

## Evaluation of Heavy Metals in Fish of the Sepetiba and Ilha Grande Bays, Rio de Janeiro, Brazil

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**Muscles, gonads, and liver tissues of fish caught in Sepetiba and Ilha Grande Bay were analyzed to assess levels of heavy metal concentrations of Cd, Fe, Zn, Pb, Ni, Cu, and Cr. Levels of Cr surpassed the maximum permissible concentration in muscle, followed by Zn in some species. Pb, Cu, and Cd presented concentrations above maximum permissible levels in gonads and liver only. Fe presented concentrations in viscera comparable to those of highly polluted areas, although there are no standards available for this metal. Ni was the only metal that did not present contamination in the fish tissues examined. Overall, fish caught in Sepetiba Bay showed higher metal concentrations than those from Ilha Grande Bay, but the latter also presented high metal concentrations in several samples.**

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**Key Words:** heavy metals; fish; Sepetiba Bay; Ilha Grande Bay; Brazil.

### INTRODUCTION

The increasing levels of pollution in aquatic systems and its influence on the biota have been widely reported (Wiese *et al.*, 1997a,b; Boyer *et al.*, 1999; Hubertz & Cahoon, 1999). Accumulation of heavy metals in aquatic organisms in one of the most striking effects of such pollution. Some metals, in small amounts, are necessary for individual metabolic processes, being assimilated by marine organisms. However, their capacity to form complexes with organic substances can reach concentrations up to 1000 times higher than their assimilation and

fixation in tissues, becoming toxic to organisms (CETESB, 1982). The effects of these pollutants can be lethal or sublethal to all components of the biota, such as phytoplankton, zooplankton, benthos, fish, birds, and, finally, humans (Coelho and Fonseca, 1986). These effects can be both teratogenic and mutagenic (Evangelista, 1994).

Most of the watershed uses of Sepetiba Bay, Rio de Janeiro, are controlled by the Metropolitan Industrial Act, which divides industrial areas into zones according to land use: Strict Industrial Zone (SIZ), Predominantly Industrial Zone (PIZ), and Multiple Use Zone (MUZ). The heavy industries located around Sepetiba Bay fall into the SIZ category and there is a high concentration of industrial plants in this area. At present there are more than 100 medium- and large-size companies, of several industrial types, which release great amounts of potentially toxic substances into the bay, especially heavy metals (SEMA, 1998). Although the industrialization process in the area is relatively recent, occurring mostly in the past 40 years, pollution levels have already matched levels of older, historically polluted industrial areas of Europe and North America (Lacerda and Pfeiffer, 1987). Additionally, there are large passive residuals in the sediment in the Bay, which is disturbed by drag operations during maintenance and enhancement of Sepetiba Harbor. These disturbances make the metals again available to be incorporated into the food web. There is also potential for even more industrial development in the Bay area and Rio de Janeiro City. If no pollution control measures are taken, a 50% load pollutant increase by 2020 is estimated, and this could have serious ecological and economic consequences, considering existing degradation conditions (SEMA, 1998). Besides the damages already observed in the landscape

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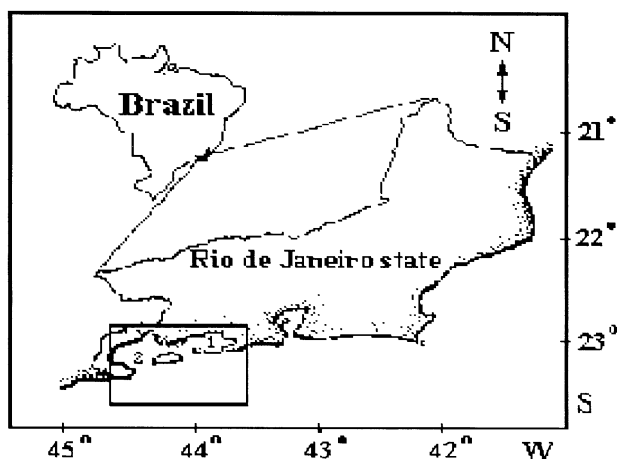


FIG. 1. Study area: 1, Sepetiba Bay; 2, Ilha Grande Bay.

and fisheries, with the latter representing about 3% of total fishery marked in the State of Rio de Janeiro (FIPERJ, 1998), a very important concern is the health of thousands of people feeding on fish from the area.

