

## Use of *Cathorops spixii* as bioindicator of pollution of trace metals in the Santos Bay, Brazil

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**Abstract** In the present study *Cathorops spixii*, was evaluated as a bioindicator fish for trace metal pollution. Concentrations of cobalt (Co), iron (Fe), selenium (Se) and zinc (Zn) were determined by Instrumental Neutron Activation Analysis in liver. Mercury (Hg) and methyl-mercury (MeHg) were analyzed by Cold Vapor Atomic Absorption Spectrometry in muscles and livers. High concentrations of Co, Fe, Se and Zn were observed in *C. spixii* from Santos Bay in comparison to fish collected in a non-polluted site in the same Brazilian coast. These trace metal concentrations were out of the permissible levels for human consumption. Although, Hg and MeHg levels were low, the *C. spixii* could still be used as an effective bioindicator to observe trace metal behaviors in the environment in function of the bioaccumulation process observed mainly by other analyzed trace metals. Thus, the use of this species is strongly recommended to monitor the effects and behavior of trace metal pollution in aquatic ecosystems in Brazil due to its bioaccumulation function.

**Keywords** Bioindicator · Contamination · Trace metals · Brazilian coast · *Cathorops spixii*

### Introduction

The coastal environment receives a large amount of trace metal pollution from different natural and anthropogenic sources, such as industrial and domestic sewage, storm

runoff, leaching from landfills, shipping and harbor activities, and atmospheric deposits (Salomons and Förstner 1984; Lacerda 1998). Some trace metals represent a serious problem due to their toxicity and their ability to accumulate in the biota (Islam and Tanaka 2004). Therefore, trace metal concentration determination in organisms should be part of any assessment and monitoring program in the marine coastal environment (Marcovecchio 2004).

The Baixada Santista estuarine system receives an intensive and continuous industrial and domestic effluent. Some authors (Cetesb 1979, 2001; Fúlfaro et al. 1983; Boldrini and Navas-Pereira 1987; Montone 1987; Braga et al. 2003; Aguiar and Braga 2007) verified high concentrations of different chemical compounds introduced into the Santos Bay. In 1983, the total flow of Santos and São Vicente waste reached 2,000 L/s most being deposited through a submarine emissary (Homem 1983) into the Santos Bay. This emissary is about 5,800 m long and deposits mainly the domestic waste into the Santos Bay which also receives other kinds of pollutants.

Little is known about the effects of the sewage disposal on demersal fish populations (Otaway et al. 1995). However, some studies show changes in abundance and in diversity (Puffer et al. 1982; Grigg 1994) with some different consequent alterations overall in the reproductive system, histopathological changes and organic enrichment and others not only exactly from sewage disposal, but from other sources that reach the estuarine system and follow to the Santos Bay.

Organisms used as pollution monitors have numerous advantages over the chemical analyses of abiotic compartments. Organisms only accumulate the biological available forms of the pollutant. Furthermore, they are always present in the marine ecosystem, consequently enabling continuous monitoring of pollutants (Bryan 1979; Phillips and Segar 1986).

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Organisms are able to integrate the fluctuations of concentration pollutants through time and to accompany the magnification afforded by bioaccumulation. This is advantageous due to the precision and expense of analyses of trace metal pollutants near the limits of analytical detection (Phillips 1977; Jones and Walker 1979).

As a consequence of trace metal excess, the organism can present alterations in growth rate, reproductive phases, cellular mutations, modifications in the enzymatic processes, behavioral alterations and even death (Heath 1987). These effects can influence individual health, population and community survival (Furness and Raibow 1990).

Most studies published on marine pollution bioindicator organisms are concentrated on invertebrates, mainly crustaceans and mollusks. However, the use of fish as bioindicators of marine pollution monitoring is widely recognized (Reddy et al. 2001).

Fish tissues have high capacity to bio-accumulate trace metals and organic compounds being sensitive to aquatic pollution (Fisk et al. 2001). Concentrations of trace metals can vary in different degrees depending on the considered tissues in the same individual; as result of the different biochemical characteristics of the tissues. Therefore, fishes represent good bioindicators for environmental studies. They tend to accumulate pollutants in their tissues, transferring the pollutants to local trophic levels (Boon et al. 2002).

