TRACE METALS ANALYSIS IN BROWN BOOBY (*SULA LEUCOGASTER)* COLLECTED FROM ILHA GRANDE BAY, RIO DE JANEIRO, BRAZIL

Aldo Pacheco Ferreira[1]

RESUMO

Concentrações de metais traço: chumbo, zinco, cromo, cádmio, níquel e cobre foram estimadas em Atobá-pardo (*Sula leucogaster*), colhidos na Baía da Ilha Grande, Rio de Janeiro, Brasil. Os níveis médios de concentração no fígado e no rim (µg.g^{-1} de peso seco), respectivamente foram 6,32955 e 6,57136 (Cd); 78,17409 e 96,89409 (Zn); 44,01727 e 65,20864 (Cu); 41,15091 e 39,62318 (Pb); 2,80091 e 4,16455 (Cr) e 9,27182 e 9,91091 (Ni). Os resultados indicam níveis relativamente elevados de contaminação por metais traço em *S. leucogaster* e os dados obtidos são preocupantes pela extensão que pode causar para o nível trófico da fauna marinha na região estudada.

Palavras-chave: Metais-traço; Contaminação; Baía da Ilha Grande; *Sula leucogaster.*

ABSTRACT

Concentrations of the trace metals: lead, zinc, chromium, cadmium, nickel, and copper were estimated in Brown Booby (*Sula leucogaster)*, harvested from Ilha Grande Bay, Rio de Janeiro, Brazil. Mean concentration levels in liver and kidney (µg.g^{-1} dry weight), respectively were 6,32955 and 6,57136 (Cd); 78,17409 and 96,89409 (Zn); 44,01727 and 65,20864 (Cu); 41,15091 and 39,62318 (Pb); 2,80091 and 4,16455 (Cr); and 9,27182 and 9,91091 (Ni). The results indicate relatively high trace metal contamination in *S. leucogaster* and the data obtained are worrying by the extension that may cause to the trophic level of marine fauna at this studied region.

Keywords: Trace metal; Contamination; Ilha Grande Bay; *Sula leucogaster.*

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[1] Escola Nacional de Saúde Pública Sérgio Arouca, Centro de Estudos da Saúde do Trabalhador e Ecologia Humana (Cesteh/Ensp/Fiocruz). Rua Leopoldo Bulhões, 1480, CEP 21041-210, Manguinhos. Rio de Janeiro, Brasil. E-mail: aldoferreira@ensp.fiocruz.br

INTRODUCTION

Increased human activities such as industrialization, coupled with over-population and increased ambient temperature amongst other factors, have become major environmental issues in recent years.

Exposure to very low levels of elements such as lead, cadmium and mercury have been shown to have cumulative effects since there is no homeostatic mechanism which can operate to regulate the levels of these toxic substances (PEREIRA & EBECKEN, 2009). The major pollutants from industrial discharge have been shown to be lead, mercury, nickel, arsenic, zinc and copper. Lead intoxication has been reported to be associated with neurological problems, renal tubular dysfunction and anemia (MORAES & JORDÃO, 2002). Although zinc and copper are essential trace elements which may also serve as plant nutrients, they may be used as components of paint pigments. Consequently, their undue presence in the environment through industrial discharge can also be hazardous to man (SANTANA & BARRONCAS, 2007).

The nature of metals from both natural and anthropogenic sources combined with their necessity in biological processes produces a multifaceted system for assessment. Metal distributions in abiotic and biotic systems should be examined to precisely evaluate impact on ecosystems. Wildlife studies of exposure and effect can be challenging, but the results are more complete than evaluation of only metal concentrations. Birds are good sentinel species because they are observable, sensitive to toxicants, and live in different trophic positions. Consequently, studies assessing avian population status, reproductive success, and toxicological importance of metal exposures can be extrapolated to other wildlife and probably humans (FERREIRA et al., 2010).

Sula leucogaster (BODDAERT, 1783) breeds in some coastal and oceanic islands of Brazil, and uses as food a great diversity of prey, captured in flat diving, between 10 to 15 m, beyond ictiofauna discarded in shrimps fisheries. As a type of bird with a large number in diversity at study site, it was then chosen as an indicator, corroborating other studies in the same line (BURGER et al., 1992; NOERNBERG et al., 2008).

