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Baseline

Bioaccumulation of heavy metals in marine organisms and sediments from Admiralty Bay, King George Island, Antarctica

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ABSTRACT

The Antarctic continent is considered a low-impact environment; however, there is a tendency to increase the contaminants' levels due to human activities in the research stations. In this study, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn levels in sediment and biota were determined in the environmental samples from Admiralty Bay (King George Island, Antarctica) collected in 2003. The results demonstrated high concentrations of Cu and Zn in the sediments. There was bioaccumulation of As in the biota from Admiralty Bay and bioaccumulation of Zn specifically in the biota from Martel Inlet. In addition, the results were useful in order to understand the heavy metal levels for the pre-accident condition of Comandante Ferraz Antarctic Station, where an accident occurred in 2012, and also for the comparison with current conditions within the monitoring work developed by INCT-APA (National Institute of Science and Technology for Environmental Research Antarctic).

The Antarctic continent presents unique characteristics due to its geographic isolation, enabling it to be one of the remaining regions on the planet where human activities have little direct impact (Xuebin et al., 2006). Human activities expanded in the continent due to the installation of permanent research stations (Santos et al., 2005; Vodopivez et al., 2001).

Admiralty Bay is located in Western Antarctica (SE coast of King George Island). In this bay there are three research stations: Henryk Arctowski (Poland), Comandante Ferraz (Brazil) and Machu Picchu (Peru) (Montone et al., 2001; Ribeiro et al., 2011; Santos et al., 2006, 2007).

As a result of the increasing research interest and, therefore, human presence, there is a trend toward increasing levels of certain contaminants in the bay, such as heavy metals and metalloids (Islam and Tanaka, 2004). The organisms in the bay are able to integrate the variations of metal levels over time through bioaccumulation, which is the transfer of metal from a source, such as water, sediment or food, to an organism. The bioaccumulation depends on the contamination level in the environment and on biotic factors, such as diet and the trophic position that the organism occupies. Therefore, bioaccumulation reflects the amount of these elements that has been ingested, excreted, and retained, and the bioavailability of the metals, which cannot be studied through the concentration in sediments. Evaluating the bioavailability also enables the early detection of harmful effects on the Antarctic marine ecosystem (Ahn et al., 2002; Marcovecchio, 2004).

In this study, levels of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn) and mercury (Hg) were investigated in biota and sediments from Admiralty Bay. Information from these results enables the monitoring and a deeper understanding of the anthropic impacts on the Antarctic environment. The levels of these elements in biota in areas that are relatively uncontaminated have great relevance because they could be considered baseline levels or even a worldwide reference (Berkman and Nigro, 1992; Jerez et al., 2011).

In polar ecosystems the contaminant concentrations tend to increase due to natural and anthropic inputs (Farías et al., 2007). An unexpected increase in this particular Antarctic region may have occurred after a fire at the Comandante Ferraz Antarctic Station in February 2012. Within this context the evaluation of past data for such events allows for more thorough monitoring of future environmental impacts (Mauri et al., 1990).

The sampling campaign was carried out from November 25 to December 2, 2003 in Admiralty Bay. Samples were collected aboard the R/B SKUA, and the four sampling sites (Fig. 1) are areas of muddy bottom sediments (20 m deep). At each site, samples of surface sediments, benthic invertebrates, one fish, macroalgae and microphytobenthos were obtained with a van Veen grabber. Sample collection and processing were performed by the Antarctic Bentos Laboratory of the Oceanographic Institute of the University of São Paulo.

The technique of acid digestion was chosen to extract As, Cd, Cr, Cu, Ni, Pb and Zn from samples of biota. In this method, 0.35 g of each dried

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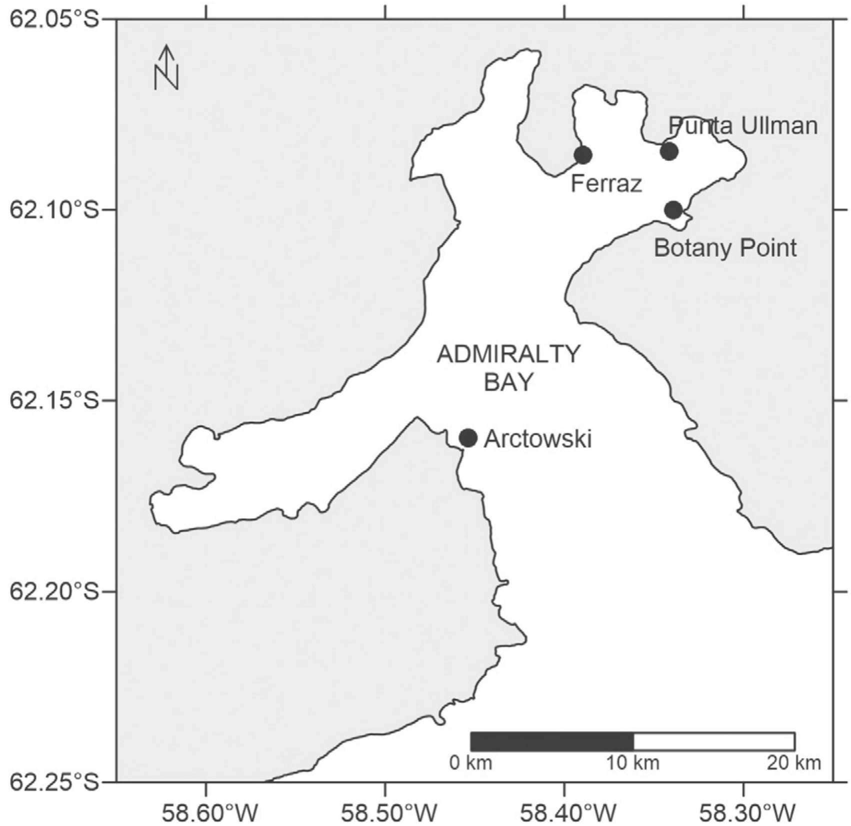

