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Science of the Total Environment 323 (2004) 219–226

Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

The use of *Micropogonias furnieri* and *Mugil liza* as bioindicators of heavy metals pollution in La Plata river estuary, Argentina

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Received 31 May 2003; accepted 19 September 2003

Abstract

This paper presents, the concentrations of total Hg, Cd and Zn in edible muscle tissue, and in the liver of the fish *Micropogonias furnieri* and *Mugil liza* from the Samborombon Bay, La Plata river estuary, Argentina. The highest accumulation of the three metals was observed in liver samples, whereas in muscle tissue concentrations they were always lower, values even lower than the detection limit of the analytical method used. A marked relationship between metal contents of the studied species and their trophic and ecological habits was observed. In all cases, metal levels found in edible muscle tissue were lower than the international standards of reference for organisms directed to human consumption. Finally, the validity of using these two species as bioindicators of heavy metal pollution in the assessed ecosystem was discussed.

Keywords: Monitoring; Heavy metals; Fish; Muscle; Liver; Estuary

1. Introduction

The wide diversity of human activities that introduce pollutants into the environment, as well as their magnitudes make the assessment of environmental impact a subject of utmost interest. Contamination of aquatic environments with potentially harmful substances, in particular non-degradable heavy metals, and its subsequent impact on organisms, is more dramatic within estuaries and semi-closed coastal zones, especially when they are near highly populated or industrial areas. Heavy metals may enter an estuary from different natural and anthropogenic sources, including industrial or domestic sewage, storm runoff, leaching from landfills, shipping and harbor activities, and atmospheric deposits (Salomons and Förstner, 1984; Lacerda, 1998).

The study of organisms as pollutant monitors has several advantages over the chemical analysis of abiotic compartments. Organisms only accumulate the biologically available forms of the pollutant and are always present in the environment, thus enabling the continuous monitoring of pollutants. Organisms integrate fluctuations of pollutant concentration through time and the magnification afforded by bioaccumulation may be advantageous concerning the accuracy and expense

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doi:10.1016/j.scitotenv.2003.09.029

of analysis of trace pollutants near the limits of analytical detection. Most of the papers published on organisms as pollution bioindicators have concentrated on invertebrates, mainly mollusks and crustaceans. However, the use of fish as indicators for marine pollution monitoring is at present widely recognized (Phillips, 1977; Jones and Walker, 1979; Bryan et al., 1985; Phillips and Segar, 1986; Reddy et al., 2001). According to Markert et al. (1997) the concepts of *bioindicator* (organisms which only provide information on the quality of the environment or its change) and *biomonitor* (that who make it possible to determine the quantity of the environment or its change) must be clearly indicated.

In the present paper, the concentrations of Hg, Cd and Zn in edible muscle tissue and in the liver of the fish *Micropogonias furnieri* and *Mugil liza* were studied. These are two of the most often captured species in the Samborombon Bay (in the outer zone of the Río de la Plata estuary), in Argentina. An attempt was made to understand variations of metal concentrations among organisms and species; as well as the relationship between metal content and the size of the fish. Finally, the use of *M. furnieri* and *M. liza* as pollution bioindicator species was assessed.

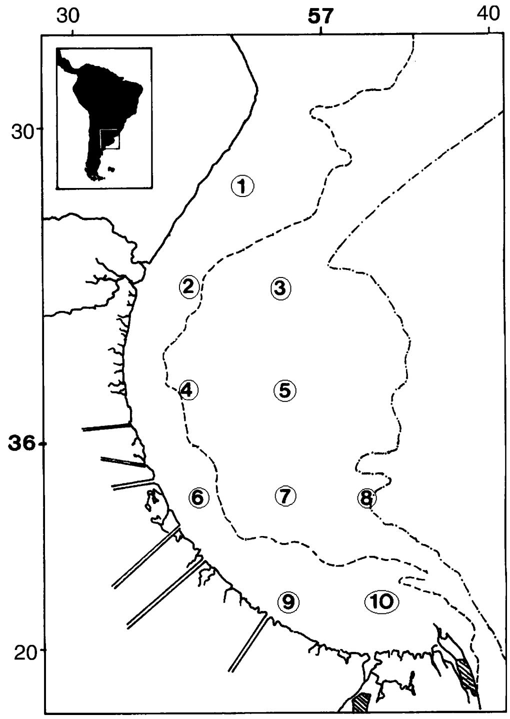

Fig. 1. 'Location of sampling stations at Samborombon Bay'.