Pollution in the marine environment has become an issue of great concern, especially to coastal states (PEREIRA & EBECKEN, 2009). The oceans cannot provide an infinite sink for anthropogenic wastes but little attention has been given to evaluating the limits of capacity of coastal areas for waste assimilation (JURESA & BLANUSA, 2003). Consequently, instances of fisheries closures, spoiled beaches, destroyed coral reefs and wildlife habitat, toxic blooms and lost coastal ecological communities are widespread, with a corresponding determination of cost benefit. Recent concerns about connectivity of ocean health issues and the relationship to human disease highlight an important area for study.

The aquatic environment with its water quality is considered the main factor controlling the state of health and disease in both man and animal. Nowadays, the increasing use of the waste chemical and agricultural drainage systems represents the most dangerous chemical pollution (LACERDA & MOLISANI, 2006). Knowledge of the ocean and the impact of human activities on it can reveal the complexity and interdependence of all aspects of the system (COSTANZA & FARLEY, 2007). Improved acquaintance and predictive capabilities are required for more effective and sustained development of the marine environment to obtain associated economic benefits and to preserve marine resources.

The goal of this work was to evaluate selected metal concentrations in different tissues of *S. leucogaster* collected from Ilha Grande Bay, which is situated in the southern Atlantic Coast of Rio de Janeiro State, Brazil. Additionally, this study aims to obtain and assess levels of trace metals, allowing a better understanding of Ilha Grande bay and provide subsidies to mitigate the possible contamination caused by industrial activities, urbanization without adequate planning and sewage systems.

TRACE METALS IN MARINE CONTAMINATION VIEW

The levels of Cd, Zn, Pb, and Cu found in seabirds are the result of two main processes: bioaccumulation through food and biodegradation of environmental processes (JOHANSEN et al., 2006). According to Schmitt-Jansen et al. (2008) the sub-lethal effects on birds include growth retardation, suppression of egg production, egg shell thinner and changes in behavior.

Cadmium is known for its long half-life in biological systems (decades in humans and years in birds), and 0.1-1.0% of ingested Cd absorbs through the avian gastrointestinal tract to be distributed to kidney and liver. Also, Cd can connect to the liver to **metallothionein** (SEEBAUGH et al., 2005), which is responsible for liaison alleviate the potential toxic effects. The high levels of Cd detected in the kidneys are major than expected, and on the other hand, when compared to the liver, may indicate high exposure (THOMPSON et al., 2007). The metallothionein are a group of soluble molecules of low molecular weight, characterized by its stability to high temperature, high content in cysteine and the absence of amino acids flavored. These proteins act in the transport and storage of elements. Also provide protection for the effects of certain toxic metals, sequestering them and decreasing the amount of free metal ion (BUSTAMANTE et al., 2008).

The levels of essential metals such as Zn are metabolically regulated in seabirds tissues. Zn has an important role in many metabolic processes, especially in the activation of enzymes and the regulation of gene expression, and therefore its higher concentration (SAVINOV et al., 2003). In fact, levels of Zn were higher in both the kidney and in liver.

Lead absorption from the gastrointestinal tract ranges from 4-70 % depending on the form of Pb ingested and the age of the exposed individual. A large amount of lead is deposited into bone, which acts as a depot that provides a reliable indication of long-term exposure.

At the present time there are unprecedented pressures on natural resources (LAUWERYS & HOET, 1993). Sustainable development of these resources is hindered by an inability to detect emerging environmental problems at an early stage when remedial measures can still be effective. Nowhere is this inadequacy so pronounced as in the marine environment. Global energy cycles and the biological processes upon which all life depend are critically influenced by the ocean (PAIN et al., 1998; PEREIRA & EBECKEN, 2009).

The assessment of environmental variables and biological effects in seabirds will provide critical insights into the level and extent in public health effects associated with marine areas and resources. Also, the direct contaminant loads and exposure will assist regional, and consequently, national decision makers in efforts to ensure the sustained protection to marine ecosystems.

