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Scientific Note

Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn IN MUSSELS COLLECTED IN SANTOS BAY, SÃO PAULO, BRAZIL: LIMITS REQUIRED BY LOCAL LEGISLATION

Marcos Bührer CAMPOLIM[1]

Marcelo Barbosa HENRIQUES[2]

Edison BARBIERI[3]

[1] Instituto Florestal, Rua do Horto, 931, CEP 02377-000, São Paulo, SP, Brasil. E-mail: marcoscampolim@yahoo.com.br (corresponding author).

[2] Instituto de Pesca, Centro APTA do Pescado Marinho, Avenida Bartolomeu de Gusmão, 192, Ponta da Praia, CEP 11030-906, Santos, SP, Brasil.

[3] Instituto de Pesca, Núcleo de Pesquisa e Desenvolvimento do Litoral Sul, Avenida Professor Wladimir Besnard, CP 43, CEP 11990-000, Cananéia, SP, Brasil.

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ABSTRACT

This study quantified and evaluated the concentrations of trace elements Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in mussels *Perna perna* collected in Urubuqueçaba island, Santos Bay, São Paulo, Brazil. This region presents port and industrial activities, as well as high population densification. The collections in natural mussel beds occurred in eight campaigns, two per season of the year, totaling 240 samples, from April 2010 to June 2011. The determination of the concentration of trace elements was performed using the Atomic Absorption Spectrometer (AAS) Flame. The statistical analysis used the PAST Software 1 using $p < 0.05$ as significant. Average concentrations in µg g^{-1} wet weight obeyed the order Cd (0.11), Cr (0.37), Pb (0.38), Cu (1.63), Ni (2.31), Mn (2.33), Zn (27.11), Fe (179.97) and Al (375.23). The results were compared with other studies of mussels and Brazilian standards that establish maximum allowable concentrations for human consumption, only Cr showed concentrations above those permitted by Brazilian standards.

Key words: bioaccumulation; bivalve mollusks; marine pollution; *Perna perna*; trace element.

Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb E Zn EM MEXILHÕES COLETADOS NA BAÍA DE SANTOS, SÃO PAULO, BRASIL: LIMITES PRECONIZADOS PELA LEGISLAÇÃO BRASILEIRA

RESUMO

Este estudo quantificou e avaliou as concentrações dos elementos traços metálicos Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb e Zn em mexilhões *Perna perna* na ilha Urubuqueçaba, baía de Santos, São Paulo, Brasil. Esta região apresenta atividades portuárias e industriais, além de alta densidade populacional. As coletas em bancos naturais do mexilhão ocorreram em oito campanhas, duas por estação do ano, totalizando 240 amostras, no período de abril de 2010 a junho de 2011. A determinação da concentração dos metais foi realizada empregando Espectrometria de Absorção Atômica – AAS. O tratamento estatístico utilizou o Software PAST 1 utilizando $p < 0{,}05$ como significativo. As concentrações médias, em µg g^{-1} de peso úmido obedeceram a seguinte ordem: Cd (0,11), Cr (0,37), Pb (0,38), Cu (1,63), Ni (2,31), Mn (2,33), Zn (27,11), Fe (179,97) e Al (375,23). Os resultados foram comparados com outros estudos realizados com mexilhões e com as normas brasileiras que estabelecem concentrações máximas permitidas para o consumo humano e somente o Cr apresentou concentrações acima do permitido pelas normas brasileiras.

Palavras-chave: bioacumulação; moluscos bivalves; poluição costeira; *Perna perna*; elemento traço.

INTRODUCTION

Individually or in combination, metallic ions represent a risk to the environment and are considered important coastal pollution factors (AMADO-FILHO *et al.*, 2008; BARROS and BARBIERI, 2012; CAMPOLIM *et al.*, 2017). At low concentrations they are essential for the metabolism of plants and animals, however, at high concentrations, they present toxicity (ZAGATTO and BERTOLETTI, 2006; CARMO *et al.*, 2011; DAMATO and BARBIERI, 2011; FERREIRA *et al.*, 2013; MARENGONI *et al.*, 2013; SANTOS *et al.*, 2014).

Trace elements, with the exception of Al and Fe, occur naturally in the environment, but anthropic activity has increased its concentrations causing contamination of the ecosystems; the organisms that inhabit the affected areas become exposed to the new environmental conditions (LAMPARELLI *et al*., 2001, CARVALHO *et al*., 2001, DAMATO and BARBIERI, 2003).

