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Este Trabalho Técnico Científico foi preparado para apresentação no 3º Congresso Brasileiro de P&D em Petróleo e Gás, a ser realizado no período de 2 a 5 de outubro de 2005, em Salvador. Este Trabalho Técnico Científico foi selecionado e/ou revisado pela Comissão Científica, para apresentação no Evento. O conteúdo do Trabalho, como apresentado, não foi revisado pelo IBP. Os organizadores não irão traduzir ou corrigir os textos recebidos. O material conforme, apresentado, não necessariamente reflete as opiniões do Instituto Brasileiro de Petróleo e Gás, Sócios e Representantes. É de conhecimento e aprovação do(s) autor(es) que este Trabalho será publicado nos Anais do 3º Congresso Brasileiro de P&D em Petróleo e Gás

HEAVY METALS AND PETROLEUM HYDROCARBONS IN SEDIMENTS OF THE MANGROVE FROM SÃO FRANCISCO DO CONDE REGION – TODOS OS SANTOS BAY - BAHIA.

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Abstract - As part of the environmental assessment within Todos os Santos Bay, located in Recôncavo Bahiano, in summer of 2001, sediments samples of the mangrove were collected at eight locations to determine the spatial distribution of anthropogenic pollutants in the São Francisco do Conde Region. Muddy sediments with high organic matter content dominate the study area. Heavy metal levels indicated that sediments were moderately polluted with Zn (overall mean: 89 +/- 16 µg. g⁻¹ dry sediment), Pb (20 +/- 8), Cu (45 +/- 11), Cr (62 +/- 10), V (70 +/- 18), Ni (29 +/- 7) and Cd (0,3 +/- 0,5). Depending on location, aliphatic hydrocarbons reached from 8704 to 1899406 µg. g⁻¹, while the unresolved complex mixture represented up to 95% of the total aliphatic fraction. Total PAH concentrations ranged from 30 to 1754 µg. g⁻¹ except at one location, petroleum derivatives were identified as main local source. The results pointed out that almost all the area presented some substances that can cause adverse biological effects, especially in the inner region where all metals are above PEL levels.

Keywords: Heavy metals; Hydrocarbons; Sediments; Mangrove; Todos os Santos Bay.

Resumo – O município de São Francisco do Conde situado na porção norte da Baía de Todos os Santos foi palco da instalação da primeira refinaria de petróleo no Brasil, constituindo em ponto de partida para construção e consolidação da infraestrutura que se mostrou capaz de sustentar, nos anos seguintes, o processo de industrialização da região de todo Recôncavo Baiano. Com base na geoquímica de metais pesados caracterizaram-se dois ambientes distintos: um com maior influência das contribuições antrópicas oriundas das águas do rio Subaé e outro sob maior influência de atividades petrolíferas. Com o uso de biomarcadores moleculares específicos (alcanos saturados e hidrocarbonetos policíclicos aromáticos), avaliaram-se as contribuições naturais e antrópicas, estas últimas relacionadas ou não ao complexo petrolífero instalado. Comprovou-se que, ao longo das últimas décadas, volumes consideráveis de petróleo e derivados, com características distintas, foram introduzidos às regiões de manguezal na região de São Francisco do Conde ao norte da Baía de Todos os Santos.

Palavras-Chave: Metais pesados; Hidrocarbonetos; Sedimentos; Manguezais; Baía de Todos os Santos.

1. Introduction

The Subaé estuary, in São Francisco do Conde region, is part of the Todos os Santos Bay, which covering an area of around 1200 km² (Fig. 1); water depth reaches 6 m except in navigation channels (9–11 m depth). The Subaé estuary is a microtidal environment and its hydrodynamic is controlled mainly by ocean flow (Leão & Dominguez, 2000). Water temperature distribution in the Subaé estuary, shows a warm season from December to March.

The bay receives municipal effluents (either discharged untreated or with only primary treatment) of 1.5 million people (São Francisco do Conde, Santo Amaro and Feira de Santana city). In addition, it is the receptor of multiple industrial discharges including those of a metallurgic centre from Santo Amaro city and a major petroleum refinery Landulfo Alves – Mataripe (LAM) (Fig. 1). To date, information regarding the local pollution level and its effects is very limited. Veiga (2003) and Santos (2002) studied hydrocarbon and heavy metal concentrations in intertidal sediments retrieved along the coast of the São Francisco do Conde area and found sediments at the mouth of the Subaé stream, to be contaminated particularly by chromium, a metal released with the untreated wastewaters. Here, we present results regarding the distribution and sources of heavy metals and hydrocarbons, and discuss their potential impacts in the context of other relevant environmental characteristics.