2. Materials and methods

2.1. Studied area

The large La Plata river estuary is a system of vital importance at the north-eastern littoral of Buenos Aires Province, not only from the physical viewpoint but also because of its ecological significance (Boschi, 1988). It has been described as a typical frontal system, which simultaneously presents a relative abundance of nutrients on surface, and a highly stable water column (Carreto et al., 1986). The main flux of the La Plata river presents a north-northeast drift, although important fluctuations indicate spatial-seasonal variability of the estuarial system (Brandhorst and Castello, 1971). It is a brackish water system, with a wide range of salinity variation; this parameter is strongly regulated by freshwater from the river, and by the penetration of marine water (controlled by currents and meteorological conditions) (Boschi, 1988; Simionato et al., 2001). Besides, the river transports a large mass of suspended material from its basin. These fine particles of fluvial origin settle within the estuary and form large wetland areas in the region.

The Samborombon Bay of the La Plata river estuary was selected because its size allows intensive studies over short periods. The bay is located southwest of the outlet of the La Plata river, between Punta Piedras (32°57′S and 57°08′W) and Punta Rasa (36°18′S and 56°48′W) on the north-eastern coast of Buenos Aires Province (Fig. 1). In addition to high freshwater and sediments discharged through the La Plata river, the bay receives the contribution of many rivers and channels (the Salado river basin, the Samborombon river, etc.), through which waters from the whole Buenos Aires Province drain. Therefore, important amounts of pollutants may enter the bay from the

Table 1
Percentages of recovery in the analysis of NIES reference material (mussel tissue flour) for AQ assessment

Metal analyzed	Percentage of recovery (range %)
Cd	91.4–99.3
Zn	96.5–102.3
Hg	93.7–98.8

biggest urban and industrial centers of Argentina (located beside the La Plata river or its tributaries).

2.2. Sampling and analysis

During the study period eight fishing expeditions were carried out in the Samborombon Bay. Catches were obtained from ten (10) sampling stations (Fig. 1) by pair trawling with commercial fishing vessels from the San Clemente del Tuyú harbor.

Morphometric data on the collected specimens of *M. furnieri* and *M. liza* were taken and, subsamples of dorsal muscle tissue (from the post-cephalic region) and liver were obtained. The samples were frozen at −20 °C until treated in the laboratory to determine total mercury, zinc and cadmium.

After an acid mineralization, mercury concentrations were measured through cold vapor atomic absorption spectroscopy, following a domestic modification of the method opportunely described by Uthe et al. (1970). For cadmium and zinc determination samples were digested with acid followed by atomic absorption spectroscopy with air/acetylene flame and deuterium lamp background correction. Details on sample preparation and analysis were published elsewhere (Marcovecchio et al., 1988a).

All samples were analyzed on a AA-2380 Perkin-Elmer spectrophotometer. Analytical grade reagents were utilized to establish calibration curves and blank assays. Analytical quality (AQ) was checked against reference material (mussel tissue flour), provided by the National Institute for Environmental Studies (NIES), from Tsukuba (Japan). Corresponding data on reference material recovery test's are shown in Table 1.

3. Results

Total concentrations of Hg, Cd and Zn in muscle tissue and liver of *M. furnieri* and *M. liza* from the Samborombon Bay (Table 2) are useful to assess trace metal contents in the organisms taken from the environment under study, and may be used as a quality index for its evaluation. Furthermore, considering that these fishery products are used for human consumption, it is important to know the metal contents of the species caught.

3.1. Cadmium

In the case of *M. furnieri*, Cd concentrations in liver varied between 0.95 and 5.34 μg/g (wet wt.), with an average of 3.13 μg/g (wet wt.); on the other hand, muscular-Cd contents were always lower than the detection limit of the method used.

Table 2
'Trace metals distribution in muscle and liver of the fish species studied at Samborombón Bay'

	Analyzed tissue	*Micropogonias furnieri*				*Mugil liza*			
		X	S.D.	C.V.%	Min–max	*X*	S.D.	C.V.%	Min–max
Cd	M	n.d.	–	–	–	0.34	0.05	14.7	0.20–0.44
	L	3.13	1.04	33.1	0.95–5.34	9.15	1.25	13.7	7.85–12.4
Zn	M	20.5	4.86	23.7	10.7–31.2	48.8	3.99	8.18	40.8–59.8
	L	44.3	6.20	14.0	30.6–60.1	52.0	4.14	7.96	44.2–60.2
Hg	M	0.11	0.04	37.7	0.03–0.19	0.40	0.06	14.3	0.30–0.50
	L	0.13	0.04	29.7	0.04–0.21	0.53	0.11	20.6	0.27–0.79

X, mean concentration in μg/g, wet wt.; S.D., standard deviation; C.V.%, coefficient of variation; min–max, minimum and maximum values as found.

