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ECOSYSTEMS

Seasonal arsenic in catfish (Siluriformes, Ariidae) and the hydrochemical conditions of two areas in a Ramsar site on the Brazilian coast

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Abstract: The construction of a data bank concerning metal and metalloid content of bioindicator fish from coastal areas is very important as it can help environmental managers in decision making. In natural conditions, the concentration of elements can be influenced by abiotic parameters such as water salinity. In this study, catfish Cathorops spixii were evaluated concerning the total arsenic (As) concentration in the muscle tissues of individuals subjected to different abiotic conditions in the Cananéia-Iguape Estuarine-Lagoon Complex (CIELC), which was recently included on the Ramsar list of wetlands of international importance. Seventy-four catfish were seasonally caught in the northern and southern regions of the CIELC and their hydrochemical parameters were obtained. C. spixii from the southern, best preserved, area showed arsenic concentrations around ten times higher than the maximum limit established for fish intended for human consumption. However, these high concentrations of arsenic could be associated with the abiotic parameters of the water, such as salinity variations, in this area.

Key words: Arsenic, *Cathorops spixii*, estuary, environmental protection area, salinity.

INTRODUCTION

Arsenic (As) is a semi-metal and although it has no function for marine organisms, it can be easily assimilated as a micronutrient and occurs in a wide range of chemical forms (Francesconi & Edmonds 1993). Additionally, it is considered the most toxic and dangerous substance among the 275 classified by CERCLA (ATSDR 2007). In marine organisms such as fish, the predominant arsenic compound is arsenobetaine, which is widely considered non-toxic and is involved in the regulation of osmotic stress (Peshut et al. 2008, Urgast et al. 2010).

In general, studies of As levels in aquatic organisms take into account only the permissible limit for human consumption. Therefore, increases in the toxic effects related to the chemical speciation of arsenic compounds, such as their organic and inorganic forms and the influence of abiotic factors – such as water salinity – in this transformation, need attention.

The Madamango sea catfish *Cathorops spixii* (Siluriformes, Ariidae) inhabits tropical regions and is one of the most common species of catfish on the Brazilian coast. This species is euryhaline and has benthic feeding habits (Figueiredo & Menezes 1978). It is widely consumed by traditional communities and the low-income population. For biomonitoring purposes, this species is recommended as a bioindicator of contamination in estuaries such as the Cananéia-Iguape, Brazil, and the Santos-São Vicente, Brazil, due to its capacity to accumulate and participate in the dynamics of essential and non-essential metals (Azevedo et al. 2009, 2012). Moreover, *C. spixii* are responsive to metal exposure and exhibit acute and chronic responses indicating biochemical, genotoxic, and histopathological damage (Azevedo et al. 2013). Thus, the concentrations of trace elements in fish muscle may indicate the quality of the ecosystem and the potential risk to human health (Azevedo et al. 2009). Concerning arsenic content, the measurement and monitoring of bioindicator fish species such as *C. spixii* from estuarine regions is of great importance for conservation and avoiding risks to human beings, while also contributing to an increased understanding of arsenic's metabolic role in organisms as linked to the salinity of water.

The Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) on the southern coast of the São Paulo State (Brazil) is an ecosystem influenced by a set of anthropogenic factors. The CIELC is composed of a group of four islands near the mainland; namely, Cananéia, Cardoso, Comprida, and Iguape (Figure 1). The latter is an artificial island that was formed due to the opening of the Valo Grande Channel in the city of Iguape in the north of the system. The island of Cananéia is separated from the continent by a channel called Mar de Cubatão, and the island of Comprida is separated from the continent by a channel called Mar de Cananéia. These two channels in the southern area of the system interconnect in Trapandé Bay. This part of the estuarine complex is better preserved than the northern area of the estuarine complex system because it is significantly influenced by the ocean, which conserves the natural conditions attributed to tide influxes and sea hydrodynamics (Braga & Chiozzini 2008, Chiozzini et al. 2010). The northern region of this estuary receives a high freshwater inflow due to its proximity to the Ribeira de Iguape River, which brings with it an inflow of different materials from the continent as it passes through the Valo Grande (an artificial drainage channel) (Cornaggia et al. 2018).