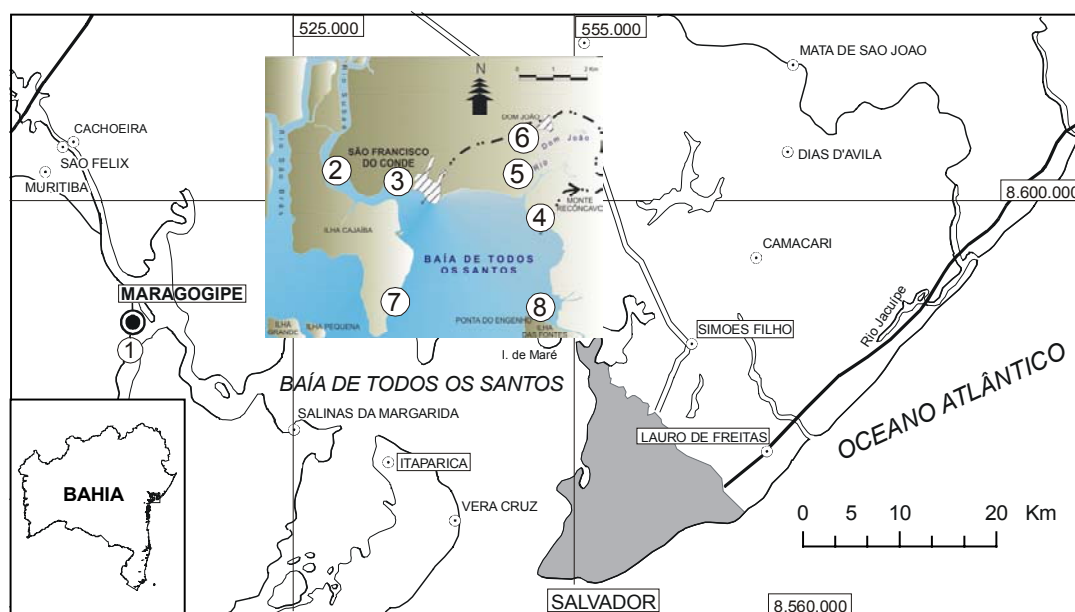


Figure 1 – Location of Todos os Santos Bay and the eight stations marked 1 in Maragogipe and 2 to 8 in São Francisco do Conde Region.

2. Material and methods

2.1. Sample collection and storage

On, February, March and December of 2001, sediments were collected at eight locations within Subaé Estuary in São Francisco do Conde (SFC) area; the exact position of each was recorded using a global positioning system. Stations 7 and 8 represented the harbor openings, while stations 4, 5 and 6 corresponded to intermediate locations. Stations 2 and 3 were more coastal sites in the fluvial basin; station 1 was located just off the Subaé Estuary (Fig. 1).

At each station, 3 sediment samples were collected with manual corers of 4.5 cm internal diameter. Granulometric analysis was performed on three cores, the upper centimeter of the sediments of three other corers, stored in a PE vial in the cold, served for quantification of organic matter. Sediments contained in three metallic corers were transferred to tin foil and frozen in aluminum bottles until analysis of hydrocarbons. Two acrylic corers were stored in vertical position in the cold; upon arrival at the laboratory, one of them was used for heavy metal analysis and the other one was used to measure pH.

2.2. Digestion of samples and quantification of heavy metals

Samples were prepared at the Mangrove Biogeochemistry Studies Laboratory of the Federal University of Bahia – Geosciences Institute (UFBA-IGEO) and analyses done at the Pedro Ribeiro Technology Industrial Center (CETIND). The superficial five centimeters of the corer sediments that passed through a PE-mesh of 63 µm were dried at 85 °C to constant weight, prior to homogenization by an agate mortar and pestle. In order to avoid interference of organic matter in the results, and convert the metals to their free form, applying method no. 3051 of the EPA

(Anonymous, 1990), duplicates of sub-samples (0.5–1 g) were mixed with 10 ml concentrated nitric acid and digested by microwave (CEM, MDS 2100) in a closed fluorocarbon vessel.