Cd levels found in muscle tissue of *M. liza* varied between 0.20 and 0.44 μg/g (wet wt.), with a mean content of 0.34 μg/g, while in liver the observed variations were between 7.85 and 12.4 μg/g (wet wt.), with a mean concentration of 9.15 μg/g.

Cd concentrations in both species were rather constant with small coefficients of variation for both species. This indicates a low individual variability of Cd concentrations in these fish species. Liver tissues of both species have clearly shown a higher capacity to accumulate Cd compared to muscle tissues. The ratio muscular-Cd to hepatic-Cd was 1:27 for *M. liza* and even higher for *M. furnieri*, since Cd concentrations in muscle tissues of this species were below our analytical detection limit. Cadmium concentrations found in edible muscle tissue of *M. furnieri* and *M. liza* were always lower than the standards internationally accepted as apt for human consumption (Nauen, 1983).

3.2. Zinc

Zn concentrations in muscle tissue of *M. furnieri* varied between 10.7 and 31.2 μg/g (wet wt.), with a mean concentration of 20.5 μg/g. Those in liver ranged between 30.6 and 60.1 μg/g (wet wt.), with a mean of 44.3 μg/g. Zinc contents in the muscle tissue of *M. liza* varied between 40.8 and 59.8 μg/g (wet wt.), with a mean of 48.8 μg/g. Those in liver ranged between 44.2 and 60.2 μg/g (wet wt.), with a mean of 52.0 μg/g. The same as for Cd, inter-individual variability of Zn was rather small and Zn accumulation was also higher in liver tissue than in the muscle one. Muscle-Zn to hepatic-Zn ratio was 1:2.2 for *M. furnieri*, and 1:1.2 for *M. liza*. Zinc concentrations found in the edible muscle of both species were also lower than the standards internationally recommended for human consumption (Nauen, 1983).

3.3. Mercury

Total Hg concentrations in the muscle tissue of *M. furnieri* varied between 0.03 and 0.19 μg/g (wet wt.), with a mean concentration of 0.11 μg/g, while in liver they ranged between 0.04 and 0.21 μg/g (wet wt.), with a mean of 0.13 μg/g. Total Hg concentrations in the muscle tissue of *M. liza* ranged between 0.30 and 0.50 μg/g (wet wt.), with a mean of 0.40 μg/g, while in liver they varied between 0.27 and 0.79 μg/g (wet wt.), with a mean value of 0.53 μg/g. High coefficients of variation observed suggest the existence of individual variability of Hg for both species (Table 1).

Both tissues of *M. furnieri* have shown a similar ability for Hg accumulation (1:1), even though *M. liza* seemed to have a slight increase in the hepatic capability (1:1.35). Total Hg concentrations in edible muscle of *M. furnieri* and *M. liza* were lower, in all cases, than the standards internationally accepted as apt for human consumption (Nauen, 1983).

In the case of Hg, a strong relationship between the metal concentration and the size of the analyzed organism was observed in both species (Figs. 2 and 3), which suggests, notwithstanding the low concentrations found, that Hg bioaccumulation has occurred in these species, and explains most of the inter-individual variability in mercury concentrations.

4. Discussion

The use of fish as biological indicators in programs of pollution monitoring in aquatic environments is widely recognized. The main purpose of monitoring has been to provide continuous and reliable information on the quality of marine foodstuffs concerning human health, as well as to check processes occurring in affected areas from an environmental viewpoint. In the pertaining literature the following concepts have been clearly defined: (i) *active biomonitoring* (selected organisms bred in laboratories are exposed in a standardized form in the field for a period of time, after which the effects provoked on organisms are analyzed); and (ii) *passive biomonitoring* (organisms already present naturally in the ecosystem are examined to study their reactions) (Markert et al., 1999). The present study constitutes a case of passive monitoring within the Samborombón Bay ecosystem, in the Rio de la Plata estuary.