A similar semiclosed system, but less impacted, is Ilha Grande Bay, located near Sepetiba Bay. In the current study, fish from this area are examined for metal concentration, aiming to compare the situation between these two Bays (Fig. 1). This work seeks to evaluate the present levels of heavy metal concentrations in fish from Sepetiba Bay and Ilha Grande Bay and to establish comparisons with maximum permissible concentration standards.

## MATERIALS AND METHODS

A total of 120 fish, from both Sepetiba Bay (60 individuals) and Ilha Grande Bay (60 individuals), obtained from a local fish market from December 1999 to May 2000 were examined. Four species were selected to test for cadmium, lead, chromium, nickel, iron, copper, and zinc concentrations: *Mugil lisa*, *Cynocion leiarchus*, *Micropogonias furnieri*, and *Genidens genidens*. Thirty-six *M. lisa*, *C. leiarchus*, and *M. furnieri* and 12 *G. Genidens* individuals were used.

TABLE 2

Recovered Values (%) for all Analyzed Methods

Cd	Pb	Cu	Cr <sup>t</sup>	Fe	Ni	Zn
97	90	93	97	98	102	96

Each sample comprised three individuals of varied sizes, in three replications, from each tissue examined: muscle, gonads, and liver (Table 1). For *G. genidens*, only two individuals composed the sample, with three replications. Fish species selection aimed to include different ecological niches, as well as those commonly used for human consumption.

Muscle analyses were used to investigate possible transfer of heavy metals to human populations via fish consumption. Liver analyses were used to determine recent metal accumulations, while gonad analyses were for assessing possible transfer and/or influence of metals through the reproductive processes and also human consumption.

Fish were dissected for liver and gonad samples, and sliced for muscle samples, using plastic knives on polyethylene film, which were discharged after each tissue extraction. The digestion procedure followed McDaniel (1992), and metal extraction was performed according to Creed *et al.* (1992). One gram of lyophilized sample was added to 5 ml of nitric acid P.A. and 5 ml of 30% peroxide hydrogen and heated at 80°C for 1 h. The solution was recovered in 1 ml chloridic acid and filtered on glass fiber paper. Metal analyses were performed using an atomic absorption spectrophotometer (AAS) (GBC Scientific PTY Ltd. Avanta). Results were expressed as micrograms of metal per wet weight gram of fish. The maximum permissible concentrations (MPC) were those established by the Brazilian Ministry of Health (1977). The laboratory reference material used was lobster hepatopancreas TORT. Blank values were zero for all metals examined (Cd, Pb, Cu, Cr<sup>t</sup>, Fe, Ni, Zn) and the recovered values (in %) are as described in Table 2.

TABLE 1

Fish Species Examined and Their Ecological Characteristics

Popular name	Scientific name	Feeding habit	Biotic compartment
Mullet	<i>Mugil lisa</i>	Filter/herbivorous	Water column/substrate
Drums	<i>Cynocion leiarchus</i>	Carnivorous	Water column/substrate
Croaker	<i>Micropogonias furnieri</i>	Omnivorous	Substrate
Marine catfish	<i>Genidens genidens</i>	Omnivorous	Substrate

