

ECOTOXICITY AND CONTAMINATION ASSESSMENT INTO CUBATÃO RIVER SEDIMENTS, SP-BRAZIL

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ABSTRACT

Cubatão River Basin is located between São Paulo and Baixada Santista (coast), covering approximately 177km² area. Cubatão River as the main water source for the region which supply water to Cubatão and its industrial area, including Santos, São Vicente and partially to Praia Grande and Guarujá municipalities. Besides the huge importance of this river associated to the economical aspects, different types of environmental problems are faced in the region. CETESB confirmed toxicity in water during 2009 probably due to the influence of several industrial activities, especially phosphate fertilizer plant, oil refineries, chemical and steel industries. The objective of this paper was the assessment of acute and chronic biological effects through the exposition of different classes of organisms to water and sediments at laboratory conditions. *Ceriodaphnia dubia* and *Vibrio fischeri* bacteria were exposed to Cubatão water and *Hyalella azteca* were exposed to the sediments (100g of sediment + 200 mL of water, the same water used for growing the living organism). The following sites were sampled for sediments: **S0** (spring of water); **S2** (near the WTP - Water treatment plant for water supply); **S4** (near Companhia Brasileira de Estireno); **S5** (near Carbocloro S. A.); **S7** (Perequê River-influent at Cubatao); **S8** (Pilões River – influent at Cubatão). Neutron Activation Analysis was applied to the sediment samples in order to quantify some metals and trace elements. Point **S0** presented the highest concentration for Mn; **S2** for As and Ba; **S4** for Br, Cr, Fe, Mg and Na. Points **S5** and **S8** presented the highest concentration for all the rare earth elements (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb), Hf, Th and U. Point **S8** also presented the highest concentration for Ca, Ti, V and Zn. The Enrichment Factor (EF) and Geoaccumulation index (Igeo) were used to assess metals and trace elements contamination in the sediment samples. The EF was calculated using Sc as reference element for normalization purposes and Upper Continental Crust (UCC) as reference values. The ecotoxicity results evidenced sign of effects only on *V.fischeri* and non negative effects were observed on *C.dubia* when living organisms were exposed to the water of Cubatão. On the contrary for sediments samples, higher signs of effects were detected by *H.azteca* when exposed to the sediments.

Keywords: ecotoxicity, metals, NAA, sediments, trace elements.

1. INTRODUCTION

Aquatic environment faces huge impacts due to population growth, industrial activities and excessive use of waters which are commonly discharged in a worst contamination condition compared to raw water. Taking into consideration only health care products and pharmaceutical items hundreds of contaminants are discharged into waters everyday. Nevertheless it is not common to obtain acute toxicity in natural water even at impacted rivers and it is one of the reasons to include sediments evaluations at environmental monitoring programs and research.

Concentrations of contaminants in sediment may be several orders of magnitude higher than in the overlying water. Monitoring sediments are often recommended once they provide habitat for many aquatic organisms and is a repository for several persistent chemicals introduced at a given aquatic system [1].

Cubatão River Basin is located between São Paulo Metropolis and Baixada Santista (the coast), providing drinking water to several districts (Cubatão, Santos, São Vicente and partially to Praia Grande and Guarujá population). Besides the water supply for drinking, the water used at industrial activities are also supplied by Cubatão River [2].

Previous studies at Cubatão River Basin demonstrated benzo(a)pirene at sediments, heavy metals, mainly Hg and also mutagenicity and chronic toxicity, close to the sites sampled at COSIPA (steel industry) and Santos harbor Hg nos sedimentos [3, 4].

2. OBJECTIVE

The objectives of the present paper were to assess the acute and chronic toxicity into water and sediment from Cubatao River. Three classes of living organisms were exposed to those samples. Neutron Activation Analysis (NAA) technique was applied for some metals and trace elements determinations in the sediment samples.

3. METHODOLOGY

Water and sediment from Cubatão River have been sampled since March 2010 up to July 2011. During the samplings two rainy seasons were included (March 2010 and February 2011). Seven sites were sampled during the monitoring program and two of them are Piloes and Pereque Rivers, of interest once they are contributors and flows through Cubatão direction. Figure 1 shows the sampling sites location which allows the observation of the area and its use by concentrated local population and industrial production.