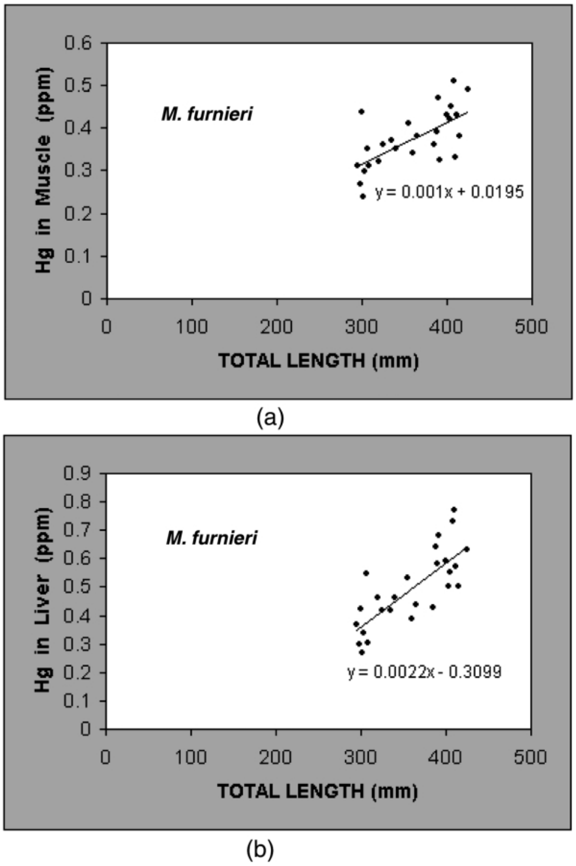

Fig. 2. 'Muscular mercury and hepatic mercury concentrations vs. size relationship for *M. furnieri*'.

Concentrations of cadmium, zinc and mercury determined in muscle tissue and liver of *M. furnieri* and *M. liza* from the Samborombon Bay were relatively low, as compared with reports from other authors for related species in different ecosystems in the region as well as in the world. Heavy metal concentrations found in this study were similar to those reported by Eustace (1974) for *Mugil cephalus* from the Derwent estuary, Australia; by Stenner and Nickless (1975) for *Mugil* sp. from S.W. Spain and Portugal; by Menasveta and Cheevaparanapiwat (1981) for *Mugil dussumerii* from estuaries of Thailand; and by Pfeiffer et al. (1985) and Marins et al. (1998) for *Mugil* sp. and *Micropogonias* sp. from Sepetiba Bay (Brazil). The results from the Samborombon Bay also compare with those from other environments in Argentina, such as those reported by Perez et al. (1986) for *M. furnieri* from the Argentinean continental shelf. However, they are significantly lower than those reported by Marcovecchio et al. (1988a,b) for *M. furnieri* and *Mugil* sp. from the Bahía Blanca estuary. The extensive wetlands surrounding the upper reaches of the La Plata river estuary may reduce the transport of pollutants from the Buenos Aires metropolitan area into the Samborombon Bay.

The process of trace metals bioaccumulation is of utmost environmental significance, and many results for different animal groups indicate the occurrence of bioaccumulation (Boyden, 1977; Bryan, 1979; Marcovecchio et al., 1986). The

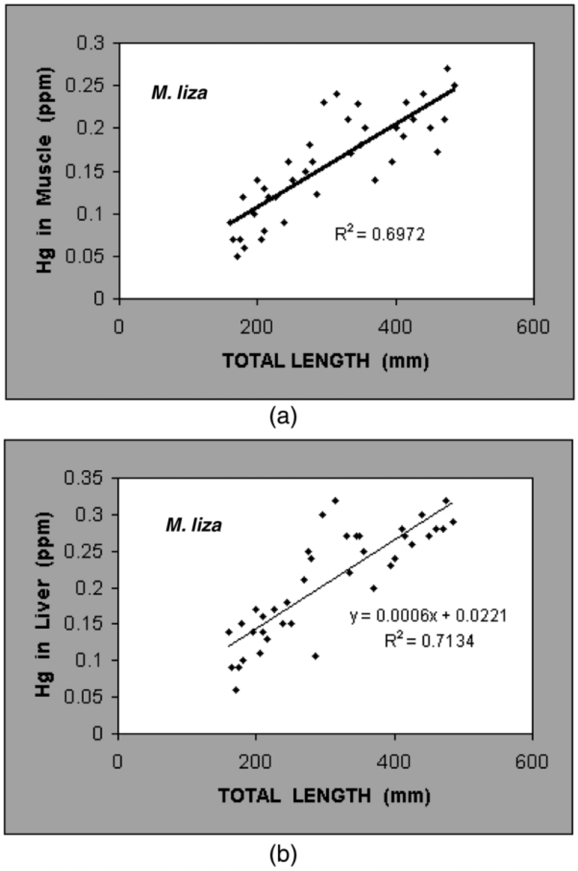

Fig. 3. 'Muscular mercury and hepatic mercury concentrations vs. size relationship for *M. liza*'.