In previous studies, it was found that toxic metals such as Pb and Cd are present in sediments (Mahiques et al. 2009, 2013, Tramonte et al. 2018) and the tissues of catfish (Azevedo et al. 2012), and that they cause biochemical disturbances in these fish (Azevedo et al. 2013). Residues of Pb, Ag, Cd and Zn from past mining activities and refinery (Company Plumbum) in the upstream cities of the Alto do Ribeira region were detected in sediment from the Mar Pequeno (Tramonte et al. 2018). With respect to arsenic content in sediment, some authors consider it part of the natural enrichment process in the Ribeira de Iguape basin and along the estuary as a consequence of sediments being deposited by continental rocks (Figueiredo et al. 2007, Angeli et al. 2019, Santos et al. 2020). The riverine flow into the estuarine system through the drainage basin of the Ribeira River, which passes through the Valo Grande Channel, follows seasonal rain patterns, with high discharge during the rainy months (mainly in the summer) – with a maximum output of 1751 $m^3 s^{-1}$ and an annual mean of 773.56 $m^3 s^{-1}$ (Bérgamo 2000).

Finally, the assessment of the degree of contamination of estuarine organisms by trace elements is necessary due to the risk to the biodiversity of the regions in this study. Another important issue is that when these organisms are contaminated and consumed by humans this may cause public health problems. Therefore, the goal of this study was to compare concentrations of As in the muscle tissue of wild catfish *C. spixii* from the northern and southern areas of the CIELC in the summer and winter period.

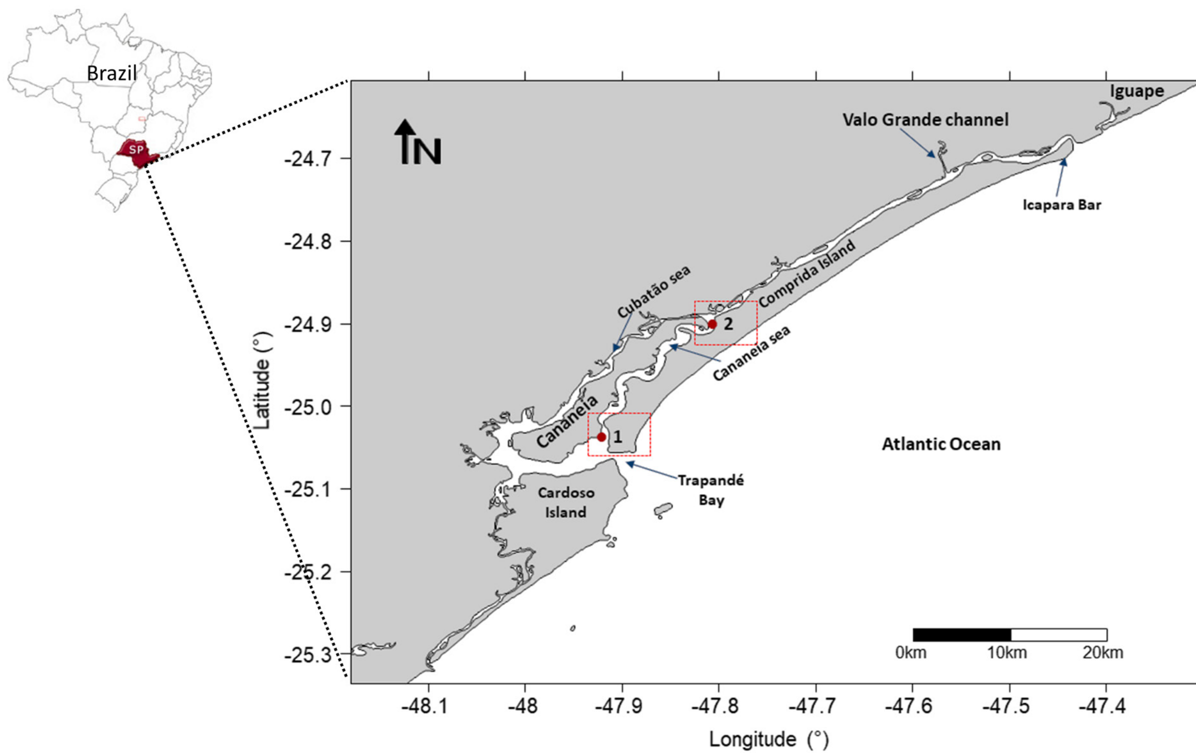

Figure 1. **Sampling sites in the Cananéia-Iguape Estuarine Lagoon-Complex (CIELC), São Paulo State, Brazil.**