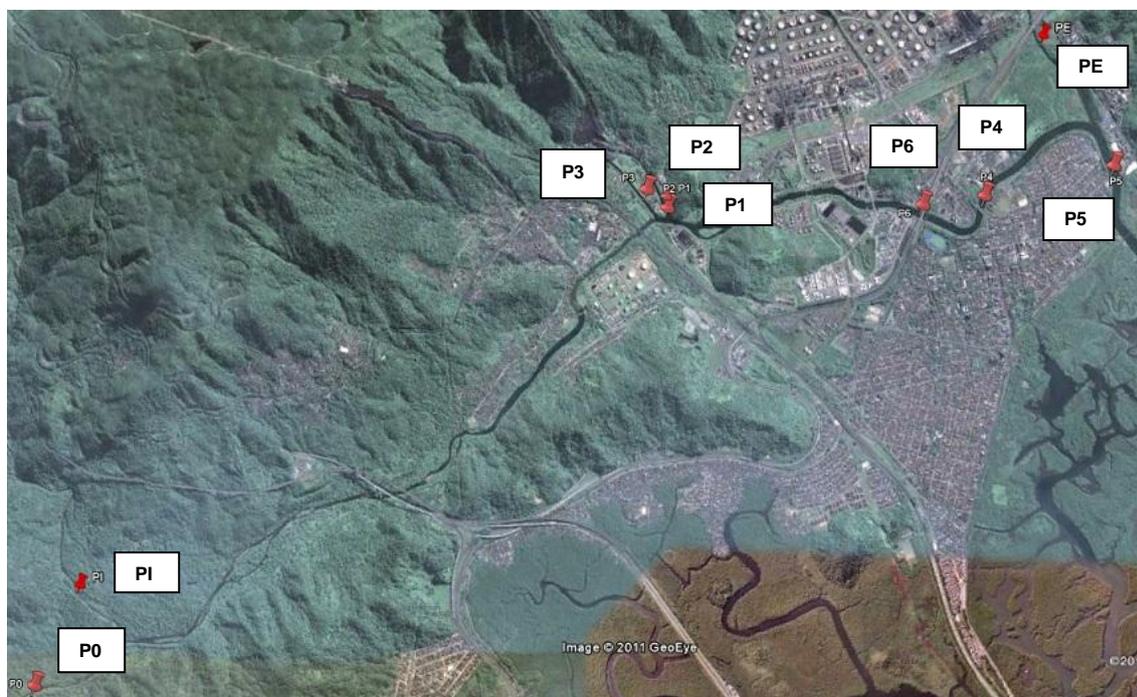


Figure 1. Indicative position of sampled sites at Cubatao region (Cubatão, Piloes and Pereque Rivers).

The toxicity assays were applied in order to assess the acute and chronic effects to exposed living organisms: *Vibrio fischeri* and *Ceriodaphnia dubia* were exposed to waters and *Hyalella azteca* was exposed to integral sediments. And besides, the inorganic and organic contaminants are being determined in order to complete the research and establish a relationship cause-effect of toxicity. All toxicity assays were carried out at LEBA/IPEN using living organisms from a proper growth.

The assays which applied *Vibrio fischeri* were carried out according to NBR 15411-2: 2006 [5], Microtox®, M-500 model, Microbics equipment which measure the bacterial luminescence in the presence of samples of interest. These assays initiated by a salinity sample adjustment (NaCl 20%) and the following sample concentrations were performed during this work: 20.7%, 31.6%, 46.6% and 70%. Linear regression analysis was performed to achieve the final results which were expressed as EC₅₀ (% v/v, 15 min), once exposure time was fixed in 15 minutes.

The chronic effects search for Cubatão water samples were performed on *Ceriodaphnia dubia* according to NBR 13373:2005 [6]. One neonate was exposed to water samples (10 replicates) for eight days and their growth and reproduction were registered and compared to the control samples (natural water used for keeping living cladoceras at Laboratory). KCl was the adopted reference substance and the assays were validated when at least 15 neonates were obtained at the control samples during the assays at the same conditions. Bioequivalence factor 0.79 and Toxstat (3.5) was the statistic program applied for running data [7, 8]. Samples were considered as Toxic or Not Toxic.

The sediments ecotoxicity assays were performed on *Hyalella azteca* according to NBR 15470:2007 [9]: 100 mL of sediments was mixed to 200 mL of natural dilution water and after 12 hours the *H. azteca* were introduced to the mixtures. Fish ration was the basic food for this specie. The exposition period was 10 days, when the organisms were keep in the sediments. To ending the assay the living organisms were registered and numbers were compared to the death results obtained in the control. KCl was the adopted reference substance and the assays were validated when at least 15 neonates were. T Test and bioequivalence were applied (B = 0.89 for *H. azteca*) and TOXSTAT, 3.5 [7]. To the control samples it was used an artificial net for keeping the organism as if it was the sediment. Samples were considered as Toxic or Not Toxic.