Although well regulated in some countries, industry has been the source of many contaminants and chemicals in food. Major industrial activities have the potential for generating air emissions, waste water effluence and solid wastes, all of which enter the food chain and cause danger to man, animals and plants. In view of these findings, there is need to monitor more closely the environment under review and put in place appropriate checks and balances to preserve the health of communities within the vicinity of the industrial areas, particularly as the effects of metals are bioaccumulative and pose great dangers to the health of humans, animals and plants.

Anthropogenic inputs of pollutants such as trace metals into the marine environment have increased their levels to large extents within past a few decades. These pollutants tend to accumulate in the bottom sediments (FERREIRA et al., 2010). As a result, ecosystems such as seaports or other industrialized coastal areas that have chronic inputs of metals have highly contaminated sediments.

This characteristic has led to concerns over the ecological effects that may be associated with sediment quality. Of particular concern are toxic effects and the potential for bioaccumulation of metals in biota exposed to the sediments (JOHANSEN et al., 2006). The availability of trace metals to the biomass of a polluted region is the prime concern both in terms of the prediction of the effects of metal pollution on an ecosystem and in terms of possible human health risks.

With growing interest on environmental issues, several intriguing questions related to trace metals are often raised. This review addresses the basic concepts, sources, speciation, mode of action, levels, analytical measurement, bioavailability, bioaccumulation, biological role and toxicity of trace metals in the marine environment. Lead, zinc, chromium, cadmium, nickel, and copper are selected because these metals are common and are often at measurable levels in marine samples. An attempt has been made to answer the queries presented by the environmentalists working on various aspects of trace metal pollution in the marine environment

METHODOLOGY

STUDY AREA

Ilha Grande Bay is located in the State of Rio de Janeiro, southeastern Brazil (22°50’ S - 23°20’ S, 44°45’ W - 44°00’ W), an area rich in islands, inlets and smaller bays (Figure 1). An accelerated growth process has been shown by several urban centers along the Ilha Grande Bay coastal zone, including old cities such as Angra dos Reis and Parati, and villages like Monsuaba, Bracuí, Frade and Perequê. The main economic activities of this region are directly and indirectly related to the sea, such as fishery, tourism, aquatic sports and commercial shipping.

