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Study of the Toxicity of Marine Sediments of Babitonga Bay – Brazil

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ABSTRACT

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The contamination in aquatic environments, in the last decades, is undeniable. One of the most important sources of contamination are industrial wastewaters. For this reason, the study of pollutants coming from anthropic origin on the Babitonga Bay should be considered as an important tool for the local government, in order to create programs for preserving this kind of ecosystems. One of the ways for determining pollution in aquatic systems is studying bio-availability and toxicity of trace metals in contaminated sediments available to aquatic animals, by the use of speciation techniques and bioaccumulation studies. The heavy metals studied for this purpose were Cr and Zn. According to results obtained, the concentration values for Zn were very high at the first (0.0 – 17.78 mg.kg⁻¹ dry sediment), second (0 – 64.27 mg.kg⁻¹ dry sediment) and third (11.8 – 290.77 mg.kg⁻¹ dry sediment) GPHs for all site samples, as well as the high concentration values for Cr at the third (1.12 – 13.7 mg.kg⁻¹ dry sediment) GPH. Approximately, 85% of Zn and 45% of Cr were found at the first three phases. These results indicate a relatively polluted sediment. Then, in order to verify the bio-availability of the metal content of Babitonga Bay sediments to the water column, bioaccumulation analysis were performed. Three commercial species of edible fish, caratinga (*Eugerres brasiliensis*), robalo (*Centropomus parallelus*) and tainhoa (*Mugil platanus*) were selected and collected for this study. The levels of metals detected on the fish muscles of all the mentioned species are acceptable for human consumption.

ADDITIONAL INDEX WORDS: *heavy metals, sediments, speciation, fish.*

INTRODUCTION

Babitonga Bay is located on the northern coast of Santa Catarina State, Brazil, between the continent and the island of São Francisco do Sul (26°00' – 26°26' S and 48°29' – 49°12' W, Figure 1). The Babitonga Bay has an extension of 154 km², representing one of the most important estuarine formations in the south of Brazil. However, agricultural runoffs, agricultural and domestic effluents go directly into the bay through drains, channels and rivers. In addition, smelting, galvanic and textile factories located on the vicinity of the bay also discharge effluents into the bay.

Bottom sediments are known as the principal sink for heavy metals in an aquatic environment, and may be introduced to water by both natural and anthropogenic sources (PEMPKOWIASE *et al.*, 1999). However, when the environmental conditions change, as a result of either physical disturbance (pH, sediment redox potential, etc.) (BOUGHRIET *et al.*, 1992), or diagenesis (PETERSEN *et al.*, 1995), sediments can act as a source of pollutants even after a long time of the cessation of direct discharges.

To assess the environmental impact of polluted sediments, the determination of the total concentration of metals does not give any information regarding the form in which metals are bounded to the sediments (metal carbonates, oxides, sulfides, organometallic compounds, etc.). The chemical form of the metals found on the sediments is very useful for determining the degree

of association of metals in the sediments, to what extent they may be remobilised to the environment, and also for distinguishing metals of lithogenic origin from those of anthropogenic origin.

The main goal of operational speciation studies is to convert the metals bound on the sediment phases into soluble forms by the use of chemicals for decreasing pH and increasing oxidizing strength in order to remove the operationally-defined host fractions. Many of the sequential extraction schemes employed are based on the five-stage procedure of TESSIER *et al.* (1979): (1) loosely metals adsorbed by the surface of sediments particles; (2) bounded to carbonates; (3) bounded to iron and manganese oxides/hydroxides; (4) complexed by organic matter; and (5) incorporated into clay mineral lattices (Fergusson, 1990). According to RUBIO *et al.* (1991), metals of anthropogenic origin are mainly obtained on the first extractions.

Any study has determined metal speciation on the Babitonga sediments, although this is of critical importance in order to determine the likely behaviour of metals in aquatic systems and their potential for biological uptake.