In the present investigation, the concentrations of some trace metals were measured in different tissues of *Cathorops spixii* from the Santos Bay. Cobalt (Co), iron (Fe), mercury (Hg), selenium (Se) and zinc (Zn) concentrations were determined in liver samples; mercury (Hg) and methyl-mercury (MeHg) were also determined in muscle of *C. spixii*. For comparison, the same trace metals were determined in *C. spixii* from a non-polluted site. An attempt was made to understand variations of the trace metal concentrations among organisms, as well as the relationship between metal concentrations and fish sizes. These analyses will subsidize the hypothesis that *C. spixii* is a good bioindicator species of trace metal pollution to a system strongly impacted by domestic and industrial sewage (Santos Bay) in comparison to a non-polluted site in the Brazilian coast.

## Materials and methods

### Studied sites

The Santos Bay is located in São Paulo state (24°00'S; 46°21'W), at the central part of this state coast. The climate is typically tropical (subtropical) with humid forest and a rainy summer season. This region represents an important

economic area. Besides tourism, the secondary activity of the city, the largest commercial harbor of South America operates in the city. Brazil's most important petrochemical and metallurgical complex composed of more than 1,100 industries, is located in the region. The increase of urbanization and industrialization along banks of estuary, especially over the last 50 years, has been responsible for the degradation of the mangrove vegetation due to the industrial and domestic effluents and the disposal of solid residues. The input of pollutants acts as an unbalancing agent of the ecosystem. The presence of some human activities contributes directly or indirectly to the input of trace metals in this area.

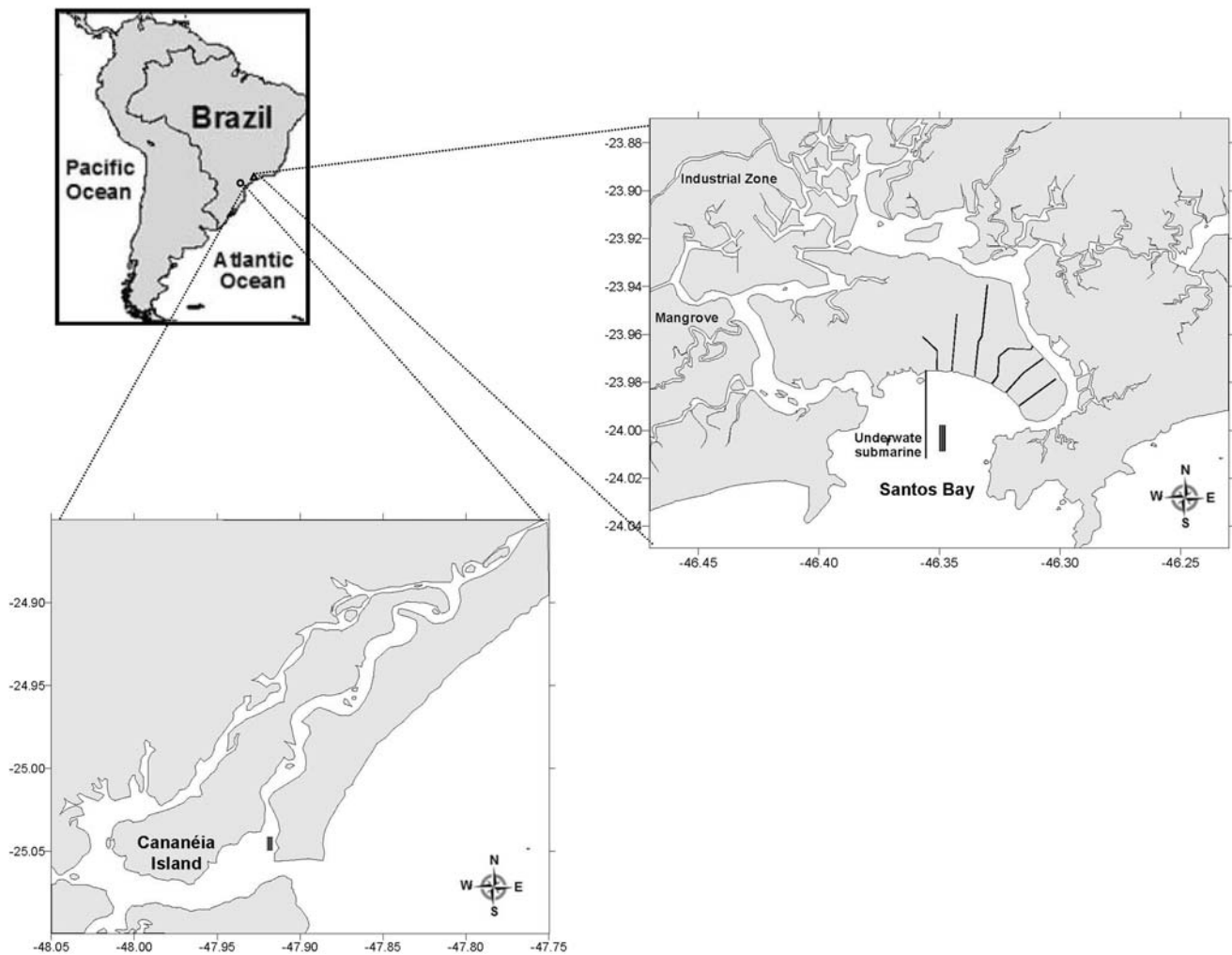
Cananéia estuarine-lagoon complex is located at south of São Paulo State coast (25°S; 48°W) and was used as non-polluted site due to the low human activity. The inner section of the estuarine-lagoon complex is subject to tidal cycles and to fresh water inputs. Externally, drift currents exists. The tidal movements and the fresh water discharges define the general circulation, the distribution processes and the water mixture in this estuarine-lagoon complex. This region is an important area for monitoring and contamination studies due to low anthropogenic influence.