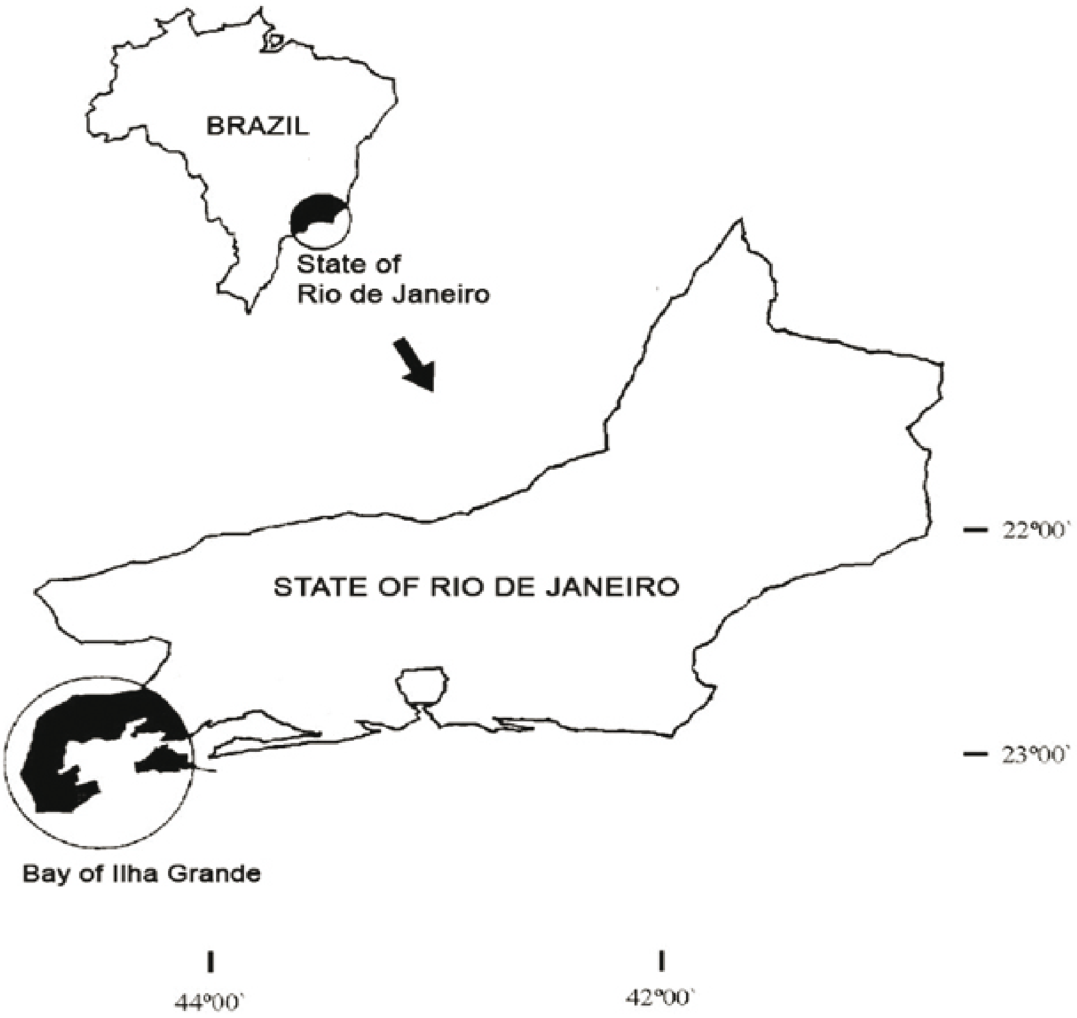


Figure 1. Study area: Ilha Grande Bay, Rio de Janeiro, Brazil

COLLECTION OF SAMPLES

We analysed thirty nine specimens (adults) found stranded or dead in areas related to the study site, between March 2007 and December 2009. After collection the birds were brought to the laboratory, and immediately the carcasses were necropsied according to Jauniaux et al. (1998), while putrefactive specimens were discarded. Organs were removed (liver, kidney), weighed, and kept frozen (-20°C) prior analysis.

PREPARATION OF SAMPLES

In the laboratory, two identical samples were prepared from liver and kidney and weighted approximately 100 mg each. One of the samples of each tissue was kept for the toxicological analysis and the other was taken to dry in oven at 60°C until a constant weight to allow turning the concentrations of various elements, obtained primarily in terms of wet weight of sample concentrations on the dry weight of sample analyzed.

Aliquots of each homogenised dried sample were digested in 5 ml of 14 N nitric acid at 60 °C on a hot plate until the solution was clear. After evaporation, the residue was dissolved in 10 ml of 0.3 N nitric acid.