Aquatic organisms may accumulate metallic trace elements in their tissues, even when the water has concentrations of these compounds below the maximum concentration tolerated by legislation, which leads to contamination risks within the food chain (NIENCHESKI *et al*., 2014). Benthic marine species have been widely used as biological indicators for monitoring trace elements, mainly because of their ability to accumulate such substances at concentrations many times higher than those found in the environment (RESGALLA JUNIOR *et al*., 2008; WALLNER-KERSANACH and BIANCHINI, 2008). Mussels are used as bioindicators or biomonitors because they have a wide geographic distribution, are sessile animals and have had their biology studied (AVELAR *et al*., 2000; CARVALHO *et al*., 2001; LAMPARELLI *et al*., 2001; RESGALLA JUNIOR *et al*., 2008; GALVÃO *et al*., 2009; FERREIRA *et al*., 2013; MARENGONI *et al*., 2013; LINO *et al*., 2016). International programs to monitor pollutants in the marine environment recommend the use of bivalve mollusks such as the "Mussel Watch" in the United States (GOLDBERG, 1975) and the United Nations Environment Program (UNEP, 2004).

The concentrations of trace elements in mussels are controlled to a large extent by local environmental levels and are related to the hydrological parameters of the environment and physiological processes that control the reproductive activity (FRANCIONI *et al.*, 2004; MAANAN, 2008; KUMAR *et al*., 2015).

The mussels of the *Perna perna* species, besides being collected by extractivists in natural banks, are the most cultivated marine bivalve mollusks in Brazil (HENRIQUES *et al*., 2004; SILVA *et al*., 2009). The production by means of marine crops in the state of Santa Catarina is already an important economic activity, and in the states of Rio de Janeiro and São Paulo it has been highlighted as potential activity for development (FERREIRA *et al*., 2013).

In the estuaries and bays of Santos Bay, *P. perna* mussels are the most abundant bivalves (PEREIRA *et al*., 2002) and even with the presence of contaminants, the local population extracts this mollusk in Santos Bay for commercialization (HENRIQUES *et al*., 2000; LAMPARELLI *et al*., 2001; PEREIRA *et al*., 2002; HENRIQUES *et al*., 2004; HENRIQUES and CASARINI, 2009; SILVA *et al*., 2009; CASARINI *et al*., 2010). The island of Urubuqueçaba is a traditional *P. perna* extraction site for personal consumption and for commercial purposes (HENRIQUES *et al*., 2001; SILVA *et al*., 2009).

The estuarine system of Santos and São Vicente, inserted in the Metropolitan Region of the Santos Bay in the state of São Paulo, represents one of the most important Brazilian examples of environmental degradation due to water and atmospheric pollution of industrial origin in coastal environments (LAMPARELLI *et al*., 2001). Chemicals enter the estuarine system of Santos and São Vicente and the adjacent marine area through runoff water, the release of industrial, port and domestic liquid effluents, leaks and environmental accidents, the atmospheric deposition of pollutants, improper disposal of domestic and industrial solid waste in several sites of the contribution basins, contaminating surface and groundwater, and by contaminated sediment releases resulting from the dredging activity in the port canals (LAMPARELLI *et al*., 2001; LOURENÇO and LANDIM, 2005; ABESSA *et al*., 2008; BURUAEM *et al*., 2012).

Depending on the type and concentration, trace elements may cause damage to human health due to its toxicity, carcinogenicity and mutagenicity (CARMO *et al*., 2011). In Brazil, the standards that establish maximum limits for inorganic contaminants in food are Resolution RDC No. 42, of 08/29/2013 of the National Agency of Sanitary Surveillance, for Cd and Pb (BRASIL, 2013) and Decree No. 55.871, of 03/23/1965, regarding the regulatory norms for the use of food additives, for Cr, Cu, Ni and Zn (BRASIL, 1965). For Al, Fe and Mn no regulations were found.

Although previous works with the objective of identifying aspects of contamination of trace elements in the *Perna perna* mussel in the Santos Bay region, concluded that there was no contamination for this species, higher than allowed by the Brazilian standards that establish limits for human consumption (HENRIQUES *et al*., 2000; LAMPARELLI *et al*., 2001; PEREIRA *et al*., 2002; CASARINI *et al*., 2010). These authors point out the need for continuous monitoring as a result of the contamination context that exists in the region.