### Sampling

The sampling took place in January 2005, during the summer period corresponding to the rainy season. Fish were collected on board of the R/B Albacora ship, using a bottom Otter Trawl (1.6" mesh wall and 1.2" mesh cod end) 11 m length and, set at 8.8 m depth. Specimens of *C. spixii* were collected in Cananéia estuarine-lagoon complex ( $n = 05$ ) and in Santos Bay ( $n = 23$ ; Fig. 1) and the fish captured were transported to the laboratory in a thermal flask with ice. The identification followed Figueiredo and Menezes (1978) descriptions. In the laboratory, morphometric data of each fish was taken and ~1.0 g of the epaxial muscle from the dorsal fish surface and the liver sample were dissected, washed with distilled water, packed in polyethylene identified bags and kept at -15°C until analysis, in the Neutron Activation Analysis Laboratory.

### Analytical procedures

Mercury and methyl-mercury were determined using Cold Vapor Atomic Absorption Spectrometry (CV AAS) using FIMS from Perkin Elmer. About 200–500 mg of fish muscle and liver were digested with a mixture of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acids in Teflon vials. For MeHg determination, the methodology was based on the leaching of the sample with 6 M HCl. The separation of organic from inorganic mercury was performed by the use of an ionic exchange resin. Finally, the measurement of mercury



**Fig. 1** Study area with sampling station in Santos Bay and Cananéia Estuary, Brazil

content followed by CV AAS determination. The analytical procedure used (wet digestion) followed Horvat (1996) with some modifications. All reagents were of analytical grade with low levels of mercury. High purity water, of  $18 \text{ M}\Omega \text{ cm}^{-1}$  conductivity was obtained using Milli-Q system. The Hg stock solution ( $1,255 \text{ mg L}^{-1}$ ) was acquired by dissolving HgO (Johnson Matthey Chemicals Limited) in  $\text{HNO}_3$ .

Methodology validation for total Hg and MeHg determination was carried out by means of reference material analyses of Dogfish liver (DOLT-1, NRCC), Dogfish liver (DOLT-3, NRCC) and Dogfish muscle (DORM-1, NRCC). The detection limit for this method was established in agreement with studies found in the literature for Hg determination (Skoog et al. 2002). The detection limit was calculated using the formula ( $\text{LD} = X + 3s$ ) and the value  $0.5 \text{ ng mL}^{-1}$  was found. The quantification limit ( $\text{LQ} = X + 5s$ ) was  $0.7 \text{ ng mL}^{-1}$ . The detection limit of this procedure, considering sample mass and dilution of solutions was  $0.03 \text{ }\mu\text{g g}^{-1}$ .

The Co, Fe, Zn and Se chemical determination by Instrumental Neutron Activation Analysis (INAA) used  $\sim 150 \text{ mg}$  of fish tissues and reference materials accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Synthetic standard was prepared by pipetting convenient aliquot of each metal standard solution (SPEX CERTIPREP) onto small sheets of Whatman no. 41 filter. Fish tissue samples, reference materials and Co, Fe, Zn and Se synthetic standards were irradiated for 8 h, under a thermal neutron flux of  $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$  in the IEA-R1 nuclear research reactor at IPEN. Details for the INAA experimental procedure have been described by Fávaro et al. (2000).