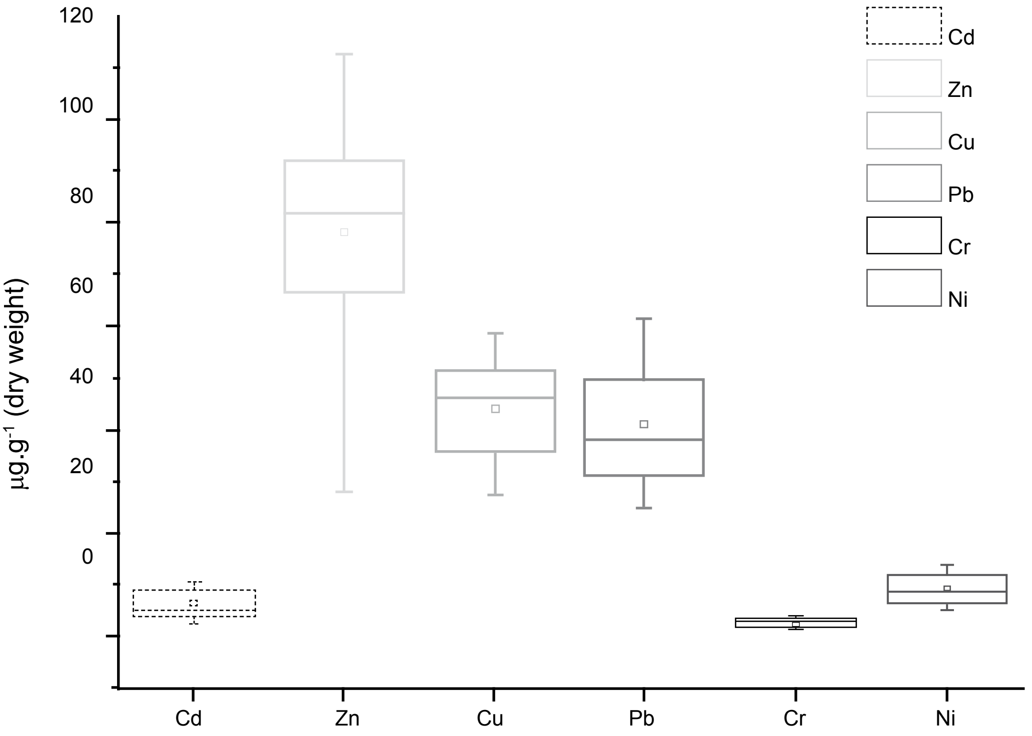
Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the determination of chromium, copper, nickel, lead, zinc, and cadmium; with the advantage of determining multi-elements in larger amounts, minors, and traces without changes in experimental parameters. The following absorption lines were used: Cr 267.716 nm; Cu 324.754 nm; Ni 231.604 nm; Pb 220.353 nm; Zn 213.856 nm; and Cd 226.502 nm. Accuracy and reproducibility of the methods were tested using muscle (Dorm-2, National Research Council, Canada) certified material. Standard and blanks were analysed along with each set of samples. Concentrations are expressed as $\mu g.g^{-1}$ wet weight (w.wt.).

STATISTICAL ANALYSIS

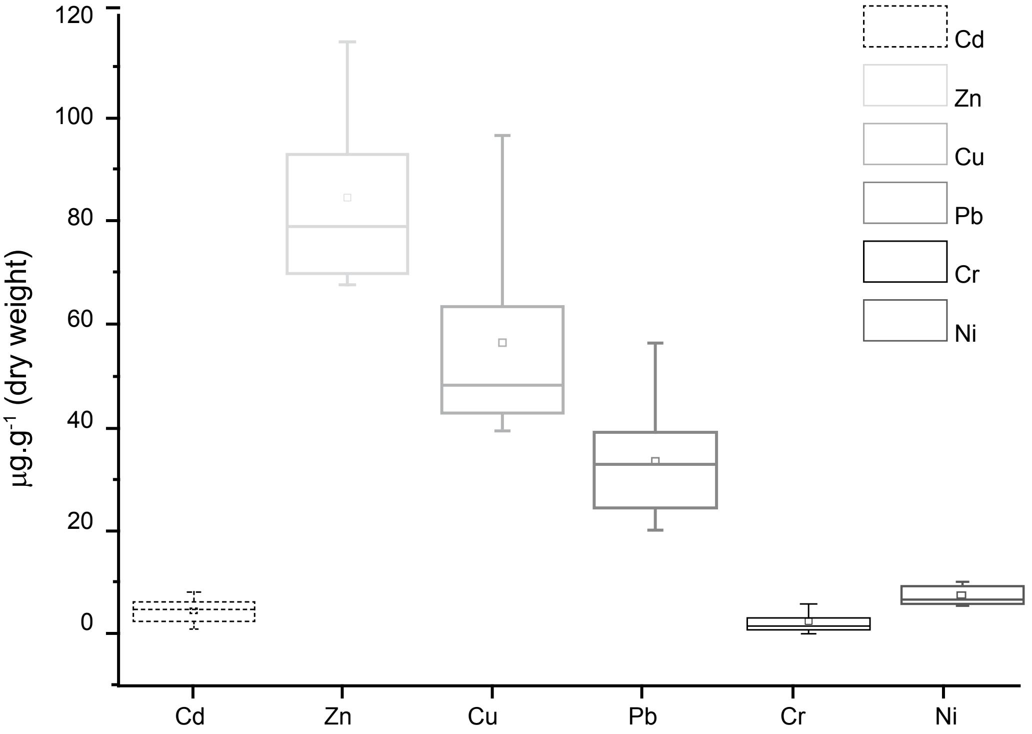
Statistical analysis was performed using Origin 7.5 software package (OriginLab Corporation). The average distribution of metals by the *S. leucogaster* was assessed using analysis of variance (ANOVA), testing inter and intragroup mean differences between organs. In order to determine which organ were significantly different from each other, a post-hoc comparison with the Tukey`s multiple comparation test was carried out. For all tests, *p*-values of < 0,05 were used to determine significant differences.

