HEAVY METALS LEVELS IN LARUS DOMINICANUS. CASE STUDY: COROA GRANDE MANGROVE, SEPETIBA BAY, RIO DE JANEIRO, BRAZIL

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ABSTRACT

Samples of liver and kidney of Kelp gull (Larus dominicanus) collected on Sepetiba Bay, Rio de Janeiro, Brazil, were analysed for their copper, zinc, cadmium, lead, chromium and nickel content. All the analyses were made using the inductively coupled plasma optical spectrometry method (ICP-OES). The investigation focused on the variability of the elements content in kidney and liver from a number of sampling seabirds and over different seasons. The results were interpreted using the analysis of variance test (ANOVA). This has revealed differences in concentration for the majority of elements with regard to organs, and how different sampling metals and organs are related to each other. Results indicate relatively high trace metal contamination in L. dominicanus, showing potential power of widespread biological and mutagenic adverse effects in trophic levels, and therefore, signalling risk to human health.

Keywords: Heavy metals; Marine environment; Contamination; Sepetiba Bay

RESUMO

Amostras de fígado e rim de gaivotão (Larus dominicanus) coletadas na Baía de Sepetiba, Rio de Janeiro, Brasil, foram analisadas quanto às concentrações-traço de cobre, zinco, cádmio, chumbo, cromo e níquel. Todas as análises foram feitas utilizando o método de Espectrometria de emissão óptica por plasma acoplado indutivamente (ICP-OES). A investigação centrou-se na variabilidade do conteúdo dos elementos no rim e no fígado de um número de amostras de aves marinhas em épocas diferentes. Os resultados foram interpretados por meio da análise do teste de variância (ANOVA). Isto revelou diferenças na concentração para a maioria dos elementos em relação aos órgãos, e como os diferentes metais pesquisados e os órgãos estão relacionados uns aos outros. Estes resultados indicam que a Baía de Sepetiba apresenta níveis preocupantes de metais, baseando-se neste estudo com L. dominicanus como indicador da avifauna local, evidenciando potencial poder de generalização adversa de efeitos biológicos e mutagênicos em níveis tróficos e, por conseguinte, sinalizando risco para a saúde humana.

Palavras-chave: Metais pesados; Ambiente marinho; Contaminação; Baía de Sepetiba

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INTRODUCTION

The pollution of aquatic systems is due not only to natural causes but above all to anthropogenic activity such as discharges of domestic or industrial effluents, leaching and runoff of pesticides in agricultural lands, among others (MORLEY, 2010). 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.

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. The high levels of Cd detected in the kidneys are higher 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 flavoured. 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 seabird tissues. Zn has an important role in many metabolic processes, especially in the activation of enzymes and the regulation of gene expression (SAVINOV et al., 2003). Therefore its higher concentration may impair physiological functions of birds, as well as contributing to decline in species populations. 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.

Because seabirds are conspicuous animals they are a suitable choice to play a role as sentinel organisms; unexpected changes in their numbers, health or

breeding success provide an alarm that may indicate an unknown pollution or food food supply problem. Seabirds are top consumers in marine foodchains which offer opportunities to detect and assess the toxicological effects of different inorganic elements on the marine ecosystem. Consequently, studies assessing avian population status, reproductive success, and toxicological importance of metal exposures can be extrapolated to other wildlife and probably humans (FERREIRA, 2010; MALLORY et al., 2010). Quantification of trace element levels in different tissues of the organism is an indicator of the bioavailable fraction of the element in the environment (SPALDING et al., 1997; SEEBAUGH et al., 2005; JOHANSEN et al., 2006; STORELLI et al., 2007; FERREIRA, 2009;).

Larus dominicanus (Lichtenstein, 1823, Charadriiformes: Laridae) inhabits the coast and coastal islands of the Pacific and Atlantic South America, Earth del Fuego to northern Peru, on the coast of Brazil are found in Rio Grande do Sul to Espírito Santo. Also is found in South Africa, Australia, New Zealand and islands Subantarctic (BARBIERI, 2008). This gull is a bird of natural wetlands, fresh or salt, grass or forested. It feeds in shallow to deep water along lake shores, rivers, estuaries, and beaches. Due to present a large number of this specie at study site, it was then chosen for this research.

Heavy metals are naturally present in various natural segments. However, human activity exerted for stimulus provided by industrial development, has changed the biogeochemical cycles influencing the transfer of these elements (PEREIRA; KUCH, 2005). Many of them have a wide range of toxic effects in humans, in terrestrial and aquatic life and in plants, and also have the potential to be bioaccumulative (ESTEBAN; CASTAÑO, 2009).

Pollution in the marine environment has become an issue of great concern, especially to coastal states (SCHMITT-JANSEN et al., 2008). 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. 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 (SCHEREN et al., 2004). Recent concerns about connectivity of ocean health issues and the relationship to human disease highlight an important area for study.

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 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). Heavy metals are natural components of marine ecosystems, but their levels may be elevated as a result of increased input into the oceans resulting from industrial activities. In some cases the concentrations of certain metals in marine waters have reached levels which cause damage to wildlife populations and created serious human health problems. Identifying levels in wildlife which are elevated as a result of pollution is difficult, since very few data have been reported concerning the natural levels of metals in any species of marine vertebrates (STORELLI et al., 2007).