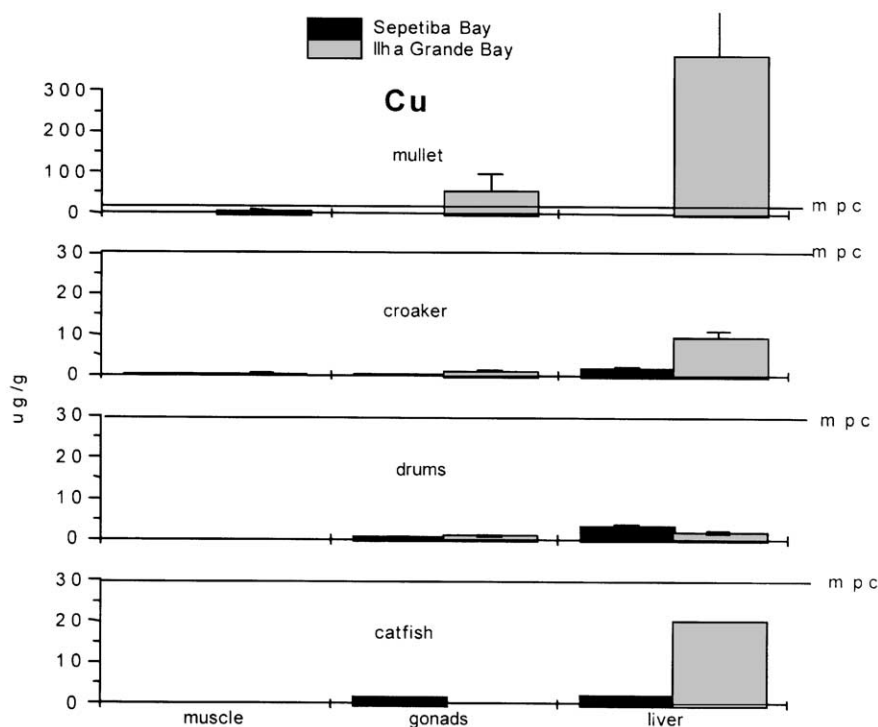


FIG. 2. Concentrations of copper in fish tissues from Sepetiba and Ilha Grande Bay. mpc, maximum permissible concentration.

## RESULTS AND DISCUSSION

### Copper

Copper levels (Fig. 2) were below the MPC for human consumption in all studied fish tissues, except for liver and gonads of mullet in Ilha Grande Bay. All other species analyzed also presented the highest concentrations in the liver in the Ilha Grande Bay.

This metal accumulates by several means, depending on environmental conditions and habits of the species (Saward *et al.*, 1975). Phytoplankton is the most likely biota compartment for Cu concentration (EPA, 1972), along with sediments, due to the great capacity of Cu for precipitation. Therefore, the highest concentrations of Cu being found in mullet could be due to the filter/herbivorous habits of this fish as well as the large amount of sediment in the Bay. These results are in agreement with those previously found for Sepetiba Bay by Pfeiffer *et al.* (1985) and for Santos Bay by Lee (1980). Copper is essential for animals and plants, as it takes part in enzyme formation and participates in respiratory processes, with accumulation levels varying widely among aquatic organisms; variations in Cu concentration are related to levels of tolerance and toxicity symptom outbreaks, depending on species and

period of passive accumulation (CETESB, 1984). High Cu concentration in fish liver is rather uncommon, and fish liver is not used for human consumption. On the other hand, gonads are consumed by humans, and high Cu accumulation in the viscera indicates high concentrations in other organs, suggesting the need for careful monitoring of its levels.

### Iron

High Fe concentrations (Fig. 3) in the liver of all studied species in Sepetiba Bay was recorded, mainly for marine catfish. This metal is present in soil, water, and atmosphere, and Fe compounds occur in several types of industrial processes. Fe participates in the hepatic process, and it is also associated with hemoglobin through the transport of oxygen. No standards for MPC have been established for iron, making results difficult to interpret. The values found in liver for fishes in the Sepetiba Bay are similar to those found in viscera in species of the Paraíba do Sul River, where Fe pollution is considerable (Azcue *et al.*, 1988). Also, waters from the Paraíba River are diverted to the Sepetiba Bay via Guandú/Ribeirão das Lajes system, and this could contribute to Fe pollution in the Bay.