Quality control included procedural blanks, measurement of standards obtained from the National Institute of Standards and Technology and spiked samples. Results presented in $\mu\text{g. g}^{-1}$ dry sediment ($< 63 \mu\text{m}$) for Cd, Zn, Cu, Cr, Ni, Pb and V, correspond to mean values of duplicate analyses. Variation between duplicates was always less than 5%.

2.3. Extraction and quantification of aliphatic and aromatic hydrocarbons

Following drying at 50 °C to constant weight, 30 g of the sample was extracted for 8 h by Soxhlet with a ultrapure hexane. The organic extracts were concentrated using a rotary evaporator, and purified and fractionated by silica/alumina gel chromatography into aliphatic and aromatic hydrocarbons. Aliphatic fractions were injected into a Hewlett Packard 6890 gas chromatograph with flame ionisation detection. Aromatic hydrocarbons were measured in a HP-MSD 5973 system, with mass detection in selected ion monitoring mode. In both instruments a 25-m HP Ultra II capillary was used, programmed 40–60 °C at 10 °C min⁻¹ and 60–300 °C at 4 °C min⁻¹. Quantification was performed using internal standards. The analytical program was conducted under a laboratory quality assurance protocol, including analysis of reference material (NIST-1941), procedural blanks and participation in international inter-calibration exercises.

2.4. Data analyses

The results of heavy metals, n-alkanes, as well as aliphatic and total PAHs were compared using Student's t-test. Pearson linear correlation analyses were performed to determine the degree of relationship between the variables studied. Variables detailed in Table 1.

Table 1 – Variables analysed in surface sediments at eight sampling stations in São Francisco do Conde Region.

	Stations Sample	Maragóipe* 1	Subaé* 2	S.F. Conde 3	Dom João 4	Dom João* 5	Dom João* 6	Ilha Cajaliba* 7	Ilha Fontes* 8
Granulometry (%)	Coarse Sand	53,00	1,00	1,00	1,00	1,00	1,00	20,00	61,00
	Fine Sand	7,33	5,33	5,33	10,00	10,00	11,00	12,00	4,00
	Silt	14,00	12,67	16,67	13,00	22,00	23,00	13,00	3,00
	Clay	25,66	81,00	77,00	76,00	67,00	65,00	55,00	32,00
Physico-chemistry	pH	6,12	6,50	7,11	7,17	7,13	7,18	7,64	6,51
	Delta pH	0,23	-0,09	-0,15	-0,20	-0,41	-0,26	-0,29	-0,15
	O.M. (%)	36,31	44,01	42,71	54,31	49,89	52,40	29,69	25,52
Metals	C/N	421,20	127,67	148,33	350,00	289,00	338,00	246,33	165,00
	Fe (%)	3,47	3,65	4,27	4,16	3,84	4,17	6,13	3,35
Heavy Metals (ppm)	Al(%)	5,03	3,76	5,42	5,29	5,83	6,02	6,71	4,48
	Pb	8,67	30,33	29,33	18,00	23,00	21,00	10,33	23,66
	Cd	0,04	0,81	1,29	0,06	0,12	0,05	0,28	0,02
	Zn	50,33	98,00	100,00	99,00	95,00	95,00	87,67	89,00
	Cu	22,67	41,00	42,00	45,00	46,00	47,00	55,67	58,67
	Cr	56,67	45,33	62,00	68,00	69,00	71,00	75,33	50,67
	V	56,00	51,33	71,00	66,00	74,00	75,00	107,67	55,67
	Ni	17,67	32,00	25,33	33,00	31,00	32,00	39,67	24,33
Other hydrocarbons	HTP	8704,24	120646,28	111541,03	47710,12	1899406,52	53069,61	132701,38	93905,71
	HRP	1644,24	98495,28	77897,03	2536,12	1074571,50	34979,61	72214,38	63920,71
	UCM	7060,00	22151,00	33644,00	45174,00	824835,02	18090,00	60487,00	29985,00
	n-alkanes	235,85	2759,55	2361,46	1297,36	6738,83	432,75	2748,27	2035,99
	n-alk/HTP(%)	2,71	2,29	2,12	2,72	0,35	0,82	2,07	2,17
	n-alk/HRP(%)	14,34	2,80	3,03	51,16	0,63	1,24	3,81	3,19
	UCM/HTP	0,81	0,18	0,30	0,95	0,43	0,34	0,46	0,32
	HRP/HTP	0,19	0,82	0,70	0,05	0,57	0,66	0,54	0,68
Polycyclic Aromatic Hydrocarbons (PAHs) - ng/g	Naftalene	6,37	9,49	17,60	11,00	27,35	11,24	7,94	12,36
	Acenafilene	n.d.	n.d.	41,30	0,50	18,97	n.d.	n.d.	n.d.
	Acenafthene	n.d.	n.d.	45,80	n.d.	n.d.	n.d.	22,20	6,40
	Fluorene	n.d.	n.d.	10,40	2,00	n.d.	n.d.	28,87	8,38
	Anthracene (An)	n.d.	2,22	n.d.	12,00	n.d.	1,02	97,37	26,08
	Phenanthrene (Phe)	3,83	3,65	56,20	69,90	n.d.	6,28	258,71	81,42
	Fluoranthene (Fit)	3,60	3,45	207,8	201,30	n.d.	5,96	280,82	90,61
	Pyrene (Py)	3,67	3,28	128,3	149,30	44,17	4,51	209,37	62,71
	B(a)anthracene (BaA)	2,89	2,86	64,1	80,90	25,87	2,35	124,52	41,67
	Chrysene (Chry)	3,50	4,95	114,8	149,40	169,41	5,61	170,68	53,14
	B(b)fluoranthene (BbF)	2,52	n.d.	-	-	44,2	4,31	107,83	27,68
	B(k)fluoranthene (BkF)	5,00	n.d.	141,7	182,80	54,18	7,01	136,49	51,74
	B(a)pyrene (BaP)	2,96	n.d.	72,1	182,80	123,57	4,53	130,92	33,89
	B(e)pyrene (BeP)	-	-	-	-	-	-	-	-
	Perylene (Per)	-	-	-	-	-	-	-	-
	B(g,h,i)perylene	2,44	n.d.	32,3	111,40	n.d.	4,30	74,81	22,58
	Indeno(1,2,3-cd)pyrene (IPy)	2,21	n.d.	72,6	110,90	n.d.	3,44	70,44	19,57
	Dibenzo(a,h)anthracene (DBA)	n.d.	n.d.	-	-	n.d.	n.d.	33,08	9,60
	Total PAH's	38,99	29,90	1005,00	1264,20	507,72	60,56	1754,05	547,83