MATERIALS AND METHODS

Sample collection

Seventy-four catfish were collected during the summer (February) and winter (August) of 2009 in one sampling station in the northern sector of the CIELC and another in the southern sector of the CIELC (SP, Brazil) (Figure 1). Although the samples examined in this study were over ten years old, the construction of a data bank concerning the metalloid content of bioindicator fish from coastal areas is fundamentally important, since it can support the decision making of environmental managers. Catfish were collected on board the *Albacora* research vessel by the Oceanographic Institute of São Paulo University. To catch the fish, a bottom otter trawl net (1.6" mesh wall and 1.2" mesh cod end) of 11 m length was used. All analyzed and collected *Cathorops spixii* specimens were authorized by ICMBio (Instituto Chico Mendes de Conservação da Biodiversidade – Sisbio process nº 18803-1). The voucher species MZUSP-48529 is deposited in the ichthyological collection of the Museu de Zoologia da USP.

After collection, the fish were identified following Figueiredo & Menezes (1978), biometric data – such as the total length (TL) and total weight (TW) – were obtained, and, finally, the fish were dissected to facilitate the removal of the epaxial muscle tissue, and immediately stored at -20°C so that arsenic levels could later be determined. The condition factor (CF) was calculated as CF = [total weight (g)/total length (cm)^3]*100 in accordance with Vazzoler (1996).

Hydrochemical analysis

Before the *C. spixii* were caught, the water was sampled at the same sites and during the same time period as the catfish were collected; that is, in the summer (February) and winter (August) of 2009. The bottom water samples were obtained using a Nansen sampler by Hydrobios®. The local depth of the sampling site was obtained using the echosounders of the research vessels. The water temperature was measured *in situ* using protected reversing thermometers, calibrated in degrees Celsius (°C), and packed in cartridges with auxiliary thermometers aggregated to the sampler bottle. The accuracy of the reading was ± 0.02°C. The salinity of the bottom water was determined by an inductive method using a Beckman® model RS-10 salinometer with an accuracy of ± 0.001. The equipment was calibrated using ampoules of standard seawater. Following the recommendations of Aminot & Chaussepied (1983), the pH measurement was made using an Orion® potentiometer equipped with a combined glass electrode with a precision of ± 0.001. The silicate levels were determined using a colorimetric technique following the methodology proposed by Grasshoff et al. (1983).

Arsenic determination

Arsenic (As) concentrations were obtained using Instrumental Neutron Activation Analysis (INAA). For sample preparation, the muscle tissues were lyophilized using a Liobrás® model L101 Lyophilizer and the moisture content obtained was 80.1± 0.2 %. All the concentration results obtained in the present study were corrected to dry basis. Approximately 150 mg of muscle tissue and certified reference materials were used as standards and then accurately weighed and sealed in pre-cleaned polyethylene bags for 8 hours of irradiation under a thermal neutron flux of 10^{12} cm^{-2} s^{-1} in the IEA-R1 nuclear research reactor at the Nuclear and Energy Research Institute (IPEN). After one week of decay, the measurement of induced gamma activity was performed with a gamma ray spectrometer consisting of a German hyperpure GMX20190 CANBERRA coupled to a multichannel analyzer S-100 and the computer program Version2, which is capable of locating the photopeak of arsenic and calculating its area. The total As concentration was expressed as μg g^{-1} dry weight (d.w.) and wet weight (w.w.) for comparison with other authors. Quality assurance of the analyses was done by analyzing the certified reference materials DOLT-1 (Dogfish Liver Certified Reference Material for Trace Metals, NRCC) and DORM-1 (Dogfish Muscle Certified Reference Material for Trace Metals, NRCC). The relative standard deviation obtained was lower than 5% and the relative error was lower than 7.5% for ten determinations of these materials, thus verifying both the precision and accuracy, respectively, of the analytical methodology.