The objective of this study was to determine trace element concentrations (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in *Perna perna* mussels collected on the island of Urubuqueçaba, Santos Bay, and to compare the results with Brazilian standards which establish maximum permissible concentrations for human consumption.

METHODS

The samples of *Perna perna* mussels consisted of adult animals (> 50 mm), collected from April 2013 to June 2014, in natural banks of the intertidal region on the island of Urubuqueçaba (coordinates of latitude 23°58'26 "S and longitude 46º21'08" W), located in the Santos Bay, central coast of the state of São Paulo (Figure 1).

For this study, two hundred and forty samples were used, collected in eight collection campaigns, two per yearly season. The collected animals were cleaned of the fouling material and stored in plastic bags moistened with local water, appropriately identified. The transport to the laboratory of the Fisheries Institute was carried out in Styrofoam boxes with ice and the samples were frozen.

The treatment of the samples consisted in the removal of the meat from the shells of the mussels and drying them to a constant weight in an air circulating oven at 60 °C. The opening process consisted of adding 10 mL of pure supra HNO_3 in 0.5 g of mussel tissue, with subsequent heating at 60ºC for 2 hours, for the destruction of resistant fats (BARROS and BARBIERI, 2012). The aperture solutions were transferred to a 50 mL volumetric flask and completed to the flask's mark with ultrapure water. Three white solutions were prepared similarly to the samples for quality control of the analyses. The Atomic Absorption with Flame Spectrometer (Shimadzu, model AA-6800, USA, Tampa) and standard reference material of 15 SRM certified oyster tissue (No. 1566b oyster fabrics) were used. The recovery percentages