Neutron Activation Analysis Determination (NAA): sediment samples were previously dried at 45°C in a ventilated oven until constant weight. After this step, sediment samples were passed through a 2 mm sieve, ground in a mortar, once again passed through a 200 mesh sieve and then homogenized before analysis. The total fraction (< 2 mm) was analyzed. Approximately 200 mg of sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Sediment samples and reference materials were irradiated for 8 hours, under a thermal neutron flux of 10^{12} n cm⁻² s⁻¹ in the IEA-R1 nuclear reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ⁵⁷Co and ⁶⁰Co, respectively. The elements determined by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The analysis of the data was done by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by errors propagation. The methodology validation was verified by measuring the reference materials Buffalo River Sediment (NIST SRM 8704), Soil 7 (IAEA) and BEN (Basalt –IWG-GIT). Details of the analytical methodology is described at Larizzatti *et al* [10].

4. RESULTS AND DISCUSSION

As already pointed out the obtained data include water and sediments for toxicity evaluation and only sediments for inorganic determinations. Chronic effects data on *Ceriodaphnia dubia* was presented at Figure 2: comparative reproduction of microcrustacea in the presence of natural river water. When *Vibrio fischeri* luminescent bacteria was exposed to the same samples the light reduction numbers were organized at table 1.

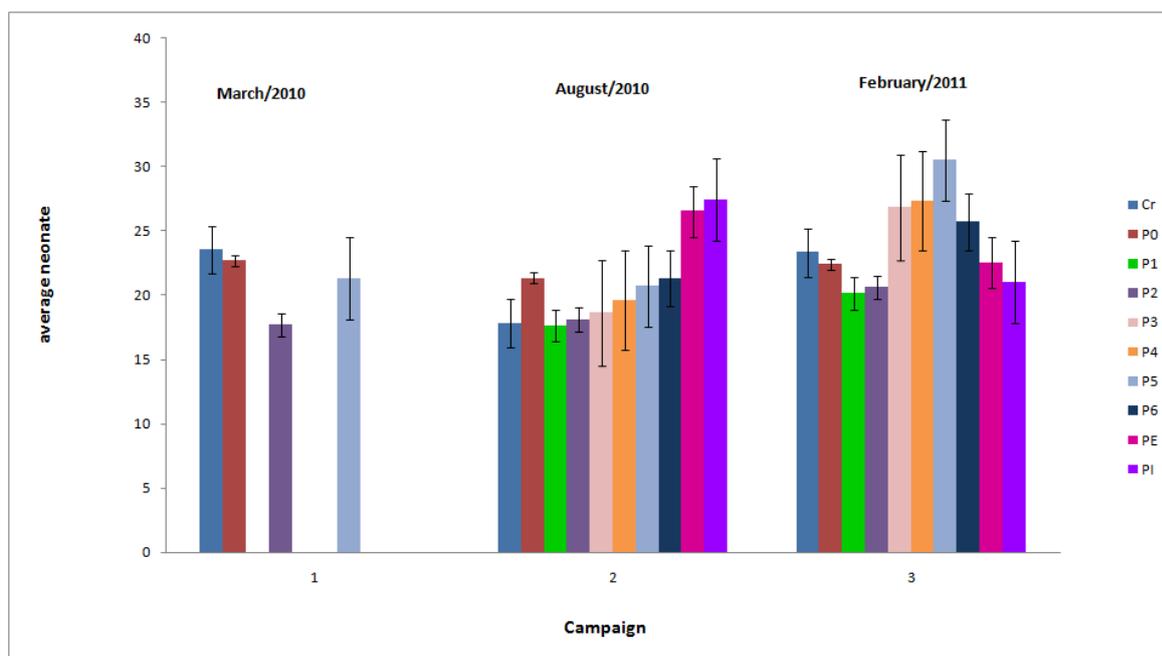


Figure 2. Average *C. dubia* neonates obtained during the exposition to water sampled at different sites.

Table 1. Effective average concentration of natural waters which reduced 50% of light (EC_{50}) *V. fischeri*.