3. Results and discussion

3.1. Surface sediment characteristics

Muddy fractions ($< 63 \mu\text{m}$) dominate the sediments in SFC area (Table 1). This is also the prevailing

type of sediment in the outermost region of Todos os Santos Bay (Lessa et al., 2000), and is in accordance with the general pattern determined for the Subaé estuary. This is not surprising, since fine sediments carried into the basin through fluvial discharge are likely to form sharp suspended sediment gradients at estuarine fronts (Pinckey and Dustan, 1990) such as the one that characterizes SFC coastal zone. Fronts in an estuary tend to inhibit exchange and to trap effluents or fine sediments within restricted water masses (Duck and Wewetzer, 2001). Fine particulate material tends to flocculate and sediment out of the water column, increasing ion scavenging, and concentrating sediment-associated contaminants in these areas (Duck and Wewetzer, 2001).

In general, the organic matter content of sediments was higher than of the nearby regions (Veiga, 2003), with a spatial gradient from the inner (station 2) to the outer region (station 7) of the harbor. As the entire study area is dominated by muddy (silt and clay) sediment fractions, weak correlation between sediment fractions and organic matter content could be detected as it would be expected (Gray, 1981). The deposition of complexes formed by organic and clay particles commonly occurs in areas of reduced hydrodynamic energy and leads to organic enrichment of the sediments, and consequently, depletion of oxygen. Reduced conditions were detected at sampling stations 2 and 8.

3.2. Heavy metal concentrations and distribution

A wide range of values for heavy metal concentration was observed for the surface sediments of SFC area (Table 1). The lack of correlation between heavy metal concentration and granulometric fractions is explained by the fact that in the study area the surface sediment is fairly homogeneous (Table 1).