Fig. 1. Admiralty Bay, King George Island. Location of the sampling sites.

sample was digested with 4 mL of nitric acid, followed by the addition of 1 mL of hydrogen peroxide. After 18 h the treated analytes were disposed of in a heated digester block for 3 h, and the final solution was filtered and diluted to 35 mL.

Specifically for Hg digestion in the samples of both matrices (biota and sediment) an adapted version of method 7471 A (USEPA, 1994) was used. For digestion of the sediment samples for all elements of interest, method 3050B of acid digestion for sediments was used (USEPA, 1996).

For analysis of heavy metals, an Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES - Varian equipment, model 710ES) was used, and the VGA (Vapor Generated Accessory) was coupled to it only for Hg analysis. Sixty-five biota samples were analyzed in total, representing thirty different taxa, and four sediment samples (i.e., one from each sampling site).

For quality control the generated data, the parallel analysis of SRM 2976 (Mussel tissue - Trace elements and methylmercury – freeze dried of the National Institute of Standards and Technology) and DORM-2 (NRCC - National Research Council Canada) certified reference materials was performed, which showed recoveries between 87 and 100% (Table 1).

Furthermore, the limit of quantitation of the method (LQM), (level below which the heavy metals concentration is considered as not quantifiable) was calculated for each element of interest. The results were: As 2.96 mg kg^{-1}, Cd 0.38 mg kg^{-1}, Cr 0.60 mg kg^{-1}, Cu 0.42 mg kg^{-1}, Ni 0.31 mg kg^{-1}, Pb 0.80 mg kg^{-1}, Zn 0.93 mg kg^{-1} and Hg 17.70 μg kg^{-1}.

The concentrations of all the elements were similar in the four sampling sites (Fig. 2), it can be inferred that there is little spatial variation in their levels in sediments. In all sediment samples, Cd and Hg concentrations were lower than the LQM.

The elements with the highest average concentrations were Cu (62.7 mg kg^{-1}) and Zn (62.5 mg kg^{-1}), and these levels are in agreement with values obtained by Santos et al. (2007) and by Ribeiro et al. (2011).

The high concentration of Cu in the sediments has been discussed by previous authors, such as Machado et al. (2001), who indicated that Cu can be associated with the mineralization of chalcopyrite (sulfide of Cu and Fe) in the area. In addition, Fourcade (1960) believes that the high concentration of Cu in the sediments of the bay are due to their mineralogy, which is a result of the glacial erosion of volcanic rocks, such as basalt–andesite. During the magmatic distinction process, Cu and other metals, such as Zn, are incorporated into olivine, pyroxene and plagioclase, which compose rocks such as basaltic andesite (Salomons and Förstner, 1984). Therefore, the high concentration of Cu and Zn in sediments could be associated with the natural/basal levels in the Admiralty Bay.

The organisms were classified according to the trophic group classification of Corbisier et al. (2004) (Table 2). The occurrence of taxa and the accumulation of elements were different at each sampling site (Fig. 3).

Table 1
Certified and observed values (average ± standard deviation) for heavy metals (mg kg^{-1}) and mercury (μg kg^{-1}) in certified reference materials SRM 2976 and DORM-2 (only for Hg), and recovery levels.

Element	Certificate value	Observed value	Recovery (%)
As	13.1 ± 1.8	13.4 ± 0.3	100.61
Cd	0.82 ± 0.16	0.74 ± 0.04	90.67
Cr	0.5 ± 0.16	0.44 ± 0.01	87.85
Cu	4.02 ± 0.33	4.35 ± 0.24	108.09
Ni	0.93 ± 0.12	0.86 ± 0.18	92.83
Pb	1.19 ± 0.18	1.20 ± 0.06	100.65
Zn	137 ± 13	133 ± 3	97.25
Hg	4.64 ± 0.26	4.53 ± 0.20	97.72