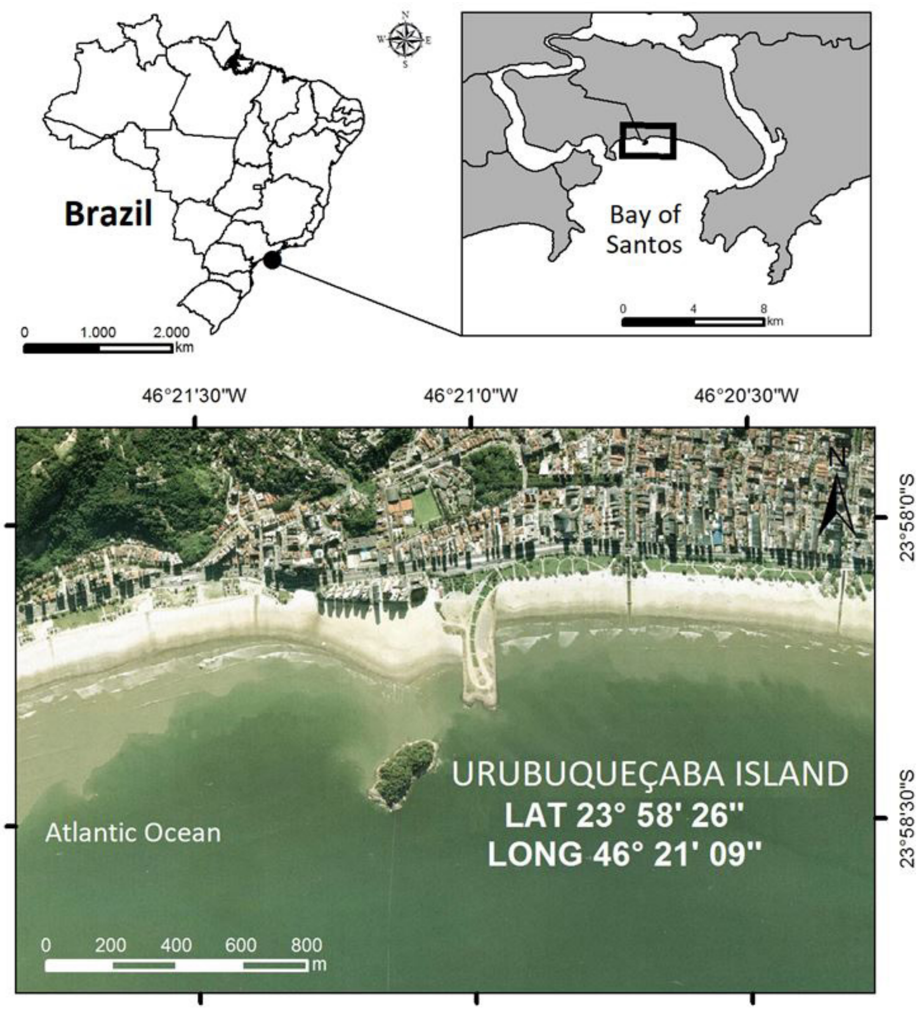

Figure 1. Location of the island of Urubuqueçaba, Santos Bay (SP), collection area of *Perna perna* mussels.

Table 1. Recovery of the sample certified by metallic trace element.

Element	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Recovery	101%	98%	84%	102%	99%	87%	93%	96%	88%

of the metalic trace element sample showed good precision and accuracy of the analytical methods employed (Table 1).

Mean trace element concentrations were based on analysis of thirty mussel samples and expressed in μg g^{-1} dry weight. The statistical analysis used the Past Software 1 (HAMMER *et al.*, 2001) using $p < 0,05$ as significant.

The mean concentrations of the trace elements analyzed were compared with other studies developed with mussels in the southeastern region of Brazil, in the states of São Paulo and Rio de Janeiro, and with Brazilian standards that establish maximum permissible concentrations for human consumption: Decree No. 55.871, of 23/03/1965 on the regulatory norms for the use of food additives (BRASIL, 1965); and Resolution RDC No. 42, of 29/08/2013 of the National Health Surveillance Agency, provides for the MERCOSUR Technical Regulation on Maximum Inorganic Contaminant Limits in Food (BRASIL, 2013).

The maximum permissible concentration values of contaminants adopted by standards in force in Brazil are expressed in μg g^{-1} wet weight. To compare the results of this study with the Brazilian standards that adopt the wet weight, the results obtained for dry weight were multiplied by 0.3 (considering that these organisms have about 70% of their body mass composed of water) to obtain the values of trace elements in mussels by wet weight (Carvalho *et al*., 2001; LAMPARELLI *et al*., 2001). For the comparative analysis with other studies performed, the original concentrations in dry weight were transformed to wet weight.

Table 2. Minimum, maximum, mean and standard deviation of trace elements analyzed, and maximum concentrations allowed in foods according to Brazilian standards - RDC 42/2013 and Decree 55871/1965 (µg g^{-1} wet weight).

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	300.00	0.07	0.15	1.20	129.60	1.50	1.35	0.09	19.20
Maximum	529.20	0.26	0.75	2.43	231.00	2.89	3.40	0.75	48.00
Mean	375.23	0.11	0.37	1.63	179.97	2.33	2.31	0.38	27.11
Deviation	56.46	0.03	0.09	0.29	24.62	0.36	0.48	0.19	6.12
RDC 42/2013	-	2.00	-	-	-	-	-	1.50	-
Dec. 55871/65	-	-	0.10	30.00	-	-	5.00	-	50.00

RESULTS

The minimum, maximum and mean concentrations of trace elements corrected from µg g^{-1} of dry weight to µg g^{-1} of wet weight and the maximum permissible concentrations according to current standards in Brazil (RDC 42/2013 and Decree 55871/1965) are presented in Table 2.

The mean concentrations, in µg g^{-1} wet weight, per growing order were Cd (0.11±0.03), Cr (0.37±0.09), Pb (0.38±0.19), Cu (1.63±0.29), Ni (2.31±0.48), Mn (2.33±0.36), Zn (27.11±6.12), Fe (179.97±24.62) and Al (375.23±56.46).

Cr was the only quantified trace element that presented concentrations above that allowed by Brazilian legislation. For Al, Fe, Mn no national standards for maximum concentrations permitted for mollusks and other foods were found.

DISCUSSION

Aluminum

In Brazil, the trace element Al does not have a maximum permissible concentration standard for aquatic organisms. The average concentration obtained in the present study of 375.23 µg g^{-1} of wet weight was close to the result found by CARVALHO *et al*. (2001) in Macaé, of the State of Rio de Janeiro coast, with a mean of 395.00 µg g^{-1} wet weight. CARVALHO *et al*. (2001) suggest that the high concentrations may be related to the suspended particulate matter from the Macaé river discharge and the oxidation of ship hulls due to the intense traffic of vessels. The Santos Bay region has similarities with Macaé in that they are port cities, with industrial poles and great population densities. Concentrations above 300.00 µg g^{-1} of dry weight obtained by CARVALHO *et al*. (2001) and the present study may characterize environments with large anthropogenic interventions, given the similarity of the data obtained and local contexts of the studied regions.