EC_{50} (% _{v/v} , 15min)			
	<i>Campaign 1</i>	<i>Campaign 2</i>	<i>Campaign 3</i>
<i>P0</i>	71.61 (18.46-277.72)	47.92 (25.43-90.29)	36.33 (20.47-64.48)
<i>P1</i>	NR	32.98 (8.34-130.40)	37.90 (21.86-67.51)
<i>P2</i>	50.43 (32.25 - 78,85)	39.83 (12.41 – 127.77)	44.84 (26.15 – 76.87)
<i>P3</i>	NR	31.76 (8.14 – 123.85)	39.11 (27.97 – 54.68)
<i>P4</i>	NR	40.77 (23.57 – 70.51)	35.66 (18.46 – 68.87)
<i>P5</i>	51.89 (35.32-76.24)	31.15 (14.25 – 68.08)	34.43 (19.08 – 62.10)
<i>P6</i>	NR	34.00 (15.31 – 75.51)	41.04 (27.47 – 61.32)
<i>PE</i>	NR	37.93 (10.39 – 138.46)	32.64 (11.67 – 91.24)
<i>PI</i>	NR	59.90 (9.53 – 107.43)	35.55 (16.63 – 75.99)

NR – Not determined

The ecotoxicity data obtained for sediments were presented at Figure 3 and chemical determination at Table 2. The samples were reported as toxic when a significant mortality of organisms was obtained after compared to the data obtained at control samples and were indicated (*). From the results obtained for water samples it is possible to observe some indication of acute effects for *V.fischeri*, specially to the samples from sites: P2, P3 and P4 and most of samples resulted in a range of EC₅₀ value from 31,15% and 71,61%. Regarding to chronic effects to *C.dubia* although not possible to be determined once all the samples resulted in suitable reproduction numbers, it is easily to observe that when the test-organisms were exposed to samples from P1 and P2 their reproduction was lower if compared to the other sampling sites (Fig 2).

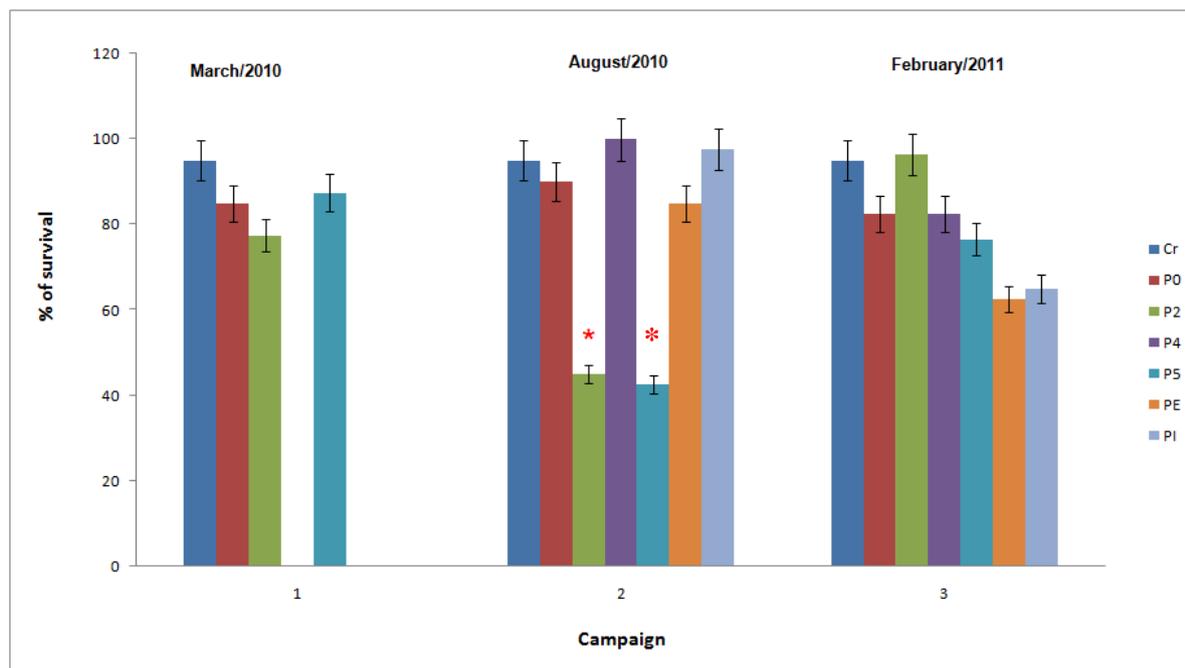


Figure 3. Surviving percentage of *H. azteca* when exposed to raw sediments.