RESULTS AND DISCUSSION

Concentrations of the elements analyzed in the livers and kidneys of adult *S. leucogaster* are presented in Figure 2 and Table 1. Mean concentration levels in liver were 6.32955 (2.63 – 10.87)(Cd); 78.17409 (28.3 – 112.71)(Zn); 44.01727 (27.1 – 60.17)(Cu); 41.15091 (23.17 – 62.12)(Pb); 2.80091 (1.22 – 4.33)(Cr); and 9.27182 (4.79 – 11.95)(Ni). Mean concentration levels in kidney were 6.57136 (2.15 – 11.09) (Cd); 96.89409 (77.7 – 132.1)(Zn); 65.20864 (43.11 – 115.7)(Cu); 39.62318 (24.1 – 67.15)(Pb); 4.16455 (1.34 – 9.44) (Cr); and 9.91091 (7.23 – 14.15) (Ni).



Liver



Kidney

Figure 2. Cadmium (Cd), zinc (Zn), copper (Cu), lead (Pb), chromium (Cr) and nickel (Ni) concentrations (in µg.g-1 dry weight) in liver and kidney of Sula leucogaster. Box-plots illustrate the 10%, 25%, 50% (median), 75% and 90% percentiles and the outliers (*).

Table 1. Concentrations of elements analyzed (μg.g^{-1} metal, wet weight) in livers and kidneys of Sula leucogaster (n=39**)**

Element	**Liver (µg.g-1)**									
	Mean	**sd(yEr±)**	**se(yEr±)**	**P25**	**P75**	**P95**	**Min**	**Max**	**Range**	**Median**
Cd	6,32955	2,65676	0,56642	4,04	9,01	10,58	2,63	10,87	8,24	5,95
Zn	78,17409	23,6278	5,03746	66,65	92,15	112,7	28,3	112,71	84,41	82,8
Cu	44,01727	10,42818	2,22329	35,73	51,74	58,59	27,1	60,17	33,07	46,415
Pb	41,15091	12,31526	2,62562	31,17	50,14	61,24	23,17	62,12	38,95	38,745
Cr	2,80091	1,02228	0,21795	1,86	3,67	4,21	1,22	4,33	3,11	2,955
Ni	9,27182	3,20751	0,68384	6,64	12,01	13,89	4,79	16,74	11,95	9

Element	**Kidney (µg.g-1)**									
	Mean	**sd(yEr±)**	**se(yEr±)**	**P25**	**P75**	**P95**	**Min**	**Max**	**Range**	**Median**
Cd	6,57136	2,62989	0,56069	4,25	8,39	11,02	2,15	11,09	8,94	6,885
Zn	96,89409	18,41633	3,92637	80,07	106,45	131,11	77,7	132,1	54,4	92,315
Cu	65,20864	21,92692	4,67484	49,87	73,62	110,78	43,11	115,7	72,59	56,22
Pb	39,62318	12,60071	2,68648	28,7	45,2	65,1	24,1	67,15	43,05	38,96
Cr	4,16455	2,30925	0,49233	2,34	5,19	8,15	1,34	9,44	8,1	3,615
Ni	9,91091	2,09964	0,44764	7,92	11,87	13,13	7,23	14,15	6,92	9,155

According to the ANOVA test, significant differences (P=0.05) were found for all metals in liver (F = 137.84771; P= 0), and in kidney (F= 189.04542; P= 0). In individual analysis for each metal in liver and kidney, Cd presented no significant differences (F= 0.09206; P= 0.76308); Zn presented significant differences (F=8.59076; P= 0.00545); Cu presented significant differences (F=16.75829; P= 0.00019); Pb presented no significant differences (F= 0.16540; P= 0.68630); Cr presented significant differences (F= 6.41439; P= 0.01514); and Ni presented no significant difference (F= 0.45813; P= 0.50221).