Cadmium

The maximum concentration of Cd for bivalve mollusks permitted by Brazilian legislation is 2.0 µg g^{-1} wet weight (BRASIL, 2013). All concentrations identified in the present study did not exceed those established in the legislation (Table 2). Studies in the Baixada Santista with quantification of Cd in aquatic organisms (fish, siris, crabs, mussels and oysters) in 1981, 1990 and 2001, show a reduction in the presence of this trace element in the aquatic biota, and all species analyzed have concentrations below the limit allowed by the legislation, and the average value observed in mussels was 0.21 µg g^{-1} wet weight (LAMPARELLI *et al*., 2001). More recently, PEREIRA *et al*. (2012) obtained concentrations between 0.05 to 0.08 µg g^{-1} for mussels collected at two points in Santos Bay. The present study confirms the non-contamination in mussels, obtaining a maximum value of 0.26 and a mean of 0.11 µg g^{-1} of wet weight.

The levels of Cd in the sediment of Baixada Santista present concentrations with the possibility of causing a toxic effect to the biota (LAMPARELLI *et al*., 2001; BURUAEM *et al*., 2012). Therefore, continuous monitoring is necessary because it is an estuarine region where there is a continuous upwelling of sediments by tidal currents and by dredging to maintain flow for vessels.

Other studies carried out in the Baixada Santista region with mussels collected in the years 1996 and 1997 (PEREIRA *et al*., 2002), 2006, 2007 and 2008 (CASARINI *et al*., 2010), 2008 and 2009 (CATHARINO *et al*., 2012) and 2010 (PEREIRA *et al*., 2012), also detected concentrations below the permitted limit.

Limits below that allowed in mussels were also identified on the north coast of the state of São Paulo, in Ubatuba Bay (AVELAR *et al*., 2000), at Cocanha beach in Caraguatatuba (CATHARINO *et al*., 2012; PEREIRA *et al*., 2012), in Ilhabela (PEREIRA *et al*., 2012), and in the state of Rio de Janeiro (CARVALHO and LACERDA, 1992; CARVALHO *et al*., 1993; CARVALHO *et al*., 2001; FERREIRA *et al*., 2004; FRANCIONI *et al*., 2004; KEHRIG *et al*., 2007; LINO *et al*., 2016). The Cd does not appear to present problems on the coast of São Paulo and Rio de Janeiro in relation to concentrations in mussels according to the developed studies.

Chrome

Cr does not have a specific standard for aquatic organisms in Brazil. The concentration used to interpret the data is given by the standard that regulates food additives (BRASIL, 1965) and stipulates the value of 0.10 µg g^{-1} wet weight. All the analyzed samples exceeded this limit and the average obtained was 0.37 µg g^{-1} wet weight (Table 2). It is worth noting that of the total concentration obtained for Cr, only that relative to Cr^{6+}, is toxic for living beings.

For Santos Bay, a previous study found average concentrations of 0.60 and a maximum of 0.88 µg g^{-1} of wet weight in mussels collected in 1999 (LAMPARELLI *et al*., 2001). PEREIRA *et al*. (2012) obtained concentrations between 0.21 and 0.70 µg g^{-1} of wet weight in mussels collected in 2010. The results of the present study indicate the maintenance of the bioavailability of Cr by mussels in the region.

On the coast of Rio de Janeiro, in the Macaé port region, CARVALHO *et al*. (2001) identified a mean concentration of 0.38 µg g^{-1} wet weight, FERREIRA *et al*. (2004) identified 0.57 µg g^{-1} wet weight (original concentration in dry weight) for 3 regions studied, KEHRIG *et al*. (2007) found values above that allowed for the Guanabara Bay, and FRANCIONI *et al*. (2004) found that concentrations in five of the six studied regions were higher than those permitted for food. In Ubatuba Bay, northern coast of the State of São Paulo, AVELAR *et al*. (2000) that mussels collected and analyzed in 1995 reached maximum concentrations of 14.55 and average of 1.53 µg g^{-1} of wet weight (original concentrations were in dry weight).