Statistical analysis

The differences in the biological variables and arsenic content in the catfish were tested using a non-parametric test; namely a Kruskal-Wallis with Dunn's multiple comparisons test. All the tests were evaluated for significance at $\alpha=0.05$, and the statistical calculations were executed using Past 3.0.

RESULTS

The hydrochemical data obtained in this study showed a seasonal profile of the rainy summer region, with high values for temperature and lower salinity in the summer of 2009 (Table I). In both sectors, the water temperature in the winter was between 20°C and 22°C, and over 27°C in the summer. During the summer, thermal stratification was observed in the northern region, with colder water values at depth. During the winter, in both sectors, the deeper water was found to be slightly warmer. With the exception of temperature, no significant seasonal variation was observed for these parameters in either of the regions (southern or northern) of the CIELC.

Table I. **Average seasonal concentration of hydrochemical parameters in the bottom waters of the Cananéia-Iguape Estuarine Lagoon-Complex (CIELC).**

Region	Depth (m)	Temperature (°C)	pH	Salinity (‰)	DO (mL L^{-1})	Silicate (mL L^{-1})
Summer						
Northern	5	27.50	6.96	0.06	4.45	193.52
Southern	5	28.05	8.18	24.37	3.81	26.40
Winter						
Northern	5	20.85	7.28	0.65	5.57	168.38
Southern	5	21.70	8.43	28.98	5.11	29.41

Concerning biological variables, such as TL and TW in *C. spixii* from both regions and with respect to seasonality, no statistically significant differences were observed ($p>0.05$), indicating the homogenous morphometric conditions of the fish (Table II). On the other hand, a seasonal and sectoral profile of As content was observed with outlier values during the winter period and in the southern region of the CIELC (Table II, Figure 2). With respect to the condition factor (CF), there were also observed seasonal differences in *C. spixii* in both areas (northern and southern) (Table II). The lowest CF values were found in catfish collected in the southern area during the winter period (CF= 0.88 ± 0.09), and the highest values were found in *C. spixii* sampled in the northern sector during the summer period (CF= 0.99±0.06). It is noteworthy that fish with the lowest CF values had the highest arsenic content.

A correlation matrix of all the studied variables was analyzed for *C. spixii* (Table III). These data were used as a guide to clarify the possible correlations among the variables. As anticipated, significant and positive correlations were observed between the length and weight of *C. spixii* from both sites, as well as the length and condition factor of the fish. In addition, a significant and positive correlation was also found between the arsenic content and the CF of *C. spixii* from the southern area sampled in the summer period ($r_s=0.619$, $p<0.01$).

DISCUSSION

The measurement and monitoring of metalloids such as arsenic (As) and their effect on aquatic organisms including fish species is of great importance for conservation. In both seasonal periods, the number of fish collected in the southern region of the Cananéia estuary was smaller than in the northern region. These differences probably occur as a result of the availability of individuals of this species in both regions. Therefore, the water characteristics in these two areas may have an influence on the availability of fish.

The northern sector showed a high amount of dissolved silicate and lower salinity as a consequence of the freshwater inflow from the Valo Grande Channel due to the proximity of the Ribeira de Iguape River. Silicate is a strong indicator of terrestrial contribution and dilution processes and is normally inversely associated with salinity values (Braga & Chiozzini 2008). Other studies conducted in the same areas of the CIELC (Braga & Chiozzini 2008, Chiozzini et al. 2010, Eschrique et al. 2010, Azevedo & Braga 2011) support the data obtained in this study

Table II. Biological variables, including total length (TL – mm), total weight (TW – g), condition factor (CF), and arsenic (As) concentration, in the muscle tissue of *Cathorops spixii* seasonally sampled in the northern and southern sectors of the CIELC. Data are shown as mean ± standard deviation, minimum and maximum.

