

Arsenic and Heavy metals in Sediments near Paranaguá Port, Southern Brazil

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ABSTRACT

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Four sampling campaigns were carried out in 2001 to investigate the contamination rate by metallic at 11 sample stations around FOSPAR industry and one control point. In each sample, levels of metallic trace elements Cu, As, Cd, Cr, Hg, Ni, Pb and Zn were determined by atomic absorption spectrometry. Two extractions for metallic elements were performed, one strong with hydrofluoric acid (HF) and HNO₃ and one weak with HCl 0,1 N during 12 hours. From all investigated elements only As, Zn and Ni levels showed higher concentrations than critic limits adopted in this work. Maximum and minimum values were 0,1 and 81,5 ppm for As, 1,0 and 38,3 ppm for Ni, and 0,7 and 310,8 ppm for Zn. Our results indicate an high input of the element As, probably derived from human activities or geochemical anomaly.

ADDITIONAL INDEX WORDS: *Contaminants, bottom sediments, organic carbon.*

INTRODUCTION

The Paranaguá Estuarine Complex is in the south coast of Brazil between 2516' and 2534' S and 4817' e 4842' W coordinates and is formed by the Paranaguá, Antonina and Laranjeiras Bays. The Paranaguá Port is one of the bigger ports of Brazil and exports the agricultural and industrial production of several states and countries. Despite the crescent occupation of the coastal and estuarine areas the could be considered as one of the most preserved environments of Brazil.

Due to crescent requests of environment impact evaluations of port activities, heavy minerals contamination data is quite important. The aim of this work is to investigate the occurrence of arsenic and trace metals in the bottom surficial sediments at Paranaguá Port area.

METHODS

There were taken 11 samples of bottom surficial sediments with a Petite Ponar equipment near FOSPAR Fertilizer Industry (Figure 1) and one control sample in Laranjeiras Bay.

There were measured Arsenic (As) and the trace metals Copper (Cu), Cadmium (Cd), Chromium (Cr), Mercury (Hg), Nickel (Ni), Lead (Pb) and Zinc (Zn) rates by atomic absorption spectrophotometry (AAS).

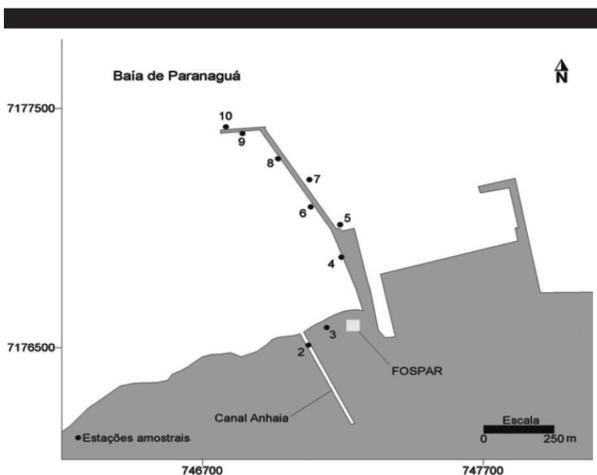


Figure 1. Map of FOSPAR area showing the sample points.

RESULTS

Elements concentrations are presented in table 1 and the rates of As, Zn, and Ni in figures 2 to 4. Arsenic, Zinc and Nickel occurs with values beyond detection limits adopted in this work. The limits were 7,24 ppm for Arsenic, 124 ppm for Zinc and 15,9 ppm for Nickel. Although the absence of background levels for the area, these values could be considered as rigorous because we had to assume conservative limits. Arsenic total concentrations present a significant increment ($p < 0.0003$) during this work. The higher total rates occur in November at 4,8,10,11 and 12 sample stations (Figure 2). The higher total rate was found at station 12 (reference station) in a local that had no impact of port activities.

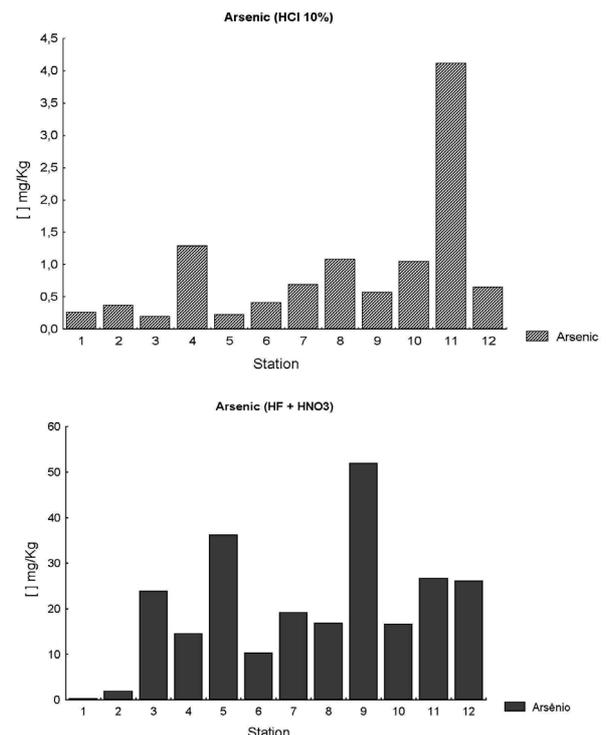


Figure 2. Total and partial Arsenic concentrations in bottom sediments.