Methodology validation for metals (Co, Fe, Se and Zn) determination by INAA was carried out by means of the reference material analyses Oyster tissue (NIST SRM 1566b) and Dog fish muscle (DOLT-1, NRCC).

All metal concentrations in fish tissues were reported in  $\text{mg kg}^{-1}$  dry weight and wet weight for comparison with other authors. Water contents were determined in the

sample tissues by weight determination before and after the freeze drying process. Fifteen replicates of each tissue were evaluated with standard deviation smaller than 3%.

### Statistical analysis

All statistical tests were performed using Bioestat version 4.0. Summarized data as a mean, standard deviation and ranges.

## Results

Fish sampling in Santos Bay showed high values of total length and weight ranging of 188–290 mm and 59.5–148.8 g, respectively. For *C. spixii* from Cananéia, the ranges to total length and weight were of 175–296 mm and 55.3–152.6 g, respectively. The obtained data indicated only adult individuals according to Rios (2001) value proposed for the first maturation ( $LC_{50} = 95.9$  mm) of *C. spixii*. Therefore, above of that value the individuals can be considered as adults.

### Trace metal determinations

Methodology validation for metals (Co, Fe, Se and Zn) determination by INAA was carried out by means of the reference material analyses Oyster tissue (NIST SRM 1566b) and Dogfish muscle (DOLT-1, NRCC) showing relative standard deviation from 1.0 to 28% and relative

error from 1.0 to 13% (Table 1). The methodology validation for total and methyl-mercury by CV AAS was carried out by means of reference materials analyses showing relative standard deviation from 4.3 to 8.5% and relative error from 0.8 to 9.3%, indicating good precision and accuracy (Table 2). The results indicated good agreement between the certified and the analytical values.

The trace metals Co, Fe, Se, Zn and total mercury (Hg) were determined in liver samples, being that, the latter was also determined in muscle. Methyl-mercury (MeHg) was analyzed in muscle and in liver samples. The average metal concentrations in liver of *C. spixii* from Cananéia and Santos Bay are given in Table 3. The concentrations of Hg in liver were lower than those of other metals (Table 4). On the other hand, Fe concentrations showed the highest level in examined tissues for Santos Bay and for Cananéia fish. The Brazilian environmental legislation (Anvisa 1998) only considers limit values for toxic inorganic metals such as Pb, Cd, Cu and Hg. Thus, due to the absence of limit values for the analyzed metals (Co, Zn, Fe), the results were compared with *C. spixii* collected in a non-polluted site (Cananéia estuarine–lagoon complex), with other fish species and considering the international maximum values proposed by EPA (1999).

The results obtained for Co, Fe, Se, Zn and Hg contents in liver of *C. spixii* are also presented in Fig. 2. For comparison, the maximum values proposed by the Environment Protection Authority (1999), established for human consumption were presented together with each trace metal

**Table 1** Trace metal concentrations in standard reference materials for Co, Fe, Se and Zn by INAA (Instrumental Neutron Activation Analysis)

Trace metal	Dogfish muscle (DOLT-1 NRCC)		RSD (%)	RE (%)	Oyster tissue (NIST SRM 1566b)		RSD (%)	RE (%)
	Determined	Certified			Determined	Certified		
Co	0.136 ± 0.038	0.157 ± 0.037	28	13	0.368 ± 0.023	0.371 ± 9	6.0	1.0
Fe	0.718 ± 0.067	0.712 ± 0.048	9.0	1.0	0.210 ± 0.011	0.205 ± 6.8	5.2	2.1
Se	7.188 ± 0.321	7.340 ± 0.420	4.0	2.0	2.234 ± 0.093	2.060 ± 0.150	4.2	8.4
Zn	0.096 ± 0.001	0.092 ± 0.002	1.0	4.0	1.491 ± 0.102	1.424 ± 0.046	6.8	4.7

Data represent mean ± SD ( $n = 3$ ) expressed in mg kg<sup>-1</sup>

RSD relative standard deviation, RE relative error

**Table 2** Total mercury (Hg) and methyl-mercury (MeHg) concentrations in standard reference materials determined by CV AAS (Cold Vapor Atomic Absorption Spectrometry)