On the other hand, the effects measured on *H. azteca* exposed to sediments revealed acute toxicity at P2 and P5, when more than 55% of test-organism dead, sampling from august 2010, and from the figure 3 it can also be observed that in February 2011 lower surviving of *H. azteca* was obtained to samples from Pereque and Piloos Rivers.

In general the samples collected during the dry season resulted in more biological effects than the others, allowing to a conclusion of more concentrated contaminants if compared to other samples. The effects observed at P2, P3, P4 and P5 are in accordance to the huge industrial activities developed there. CETESB [11, 12] also reported toxic effects on *V. fischeri* and *C. dubia* at these sites (Canal de Fuga II and Perequê River).

Neutron Activation Analysis (NAA) Results

Table 2 shows the results obtained for the sediment samples collected at Cubatão River in 6 sampling points and the reference values Upper Continental Crust (UCC) [13] and North American Shale (NASC) [14]. As we do not have these reference values (background values) for the region studied, it is commonly used to compare with these International Reference Values and considered them as our background values. The following sites were sampled for sediments: **S0** (spring of water); **S2** (near the WTP - Water treatment plant for water supply); **S4**

(near Companhia Brasileira de Estireno); **S5** (near Carbochloro S. A.); **S7** (Perequê River-suffers influence from Cubatao industrial pole); **S8** (Pilões River – suffer influences from Cubatao industrial pole). Point **S0** presented the highest concentration for Mn; **S2** for As and **Ba**; **S4** for Br, Cr, Fe and Na. Points **S5** and **S8** presented the highest concentration for all the rare earth elements (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb), Hf, Th and U. Point **S8** also presented the highest concentration for Ca, Ti, V and Zn.

Table 2. Results obtained (mg kg⁻¹) for the sediment samples (duplicate) from Cubatão River, by NAA technique (short and long irradiations) (concentration ± standard deviation), UCC and NASC values [13,14].

points	S0		S2		S4		S5		S7		S8		UCC	NASC
	Conc	St dev												
As	11.4	0.3	21.2	0.5	11.5	0.3	6.6	0.2	11.9	0.3	5.4	0.3	2	2
Ba	870	33	905	37	687	36	541	29	700	33	564	27	668	636
Br	1.2	0.1	1.4	0.1	26.9	0.3	11.5	0.2	1.9	0.1	4.0	0.1	1.6	0.69
Ca (%)	0.72	0.03	0.97	0.04	1.20	0.04	1.01	0.04	0.86	0.04	1.49	0.07	2,945	2.59
Ce	69.0	2.0	75.5	2.2	97.0	2.9	202	6.2	81.5	1.3	319	5	65.7	73
Co	9.9	0.1	10.4	0.1	13.7	0.2	10.3	0.2	11.8	0.2	10.7	0.2	11.6	28
Cr	52.7	1.0	71.3	1.3	76.9	1.4	56.4	1.0	77.0	1.5	76.9	1.5	35	125
Cs	4.7	0.2	5.6	0.2	6.8	0.6	5.6	0.5	5.0	0.3	3.6	0.2	5.8	5.2
Eu	0.87	0.04	1.12	0.05	1.25	0.05	1.34	0.06	0.98	0.04	2.26	0.14	0.95	1.24
Fe (%)	2.76	0.02	3.78	0.02	4.46	0.03	3.34	0.02	4.16	0.03	4.33	0.04	3,089	4
Hf	6.5	0.2	8.7	0.3	11.5	0.4	17.0	0.6	10.3	0.4	32.8	1.2	5.8	6.3
K (%)	2.3	0.2	2.3	0.3	1.9	0.3	1.8	0.2	3.1	0.3	3.0	0.3	2.86	3.29
La	31.4	0.3	38.1	0.4	46.1	0.5	79.9	1.3	39.3	0.6	163	2.4	32.3	32
Lu	0.38	0.03	0.53	0.04	0.50	0.03	0.70	0.05	0.53	0.05	1.02	0.09	0.27	0.48
Mn	979	66	679	35	590	91	457	45	832	10	555	57	527	465
Na	3394	43	3510	44	7898	107	4689	65	2791	36	2449	32	2.57	0.75
Nd	31	3	34	4	45	4	68	5	15	2	143	11	25.9	27.4
Rb	95	5	106	6	133	9	100	7	127	7	83	5	110	125
Sb	1.3	0.1	0.8	0.1	1.1	0.1	0.68	0.04	0.8	0.1	0.7	0.1	0.31	2.09
Sc	9.3	0.2	15.1	0.3	15.0	0.3	11.0	0.2	16.9	0.3	12.8	0.2	7	15
Sm	4.9	0.1	6.2	0.1	7.8	0.1	15.9	0.2	6.8	0.1	25.0	0.5	4.7	5.7
Ta	0.9	0.2	1.1	0.2	1.4	0.1	1.4	0.2	0.77	0.05	1.1	0.1	1.5	1.12
Tb	0.7	0.1	0.8	0.1	1.0	0.1	2.1	0.1	1.2	0.1	3.3	0.2	0.5	0.85
Th	12.5	0.2	15.5	0.3	19.0	0.3	28.6	0.7	15.6	0.3	51.6	1.0	10.3	12
Ti	2928	92	3130	92	3959	92	3394	92	2928	92	6119	92	0.31	0.42
U	2.7	0.1	3.2	0.2	3.7	0.2	5.4	0.1	3.0	0.1	9.7	0.2	2.5	2.7
V	47	10	58.9	0.5	63	1	47	2	66	2	85	16	53	130
Yb	2.4	0.2	3.2	0.2	3.1	0.2	4.8	0.3	2.8	0.2	6.0	0.3	1.5	3.1
Zn	60	3	75	3	99	3	77	3	72	3	104	4	52	85