Agriculture, aquaculture and fishing are the primary activities of the people living on the Babitonga Bay. Therefore, there is a very important concern regarding the people's health whom are fed by fish catch in this area. Since metal content in the tissues of fish is species-dependent, three commercial species of edible fish, caratinga (*Eugerres brasiliensis*), robalo (*Centropomus parallelus*)

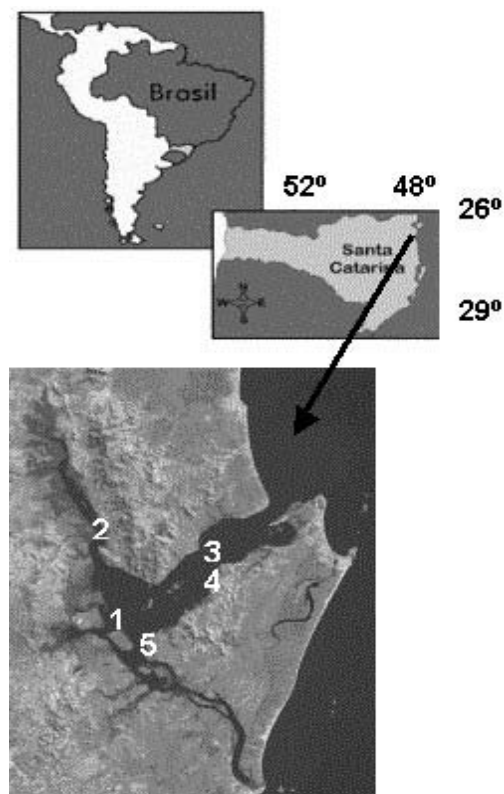


Figure 1. Geographic location of Babitonga Bay (1= Lagoa do Saguacu, 2= Rio Palmital, 3= Vila da Gloria, 4= Porto Sao Francisco do Sul, 5= Canal do Linguado).

and tainhota (*Mugil platanus*), were selected and collected from the bay for the present study.

The aims of this study are to determine: (a) the concentration of Cr and Zn in the sediments of the bay and the chemical forms in which they occur, (b) the metal bioaccumulation on the muscles of edible fish and the possible risk associated with human consumption of these fish.

METHODOLOGY

Sediment samples were collected from five sites along the Babitonga bay (Figure 1) using a Petersen dredge, getting the first 20 cm of superficial sediment, carefully screened for determining the presence of animals and for checking the colour, the structure and the smell, then put in glass jars and frozen. Depending on the bottom structure, each station was sampled several times (minimum three) to get a representative sample obtained by carefully mixing the different sub-samples.

The sequential extraction procedure was a slight modified version of the technique proposed by CHESTER AND HUGHES (1967) and TESSIER *et al.* (1979). The five GPHs obtained have the same meanings as in CHEN *et al.* (1976): i. e. phase 1, ion-exchangeable metal; phase 2, metal bounded to carbonates; phase 3, easily-reducible metal (bounded to oxides of manganese and non-crystalline lattice iron); phase 4, metal bonded to organics and sulfides; phase 5, reducible metal (bonded to iron oxides) remaining after the coating destruction by oxidative treatment of

phase 4. The geochemical phases were called GPHs, indicating with a number the extraction step.

The GPHs were determined as follows. Ten grams of dry sediment was treated with 40 ml of 1M NH₄OH, shaken for 1 h, settled overnight, filtered with 0,45µm filter, washed three times with distilled water metal-free; the residue (1) was dried overnight at 105°C. This solution contained the first GPH. Three grams of the residue (1) was mixed with 40 ml of 1M NaOAc plus 1 ml of HAc, shaken for 2 h, settled for two nights, filtered and washed. This solution contained the second GPH. The residue (2) was dried overnight like residue (1). All the residue (2) was mixed with 40 ml NH₂OH.HCl in 0.01 M HNO₃, shaken for 45 min., settled for two nights, filtered and washed. This solution contained the third GPH. The residue (3) was dried overnight like residue (1). All the residue (3), treated with 6 ml of 0.02 M HNO₃ plus 10 ml of 30% H₂O₂, was acidified with HNO₃ at pH 2, heated to 75°C for 2 h and mixed with 30% H₂O₂ at pH 2. The mixture was heated for 4 h in an oven. After cooling, it was mixed together with 15 ml of 3.2 M NH₄OAc in 20% (v/v) HNO₃, and settled for two nights. This cleared solution contained the fourth GPH. The residue (4), washed accurately, was dried in an oven overnight like residue (1). Finally, the residue (4) was mixed with 40 ml of 0.04 M NH₂OH.HCl in 25% HAc, heated to 98°C for 5 h, settled for two nights and filtered. This solution contained the fifth GPH. For HF total metal content, 0.5 grams of dry sediment was treated in a Teflon container sealed with a Teflon cap (Teflon Bomb) in an