Region	n	TL	TW	CF	As (w.w.)	As (d.w)
Summer						
Northern	20	177.3±11.5[b] (156-210)	55.97±12.28[bc] (36.08-94.30)	0.99±0.06[a] (0.90-1.11)	0.44±0.27[b] (0.07-1.12)	2.39±1.46[b] (0.37-5.92)
Southern	11	173.5±28.6[ab] (141-225)	49.94±27.99[b] (19.19-102.24)	0.88±0.09[b] (0.68-1.03)	6.75±4.06[a] (2.43-15.60)	33.90±20.12[a] (11.62-78.63)
Winter						
Northern	27	160.5±10.1[ac] (145-185)	37.37±7.16[a] (27.42-59.47)	0.90±0.07[b] (0.74-1.06)	0.84±0.77[c] (0.38-4.42)	4.46±4.01[c] (2.08-23.14)
Southern	16	171.3±21.2[ab] (152-231)	50.34±22.76[b] (30.80-123.10)	0.96±0.09[a] (0.76-1.08)	7.70±3.25[a] (1.23-12.62)	36.55±15.19[a] (6.78-60.45)

Arsenic (As) values are shown in μg g^{-1} (w.w. and d.w). *n* = number of samples. To the same variable, different letters indicate statistical differences Kruskal-Wallis test at *p* <0.05.

with regard to low salinity being related to high silicate content.

The southern area showed a more hydrodynamic profile with more oxygen dissolved values due to the influence of marine water and the tidal cycle (Table I). Tidal effects are more efficient in the southern area and cause a constant renewal of water in the region, which maintains the conditions of a stratified estuary (Chiozzini et al. 2010). A seasonal profile was also observed, with more accentuated hydrochemical variation in the northern area.

Somatic indexes, such as the condition factor (CF), provide information about an animal's physiological state, since individuals with greater mass per length have better well-being (Vazzoler 1996). CF values reflect the recent nutritional conditions and/or spending on energy reserves. Therefore, it is possible to relate the CF to the environmental conditions and the behavioral aspects of the species (Vazoller 1996). The differences found in the CF values of *C. spixii* seasonally sampled in the northern and southern regions of the CIELC may indicate the different ecological and abiotic pressures acting on these fish, which can increase competition for food and space. In fact, a significant and positive correlation between the arsenic content and the CF of *C. spixii* was observed in fish sampled in the summer period in the southern region of the CIELC.

There was a significant difference in arsenic accumulation in the muscle tissue of catfish

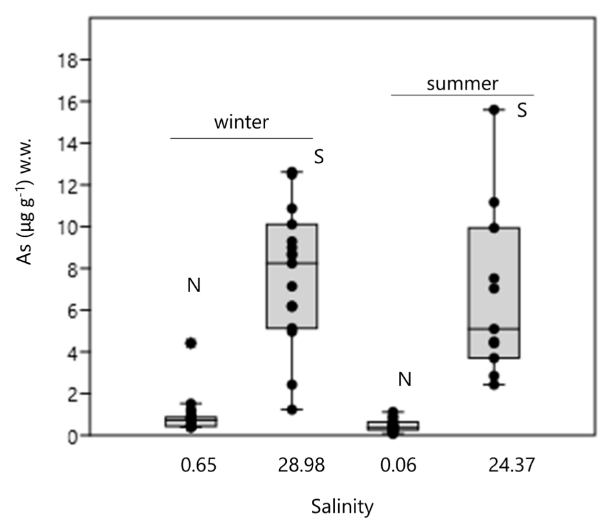

Figure 2. Box and whisker plot of the arsenic (As) concentrations (w.w.) in muscle tissues of *C. spixii* seasonally captured in the southern (S) and northern (N) regions of the CIELC. Box and jitter plots (Bars=10 and 90 percentiles; boxes=25 and 75 percentiles; vertical line=median). Outliers are indicated as * above the boxplots. The salinity of the bottom water in each sampling site is shown on the x axis.

exposed to different haline conditions not precisely related to anthropogenic influence mainly in the northern part of the estuarine system. This pattern can be explained by the osmoregulation of aquatic organisms exposed to a range of haline conditions. Euryhaline fish have developed physiological and biochemical evolutionary strategies to control dynamic changes concerning the salt balance in the environment, from active salt absorption to salt secretion and from water excretion to water retention. During osmoregulation, the gill Na^+, K^+ ATPase pump, located mainly in chloride cells, requires energy input and plays an important role in osmoregulation in both hyperosmotic and hyposmotic environments (Evans 2008). Metals can substitute other ions (i.e., Na, K, Ca, and H) and be carried into the cells by such ATPases. Gill chloride cells can assume different morphologies in Teleosts depending on the salinity of the surrounding environment (Sterzelecki et al. 2013). Moreover, there are other ionic uptake mechanisms related to changes in the function of aglomerular kidneys and proximal tubular secretion, the NaCl cotransporters in intestinal uptake, and gill and rectal gland secretion (Evans 2010).