For analysis of the contamination in mussels in Baixada Santista, LAMPARELLI *et al*. (2001) adopted the permissive maximum limit of total Cr for human consumption in fish established by the United States Food and Drug Administration (USFDA) of 13 µg g^{-1} wet weight, as reference for the discussion of the results of their monitoring. If this limit was adopted for comparison with the present study, there would be no concentrations above those allowed, and in the other studies cited, which were developed in other regions of São Paulo and Rio de Janeiro, only in Ubatuba (AVELAR *et al*., 2000) would this limit be exceeded.

The monitoring of Cr in Santos Bay is necessary due to the maintenance of the levels of contamination in sediments in the region (LAMPARELLI *et al*., 2001), which are subject to tidal currents and operational dredging of the Port of Santos, providing potential bioavailability for aquatic organisms.

Copper

In Brazil, there is no specific legislation for Cu concentrations in aquatic organisms, the standard that regulates food additives is used (BRASIL, 1965) and stipulates the maximum value of 30.0 µg g^{-1} wet weight. All concentrations of Cu identified in the present study did not exceed the maximum permitted values and the identified average was 1.63 µg g^{-1} wet weight (Table 2).

A study developed by LAMPARELLI *et al*. (2001) in the Baixada Santista region in the years 1979 and 1999, did not find concentrations above the allowed limits and the analyses in mussels in the Santos Bay presented an apparent reduction, going from 1.79 to 1.15 µg g^{-1} of wet weight. Other studies with mussels also obtained results within the concentrations allowed in Baixada Santista (PEREIRA *et al*., 2002), in Ubatuba, state of São Paulo (AVELAR *et al*., 2000) and on the coast of the State of Rio de Janeiro (REZENDE and LACERDA, 1986; CARVALHO and LACERDA, 1992; CARVALHO *et al*., 1993; CARVALHO *et al*., 2001; FERREIRA *et al*., 2004; FRANCIONI *et al*., 2004; KEHRIG *et al*., 2007).

The concentrations within the limits allowed by the Brazilian standard, found in the studies in coastal environments of São Paulo and Rio de Janeiro, may be related to the fact that Cu has a strong interaction with organic matter (humic substances), which significantly reduces its bioavailability to aquatic organisms (LAMPARELLI *et al*., 2001). Specifically, for mollusks, Cu exerts a role in oxygen transport and gas exchange in these organisms (KEHRIG *et al*., 2007).

Iron

There are no norms of maximum concentrations allowed in Brazil for aquatic organisms for the trace element Fe.

The average concentration of 179.97 µg g^{-1} wet weight (Table 2) was higher when compared to other studies conducted in Santos Bay and north coast of São Paulo that identified mean concentrations in wet weight (originally in dry weight) below 30.00 µg g^{-1} (CATHARINO *et al*., 2012). In the state of Rio de Janeiro, studies identified wet weight concentrations of 72.90 µg g^{-1} (REZENDE and LACERDA, 1986), 170.00 µg g^{-1} (CARVALHO *et al*., 2001), 339.00 µg g^{-1} (FERREIRA *et al*., 2004) and 31.6 µg g^{-1} (KEHRIG *et al*., 2007). CARVALHO *et al*. (2001) suggested that high concentrations found in their study were due to the particulate material from the Macaé river discharge and the oxidation of ship hulls, derived from port and petrochemical activities similar to Santos Bay, and the concentrations identified in both regions are equivalent. FERREIRA *et al*. (2004) attributed the high values associated with the iron oxide-rich substrates of the studied areas.

Manganese

Mn does not have a standard for maximum permissible concentrations in Brazil. LAMPARELLI *et al*. (2001) adopted as a reference for the discussion of the results of monitoring in mussels in Baixada Santista the maximum permissible limit of Mn for human consumption in fish established by the United States Government (USEPA-US Environmental Protection Agency) of 54.00 µg g^{-1} of wet weight. For Santos Bay, the authors identified a mean Mn concentration of 14.85 µg g^{-1} of wet weight and concluded that Mn is not a problem for the aquatic environment of the region.

On the island of Urubuqueçaba a mean concentration of 2.33 µg g^{-1} wet weight was found (Table 2), values lower than those identified by LAMPARELLI *et al*. (2001) for the same region.