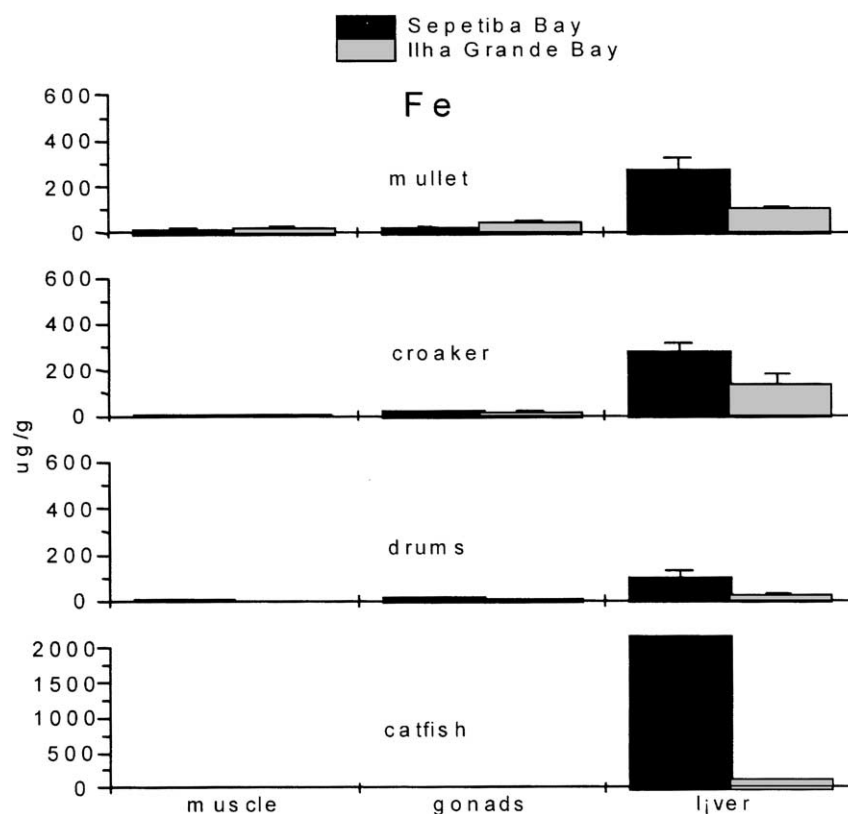


FIG. 3. Concentrations of iron in fish tissues from Sepetiba and Ilha Grande Bay.

### Chrome

Concentrations of chrome (Fig. 4) exceeded MPC in most fish species tissues studied, for both bays. This metal is used in the leather industry, in inks, and in processing of steel, among other uses (Evangelista, 1994). In Sepetiba Bay there are several of those types of industries (SEMA, 1998). Chrome presents several oxidation stages; in industrial/environmental aspects the forms  $\text{Cr}^{(0)}$ ,  $\text{Cr}^{(III)}$ , and  $\text{Cr}^{(VI)}$ , and cromats and dicromats are important.  $\text{Cr}^{(III)}$  is essential to vital processes linked to insulin function (CETESB, 1984), while  $\text{Cr}^{(VI)}$  is highly toxic, with carcinogenic and ulcerative characteristics (Evangelista, 1994; Rocha *et al.*, 1985). The highest concentrations of Cr were found in mullet gonads in Sepetiba Bay, and this is probably due to Cr affinity to lipids. Values above the MPC for human consumption were detected in fish from different areas, including Sepetiba Bay, by Pfeiffer *et al.* (1985), and it was the only metal to exceed MPC at that time. There has been criticism of the Cr MPC, concerning its very restrictive values (CETESB, 1984), yet there has been concern over the potential danger to humans who consume Cr-contaminated fish for over 15 years (Pfeiffer *et al.*, 1985).

### Zinc

Concentrations of Zn (Fig. 5) exceeding MPC were found mainly in liver samples in three of the four studied species, with the highest values in drums. Values exceeding MPC were found for gonads and muscle in mullet and drum, but lower in scale. White croaker was the only species to present Zn concentrations lower than MPC in all studied tissue types. Most of the samples with high Zn concentrations were from Sepetiba Bay. Gonads have been reported as a structure likely to present high Zn concentration due to their participation in cellular division and growth processes (Lacerda *et al.*, 1989). In the present work the highest records found in liver may characterize recent incorporation, through the digestive tract. Chipman (1958) and CETESB (1982), studying radioactive Zn, showed a high absorption rate for this metal into fish liver and kidney. Highest Zn concentrations occurred in fish associated with substrata or those which feed on it, such as marine catfish, flounder, and mullet (CETESB, 1982), and this coincides with the findings of Pfeiffer *et al.* (1985). In the present work, white croaker unexpectedly was the only species to not exceed MPC for Zn, while drum, a species less related to substrata than