Metal and metalloid accumulation and transfer are controlled by salinity (Dutton & Fisher 2011, Kalantzi et al. 2017, Zhang et al. 2018), and in less brackish waters the metals are less (or not) available (Heath 1990). Accordingly, in this study, there is a direct relationship between the As accumulation in *C. spixii* submitted to different haline conditions. The high total arsenic content found in catfish from the southern region, characterized by well-preserved conditions and high salinity, is in line with studies of fish by Dutton & Fisher (2011) and Hong et al. (2018), in which it was observed that As uptake increased as salinity increased from 6 ppt (Dutton & Fisher 2011). With respect to Brazil, Angeli et al. (2013) and Avigliano et al. (2019) found As content in the muscle tissues of catfish

Table III. Spearman Correlations (r_s) of arsenic contents (As) and total length (TL), total weight (TW) and condition factor (CF) of *C. spixii* (Cs) collected in two sites (Southern – S; Northern – N) in the winter (W) and summer (S) period in the CIELC.

	TL-SS	TW-SS	CF-SS	As-SS	TL-NS	TW-NS	CF-NS	As-NS	TL-SW	TW-SW	FC-SW	As-SW	TL-NW	TW-NW	CF-NW	As-NW
TL-SS	1															
TW-SS	0.993***															
CF-SS	0.428	0.473														
As-SS	-0.106	-0.106	-0.331													
TL-NS	0.142	0.182	0.417	0.277												
TW-NS	0.036	0.081	0.475	0.185	**0.957*** **											
CF-NS	-0.348	-0.327	0.158	-0.231	0.063	0.326										
As-NS	0.341	0.370	0.414	-0.002	0.314	0.260	-0.120									
TL-SW	0.319	0.367	**0.665** **	-0.182	**0.603** **	**0.657** **	0.241	0.305								
TW-SW	0.246	0.283	0.565	-0.112	**0.607** **	**0.658*** **	0.135	0.203	**0.959*** **							
CF-SW	-0.012	-0.057	-0.369	-0.012	-0.264	-0.311	**-0.524**	-0.277	-0.021	0.207						
As-SW	0.462	0.449	-0.209	-0.100	-0.138	-0.192	-0.359	-0.342	0.027	0.177	**0.619** **					
TL-NW	0.462	0.462	0.509	-0.349	0.266	0.204	-0.202	0.198	0.352	0.312	-0.208	0.213				
TW-NW	0.341	0.322	0.385	-0.457	0.132	0.060	-0.219	0.116	0.285	0.235	-0.135	0.165	**0.905*** **			
CF-NW	-0.451	-0.496	-0.347	-0.321	-0.434	-0.421	0.062	-0.206	-0.288	-0.318	0.162	-0.246	-0.297	0.127		
As-NW	-0.174	-0.131	0.394	-0.398	0.028	0.048	0.148	0.331	0.181	-0.006	-0.470	**-0.582**	0.077	0.197	0.264	1

SS – Southern Summer; NS – Northern Summer; SW – Southern Winter; NW – Northern Winter. **p ≤ 0.01; *p ≤ 0.05.

species (*Cathorops spixii* and *Genides barbus*) from the Paranaguá Estuarine Complex (PEC-Paraná), a coastal ecosystem with high salinity, with values closer to those obtained in this study in *C. spixii* from the southern region of the CIELC (Table IV). However, other fish species from the CIELC and PEC-Paraná had lower As content (Table IV). It is clear that the measurement and monitoring of metalloids such as arsenic (As) and their effect on aquatic organisms; for instance, fish species that are bioindicators of contamination, are important for conservation. The toxicity of As can change in different pH and redox conditions and, therefore, become problematic for the biota. This metalloid can promote changes in the energetic metabolism by reducing ATP, increasing the reactive oxygen species (ROS) and DNA damage, and, in cases of chronic exposure, it is possible that As promotes the loss of reproductive capacity (Heath 1990), which contributes to abundancy loss and, as a consequence, increased vulnerability to extinction.