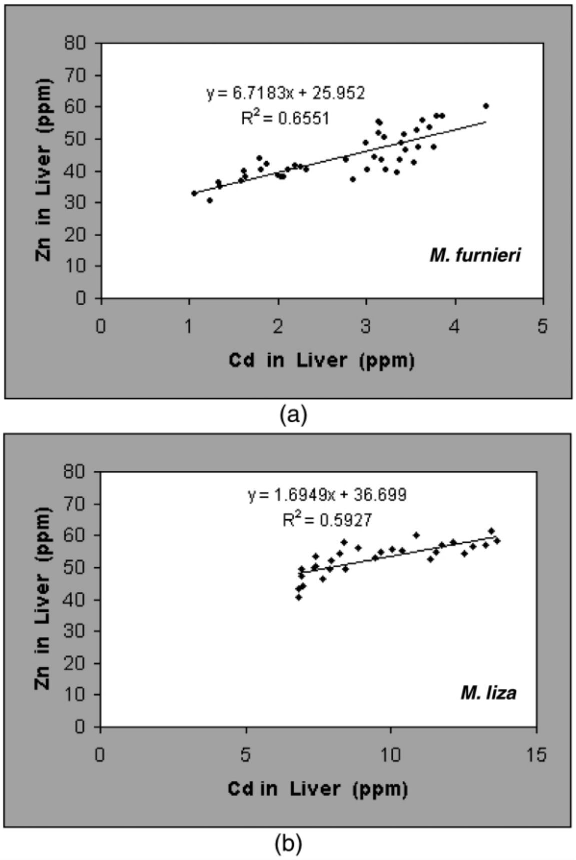

Fig. 4. 'Cadmium vs. zinc relationship in liver of *M. furnieri* and *M. liza*'.

concentrations of cadmium, zinc and mercury determined in *M. furnieri* and *M. liza* from the Samborombon Bay were relatively low, but a bioaccumulation process was verified, at least for Hg. This suggests that bioaccumulation can develop at any metal concentration without minimum level requirements, which coincides with results reported by Amiard et al. (1987) and Amiard-Triquet et al. (1987).

For both fish species analyzed, a highly significant correlation ($r=0.823$, $P<0.01$ for *M. furnieri*, and $r=0.775$, $P<0.01$ for *M. liza*) between hepatic-Cd and Zn concentrations was observed (Fig. 4). Cadmium concentration increases simultaneously with that of zinc, with a constant slope in a molar basis of approximately 5 (Zn/Cd) for *M. furnieri*, and approximately 2 (Zn/Cd) for *M. liza*. Although this kind of relationship between Cd and Zn has been described for terrestrial mammals, like horses, lambs, pigs and humans (Schroeder and Nason, 1974; Elinder et al., 1977; Elinder and Piscator, 1978) and also for marine mammals (Honda and Tatsukawa, 1983), this information is scarce for fish, and certainly unknown for the species studied here. In most of these papers the increase in Zn concentration has been proposed as a compensation for the increase in Cd concentration (due to pollution processes), and this mechanism probably includes the synthesis of metallothioneins (or metallothionein-like proteins), which would bind both Cd and Zn in a molar ratio of 1:1 (Nordberg, 1972; Wagemann et al., 1984; Das et al., 2000).

The highest concentration of trace metals was found in the tissues of *M. liza* from the Samborombon Bay. This is probably related with the trophic characteristics of this species, which being iliophagous fish (Olivier et al., 1972) reflect the metal concentrations in surface sediments and suspended particulate matter, showing high metal concentrations (Marcovecchio, 1988). These results also agree with those reported by Pfeiffer et al. (1986), who pointed out the particulate matter as the main source of metals for the biota of the Paraiba do Sul river basin in Brazil.

The use of biological indicators of pollution is efficient when basic information on biological and ecological aspects of the assessed environments is available (Olsson and Jensen, 1975). Some requirements are necessary to select suitable bioindicators, particularly abundance and facility of sampling all year round, the non-migratory nature and easy identification of the selected organisms and their capability to accumulate the pollutant of interest (Phillips, 1977; Phillips and Segar, 1986). In this scenario it is possible to determine correlations between the concentration of environmental substances and the concentration in the organism (Markert, 1996).

Considering the results of this study and the above mentioned requirements, both *M. furnieri* and *M. liza* are adequate species to be used as biomonitors of trace metal pollution in the Samborombon Bay. Thus, we recommend the use of these species as biological indicators as a tool for future monitoring programs, to evaluate the evolution of heavy metal pollution in this environment.

Acknowledgments

This paper was partially supported through grants by CONICET (National Council for Scientific and Technological Researches), from Argentina. Dr Silvia De Marco (Universidad Nacional de Mar del Plata, Mar del Plata, Argentina), Prof Berndt Markert (Zittau University, Zittau, Germany) and Prof Luiz Drude de Lacerda (Universidad Federal Fortaleza, Fortaleza, Brazil) have critically reviewed this paper, and helped to improve its content.

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