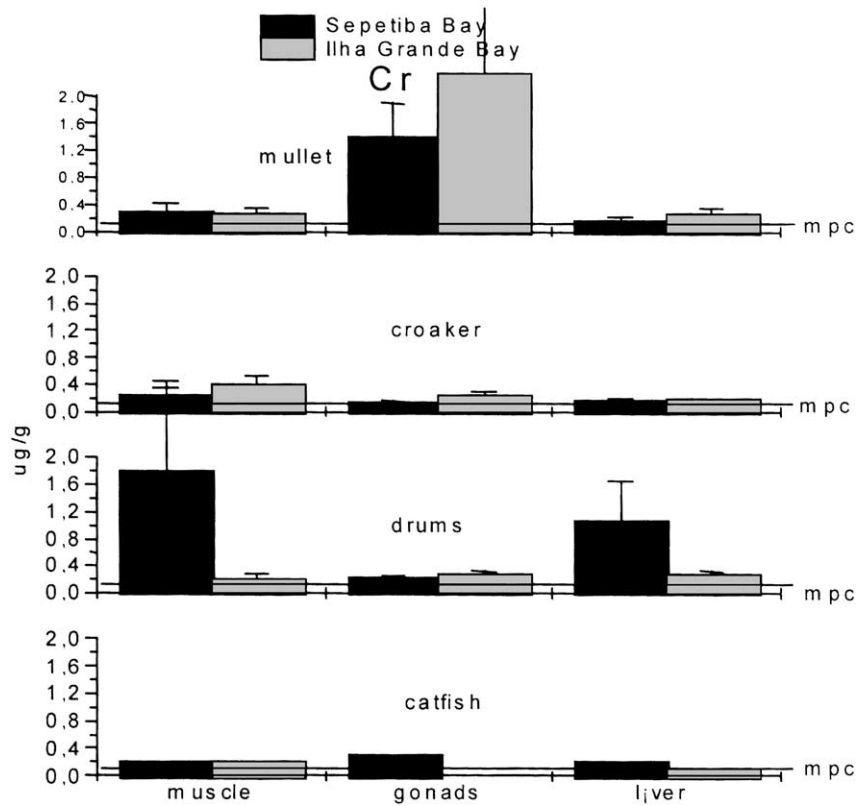


FIG. 4. Concentrations of chrome in fish tissues from Sepetiba and Ilha Grande Bay. m.p.c, maximum permissible concentration.

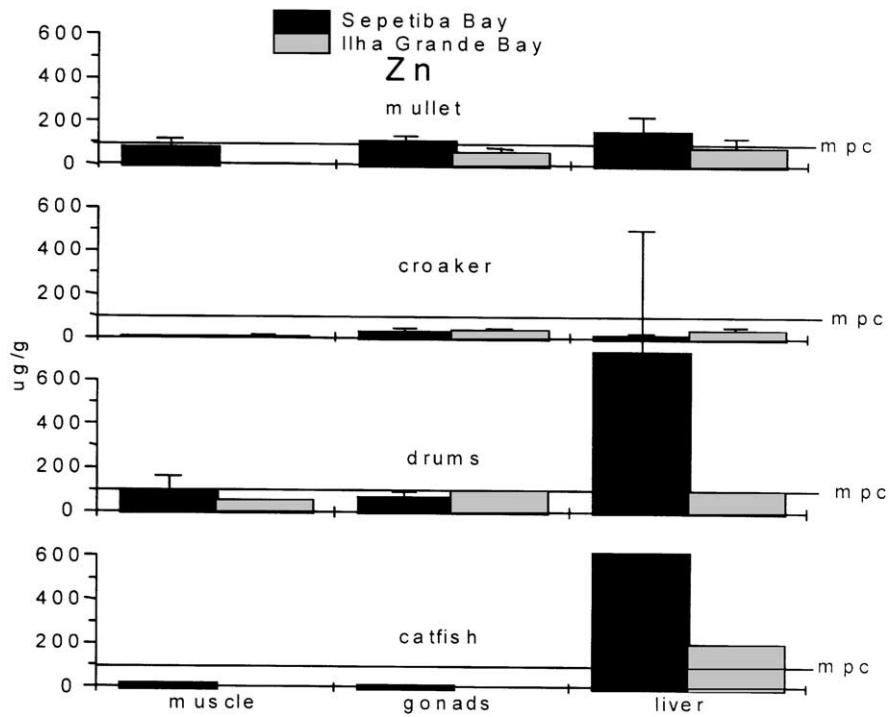


FIG. 5. Concentrations of zinc in fish tissues from Sepetiba and Ilha Grande Bay. m.p.c, maximum permissible concentration.