In order to better evaluate the difference between metals and trace element concentration in the 6 sampling points the enrichment factor was calculated. The Enrichment factor (**EF**), defined as a double ratio normalized to a reference element (**RE**), is an index used as a tool to evaluate the extent of metal and trace element pollution [15,16]:

$$EF = ([M]/[RE]_{sed}) / ([M]/[RE]_{ref}) \quad (1)$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [16]. In the present study Sc was chosen as a reference element and UCC values as reference values for sediments [13].

According to Zhang and Liu [17], if $0.5 < EF < 1.5$, the elemental concentration is probably due entirely to crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. The higher the EF value the more severe the anthropogenic contribution.

Table 3 presents the results for the Enrichment Factor calculated using the UCC values as reference values and Sc as a normalizer element.

The $EF > 1.5$ was found for the elements As and Sb at points S0 and S4, including Br at point P4 as well. Points S2 and S7 presented an $EF > 1.5$ only for As. Points S5 and S8 presented an $EF > 1.5$ for the following elements: As (S5), Br (S5), Hf, Th and rare earth elements Ce, La, Lu, Nd, Sm, Tb, Th and Yb and U at point 8 (S8). In general, all the other results present $0.5 < EF < 1.5$ indicating that the elemental concentration is probably due to crustal or natural weathering origins. As a conclusion, a strong anthropogenic influence was observed for As, Br, Hf, Th, U and rare earth elements, mainly in the points 5 and 8 located near the Carbocloro chemical industry and Pilões River that receives influence from Cubatão industrial pole, respectively.

The geoaccumulation index (I_{geo}) has been used since the late 1960s, and has been widely employed in European trace metal studies [17]. Originally used for bottom sediments, it has been successfully applied to the measurement of soil and sediment contamination. The I_{geo} enables the assessment of contamination by comparing current and pre-industrial concentrations, although it is not always to reach pre-industrial sediment layers. In the present study the I_{geo} was calculated using the equation 2:

$$I_{geo} = L_n (C_n / 1.5B_n) \quad (2)$$

Where, C_n is the measured concentration of the element in sediment samples, B_n is the geochemical background value. In this study the UCC and NASC values were used for I_{geo} calculation since we do not have regional background levels for these elements and the results are shown in Table 3.

The geoaccumulation index consists of 7 grades or classes [18]: class 0 ($I_{geo} \leq 0$), practically uncontaminated; class 1 ($0 < I_{geo} < 1$), uncontaminated to moderately contaminated; class 2 ($1 < I_{geo} < 2$), moderately contaminated; class 3 ($2 < I_{geo} < 3$), moderately to heavily contaminated; class 4 ($3 < I_{geo} < 4$), heavily contaminated; class 5 ($4 < I_{geo} < 5$), heavily to extremely contaminated; class 6 ($5 < I_{geo}$), extremely contaminated.