Zn levels at $89 \pm 16 \mu\text{g g}^{-1}$ were high and in the same range as those detected previously (Queiroz, 1992; Paredes et al. 1995) in the contiguous area of SFC area. Zn is frequently associated with sewage. Chromium ranged between 45 to $75 \mu\text{g g}^{-1}$. Taking into account the prevalent water circulation pattern, and assuming the Subaé stream as the main source of Cr in the area we can suppose that it enters the harbor basin through NE open. Usually, Cr has been considered a metal with low biogeochemical mobility, which should reduce its toxicity potential (Abel, 1989); however, lately, questions regarding bioavailability through ingested sediments have been raised (Chong and Wong, 2000).

In general, maximum levels of lead in sediments were found at stations 2 and 3 (Table 2). Pb in SFC area is distributed mainly in the carbonate and oxide fractions of the sediment, implying that a high percentage of Pb can be removed from sediments by a decline in pH (carbonate fraction) or by a decrease of redox potential (oxide fraction), due to input of organic matter or the depletion of dissolved oxygen. Thus both the low pH measured over 24 h (6.92 ± 0.49) and low redox values may contribute to the removal of Pb from the sediments. The increasing urbanisation of the region is thought to be responsible for the introduction of large quantities of Pb originating from fuel combustion, urban sewage, marine traffic and the LAM petroleum refinery. Pb has no known biological function; therefore, its effects on biological communities are very harmful (Kennish, 1992).

Copper values reported here was higher than those reported in previous studies particularly in the inner harbor where it reached up to $58 \mu\text{g g}^{-1}$ (Table 1).

The only metal that presented a fairly homogeneous distribution in the study area was Ni showing an overall mean of $29 \pm 7 \mu\text{g g}^{-1}$. Ferromanganese minerals and ferrous sulfides are among the natural sources of this element. Average nickel concentrations are $94 \mu\text{g g}^{-1}$ in igneous rocks and between 2.6 and 29 for different types of sedimentary rocks (Wedepohl, 1971).

Cadmium (Cd) presented the lowest levels (Table 1); however, it show very high toxicity to both aquatic and terrestrial organisms even at low concentrations (Kennish, 1992). For dissolved cadmium, acute LC50 values as low as $3.5 \mu\text{g l}^{-1}$ have been demonstrated for planktonic organisms (Versteeg and Giesy, 1986). Although Cd is sulphur seeking metal that tend to precipitate in anoxic sediments, experiments carried out at concentrations close to or lower than the values found in this study, show that they can still be assimilated from anoxic sediments with high organic matter content (Griscom et al., 2000; Chong and Wong, 2000; Lee et al., 2000); therefore they can potentially bioaccumulate through dietary uptake.

Comparing the overall means of the heavy metal levels (entire study area) with the EPA sediment guidelines (Anonymous, 1977) and Long et al. (1995), SFC area can't be considered as polluted by Cu, V, Cr, Pb Ni and Cd, but polluted by Zn. We used these data as reference due to the lack of references and background values from bottom sediments from Brazil. Generalizations involving metal concentrations at a regional level are difficult since the different authors have not always used the same analytical procedure, and also minor differences in geological and environmental characteristics can result in great disparities regarding metal concentrations (Lacerda et al., 1998).

Maximum levels of the heavy metals studied here were almost always recorded in the innermost harbor region (stations 2, 3 and 4). Since the circulation in the bay is clockwise, pollutants originating from Subaé and Dom João streams and the LAM refinery enter with water through the harbor opening in the NE, next to station 3, and tend to deposit within the inner region, i.e. in the areas with the slowest water circulation and least affected by dredging. Since the inner harbor is not subject to dredging activity, sediments (and pollutants) will be remobilised to a lesser extent than in the other parts of the study area.

The high degree of association between Ni, V and Cr is evident (Pearson coefficient $r \geq 0.77$, $p < 0.001$) and was reported in the literature for different urbanised and polluted areas (e.g. Spencer, 2002).

3.3. Aliphatic hydrocarbons

Total aliphatic hydrocarbon levels ranged from 8704 to $1899406 \mu\text{g g}^{-1}$ (Table 1). Our results are in the same range as those of highly contaminated areas such as Santos harbor in Brazil (Nishigima et al., 2001) and Hong Kong

(Zheng and Richardson, 1999). Following the 1991 Gulf War oil spill, total aliphatic hydrocarbon concentrations in the Arabian Gulf ranged from 5.4 to 92 $\mu\text{g g}^{-1}$ (Al-Lihaibi and Ghazi, 1997).

The UCM/n-alkanes ratio has been used as a marker for petroleum inputs, and a value above 4 represent petroleum related sources of compound (Simoneit, 1984). In most SFC samples this ratio is above 4.

