis of bad conservation and use of the region's soil. The levels of Cu were approximately seven times higher than those established by CONAMA's Resolution 344/04 (Brasil, 2004), while the Zn levels were about three times higher. Those concentrations were also higher than the ones verified by Dornfeld (2002) in Salto Grande Reservoir. Cu and Zn are considered to be vital biological elements, playing an enzymatic role in the physiological processes of the organisms, but they can also produce dangerous damages to health if consumed in high concentrations (Cotta, 2006). This study highlights the great influence of farming activities, which are the cause of higher concentrations of Cu and Zn (heavy metals which are directly related with fertilizers and wastes produced by the intensive breeding of pigs and poultries).

Exhibiting a pattern different from other metals, the lowest concentrations of Cd were obtained at site 1, while the highest ones were verified at site 3, without displaying a high variation between the different sites. In literature there is no description for cadmium as an element that brings benefits or that is essential for all living beings. In contrast, it accumulates in the tissues originating chronic and severe health effects, and a single 9.0 g dose may cause death.

The lead is a toxic, bio-accumulative metal that causes pollution, and with no identified biological functions neither for plants nor animals (Cotta, 2006). The highest concentrations of Pb were also observed at site 3 and the lowest at site 5. For all the sampled sites, the Pb was the only metal that displayed concentrations which are in accordance to legislation (Resolução 344/04 do CONAMA) which is 35.00 mg.kg^{-1}, indicating that the reservoir is not contaminated by this metal.

The values of the concentrations obtained in this research demonstrate that the maximums are often superior to the ones recommended by the legislation, and may confirm a contaminated system, with possible toxic effects for the aquatic biota.

The quality of the water of the Itá reservoir reflects the natural conditions and the amount of polluters generated by human activities, which are launched directly into the rivers that flow into the lake. In both riverbanks, besides the transport of solids containing biocides as a result of planting activities there is also an intensive pig and chicken production.

This study indicates that the high levels both of organic matter and of heavy metals are connected with the intense farming activities and with the use and occupation of soils around the basin. It is a well-known fact that high levels of some heavy metals originated by the use of agro-chemicals and high values of organic matter indicate the input of large amounts of wastes that have their origin in the farming activities that surround the evaluated area.

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