Arsenic probably comes from natural sources, and this fact is supported by other studies conducted in the CIELC (Figueiredo et al. 2007). Although the highest concentration within the total muscle tissue in catfish from the southern area of the CIELC was around ten times higher than the maximum limit established for fish intended for human consumption; namely, 1.0 μg g^{-1} w.w. (ANVISA 2013, FAO/WHO 2014), we recommend further studies on As speciation as it is probable that arsenic stored in catfish muscle is in a non-toxic form, such as in its organic form. Arsenobetaine, for example, is an organic form of arsenic that is non-toxic and whose biological function is reducing environmental stress in aquatic organisms such as estuarine fish that inhabit regions with the highest salinities (Peshut et al. 2008, Grinham et al. 2014).

Moreover, the highest As concentrations in fish from the best conserved area of the CIELC can be reflected in natural geological conditions, because high As levels were previously obtained

Table IV. Total arsenic (As) contents in muscle tissues of fish species from estuarine regions in Brazil. Data are shown as mean values±standard deviation or minimum-maximum in dry weight.

Species	Sampling site	Arsenic (mg Kg^{-1})	Reference
Cathorops spixii *Genidens genidens*	Guaraqueçaba (Paranaguá Estuarine Complex/PR)	20.52±10.29 6.06±3.13	Angeli et al. (2013)
Cathorops spixii *Genidens genidens*	Antonina/Paranaguá (Paranaguá Estuarine Complex/PR)	13.35±7.42 3.49±1.03	Angeli et al. (2013)
Genidens barbus *Paralonchurus brasiliensis*	Paranaguá Estuarine Complex/PR	14.5 ± 6.01* 2.34–22.63	Avigliano et al. (2019)
Stellifer rastrifer *Isopisthus parvipinnis*	Cananéia-Iguape estuarine-lagoon complex/SP	1.30–5.17 1.62–2.57	Trevizani et al. (2019)
Paralonchurus brasiliensis		2.59–3.25	
Stellifer rastrifer *Isopisthus parvipinnis*	Paranaguá estuarine complex/PR	1.64–6.13 1.68–9.04	Trevizani et al. (2019)

***Data in wet weight (w.w.).**

in the sediment of this region (3,000 μg g^{-1}) when compared to the sediment of the northern area (1,000 μg g^{-1}) of the CIELC (Amorim et al. 2008). A significant and positive correlation between arsenic content in the muscle of benthic fish and in sediments has also been identified in other studies (Zhang et al. 2018). Catfish are a species that have sediment feeding habits (Figueiredo & Menezes 1978) and, therefore, it is very probable that the ones that feed in more contaminated sediment present higher arsenic concentrations. These differences in the arsenic content of sediment are probably due to distinct environmental conditions such as the organic matter content of sediment and distinct granulometry. The concentrations of organic matter in the northern and southern regions of the CIELC varied from 4.5 to 10.9% and were associated with the smallest size grain of sediments (i.e. Mud= silt + clay) (Barcellos et al. 2009). Azevedo et al. (2011) reported differences concerning granulometry composition in sediments from the northern and southern regions of the CIELC. In general, these authors reported the dominance of sand in both periods; namely, summer and winter. However, the sampling points located in the innermost sectors of the CIELC (Cubatão Sea) and in the northern site showed a higher composition of mud (silt/clay), ranging of 45 to 60%. Some studies of As content in aquatic ecosystems in Brazil have linked high levels of As in coastal and estuarine sediments to the enrichment of sediments by continental rocks (Angeli et al. 2019, Kim et al. 2020, Santos et al. 2020). Therefore, the high natural concentration of As in the southern region of the CIELC may be another factor that influences the arsenic uptake of catfish from this area.

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