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Cu, Zn, Pb AND Cd BIOACCUMULATION IN THE BENTHIC FISH *Cathorops spixii* FROM CANANÉIA, SP, BRAZIL

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ABSTRACT

The purpose of this study was to determinate levels of Cu, Zn, Pb and Cd in muscle, liver and gills in order to understand some aspects of the bioaccumulation in the catfish *C. spixii*. Metals were determined by using a high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The results showed differences in the levels of metals between the tissues, as expected, showing changes in the metal accumulation. Zn and Cd presented higher concentration in the liver, following the muscle and finally the gill. The mean values obtained for Zn in these tissues were 57.58 µg kg^{-1}, 9.86 µg kg^{-1} and 188 µg kg^{-1}, respectively. Mean levels of Cd were 282 µg kg^{-1}, 16 µg kg^{-1} and 2.9 µg kg^{-1}, respectively to liver, muscle and gill. On the other hand, data of Cu and Pb showed a decreasing of the concentration in the liver toward the muscle: liver <gills <muscle, with a mean concentrations of Cu of 2.83 g kg^{-1}, 398 µg kg^{-1} and 75.70 µg kg^{-1} and levels of Pb of 190 µg kg^{-1}, 125 µg kg^{-1} and 59 µg kg^{-1}, respectively. The highest levels of metals observed in the liver confirm their important function in the detoxification mechanism. Despite low concentrations of Pb and Cd found in samples, the presence of these toxic metals in the individuals indicate the need of monitoring of this system and can be explained by the presence of an abandoned gold mining located in Ribeira do Iguape, in the North of Cananéia estuary.

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1.INTRODUCTION

Bioaccumulation is the process by which chemical compounds are accumulated in different organisms [1]. No essential metals are natural components of the environment, however, the different anthropogenic activities has been causing one significant increase of it concentration. In fish the input of metals within the organism can occur directly by ingestion of the food and/or absorption /adsorption by the gills [2].

Metals such as Zn and Cu are very important for the living organisms, because these elements have positive functions for the life, for instance acting as cofactor in some enzymes. On the other hand, it was not reported positive biological function to metals as Pb and Cd and, therefore, these are consider toxic for the living organisms [2]. About 90% of Pb is stored in bone and the excessive accumulation of this element can cause changes in the absorption of Ca [3]. Cadmium (Cd) is one the most toxic non-essential element due it high persistent in the environment and organisms, around 10 years [4], therefore can to accumulate in the food chain [5].

The Ariidae family consists of catfish that inhabit littoral estuaries and rivers. *Cathorops spixii* is found throughout the Atlantic coast of the South America [6], live in low deep water, in sandy or muddy areas [7]. The diet is composed mainly by *Polychaeta*, *Bivalvia*, *Crustácea*, *Hydrozoa* and other smaller fish [8].

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Cananéia estuary, is located in the Southeast of the Brazilian coast and is an important aquatic system because is an environmental protected area. This estuary has important contribution of the several riverine channels, located within the estuary, such as Comprida, Cardoso and

Cananéia islands [9]. For consequence of the low human influence, this aquatic system is constantly used as reference area in biomonitoring studies [10-13]. However, during the last years, some studies have been indicating the presence of toxic metals in this region [13, 14].

The main objectives of this work was identified some aspects of the metals bioaccumulation in the Ariidae catfish *Cathorops spixii*. In order to provide information concerning this process, Zn, Cu, Cd and Pb were evaluated in muscle, liver and gill.

2. SAMPLING PROCEDURES

2.1 Fish collection

Samples were taken in Cananéia estuary, using gill nets with 20mm mesh. After collection, fish were identified [15] and biometric measurements such as weight and size taken. Muscle, liver and gill were sampled, washed in ultrapure water and keep at -20°C for metal analysis.

