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Evaluation of heavy metals levels in the Paraíba do Sul River by SRTXRF in muscle, gonads and gills of *Geophagus brasiliensis*

C. Calza[a], M.J. Anjos[a,b,*], C.R.F. Castro[a], R.C. Barroso[b], F.G. Araujo[c], R.T. Lopes[a]

[a] *Laboratório de Instrumentação Nuclear, COPPE/UFRJ, P.O. Box 68509, 21945-970 Rio de Janeiro, Brazil*
[b] *Instituto de Física, Universidade do Estado do Rio de Janeiro, Brazil*
[c] *Laboratório de Ecologia de Peixes-Universidade Federal Rural do Rio de Janeiro, Brazil*

1. Introduction

It is known that fish may accumulate heavy metals through direct absorption, or via their food chain and pass them to human beings, by consumption, causing chronic or acute diseases. The metals bioaccumulation causes biochemical or pathological effects in individual fish, resulting in decrease of growth, fecundity and survival (Al-Yousuf et al., 2000). Biological strategies have evolved to detoxify metals, or to otherwise reduce the exposure of species to high concentrations of trace elements in their tissues. Total reflection X-ray fluorescence with synchrotron radiation (SRTXRF) become a competitive multi-element technique for the determination of trace elements in tissue samples (Baur et al., 2001). Since concentrations of most trace elements in tissues are lower than 100 $\mu g l^{-1}$, the direct determination of these elements is very difficult.

In this work the concentration levels of heavy metals in selected tissues (muscle, gonads and gills) of *Geophagus brasiliensis* from the Paraiba do Sul River are determined using SRTXRF. This river, located in a region between the two most important urban and industrial centers of Brazil, has been changed along the last years by the human activity. Consequently, a decline in the diversity and abundance of the species has been observed.

*Corresponding author. Laboratório de Instrumentação Nuclear, COPPE/UFRJ, P.O. Box 68509, 21945-970 Rio de Janeiro, Brazil. Tel.: +55-21-2562-7311; fax: +55-21-256-28444.
E-mail address: marcelin@lin.ufrj.br (M.J. Anjos).

2. Materials and methods

The samples of *G. brasiliensis* were collected in four distinct areas (subdivided in 18 sampling points) of the Paraiba do Sul River from December 2002 to May 2003. The fish were packed in polyethylene film and transported on ice to the laboratory, where they were kept in a freezer (−15°C). After defrosting, they were dissected, and muscle, gonads and gills separated. The samples of fish tissues were lyophilized and homogenized. The digestion procedure was performed with 100 mg of the samples and 1 ml HNO_3 65% in Teflon bombs, heated at about 120°C, during 4 h. At room temperature (25°C), the solution was diluted to 4 ml with milli-Q water. Afterwards, an aliquot of 450 μl from this solution was added to 50 μl of a selenium standard solution, with agitation to assure perfect homogeneity. Finally, 10 μl of the mixture, containing the internal standard, were deposited on the sample carrier, and the droplet was dried using an infrared lamp. The measurements were performed at the XRF beamline of the LNLS (National Synchrotron Radiation Laboratory) in Campinas, Brazil.

3. Results and discussion

The muscle analysis of *G. brasiliensis* was performed to evaluate the possible transfer of heavy metals to human beings through fish consumption. The gonads were used to study the possible transfer and/or influence of metals, through the reproductive processes (Lima Jr.

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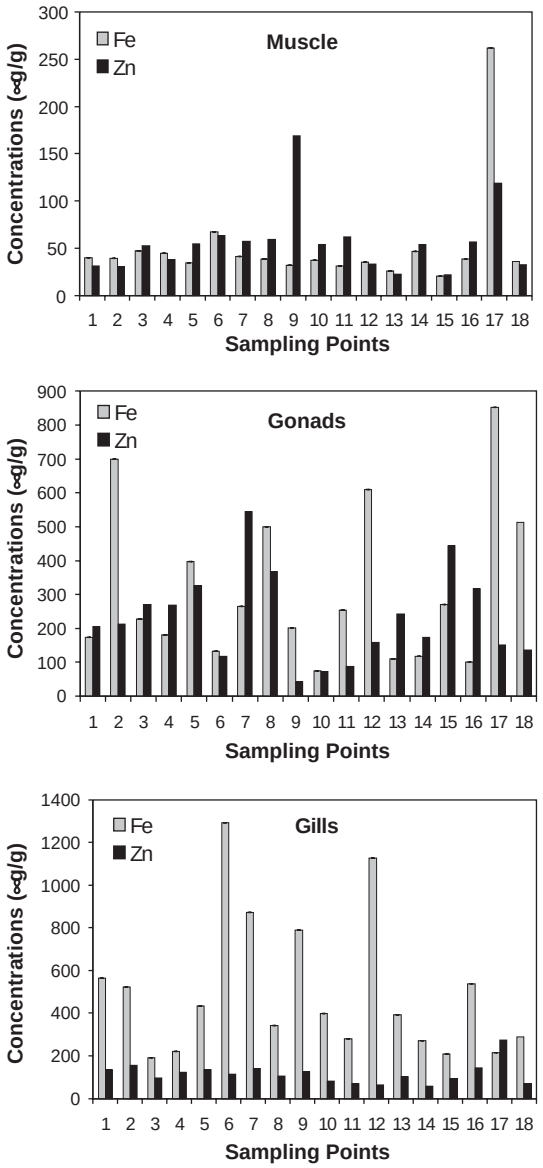

Fig. 1. Concentration levels (μg/g) of Fe and Zn in muscle (top) gonads (middle) and gills (bottom diagram) of *G. brasiliensis*.

et al., 2002). Gills are considered the primary action site for most metals (Moraes et al., 2003), which are absorbed through fish breathing and/or ionic exchanges.

The elements identified in the fish tissues were: Ti, Cr, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ba and Pb. The highest metal concentration levels observed, considering the mean values, occurred for Fe, Zn, Mn, Sr, and Rb. The concentrations found to Fe and Zn, at each sampling point, for gills, gonads and muscle are shown in Fig. 1.

The highest metal accumulation was found for Fe in the gills: (1293.2 ± 6.9 μg/g): see Fig. 1. The concentration order of iron in the tissues, considering the mean values, were: gills > gonads > muscle. Iron is present in soil, water, and the atmosphere, and its compounds occur in several industrial processes. It participates in the hepatic process, and is also associated with haemoglobin through oxygen transportation.

The metal concentrations found in the fish samples of *G. brasiliensis* were higher than those reported by Lima Jr. et al. (2002), referring to Sepetiba and Ilha Grande Bays, and Malm et al. (1988), considering the Paraiba do Sul River. Although the last one has been performed at the same region, the analyzed tissues were different from those used in this paper.

The highest concentration of Zn was observed in gonads (543.9 ± 1.7 μg/g). Considering all tissues investigated, and the average of concentrations, Zn accumulation follows the sequence: gonads > gills > muscle. The gonads may exhibit high Zn concentrations due to participation in cellular division and growth processes.

4. Conclusion

Most metals exhibited the highest concentration levels in gills, that may be associated to the direct contact to water, so that metal uptake can occur by fish breathing or ionic exchanges. Comparing the results of the present work to the Brazilian Food Legislation, Cr, Zn and Pb exceeded the maximum permissible limits.

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