3.4. Polycyclic aromatic hydrocarbons

Total PAH concentrations ranged from 30 to 1754 $\mu\text{g g}^{-1}$, i.e. similar to those observed in severely polluted areas such as Santos (Nishigima et al., 2001), Boston harbour (Shiaris and Jambard-Sweet, 1986) and the north-west coast of the Mediterranean Coast (Benlahcen et al., 1997).

In general, the highest concentrations were found at stations 3, 4 and 7, the lowest at stations 2 and 6 (Table 1). PAHs may originate from two main anthropogenic sources: the direct release of oil products and the combustion of fossil fuels. It is often difficult to identify the real source because PAHs are introduced into the environment by diverse routes and one source can be obscured by another (Wang et al., 1999). The presence of alkylated aromatic hydrocarbons (Table 1) indicates a contribution from fresh petroleum sources because the combustion of oil or its derivatives does not produce alkylated aromatic hydrocarbons (Law and Biscaya, 1994).

Numerous diagnostic ratios have been defined to differentiate the sources including the phenanthrene/methylphenanthrenes and naphthalene/methylnaphthalenes ratios. With the exception of station 1, the remaining locations always presented ratios of less than 1 (Table 1), showing that petroleum and its derivatives are the main local source.

3.5. Potential adverse effects associated with the levels of contaminants in the area

The results obtained for the metals studied was evaluated for adverse effects on biological organisms using available 'sediment quality values' (SQVs) and sediment quality guidelines. The usefulness of SQVs, generally considered site-specific, is subject to controversial discussions (Dell-Valls and Chapman, 1998). SQVs have not been established for Brazil; nevertheless, in an attempt to grossly estimate possible adverse effects of contaminants on the benthic fauna, data obtained in this study were compared to SQVs reported by DellValls and Chapman (1998) for the Gulf of Ca'diz and San Francisco Bay. Various toxicity and bioaccumulation tests can be performed to evaluate the biological significance of contaminants in sediments. Based on toxicity laboratory tests, the Threshold Effect Level (TEL) and Probable Effect Level (PEL) have been defined. Toxicity rarely occurs below the TEL and frequently above PEL (MacDonald et al., 1996).

Related to heavy metals we can partially conclude that (i) the inner region of the harbor presented heavy metal concentrations that can't cause major adverse biological effects, except for Ni and Zn; and almost all the metals are above PEL level, the exceptions are Ni and Zn that are between TEL and PEL; (ii) stations 4, 7 and 8 presented Pb and Cr levels that are below the minimum adverse biological effect level or without effects, but its concentrations are between TEL and PEL levels; (iii) Ni concentrations were always below the level of no or minimal adverse biological effects but according to the sediment quality guidelines all the values ranged between TEL and PEL levels.

Some PAHs are known to be mutagenic and carcinogenic and may cause metabolic and behavioural changes in aquatic organisms (Grimmer, 1985; Law and Biscaya, 1994). In all samples at least one of the analysed contaminants was present in excess of the TEL level, and most of them (81%) had at least one analyte in excess of PEL.

4. Conclusions

In the study area, total aliphatic hydrocarbons and PAH levels were in the same range as those determined in heavily polluted areas worldwide. PAH-ratios as well as n-alkanes show that the main local source of hydrocarbons is petroleum and its derivatives, the elevated proportions of UCM pointing to long-term petroleum contamination. At the levels present within the inner harbor region where water exchange is reduced, Cd, Zn, Cu, Cr, Pb, Ni and V may cause major adverse biological effects. Compared to a previous study, an important enrichment of Cu in sediments was detected.

The study area can be divided into three regions, with different degree of environmental pollution (Fig. 1). Even though the inner region is the most affected by human activities, most of the parameters investigated in this study indicate that the entire harbor area is impacted. Urgently, in SFC area and particularly in Subaé Estuary, an environmental monitoring system is needed. The degree of pollution is attributed to the lack of governmental control regarding anthropogenic inputs rather than the magnitude of industrialization in BTS. Therefore, efficient governmental controls for industrial and municipal discharges should be established. Taking into account the very high loads of heavy metals, hydrocarbons and organic, the present situation implies serious risks to human health.

5. Acknowledgements

The study was funded by the FINEP – CTPETRO no. 640002700 and support from CAPES.

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