Table 3 also presents the I_{geo} results calculated for both geochemical background values UCC and NASC for the results obtained by NAA technique. From the results we could conclude that:

- For most elements analyzed the I_{geo} accumulation index was $< zero$, indicating no- contamination in the sampling sites;
- As and Br presented the highest I_{geo} values; As ($1 < I_{geo} < 3$), except for S8; Br ($2 < I_{geo} < 5$) in the sampling sites S4, S5 and S8;
- The rare earth elements, Hf, Th and U presented $1 < I_{geo} < 2$ at S8 and $0 < I_{geo} < 1$ at S5.

As a conclusion from the results obtained for I_{geo} index we verified the presence of contamination for As in most sites, Br mainly at sites S4, S5 and S8 and for rare earth elements, Hf, Th, U in the sites S4, S5 and S8.

Table 3. I_{geo} accumulation index using UCC and NASC values as background values and Enrichment Factor (EF) using UCC values as background values.

	Igeo (UCC)						Igeo (NASC)						EF					
	P0	P2	P4	P5	P7	P8	P0	P2	P4	P5	P7	P8	P0	P2	P4	P5	P7	P8
As	1.9	2.8	1.9	1.1	2.0	0.8	1.9	2.8	1.9	1.1	2.0	0.8	4.3	4.9	2.7	2.1	2.5	1.5
Ba	-0.1	-0.1	-0.5	-0.8	-0.4	-0.8	-0.2	-0.1	-0.5	-0.9	-0.5	-0.8	1.0	0.6	0.5	0.5	0.4	0.5
Br	0.2	0.4	4.7	3.5	0.9	2.0	-1.0	-0.8	3.5	2.3	-0.3	0.8	0.6	0.4	7.8	4.6	0.5	1.4
Ca (%)	-2.4	-2.0	-1.7	-2.0	-2.2	-1.4	-2.6	-2.2	-1.9	-2.1	-2.4	-1.6	0.2	0.2	0.2	0.2	0.1	0.3
Ce	-0.7	-0.5	-0.2	0.9	-0.4	1.5	-0.5	-0.4	0.0	1.0	-0.3	1.7	0.8	0.5	0.7	2.0	0.5	2.6
Co	-2.1	-2.0	-1.6	-2.0	-1.8	-2.0	-0.8	-0.7	-0.3	-0.8	-0.6	-0.7	0.6	0.4	0.5	0.6	0.4	0.5
Cr	-1.8	-1.4	-1.3	-1.7	-1.3	-1.3	0.0	0.4	0.6	0.1	0.6	0.5	1.1	0.9	1.0	1.0	0.9	1.2