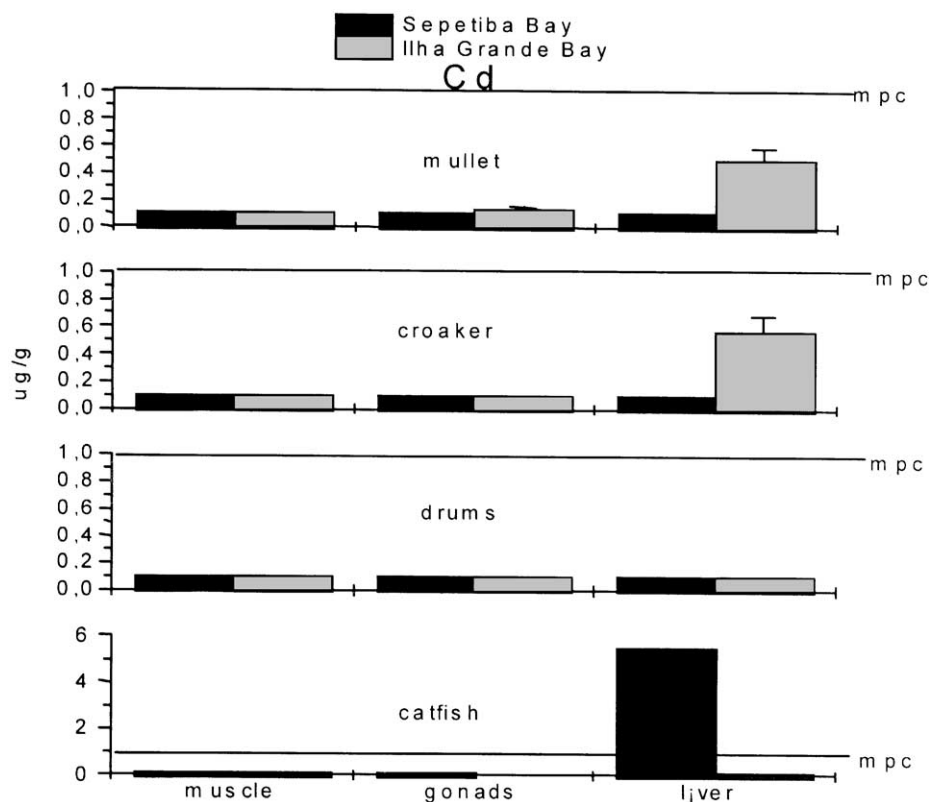


FIG. 6. Concentrations of cadmium in fish tissues from Sepetiba and Ilha Grande Bay. mpc, maximum permissible concentration.

the others, had the highest Zn concentrations. Besides its piscivorous habits, drum also feed on benthic invertebrates, preferring the muddy bottom when in shallow waters, which could explain such results (Menezes and Figueiredo, 1980).

Although zinc is an essential element to the physiology of organisms, poisoning to humans can occur, resulting in lung disease, gastroenteritis, fever, vomiting, muscular coordination problems, and dehydration. In fish, it can obstruct the interlamellae spaces, blocking breathing movement (Rocha *et al.*, 1985), as well as delay growth and maturation (EPA, 1976). Fish and mollusks contaminated by Zn present a bluish coloration, and are usually rejected by consumers (Rocha *et al.*, 1985). Zn concentrations found in this work are higher than those found by Pfeiffer *et al.* (1985), indicating a major system contamination for Zn, with MPC values higher than allowed, even in Ilha Grande Bay. There is some controversy over Zn MPC values, with both 50 and 100 µg/g being reported (Brazilian Ministry of Health, 1977).

#### Cadmium

Overall Cd concentrations (Fig. 6) were below MPC, except for liver in marine catfish in Sepetiba

Bay. As liver is not commonly consumed by humans possible Cd toxicity via fish ingestion is not likely. However, Cd is not an essential element, it is difficult to excrete once ingested, it presents high toxicity, and in Sepetiba Bay it is very widespread (FEEMA, 1997). Even subacute Cd levels can result in physiological dysfunction in fish, reducing the possibility for survival in the environment (Larsson *et al.*, 1976).