Studies developed with Mn in mussels in the state of Rio de Janeiro obtained concentrations of µg g^{-1} of wet weight of 4.02 µg g^{-1} (REZENDE and LACERDA, 1986), 5.10 µg g^{-1} (CARVALHO and LACERDA, 1992), 5.52 µg g^{-1} and 10.71 µg g^{-1} (CARVALHO *et al*., 1993), 2.46 µg g^{-1} (CARVALHO *et al*., 2001) and 6.60 µg g^{-1} (FERREIRA *et al*., 2004).

If the maximum limit defined by the American agency of 54.00 µg g^{-1} wet weight was adopted, the results of this work and the others mentioned have permissible concentrations for human consumption. As for the pH and redox potential - pH in the estuarine and coastal environment favor the precipitation of Mn in the sediment (LAMPARELLI *et al*., 2001). Reduced concentrations of this element were expected in these environments, a condition confirmed by the present study.

Nickel

For the evaluation of the Ni concentration, the standard regulating food additives was used (BRASIL, 1965), which establishes the maximum value of 5.0 μg g^{-1} wet weight. In Brazil, there is no specific norm for Ni concentrations for aquatic organisms.

The results obtained did not exceed the permitted limit and obtained a mean of 2.31 μg g^{-1} of wet weight (Table 2).

A study by LAMPARELLI *et al*. (2001) with mussels in Baixada Santista found concentrations above those allowed in the Santos estuary and within the limits allowed for the Santos Bay, with a mean concentration of 0.80 μg g^{-1} of wet weight. The authors identified an increase in Ni levels in the sediments of the Santos and São Vicente estuaries, especially with the specific sources (industrial effluents), diffuse sources (port terminals and air pollution) and also near the dumps and sanitary landfills located in Baixada Santista.

The mean concentration obtained in the present study is higher than the average found by LAMPARELLI *et al*. (2001), a condition that may indicate that the continuous increase of Ni levels in the region still occurs.

Other studies carried out in the state of Rio de Janeiro did not find concentrations above those allowed (REZENDE and LACERDA, 1986; CARVALHO *et al*., 1993; CARVALHO *et al*., 2001; FERREIRA *et al*., 2004; KEHRIG *et al*., 2007).

Lead

The maximum permissible concentration of Pb for bivalve mollusks in Brazil is 1.5 μg g^{-1} wet weight (BRASIL, 2013). All concentrations identified did not exceed the maximum permitted values (Table 2).

Previous studies developed in the Santos Bay with mussels have found values below the maximum allowed by the legislation in force in Brazil (LAMPARELLI *et al*., 2001; PEREIRA *et al*., 2002; CASARINI *et al*., 2010; CATHARINO *et al*., 2012; PEREIRA *et al*., 2012). Limits below that allowed in mussels have also occurred in the north coast of the state of São Paulo (CATHARINO *et al*., 2012) and in the state of Rio de Janeiro (REZENDE and LACERDA, 1986; CARVALHO *et al*., 1993; CARVALHO and LACERDA, 1992; CARVALHO *et al*., 2001; FERREIRA *et al*., 2004; KEHRIG *et al*., 2007). In the Ubatuba Bay, north coast of the state of São Paulo, AVELAR *et al*. (2000) recorded concentrations in mussels above the maximum allowed value, being related to the burning of fossil fuels coming from motorized vessels.

The maximum and mean concentrations obtained in the present study are one-half and one-fourth, respectively, of the maximum concentration allowed by legislation, which indicates a significant presence of Pb in the region (Table 2). It is necessary to monitor this trace element in the Santos Bay due to the intense traffic of motorized vessels in this region.

The retention and absorption of Pb in the digestive tract of mollusks are linked to several factors that must be considered, and salinity, hygroscopicity, concentration, larval phase, respiratory rate and duration of exposure can be mentioned, among others (BARROS and BARBIERI, 2012).

Zinc

Zn does not have a specific standard for maximum concentration limits for aquatic organisms in Brazil. The concentration used to interpret the data is given by the standard that regulates food additives and stipulates the value of 50.00 μg g^{-1} wet weight (BRASIL, 1965).

All samples analyzed did not exceed the maximum permitted limit and the mean concentration was 27.11 μg g^{-1} wet weight (Table 2).