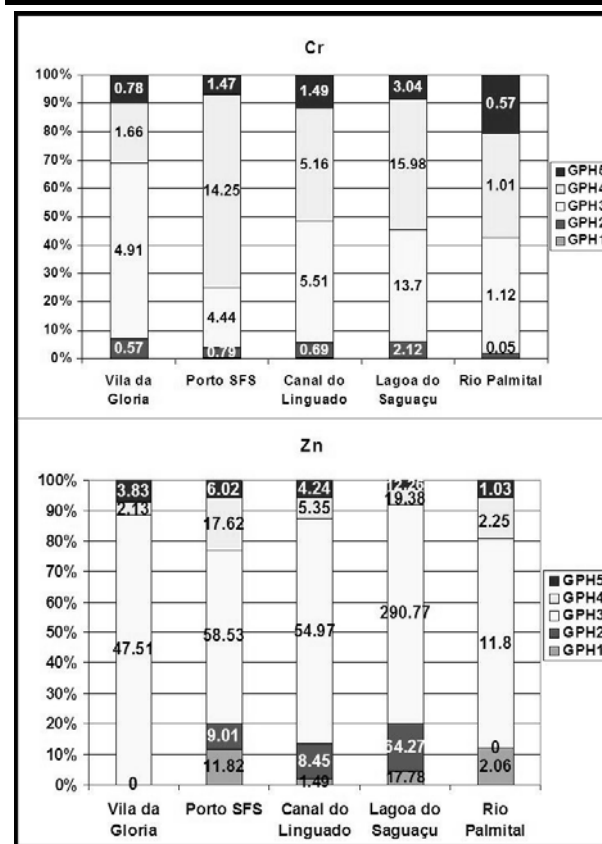


Figure 2. Percentage concentration (%) and mg.kg⁻¹ dry sediment for Cr and Zn at each of the five geochemical phases of the modified Tessier *et al.* (1979) method.

Table 1: Bioaccumulation of metals in the fish of Babitonga Bay

| Ichtic Species | Content of metals ($\mu\text{g}\cdot\text{g}^{-1}$, wet weight) \pm standard deviation | |
|--|--|------------------|
| | Zn | Cr |
| <i>Eugerres brasilianus</i> | 9.28 \pm 0.65 | 0.06 \pm 0.004 |
| <i>Centropomus paralellus</i> | 12.71 \pm 0.56 | 0.08 \pm 0.006 |
| <i>Mugil platanus</i> | 4.40 \pm 1.17 | 0.06 \pm 0.009 |
| Permitted limits of heavy metals (Health's Ministry) | 100 | 0.10 |

oven with 0.5 ml of distilled water, 1.5 ml of concentrated HF and 3.0 ml of aqua regia (HCl conc. + HNO₃, 3:1). All the solutions were examined by flame atomic absorption analysis (Spectra AA 250 plus, Varian).

The fish analysed were obtained from a local fish market, sliced for muscle samples and finally liophilized. Then, aliquots of 0.5g of an oven-dried (105°C, 18 h) and homogenized sample were wet digested in a glass vessel with 10 ml of concentrated HNO₃ and then agitated for 18 h at a room temperature. After digestion, the samples were filtered with a 0.45 μm filter and diluted with distilled metal-free water up to 50 ml. The metal analysis were carried out by using an atomic absorption spectrophotometer (Spectra AA 250 plus, Varian).

RESULTS AND DISCUSSION

The concentration in percentage (%) of Cr and Zn determined at each extraction step for the five different location of sediment samples are illustrated in Figure 2.

Partitioning patterns for Cr and Zn on the different sediment samples showed that the distribution of heavy metals is not uniform over the whole Bay. This can be explained by the differences on the heavy metals sources, the prevailing physico-chemical conditions, complex reactions such as adsorption, flocculation and redox conditions existing on the Bay.

The smallest values of Cr were observed at the first GPH (ion-exchangeable metal) and second GPH (metal bounded to carbonates) (0% to 7%), for all site samples. The highest values concentration (%) were observed at the third GPH (easily-reducible metal, bounded to oxides of manganese and non-crystalline lattice iron) (21% to 62%) and fourth GPH (metal bounded to organic substances and sulfides) (21% to 68%), in all site samples. The high values of metals found on the fourth GPH (organic phase) are not alarming, since they are not considered very mobile or available and therefore generally associated with stable, high molecular weight humic substances, which slowly release small amounts of metals (SINGH *et al.*, 1998).