Cs	-0.7	-0.5	-0.2	-0.5	-0.6	-1.1	-0.9	-0.6	-0.4	-0.6	-0.8	-1.3	0.6	0.4	0.5	0.6	0.4	0.3
Eu	-1.1	-0.7	-0.6	-0.5	-0.9	0.3	-0.7	-0.3	-0.2	-0.1	-0.5	0.7	0.7	0.6	0.6	0.9	0.4	1.3
Fe (%)	-1.1	-0.7	-0.4	-0.8	-0.5	-0.5	-0.7	-0.3	-0.1	-0.5	-0.2	-0.1	0.7	0.6	0.7	0.7	0.6	0.8
Hf	-0.5	-0.1	0.3	0.9	0.1	1.8	-0.4	0.0	0.4	1.0	0.2	1.9	0.8	0.7	0.9	1.9	0.7	3.1
K (%)	-1.1	-1.1	-1.3	-1.4	-0.7	-0.7	-0.9	-0.9	-1.2	-1.2	-0.5	-0.5	0.6	0.4	0.3	0.4	0.5	0.6
La	-0.6	-0.3	-0.1	0.7	-0.3	1.8	-0.6	-0.3	-0.1	0.7	-0.3	1.8	0.7	0.5	0.7	1.6	0.5	2.8
Lu	-0.9	-0.4	-0.5	0.0	-0.5	0.5	-0.1	0.4	0.3	0.8	0.4	1.3	1.1	0.9	0.9	1.7	0.8	2.1
Mn	0.5	0.0	-0.2	-0.6	0.3	-0.3	0.3	-0.2	-0.4	-0.8	0.1	-0.5	1.4	0.6	0.5	0.6	0.7	0.6
Na (%)	-1.7	-1.7	-0.5	-1.3	-2.0	-2.2	-3.5	-3.5	-2.3	-3.0	-3.8	-4.0	0.1	0.1	0.1	0.1	0.0	0.1
Nd	-0.4	-0.3	0.1	0.7	-1.5	1.8	-0.3	-0.2	0.2	0.8	-1.4	1.9	0.9	0.6	0.8	1.7	0.2	3.0
Rb	-1.0	-0.8	-0.5	-0.9	-0.6	-1.2	-0.8	-0.6	-0.3	-0.7	-0.4	-1.0	0.7	0.4	0.6	0.6	0.5	0.4
Sb	-1.2	-1.9	-1.5	-2.2	-2.0	-2.1	1.5	0.9	1.2	0.6	0.7	0.6	3.2	1.3	1.6	1.4	1.0	1.2
Sc	-1.3	-0.6	-0.6	-1.0	-0.4	-0.8	-0.2	0.5	0.5	0.1	0.7	0.3	1.0	1.0	1.0	1.0	1.0	1.0
Sm	-0.8	-0.5	-0.1	0.9	-0.3	1.5	-0.5	-0.2	0.1	1.2	0.0	1.8	0.8	0.6	0.8	2.2	0.6	2.9
Ta	-0.9	-0.7	-0.3	-0.3	-1.1	-0.6	-1.4	-1.1	-0.7	-0.7	-1.5	-1.0	0.4	0.3	0.4	0.6	0.2	0.4
Tb	-0.8	-0.7	-0.3	0.7	-0.1	1.4	0.0	0.1	0.4	1.5	0.7	2.2	1.1	0.7	0.9	2.6	1.0	3.6
Th	-0.5	-0.2	0.1	0.7	-0.2	1.5	-0.3	0.0	0.3	0.9	0.0	1.7	0.9	0.7	0.9	1.8	0.6	2.7
Ti (%)	-1.1	-1.0	-0.7	-0.9	-1.1	0.0	-0.7	-0.6	-0.2	-0.5	-0.7	0.4	0.7	0.5	0.6	0.7	0.4	1.1
U	-0.6	-0.3	-0.1	0.4	-0.5	1.3	-0.5	-0.2	0.0	0.5	-0.3	1.4	0.8	0.6	0.7	1.4	0.5	2.1
V	-2.1	-1.7	-1.6	-2.1	-1.6	-1.2	-0.8	-0.4	-0.3	-0.8	-0.3	0.1	0.7	0.5	0.6	0.6	0.5	0.9
Yb	-1.0	-0.5	-0.6	0.1	-0.7	0.4	0.1	0.5	0.4	1.1	0.3	1.4	1.2	1.0	1.0	2.0	0.8	2.2
Zn	-1.1	-0.8	-0.4	-0.7	-0.8	-0.3	-0.4	-0.1	0.3	0.0	-0.1	0.4	0.9	0.7	0.9	0.9	0.6	1.1

According to Silva *et al* [19], uranium and thorium radionuclides were found in the sediments from Cubatão River in high concentrations. They concluded that the presence of phosphogypsum stacks, a waste by-product derived from the wet process production of phosphoric acid, present a potential threat to the surrounding environment and to the individual occupationally exposed. The phosphogypsum may be related to the high concentration of radionuclides at Cubatão River.

Luiz-Silva *et al* [4] detected Cu, Cd, Pb, and Hg in sediments from Cubatão River.

Cubatão Basin is a distached area where mercury is a relevant contaminant probably related to industrial activities and effluents discharges [20]. The contamination of water by phenol has also been reported and possibly phenol is one of the cause for the indicative toxic effects determined on *V. fischeri* at this present paper. *Vibrio fischeri* are more sensitive to phenol if compared to water fleas (*D. similis*) [12, 21].

5. CONCLUSION

Considering the obtained results, it was observed signs of acute toxicity on *Vibrio fischeri* (indicative effects) in water samples, EC₅₀ values ranged from 31.15% up to 71.61%. Chronic toxicity tests with *C. dubia* in the water samples showed no toxicity, however, lower reproduction was obtained for *C. dubia* exposed to waters collected at P1, P2, P4 and P5, when compared with the other points. The acute toxicity of sediment to *H. Azteca* revealed toxicity in points P2 and P5 in the 2nd campaign (August/2010), when more than 50% of exposed organisms died during the exposition. The Neutron Activation Analysis results confirmed P5 as a relatively worst site, showing the sediment from points P5 and PI higher concentration of metals and rare earths.

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