Reference materials	Total Hg				MeHg			
	Certified	Determined	RSD (%)	RE (%)	Certified	Determined	RSD (%)	RE (%)
Dogfish liver (DOLT-1, NRCC)	0.225 ± 0.037	0.246 ± 0.019	7.7	9.3	–	–	–	–
Dogfish liver (DOLT-3 NRCC)	–	–	–	–	1.590 ± 0.120	1.53 ± 0.130	8.5	6.0
Dogfish muscle (DORM-1, NRCC)	0.798 ± 0.074	0.754 ± 0.035	4.6	5.5	0.731 ± 0.060	0.725 ± 0.031	4.3	0.8

Data represent mean ± SD ( $n = 3$ ) expressed in mg kg<sup>-1</sup>

RSD relative standard deviation, RE relative error

**Table 3** Trace metal concentrations Co, Fe, Se and Zn in liver of *Cathorops spixii* collected in Cananéia estuary and Santos Bay

	Co	Fe	Se	Zn
Cananéia Estuary				
w.w.	0.60 ± 0.14 (0.50–0.88)	4,838 ± 580 (3,419–5,501)	12.73 ± 1,61 (10.99–14.96)	1.11 ± 0.14 (0.95–1.21)
d.w.	2.85 (2.38–4.19)	23,038 (21,042–26,195)	60.62 (52.33–71.23)	5.28 (4.52–5.76)
Santos Bay				
w.w.	0.85 ± 0.29 (0.45–1.33)	3,082 ± 975 (1,518–5,141)	15.39 ± 2.51 (11.87–19.2)	261 ± 137 (107–566)
d.w.	4.05 (2.14–6.33)	14,676 (7,228–24,481)	73.29 (56.52–91.43)	1,243 (510–2,695)

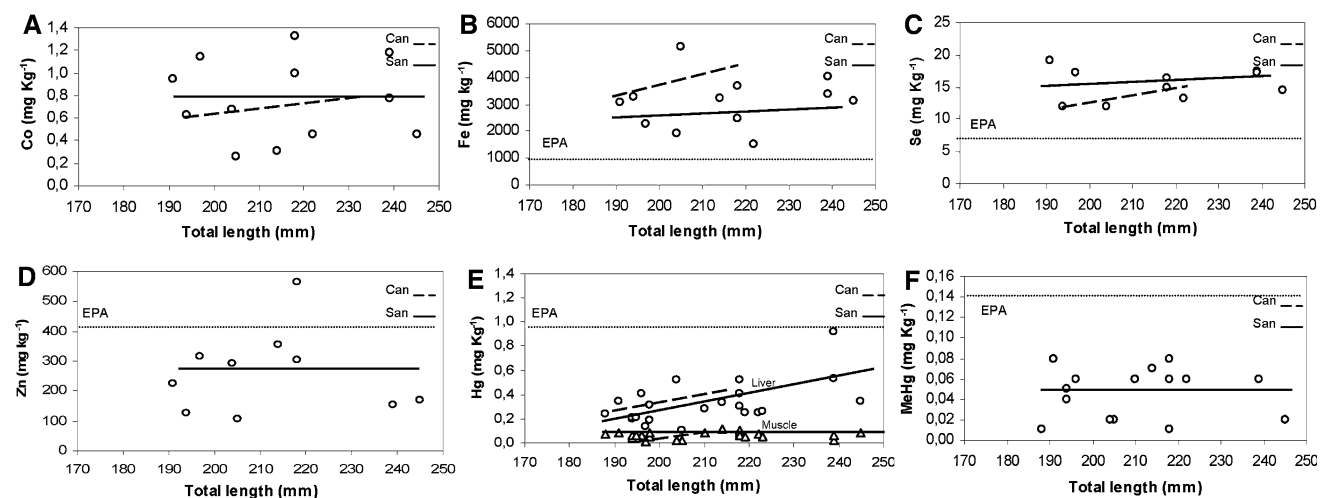
Data represent mean ± SD to wet weight (w.w.) and dry weight (d.w.) expressed in mg kg<sup>-1</sup>. The extreme values (minimum and maximum) are also presented

**Table 4** Total mercury (Hg) and methyl-mercury (MeHg) concentrations in liver and muscle of *Cathorops spixii* collected in Santos Bay and in Cananéia estuary