According to PERIN *et al.* (1997), the first, second and third GPHs are considered bio-available phases and the fourth and fifth GPHs are considered non-bioavailable phases. Due to the low values concentration observed for Cr at the first and second GPHs, this element should be considered as non-bioavailable, but since very high values concentration were obtained at the third GPH (for all the site samples), then Cr contained on the sediment samples of the Babitonga Bay must be considered bio-available to aquatic media.

According to PEMPKOWIASE *et al.* (1999), heavy metals of anthropogenic origin are generally introduced into the environment as inorganic complexes or hydrated ions, which are easily adsorbed by the sediment surface of particles through relatively weak physical and chemical bonds. Thus, heavy metals

of anthropogenic origin are found predominantly as labile extractable fractions (first GPH) in sediments.

For Zn, the highest values (at all site samples) were observed at the third GPH (69% to 89%) while for the fourth and fifth GPHs the concentration values (%) were relatively low (average 7.4%). The Zn values concentration at all bio-available phases were higher than those for Cr. This indicates that this metal is more easily available to aquatic life than Cr. Other past researchers also described a similar behavior of these metals in sediments: ALVAREZ-IGLESIAS *et al.* (2003), TOKALIOGLU *et al.* (2000) and PERIN *et al.* (1997).

Table 1 shows the heavy metal concentration on three different fish of Babitonga Bay and the permissible limits proposed by the Ministry of Health in Brazil (1977). The concentration of Zn was higher than the concentration of Cr for all species analysed. The Zn values found on the Babitonga Bay fish muscles are in concordance with the results obtained from the metal concentration studies performed in the fish of Ataturk Dam Lake (Euphrates), Turkey by KARADEDE AND UNLU (2000).

CONCLUSIONS

Trace elements concentration depends not only on industrial and household waste inputs but also on the geochemical composition of the area. However, the concentration values of Zn were very high at the first, second and third GPHs, as well as the concentration values of Cr at the third GPH. Thus, these concentrations of Zn and Cr have resulted from anthropogenic influences. The metal contents of Zn and Cr found on the Babitonga Bay sediments are characteristic of polluted sediments. In spite of this situation, the levels of Zn and Cr found on the fish muscles are acceptable for human consumption. However, if no precaution and action are taken in short term, a potential danger may occur in the future depending on the agricultural and industrial development in this region.

LITERATURE CITED

- BOUGHRIET, A., OUDANE, B., FISCHER, J.C., WARTEL, M., and LEMAN, G., 1992. Variability of dissolved Mn and Zn in the Seine Estuary and chemical speciation of these metals in suspended matter. *Water Research* 26, 1359-1378.
- CHEN, Y.K., GUPTA, S.K., SYCIP, A.Z., LU, J.C.S., KNEZEVIC, M., and CHOI, W.W., 1976. *Research study on the effect of dispersion, settling, and redimentation on migration of chemical constituents during open-water disposal of dredged materials*. Dredged Material Research Program Rep. D-76-1. Environ. Effects Lab., US Army Engineer Waterways Experimental Station.
- CHESTER, R., and HUGHES, M.J., 1967. A chemical technique for the separation of Fe-Mn minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chem. Geol.* 2, 249-262.
- PEMPKOWIASE, J., SIKORA, A., and FIERNACKA, E., 1999. Speciation of heavy metals in marine sediments vs. their bioaccumulation by Mussels. *Chemosphere* 39 (2), 313-21.
- PERIN, G., FABRIS, R., MANENTE, S., WAGENER, A., HAMACHER, C., and SCOTTO, S., 1997. A five years study on the heavy metal pollution of the sediments of Guanabara Bay (Rio de Janeiro/Brazil) and evaluation of the metal bioavailability by means of geochemical speciation. *Water Research*, 31, 3017-3028.
- PETERSEN, W., WALLMANN, K., LI, P.L., SCHROEDER, F., and KNAUTH, H.D., 1995. Exchange of trace elements of the sediment-water interface during early diagenesis processes. *Marine and Freshwater Research*, 46, 19-26.

- RUBIO, R., LOPEZ-SANCHEZ, J.F., and RAURET, G., 1991. La especiacion solida de trazas de metales en sedimentos. Aplicacion a sedimentos muy contaminados. *Anal. De Quim.* 87, 599-605.
- SINGH, S.P., TACK, F.M., and VERLOO, M.G., 1998. Heavy metals fractionation and extractability in dredged sediment derived surface soils. *Water Air Soil Pollut.*, 102: 313-328.
- TESSIER, A., CAMPBELL, P.G.C., and BISSON, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844-851.

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