Means comparison using Tukey Test indicates that in liver (p=0.05), Cd concentrations were not significantly different from Pb and Cr, but they significantly differed from Zn and Cu; Zn concentrations were statistically different from Cu, Pb, Cr, and Ni; while Cu concentrations did not differ significantly from Pb, but they were statistically different from Cr and Ni. The differences among Pb concentrations and Cr and Ni were significant as well as Cr and Ni concentrations did not differ significantly. Means comparison using Tukey Test indicates that in kidney (p=0.05), Cd concentrations were not significantly different for Cr, Ni, Zn and Pb; Zn concentrations were significantly different for Cu, Pb, Cr, and Ni; Cu concentrations were significantly different for Pb, Cr, and Ni; Pb concentrations were significantly different for Cr and Ni; Cr concentrations were not significantly different for Ni.

Metals comprise a significant part of pollutants in the marine environment. It is important to distinguish between the introduction of these metals from anthropogenic activities and those from natural weathering processes. Although sources of metals in the marine environment are relatively diverse, in Ilha Grande Bay there is great evidence of widespread adverse biological effects in fish, providing risks to human health posed by metals in seafood (KAREZ et al., 1994). The basis of toxicity for some metals support and anticipate problems due to its speciation and more effort should be focused on researches in the future.

CONCLUSION

The water system can be divided into three main compartments, the water column, the biotic and abiotic particulate matter and the sediment. It is known that the particulate material contains a chemical that is the result of chemical and physical processes that occur in the water column. As this material is decanted, i.e., with a continuous deposition, it's recorded in sediment changes that water was submitted. The focus of research in the assessment of metals in birds from Ilha Grande Bay as a representative of the top of trophic chains shows that despite being sedentary species, the degree of bioaccumulation of metals studied may be reflected also in the migratory species due to exposure. The metals contamination in one area can have harmful effects on an entire region, particularly in areas of active feeding or reproduction, or migration routes and breeding sites.

In the systematic release of trace metals into the environment, as a general analysis, it is known that cadmium is found in natural waters due to industrial discharges, such as electroplating, pigment production, welding, electronics, etc. This metal is also used as component of insecticides. It has no quality, at least known to the present, which makes it beneficial or essential to living beings. It is a metal with high toxic potential and accumulates in aquatic organisms, allowing its entry into the food chain (SAVINOV et al., 2003). Cadmium was the metal with the highest number of correlations between their levels in water and in the liver of birds. Its high bio-accumulation capacity could be an important factor in explaining this phenomenon. The action on the physiology in the trophic chain is similar to that of nickel, zinc and lead (MONTEIRO et al., 1998).

Zinc, which also showed a positive correlation between its levels in water and liver of birds, is an essential element for growth and it is a common metal in natural waters. Zinc toxic effects are associated with the respiratory system of marine animals and representatives from the top of the food webs. It is widely used in industry, mainly in electroplating, in metal and salt form such as chloride, sulfate, cyanide, etc. This metal can enter the environment through natural processes (leaching of rocks and soils) and anthropogenic, among which stands out the production of iron and steel and domestic sewage (CARVALHO et al., 2008). Similarly, lead, whose regression analysis showed a significant positive relationship between its concentrations in water and in the liver of animals, is present in water due to natural leaching of minerals or anthropogenic interference, such as industrial waste, paints, pipes, construction materials (tiles and slabs), impurities of fertilizers, pesticides. Among some potential effects on health, lead poisoning in humans can cause fatigue, irritability, anemia, dizziness, headache, muscle tremors, sensory disturbances, memory loss and reduction of neurophysiological function (BUSTAMANTE et al., 2008; CARVALHO et al., 2008).

Examination of metal uptake and accumulation in *S. leucogaster* inhabiting the site provided useful information about metal availability, uptake, and distribution that can be used to health effects assessments to determine risk and effects from such exposures (SILVA et al., 2005). There are scarce available data on levels of metals in birds in Ilha Grande Bay. Most of the research focuses on fish, a fact that initially guided the selection of metals to be included in this study. Data show worrying levels of some metals in so fish species and it was possible to expect the same levels in the analysed samples. However, all searched metals had shown higher concentrations.

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