	Hg		MeHg
	Liver	Muscle	
Cananéia Estuary			
w.w.	0.25 ± 0.001 (0.25–0.26)	0.07 ± 0.01 (0.06–0.08)	ND
d.w.	1.2 (1.20–1.24)	0.29 (0.25–0.33)	ND
Santos Bay			
w.w.	0.33 ± 0.17 (0.10–0.92)	0.06 ± 0.02 (0.01–0.11)	0.05 ± 0.02 (0.01–0.08)
d.w.	1.6 (0.48–4.38)	0.25 (0.04–0.46)	0.21 (0.04–0.33)

Data represent mean ± SD to wet weight (w.w.) and dry weight (d.w.) expressed in mg kg<sup>-1</sup>. The extreme values (minimum and maximum) are also presented

ND not detected

**Fig. 2** Trace metal concentrations in liver (Co, Fe, Se, Zn and Hg) and muscle (Hg and MeHg) versus total length of *Cathorops spixii* from Cananéia estuary (Can) and Santos Bay (San)

concentration. Cobalt levels were not compared with the national or international limits due to the absence of values for this metal. In general, it was observed that the concentrations of trace metals in *C. spixii* specimens exceeded the limit for human use.

Table 5 shows the mean values of some trace metals in liver and muscle for different fish species. The data analyses showed that Co, Zn, and Fe concentrations were greater than those found in other fish from some different areas, in the world.

**Table 5** Metal concentrations in liver and muscle of some species reported in the literature (mg kg<sup>-1</sup>)

Common name	Specie	Localization	N	Tissue	Co	Fe	Zn	Hg	Reference
Tucunaré	<i>Cichla temensis</i>	Amazon region, Brazil	53	Muscle <sup>a</sup>	–	–	–	1.1	Porvari (1995)
Pescada	<i>Plagioscion squamosissimus</i>	Amazon region, Brazil	33	Muscle <sup>a</sup>	–	–	–	1.2	Porvari (1995)
Catfish	<i>Chrysichthys nigrodigitatus</i>	Niger Delta	20	Liver <sup>a</sup>	–	–	0.02	<0.001	Eboh et al. (2006)
Catfish	<i>Silurus triostegus</i>	Ataturk Dam Lake	05	Liver <sup>a</sup>	ND	35.3 ± 6.6	20.36 ± 5.2	–	Karadede et al. (2004)
Catfish	<i>Chrysichthys nigrodigitatus</i>	Niger Delta	20	Muscle <sup>a</sup>	–	–	–	<0.001	Eboh et al. (2006)
Acara	<i>Geophagus</i> sp.	Amazon region, Brazil	02	Muscle <sup>a</sup>	–	–	–	0.03	Palheta and Taylor (1995)
Pacu	<i>Myleus</i> sp.	Amazon region, Brazil	02	Muscle <sup>a</sup>	–	–	–	0.04	Palheta and Taylor (1995)
Tilapia	<i>Oreochromis niloticus</i>	Niger Delta	20	Liver <sup>a</sup>	–	–	0.02	<0.001	Eboh et al. (2006)
Bonga	<i>Ethmalosa fimbriata</i>	Niger Delta	20	Liver <sup>a</sup>	–	–	0.02	<0.001	Eboh et al. (2006)
Smudskipper	<i>Periophthalmus koelreuteri</i>	Niger Delta	20	Liver <sup>a</sup>	–	–	0.01	ND	Eboh et al. (2006)
–	<i>Clarias gariepinus</i>	South eastern of Turkey	38	Liver <sup>a</sup>	0.003 ± 0.0	19.47 ± 2.9	4.39 ± 0.8	–	Turkmen and Cimnili (2007)
Cod	<i>Gadus morhua</i>	Labrador	12	Liver <sup>b</sup>	–	–	14–39	<0.05	Hellou et al. (1992)
Madamango Sea Catfish	<i>Cathorops spixii</i>	Cananéia estuary, Brazil	05	Liver <sup>a</sup>	0.60 ± 0.14	4,838 ± 580	1.11 ± 0.14	0.25 ± 0.001	This work
Madamango Sea Catfish	<i>Cathorops spixii</i>	Cananéia estuary, Brazil	05	Liver <sup>b</sup>	2.85	23,038	5.28	1.2	This work
Madamango Sea Catfish	<i>Cathorops spixii</i>	Santos Bay, Brazil	23	Liver <sup>a</sup>	0.85 ± 0.29	3,082 ± 975	261 ± 137	0.33 ± 0.17	This work
Madamango Sea Catfish	<i>Cathorops spixii</i>	Santos Bay, Brazil	23	Liver <sup>b</sup>	4.05	14,676	1,243	1.6	This work

Mean values ± SD

ND not detected, – not observed

<sup>a</sup> w.w., <sup>b</sup> d.w

Comparing fish size and trace metal concentrations (Fig. 2) it is possible to verify that the relation between length and all trace metal concentrations were not significant.