#### Lead

Concentrations of Pb (Fig. 7) exceeding MPC were found in mullet liver from Ilha Grande Bay. The other species and tissues had concentrations below MPC. Pb does not present beneficial or nutritional effects to organisms and is extremely toxic (CETESB, 1982). Overall it presents in very low concentrations in the biota, even when there are high concentrations in the abiotic environment. (Phillips *et al.*, 1982). This metal is used in several industrial processes and is a common residue from gasoline combustion (Evangelista, 1984). It ranks as the metal of largest diffusion through the atmosphere (SEMA, 1998). This means of dispersion could explain the high concentrations found in

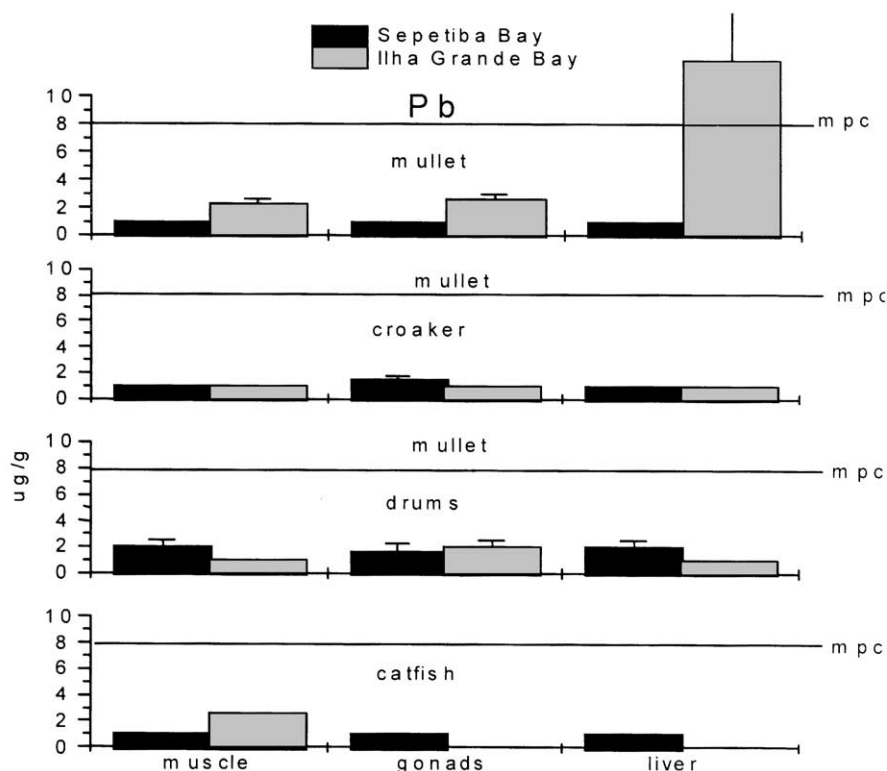


FIG. 7. Concentrations of lead in fish tissues from Sepetiba and Ilha Grande Bay. mpc, maximum permissible concentration.

mullet liver from Ilha Grande Bay, which is relatively far from the urban areas and industrial plants. Although all muscle samples are under MPC, the values obtained in the present work are higher than those found by Pfeiffer *et al.* (1985), when similar species were examined, therefore indicating an increase of lead in the environment.

#### Nickel

Nickel (Fig. 8) was the only metal that did not surpass MPC in any of the fish tissues analyzed from the two bays, being the metal with the lowest records of discharge in the Sepetiba Bay. The only means through which Ni spreads to the environment is by air diffusion, which is estimated to be 1.5 tons per year (SEMA, 1998). At present, Ni does not seem to present problems of contamination in Sepetiba Bay or Ilha Grande Bay.

#### Final Considerations

All of the metals studied, with exception of Ni, showed values exceeding MPC in at least one tissue or fish species examined. Chrome was the metal that

most exceeded the permissible levels in muscle, followed by zinc.

No evident pattern of metal incorporation was shown for certain species with regard to their position in the trophic levels. In coastal semiclosed bays, like Sepetiba and Ilha Grande, with low depth, even piscivorous fish feed on sediment when searching for invertebrates. Species feeding on plankton by filtering water also use the sediment for detritus and algae, which complement their diet. Therefore in most cases both piscivorous and planktivorous species have a close relation to the substrata, the system component most likely to be contaminated by heavy metals via sedimentation.

Liver was the tissue that presented the highest concentrations of the metals studied, indicating incorporation through digestion, which could also indicate recent incorporations, similar to gonads.