Table 1. The quality of sediment samples collected in the area based on criterias reported by [3]; minimum and maximum concentrations acquired by partial and total extractions in bottom sediment samples are expressed in ppm (mg/Kg).

Element	Critic limits *	Digest	Jan/2001	Mai/2001	Ago/2001	Nov/2001
Arsenic	7.24 (**)	Total	<0.0001-50.5	<0.0001-38.9	<0.0001-77.8	4.7-81.5
		Partial	<0.0001-5.0	<0.0001-5.9	<0.0001-5.4	<0.0001-1.6
Cadmium	0.676 (5)	Total	0.06-0.45	0.07-0.38	0.06-0.58	0.06-0.87
		Partial	<0.0001-0.11	<0.0001-0.15	<0.0001-0.17	<0.0001-0.25
Copper	18.7 (10)	Total	1.2-21.95	0.84-22.97	0.70-10.65	0.74-20.83
		Partial	0.19-4.47	<0.0001-0.10	0.10-4.17	0.18-2.70
Chromium	52.3 (25)	Total	7.48-37.3	5.05-40.50	<0.0001-29.4	6.34-44.61
		Partial	<0.1	<0.1-6.16	<0.1-6.07	<0.1-11.90
Nickel	15.9 (**)	Total	8.39-36.94	0.97-38.35	<0.1-24.79	2.61-37.29
		Partial	<0.1-1.97	<0.1-1.65	<0.1-1.9	<0.1-58.50
Zinc	124 (20)	Total	6.48-90.3	0.74-90.6	<0.4-310.8	<0.4-82.2
		Partial	0.85-44.1	0.70-42.3	0.44-39.4	<0.4-33.8
Mercury	0.13 (0.1)	Total	0.02-0.089	0.005-0.078	0.006-0.065	0.002-0.116
		Partial	ND	ND	ND	ND
Lead	30.24 (20)	Total	1.84-8.42	2.52-9.59	1.85-4.81	2.91-12.95
		Partial	<0.0001-0.2	<0.0001-0.4	<0.0001-0.2	<0.0001-0.1

Arsenic is found in the environment due to weathering of rocks and volcanic activities. In human activities Arsenic is used in pigments, medicine, glass, in metal leagues with Lead and Copper, in some pesticides, defoliants and preservatives. The source of this element was not determined in the area. Two hypothesis have been considered: a) the intense traffic of ships

and boats with anti-fouling paint is a potential source and b) a geochemistry anomaly of Arsenic in the rocks of the area. Further studies must be developed to confirm this hypothesis.

The element Nickel is abundant in earth crust and occurs associated with Sulfur, Arsenic e Antimonium. The most

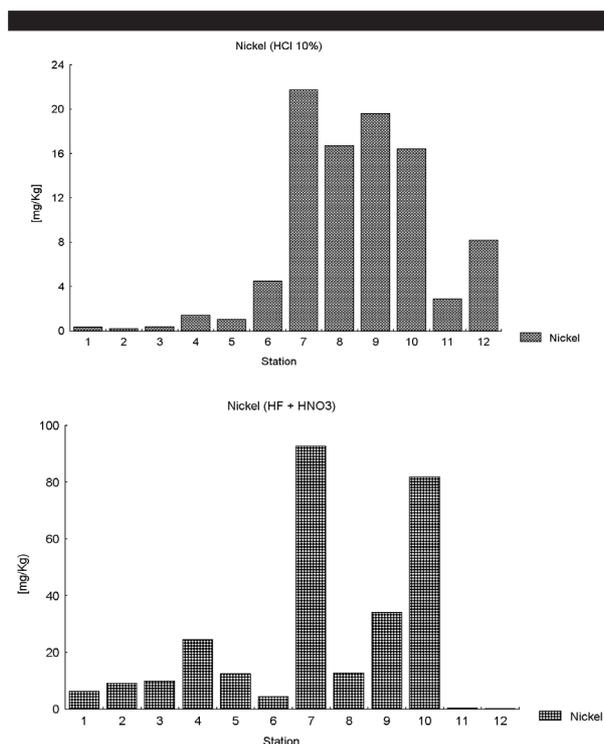


Figure 3. Total and partial Nickel concentrations in bottom sediments.