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2.2 Metals determination

Pb, Cd, Zn and Cu concentrations was based with Visnjic-Jeftic et al. [16], with some modifications. Tissues were weighed, added 65% HNO_3 and 30% H_2O_2 to 4h. After this step, the samples were taken to total digestion in a microwave (CEM Corporation, Mars 5 model), according to previously established analysis parameters. Metals were analyzed by using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Element) after a new step of dilution (1:2) in milli-Q water. 5 µg Kg^{-1} Indium was used as internal standard.
Pb and Cd were determined in the operation mode of low resolution, and Zn and Cu determined in the operation mode of medium resolution. Limits of detection and quantification calculated for each element were: 12 µg kg^{-1} and 20 µg kg^{-1} for Cu; 45 µg kg^{-1} and 63 µg kg^{-1} for Zn; 4 µg kg^{-1} and 2.0 µg kg^{-1} for Pb and; 0.15 µg kg^{-1} and 0.24 µg kg^{-1} for Cd, respectively. The analytical procedure was monitored using certified reference material (Oyster tissue, NRCC) and obtained results are show in Table 1.

Table 1. Analysis of metals in reference materials (Oyster Tissue, NIST). Data are showed as mean±sdv in mg kg^{-1} and recovery (%).

Oyster Tissue			
	Certified values	**Found Values**	**% Recovery**
Cd	4.15 ± 0.38	3.66 ± 0.07	88
Pb	0.371 ± 0.014	0.37 ± 0.06	99
Cu	66.3 ± 4.3	61.49 ± 0.85	93
Zn	830 ± 57	788.96 ± 16.71	95

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3. RESULTS AND DISCUSSION

Data about metal concentration in muscle, liver and gill of *C. spixii* from Cananéia estuary are show in the Fig. 1. The mean values obtained for Zn in these tissues were 57.5841 µg kg^{-1} to liver, 9.862 µg kg^{-1} to muscle and 188 µg kg^{-1} to gill, respectively. Mean levels of Cd were 282 µg kg^{-1} in liver, 16 µg kg^{-1} in muscle and 2.9 µg kg^{-1} in gill, respectively to liver, muscle and gill. On the other hand, data of Cu and Pb showed a decreasing of the concentration in the liver toward the muscle: liver <gills <muscle, with a mean concentrations of Cu of 2.828 g kg^{-} in the liver, 398 µg kg^{-1} in the gill and 75.7 µg kg^{-1} in the muscle and levels of Pb of 190 µg kg^{-1} in the liver, 125 µg kg^{-1} in the gill and 59 µg kg^{-1} in the muscle.

It is possible to observe differences between the tissues, as expected, showing changes in the metal accumulation. Metals as Zn and Cd presented higher concentration in the liver, following the muscle and finally the gill.

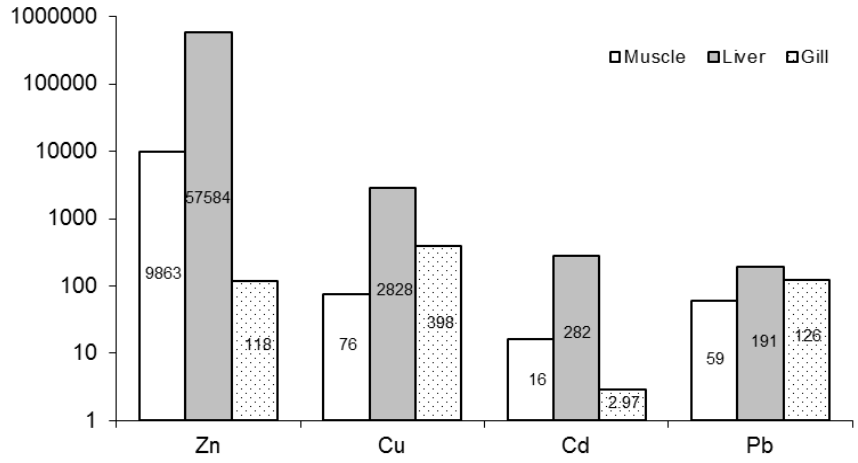

Figure 1. Metal concentrations in muscle, liver and gill of *C. spixii* from Cananéia estuary.

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4. CONCLUSIONS

The highest levels of concentration of metals observed in the liver confirm their important function in the detoxification process. Changes observed in the levels of metals between the muscle and gill can be associated to differences in the input of Zn/Cd and Cu/Pb in the environment within theses tissues. Despite low concentrations of Pb and Cd found in samples, the presence of these toxic metals in the individuals indicate the need of monitoring of this system and can be explained by the presence of an abandoned gold mining located in Ribeira do Iguape, in the north of Cananéia estuary.

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