The study developed by LAMPARELLI *et al*. (2001) in the Santos Bay with mussels did not identify values above the permitted maximum, and the average concentration in the year 1979 was 28.81 μg g^{-1} and in 1999 it was 23.95 μg g^{-1} wet weight, values close to those identified in the present study. Other studies developed in Baixada Santista with mussels obtained results within the allowed concentration (PEREIRA *et al*., 2002; CASARINI *et al*., 2010; CATHARINO *et al*., 2012).

The sediments in the marine environment of Baixada Santista present Zn values that do not cause toxic effect to the aquatic biota, whose concentrations can be considered as resulting from the constitution of the mineral matrix (LAMPARELLI *et al*., 2001). ABESSA *et al*. (2008) found an average concentration of 34.00 μg g^{-1} in sediment collected near the island of Urubuqueçaba, Santos Bay. However, in sediment removed from the channel of the Port of Santos, BURUAEM *et al*. (2012) found average concentrations ranging from 509.08 to 1077.33 μg g^{-1}, where multiple sources of contaminants are located nearby.

Due to the results obtained in the present study for the Santos Bay, Zn concentrations occur at permissible levels for human consumption. Concentrations within those allowed in mussels have also been identified on the northern coast of São Paulo (AVELAR *et al*., 2000; CATHARINO *et al*., 2012) and on the coast of the state of Rio de Janeiro (CARVALHO *et al*., 1993; CARVALHO and LACERDA, 1992; CARVALHO *et al*., 2001; FERREIRA *et al*., 2004; KEHRIG *et al*., 2007). Concentrations above those permitted were identified on the coast of Rio de Janeiro, in the vicinity of Guanabara Bay (FRANCIONI *et al*., 2004) and Sepetiba Bay with 76,20 μg g^{-1} wet weight (REZENDE and LACERDA, 1986) and 61.5 μg g^{-1} wet weight (CARVALHO *et al*., 1993).

This variation of Zn concentrations may be related to the fact that this element is necessary for mussels in the formation of several biological molecules, among them are structural proteins and enzymes (NOLAN and DAHLGAARD 1991; CARVALHO *et al*., 1993). This element is a natural constituent for the production of gametes and oxygen transport in mussels (REZENDE and LACERDA, 1986) and its concentration in bivalve mollusks is regulated by physiological mechanisms that are able to increase the bioaccumulation, especially in the products of sexual females during spawning periods, regardless of the concentration levels found in sea water (SOKOLOWSKI *et al*., 2004). The concentrations of Zn in bivalve mollusks are often high, with concentrations of oysters exceeding 1000 µg g^{-1} dry weight (LAMPARELLI *et al*., 2001).

CONCLUSIONS

For the trace elements quantified that have Brazilian standards for maximum concentrations allowed for human consumption (Cd, Cr, Cu, Ni, Pb and Zn), only Cr showed concentrations above the allowed limits.

It is necessary to establish Brazilian legislation for maximum permissible concentrations of trace elements in aquatic organisms that do not have regulations (Al, Fe and Mn) and update existing standards with specificity for aquatic organisms for the elements Cr, Cu, Ni and Zn, since the rules in force are generic for various foods.

Cr presents priority for monitoring and updating of the norm of maximum concentration allowed in aquatic organisms since it is a pollutant that can cause damage to human health. The significant concentrations in mussels on the coast of Rio de Janeiro and São Paulo and Baixada Santista, present an increasing tendency of concentrations in mussels.

Ni and Pb also need priority in monitoring for Santos Bay due to the contamination of Ni present in the sediments and mussels of the estuaries of the region, and the finding of the increase in the concentration of this element in the mussels analyzed. Also, there is the presence of significant concentrations of Pb and intense traffic of motorized vessels in the region.

Cd, even with permissible concentrations in the mussels, due to contamination in the sediment, needs attention in monitoring programs.

Mn, although there is no norm for maximum concentrations allowed in Brazil, appears not to be a relevant pollutant for the studied region, since it did not present high concentrations when compared to other studies.

Mussels are efficient indicators of bioaccumulation for the trace elements quantified. It is necessary to carry out a continuous monitoring program with mussels to verify the tendency of the concentration of metallic trace elements in Santos Bay due to the sources of pollution in the region and because of extraction for human consumption.

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