METHODOLOGY

Collection of samples and Study area

A total of thirty-nine adult L. dominicanus were collected stranded and dead in Coroa Grande mangrove, Sepetiba Bay, Rio de Janeiro State, between January 2007 and October 2009 (Figure 1).
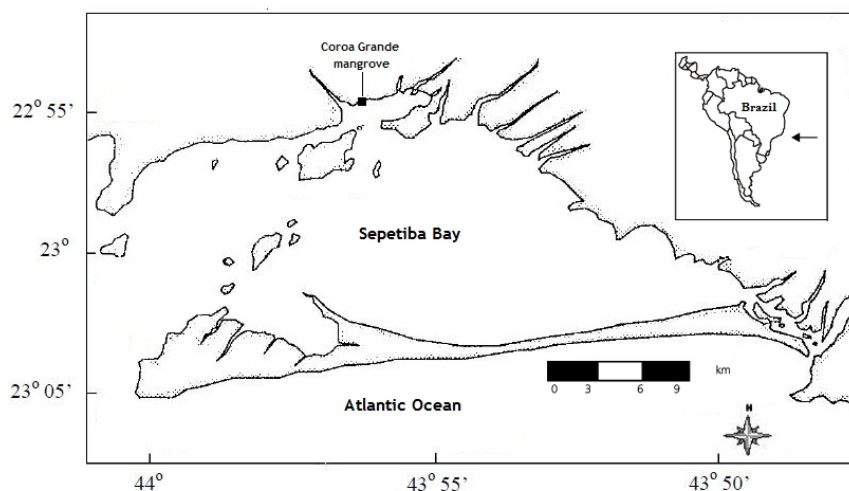

Figure 1. Study area: Coroa Grande mangrove, Sepetiba Bay, Rio de Janeiro, Brazil

Preparation of samples

The carcasses were necropsied according to JAUNIAUX et al. (1998), while putrefactive specimens were discarded. Organs were collected (liver, kidney), weighed, and kept frozen (-20°C) prior analysis. For analysis, 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 80°C by 24 hours 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 70°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 spectrometry method (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. Accuracy and reproducibility of the methods were tested by using dogfish liver (DOLT-2) and muscle (DORM-2) (National Research Council, Canada) reference standards. Standard and blanks were analysed along with each set of samples. Concentrations are expressed in µg g-1 wet weight (w.wt).

Statistical analysis

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

RESULTS AND DISCUSSION

According to the ANOVA test, significant differences (P=0.05) were found for all metals in liver (F= 66.15375; P= 0), and in kidney (F = 66.6754; P= 0). In individual analysis for each metal in liver and kidney, four of them presented no significant differences: Cd (F= 0.33628; P= 0.56631), Pb (F= 1.25953; P= 0.27064), Cr (F= 2.29712; P= 0.14008), and Ni (F= 0.60166; P= 0.44402). The other two presented significant differences: Zn (F= 6.97636; P= 0.01299), and Cu (F=20.97567; P= 0.00008).

A component of the enzymes responsible for metabolism of proteins and carbohydrates, zinc is an essential element in the animal organism. High concentrations of zinc occurred in the liver and kidneys. The concentration of zinc determined in the liver of the Kelp gulls (Table 1) was within the range of 11.39 µg g-1 w.wt to 53.6 µg g-1 w.wt. (mean 31.35313 µg g-1 w.wt). The concentration of zinc determined in the kidney (Table 2) was within the range of 22.33 µg g-1 w.wt to 81.12 µg g-1 w.wt (mean 45.37687 µg g-1 w.wt).

Copper, like zinc, is an essential metal for the well-being of an organism. The mean copper concentration determined in the liver (Table 1) was 26.89813 µg g-1 w.wt, range (12.11 µg g-1 w.wt to 39.43 µg g-1 w.wt). The mean copper concentration determined in the kidney (Table 2) was 49.78562 µg g-1 w.wt, range (22.61 µg g-1 w.wt to 89.46 µg g-1 w.wt).

Cadmium is a strongly toxic element. If absorbed into the organism through the digestive and pulmonary systems, cadmium forms complexes with proteins, in which it is easily transported and stored, mainly in the liver and kidneys and, in smaller quantities, in the pancreas, intestines and bones. Cadmium is also responsible for upsetting the activity of a number of cellular enzymes (ALLOWAY; AYRES, 1997). It produces teratogenic, mutagenic and carcinogenic effects. The concentration of cadmium in the liver of the analyzed Kelp gulls was within the range of 2.25 to 9.22 µg g-1 w.wt (mean 5.33188 µg g-1 w.wt. Table 1) and in the kidney from 2.43 to 8.17 µg g-1 w.wt (mean 5.68187 µg g-1 w.wt, Table 2).