In *C. spixii* from Cananéia, Co content ranged from 0.50 to 0.88 mg kg<sup>-1</sup>, with an mean of 0.6 ± 0.14 mg kg<sup>-1</sup>. For Santos Bay Co concentrations ranged from 0.45 to 1.33 mg kg<sup>-1</sup>, with an average of 0.85 ± 0.29 mg kg<sup>-1</sup> (Fig. 2a).

Fe concentrations in the fish from Santos Bay showed an average of 3,082 ± 975 mg kg<sup>-1</sup> ranging from 1,518 to 5,141 ± 124 mg kg<sup>-1</sup>. The average value obtained was three times larger than allowed by the Environment Protection Authority (1999; 946.29 mg kg<sup>-1</sup>). For Cananea, Fe concentrations ranged from 3,419 to 5,501 mg kg<sup>-1</sup>, with an average of 4,838 ± 580 mg kg<sup>-1</sup> (Fig. 2b). However, it is very important to consider the micronutrient function of this metal. Additionally, it should also consider the liver biotransformation function.

The average value observed for Se concentration was 15.39 ± 2.51 mg kg<sup>-1</sup> for Santos Bay and 12.73 ± 1.61 mg kg<sup>-1</sup> for Cananéia, with a variation from 11.87 to 19.21 and 10.99 to 14.96 mg kg<sup>-1</sup>, respectively. The selenium concentrations showed values twice as much as allowed by the Environment Protection Authority (1999; 6.76 mg kg<sup>-1</sup>; Fig. 2c). It is important to consider the relation between Se and Hg because the literature indicates a regulation mechanism among these two trace metals, when the organisms are exposed to a high mercury concentration (Farias et al. 2005).

The zinc concentrations ranged between 107 and 566 mg kg<sup>-1</sup> in *C. spixii* from Santos Bay and 0.95 to 1.21 mg kg<sup>-1</sup> in the fish from Cananéia. The average values were of 261 ± 137 and 1.11 ± 0.14 mg kg<sup>-1</sup>, respectively. For this metal, the Environment Protection Authority (1999) recommends a maximum value of 405.55 mg kg<sup>-1</sup>. The data showed that Zn concentrations were lower than recommended by EPA (1999; Fig. 2d).

Total Hg concentrations in livers of *C. spixii* from Santos Bay and Cananéia showed an average of 0.33 ± 0.17 and 0.25 ± 0.001 mg kg<sup>-1</sup>, respectively. The range observed were 0.10 to 0.92 mg kg<sup>-1</sup> to Santos Bay and 0.25 to 0.26 mg kg<sup>-1</sup> to Cananéia. The smallest values were found in the muscle, with a variation from 0.01 to 0.11 mg kg<sup>-1</sup> to Santos and 0.06 to 0.08 mg kg<sup>-1</sup> to Cananéia. However, total Hg concentrations were not significant among this sites (Fig. 2e).

MeHg contents in *C. spixii* muscles ranging between 0.01 and 0.08 mg kg<sup>-1</sup>, show an average concentration of 0.05 ± 0.02 mg kg<sup>-1</sup>. MeHg was not detected in the Cananéia fish (Fig. 2f). There is no limit established for MeHg in fish muscles in the Brazilian environmental legislation. However, the Environment Protection Authority

(1999) allows a maximum value of 0.14 mg kg<sup>-1</sup>. The data show MeHg values below recommended by EPA.

## Discussion

The use of fish as biological indicators in pollution monitoring program is highly recommended but not effectively used. Its use for environmental monitoring can provide continuous and reliable information of the environmental quality and can verify the contamination level in the fish consumed by humans. In both cases, a high contamination level can be dangerous for human health (Markert et al. 1999).

Few studies on trace metal concentrations exist for *C. spixii* tissues. Therefore, it is very difficult to realize a direct comparison of the obtained results in the present work with specimens from the other places. Boldini and Navas-Pereira (1987) and Farias et al. (2005) presented some results of a bioaccumulation process using *C. spixii*. These authors also did the studies in Santos Bay and Santos/São Vicente estuary. In this study, the authors chose to compare the results obtained in *C. spixii* from a polluted area (Santos Bay) with fish collected in a non-polluted estuary (Cananéia). Additionally, the data were to compare with other species (Table 5) that have the same habits as the *C. spixii*.