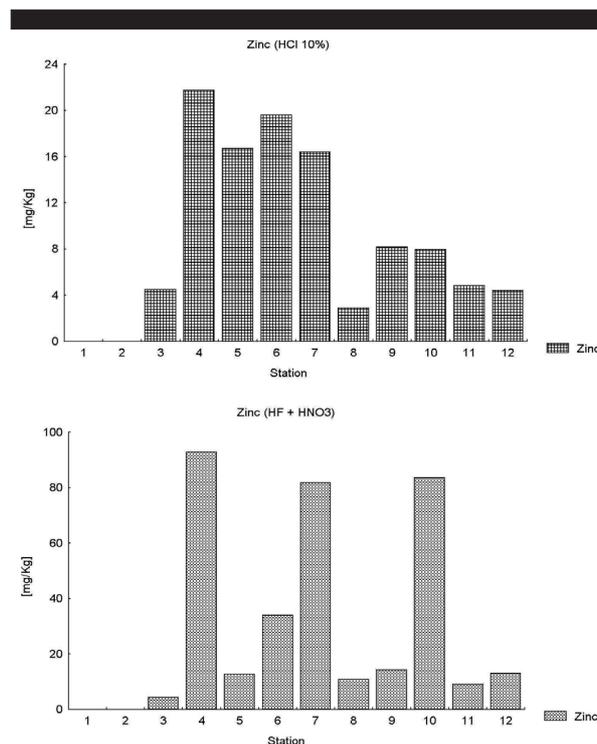


Figure 4. Total and partial Zinc concentrations in bottom sediments.

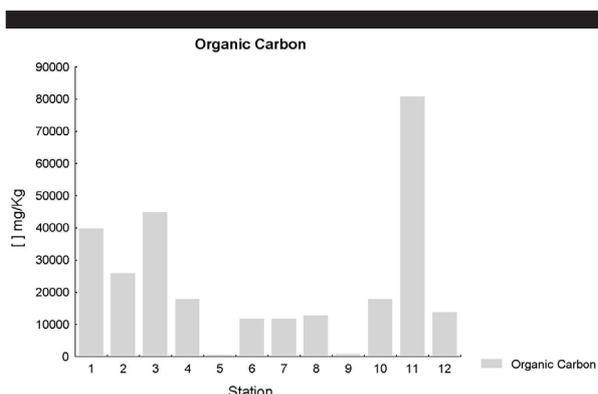


Figure 5. Total organic carbon rates in bottom sediments.

important Anthropogenic sources of Nickel includes the burn of fossil combustible, Nickel ore extraction, foundry activities, electronics, as a catalyser in industrial processes and in oil refinery. The nickel total rates exceed de critic limits in all the stations except 1 and 2 and the partial rates in station 12. In some cases the rates reaches 51.6 ppm where toxic effects is expected BUCHMAN (1999). This metal seems to be an important contaminant in the ecosystem. Nickel presence in sediments occurs as a co-precipitation of iron and manganese oxides and organic matter sorption.

The element Zinc is an essential micronutrient and its incorporation independence of the environment concentration MACDONALD (1994). Zinc can bio-accumulate in some organisms but there is no evidence of biological magnification JAAGUMAGI (1990). In neutral pH this element could be deposited in sediments by sorption by manganese and hydrated iron, clay minerals and organic matter. In low pH, Zinc stays in the sediments in insoluble sulfete forms.

A significant Zn concentration decrease during this experiment but total rates presents a distinct pattern with a maximum at August 2001 in 2, 5 and 8 stations presenting rates that reaches the critical limits of 124 ppm. The results suggest a main source of total Zn in Anhaia River. Hence, the main sources of Zn to local environment include the sewers of Paranaguá City and the burn of the city waste.

The total organic carbon (TOC) rates are presented in figure 5. The concentrations show values of 0.12% to 11.27% this one determined at station 11 in May of 2001.

The spatial distribution pattern of TOC shows the impact of urban sewers near Paranaguá Port. Stations 2 and 11 show the higher concentrations of TOC in the mouths of Anhaia and Itiberê rivers, respectively. High concentrations presented at station 3 were expected because the sample point is inside a mangrove area. The other stations are around the FOSPAR fertilizer industry pier and in the port dredged channel and

presented lower rates of TOC.

The correlation analyses did not detect significant relations of Arsenic, Nickel and Zinc rates with the TOC concentrations.

CONCLUSIONS

This work shows that background levels determination is quite important in contamination studies problems with heavy metals and Arsenic in bottom sediments. Without background levels is impossible to estimate the enhance factor of the elements, an important information in environmental impact evaluations. As an example, Arsenate (As III) is the most common form of Arsenic in oxidized marine sediments while Arsenite occurs in reduced sediment layers.

Bacteries in aerobic sediments could oxidate Arsenic III to As V. Manganese and Iron Oxi-hidroxiids abunds in oxidazed marine sediments and could also catalyze Arsenite to Arsenate oxidation NEFF (1997). Therefore, speciation investigations are necessary to comprehend fisico-chemistry dynamics relations in the environment to evaluate the impact of these polutants in marine organisms.

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