Like cadmium, lead is an element that plays no role in metabolic processes of animal organisms. It is an extremely toxic element with a wide range of harmful effects. Exposure to lead may cause kidney and nervous system problems. It can

also inhibit heme synthesis (WYK et al., 2001). The lead concentration determined determined was from 19.42 µg g-1 w.wt to 54.11 µg g-1 w.wt (mean 37.80875 µg g-1 w.wt) in the liver (Table 1) and 18.61 µg g-1 w.wt to 44.61 µg g-1 w.wt in kidney (Table 2).

The chromium concentration determined was from 4.09 µg g-1 w.wt to 3.11 µg g-1 w.wt (mean 2.21438 µg g-1 w.wt) in the liver (Table 1) and 0.69 µg g-1 w.wt to 4.23 µg g-1 w.wt in kidney (Table 2).

The nickel concentration determined was from 2.16 µg g-1 w.wt to 6.78 µg g-1 w.wt (mean 4.52062 µg g-1 w.wt) in the liver (Table 1) and 1.34 µg g-1 w.wt to 6.72 µg g-1 w.wt in kidney (Table 2).

Table 1. Concentrations of elements analyzed (µg g^{-1} metal, wet weight) in liver of _Larus dominicanus_

Element	Liver (µg g^{-1} metal, wet weight)											
	X	Sd(yEr±)	Se(yEr±)	P_{25}	P_{75}	P_{95}	X_{min}	X_{max}	R	Median	Var	CoefVar
Cd	5.33188	1.9596	0.4899	3.21	6.63	9.22	2.25	9.22	6.97	5.275	3.84003	36.753
Zn	31.35313	12.25719	3.0643	22.54	35.33	53.6	11.39	53.6	42.21	27.435	150.23866	39.094
Cu	26.89813	9.86564	2.46641	16.16	34.37	39.43	12.11	39.43	27.32	27.895	97.33078	36.678
Pb	37.80875	10.28636	2.57159	26.82	45.3	54.11	19.42	54.11	34.69	38.94	105.80929	27.206
Cr	2.21438	0.98453	0.24613	1.45	2.56	4.09	0.98	4.09	3.11	1.88	0.96929	44.461
Ni	4.52062	1.43425	0.35856	3.43	5.62	6.78	2.16	6.78	4.62	4.24	2.05706	31.727

X-arithmetic mean; Sd- standard deviation; Se- standard error; P_{25} – Percentile 25; P_{75} – Percentile 75; P_{95} – Percentile 95; X_{min}- minimum; X_{max}-maximum; R – Range; Var – Variance; CoefVar- coefficient of variation (%)

Table 2. Concentrations of elements analyzed (µg g^{-1} metal. wet weight) in kidney of *Larus dominicanus*

Element	Kidney (µg g^{-1} metal. wet weight)											
	X	Sd(yEr±)	Se(yEr±)	P$_{25}$	P$_{75}$	P$_{95}$	X$_{min}$	X$_{max}$	R	Median	Var	CoefVar
Cd	5.68187	1.41011	0.35253	4.46	6.62	8.17	2.43	8.17	5.74	5.775	1.9884	24.818
Zn	45.37687	17.34376	4.33594	25.13	56.39	81.12	22.33	81.12	58.79	44.465	300.80616	38.222
Cu	49.78562	17.38524	4.34631	36.42	56.39	89.46	22.61	89.46	66.85	49.335	302.24657	34.92
Pb	33.94125	9.176	2.294	23.61	41.16	44.61	18.61	44.61	26	36.545	84.19898	27.035
Cr	2.70125	0.82571	0.20643	2.29	3.15	4.23	0.69	4.23	3.54	2.685	0.6818	30.568
Ni	4.10375	1.60137	0.40034	2.99	5.27	6.72	1.34	6.72	5.38	3.73	2.56439	39.022

X-arithmetic mean; Sd- standard deviation; Se- standard error; P$_{25}$ – Percentile 25; P$_{75}$ – Percentile 75; P$_{95}$ – Percentile 95; X$_{min}$- minimum; X$_{max}$-maximum; R – Range; Var – Variance; CoefVar- coefficient of variation (%)

Examination of metal uptake and accumulation in L. dominicanus inhabiting the site provided useful information about metal availability, uptake, and distribution that can be used to health effect assessments to determine risk and effects from such exposures. There are scarce available data on levels of metals in birds in Sepetiba 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 many fish species and it was expected the same levels in the analyzed samples. However, all searched metals had shown higher concentrations.

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.

Heavy 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 heavy metals in the marine environment are relatively diverse, in Sepetiba 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 purpose goal of this research was to evaluate selected metal concentrations in different tissues of L. dominicanus collected from Sepetiba Bay, which is situated in the southern Atlantic Coast of Rio de Janeiro State, Brazil. This area constitutes an important natural breeding place for molluscs, crustaceans, fish, and at Coroa Grande mangrove, many species of seabirds, being L. dominicanus presenting a great number. However, several environmental problems has been brought to the Bay, due to poor sanitation conditions, including domestic and industrial sewage effluent, potentiating injuries mainly that related to heavy metals

bioaccumulation in trophic level (COPELAND et al., 2003; LACERDA; MOLISANI, 2006).

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. Additively, these metals may produce a significant effect. In part, the lack of evidence reflects the fact that relatively little research has been done. 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.

Acknowledgements

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