The trace metals as cobalt, iron and zinc are essential since they play an important role in biological systems (Ansari et al. 2004; Turkmen and Ciminli 2007) because they have a micronutrient function. On the other hand, metals such as mercury are nonessential and have toxic effects (Turkmen and Ciminli 2007). The deficiency of zinc can provoke serious consequences, as decrease of growth and sexual immaturity (Ansari et al. 2004). Some authors consider that the excess of some metals can cause harmful effects in fish as alterations in oxygen consumption, damages in the gills (Furness and Raibow 1990, Zagatto and Bertolotti 2006). There are indications that Se plays an important role in the organism protecting against toxic effects of Hg (Azevedo 2003; Farias et al. 2005) in some environmental conditions.

In the present study, the bioaccumulation processes was evaluated in a benthic feeder species that has an intrinsic association with the bottom sediment and it showed the capacity to be used as a bioindicator. The Co, Fe, Se and Zn concentrations found in *C. spixii* liver, from Santos Bay showed high values. Although total Hg in liver and muscle and MeHg in muscle showed lower values when compared to other species from different environments (Kakulu et al. 1987; Hellou et al. 1992, 1996; Voigt 1999; Farkas et al. 2003; Karadede and Unlü 2000; Canlı and Atli 2003; Agusa et al. 2005; Dural et al. 2007; Maršálek et al. 2007),

significant differences were not observed among fish from Cananéia and Santos Bay, suggesting input absence of total Hg and MeHg in both systems. Additionally, Co, Fe, Se and Zn concentrations in liver from Santos Bay *C. spixii* were useful as a trace metal diagnosis in the specimens which could be used as a quantitative index for the analyses.

In three species of the Ariidae family (*Bagre bagre*, *C. spixii* and *Netuma barba*), Boldini and Navas-Pereira (1987) obtained Zn and total Hg contents in liver of fish from Santos Bay similar to the values obtained in the present study. The same authors observed total Hg concentrations in muscle tissue lower than that showed in this investigation.

The results in trace metal concentrations obtained in this study showed the capacity of *C. spixii* to bioaccumulate trace metals from the environment, since most of the found metal contents in fish from Santos Bay were greater than metal contents in fish from Cananéia and the national (Anvisa 1998) and international (EPA 1999) maximum values established for human consumption. Therefore, the data showed that *C. spixii* is a good bioindicator for trace metal accumulation.

The biometric relations of length versus all trace metal concentrations were not statistically significant (Fig. 2). This result can be influenced by: (1) the selection process in the sampling; (2) the level of efficiency of the fishing equipment in capturing fish of smaller length; (3) the biological characteristics of the species as related to the feeding habits; (4) the degree of association of *C. spixii* to the sediment and the capacity of metabolization and/or degradation of the pollutants by this species as described by Reuther (1994) and Sinderman (1996).

Metal concentrations can vary in different tissues in function of the biochemical affinities and metabolism. Trace metals accumulation are intense in metabolic organs as liver and kidney. In these organs, the metal concentrations can be 400% higher than the contents found in the muscle tissue (Parsons 1999; Kojadinovic et al. 2007; Türkmen and Ciminli 2007). The results obtained in this study agree with first ones, since mercury levels showed significant differences in the tissues analyzed, accumulating more in the liver than in the muscle. Additionally, the largest Fe contents observed in *C. spixii* from Cananéia in comparison with Santos Bay can be related to a more effective metabolism on the fish from non-polluted site, considering the role of the Fe in the biological system with micronutrient element.

The use of fish as biological indicators of pollution is efficient when basic biological information and ecological aspects of the environment studied are available (Olsson and Jensen 1975). However, some aspects as abundance, the facility of yearly collection, non-migratory nature, easy identification and capacity to accumulate the contaminant are necessary to select the bioindicator organisms appropriately (Phillips 1977; Phillips and Segar 1986). Thus, it is

possible to determine the correlations between the xenobiotic compounds in the environment and concentrations in the bioindicator organism (Markert 1996).

## Conclusion

The results obtained in this study and the main requirements previously mentioned, the authors suggest that *C. spixii* is appropriate as a bioindicator species of trace metal pollution in Santos Bay, being recommended for biomonitoring programs, to evaluate the evolution of the contamination by trace metals.

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