Overall, the study fish from Sepetiba Bay presented higher metal concentrations than fish from Ilha Grande Bay, as expected. On other hand, fish from this latter bay, unexpectedly presented high concentrations of Cu, Pb, and Cr. The mobile nature of the fish, however, could result in a species living mostly in Ilha Grande Bay being caught in Sepetiba Bay, and vice versa. A species that is typically found

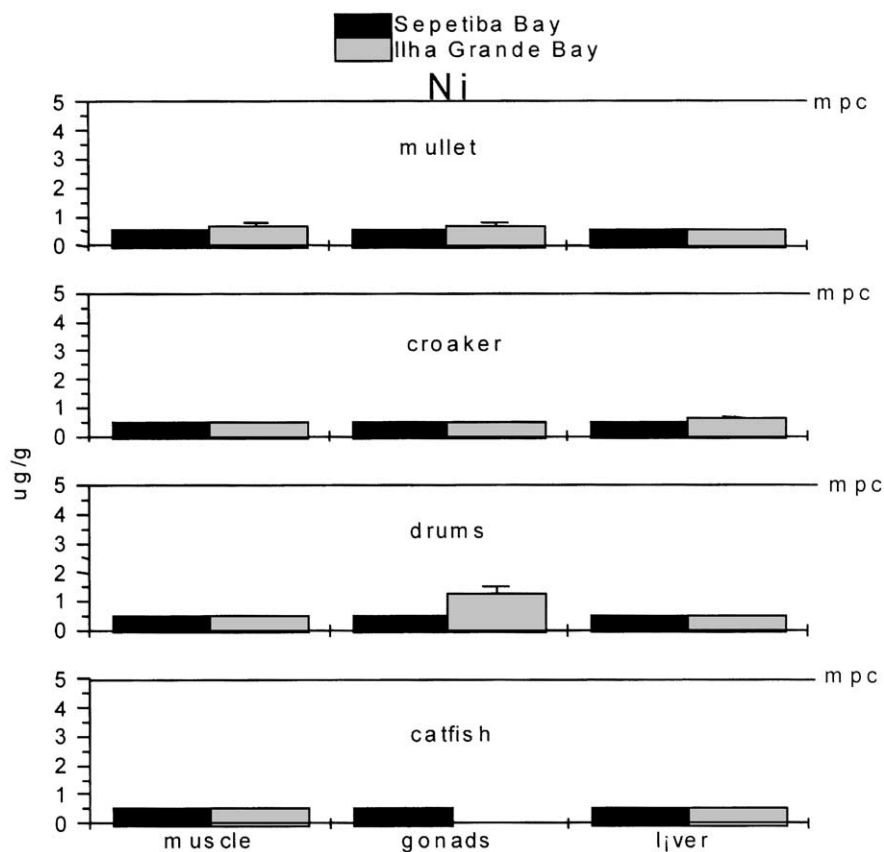


FIG. 8. Concentrations of nickel in fish tissues from Sepetiba and Ilha Grande Bay. mpc, maximum permissible concentration.

throughout the marine environment is the catfish *G. genidens*. Results from this species suggested that metal incorporation occurred in both bays, with the fish from Sepetiba Bay showing higher levels of contamination.

Drag operations for maintenance and enhancement of Sepetiba Harbor has made available to the biota sediment that has been environmentally passive for 40 years, adding more contamination to the industrial effluents that continuously come into to Sepetiba Bay. Additionally, overfishing using bottom trawling stirs the top layers of the substrata, also contributing to increased pollution in the Bay. Adding another problem is the fact that the material from the dredging is deposited inside the Bay, against the recommendations of environmental agencies, which recommend disposal in the open sea. Dispersion of this material into Ilha Grande Bay could be occurring due to the small diameter of the suspended particulate, current circulation, and proximity between the two bays. This is in addition to the contribution of atmospheric pollution. Further analyses of metals in sediments of the eastern part of

Ilha Grande Bay could better assess the levels of dispersion of this dredge material.

The results show an evident increase in contamination of the Sepetiba Bay by heavy metals, with a risk to the human population through consumption of fish. Fifteen years ago, the danger mostly involved contamination of filtering mollusks, organisms widely known as good accumulators. Ilha Grande Bay also seems to be suffering the same environmental disturbances that are occurring in the Sepetiba Bay. Regrettably, it is the last relatively preserved bay of southeast Brazil.

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