IBP 2338_08
TOTAL PETROLEUM HYDROCARBONS AND TRACE METALS IN A TROPICAL ESTUARY OF TODOS OS SANTOS BAY, BRAZIL

Joil José Celino[1], Olívia Maria Cordeiro de Oliveira[2], Jorge Alberto Trigüis[3], Antônio Fernando de Souza Queiroz[4], Karina Santos Garcia[5]

Resumo

Como parte da avaliação ambiental da baía de Todos os Santos, Bahia - Brasil, no verão de 2005, amostras de água superficial e sedimentos do manguezal foram coletados em cinco locais para determinar a distribuição espacial dos poluentes antropogênicos no estuário do rio Dom João na região de São Francisco do Conde. Sedimentos arenosos com baixo teor de matéria orgânica dominam a área de estudo. Níveis de metais traço indicaram que os sedimentos foram moderadamente poluídos com Cu (média geral: 21,48 +/- 4,76 $\mu g.g^{-1}$ sedimento seco), mas não com Pb (15 +/- 8), Zn (38 +/- 10), Cr (15 +/- 7), Ni (13 +/- 6) e Cd (0,4 +/- 0,2). Dependendo da localização, os hidrocarbonetos totais de petróleo variaram de 1,6 para 10,6 $\mu g.g^{-1}$. A análise da componente principal (ACP) revelou as principais relações entre as variáveis e as estações investigadas e confirmou os resultados analíticos. Análise das componentes principais confirma a distinção entre duas regiões de acordo com a sua qualidade ambiental. Os resultados apontam que quase toda a área apresentou algumas substâncias que podem causar efeitos biológicos nocivos, especialmente na região costeira, onde alguns metais estão acima do nível TEL.

Abstract

As part of the environmental assessment within Todos os Santos Bay, State of Bahia - Brazil, in summer of 2005, superficial water and sediments samples of the mangrove were collected at five locations to determine the spatial distribution of anthropogenic pollutants in the Dom João estuary at the São Francisco do Conde Region. Sandy sediments with low organic matter content dominate the studied area. Trace metal levels indicated that sediments were moderately polluted with Cu (overall mean: 21.48 +/- 4.76 $\mu g.g^{-1}$ dry sediment), but not with Pb (15 +/- 8), Zn (38 +/- 10), Cr (15 +/- 7), Ni (13 +/- 6) and Cd (0.4 +/- 0.2). Depending on location, total petroleum hydrocarbons ranged from 1.6 to 10.6 $\mu g.g^{-1}$. To discriminate pattern differences and similarities among samples, principal component analysis (PCA) was performed using a correlation matrix. PCA revealed the latent relationships among all the stations investigated and confirmed our analytical results. Principal components analysis confirmed two regions according to their environmental quality. The results pointed out that almost all the area presented some substances that can cause adverse biological effects, especially in the outermost region where some metals are above TEL level.

1. Introduction

Coastal wetlands are among the most biologically important and productive ecosystems on earth. Coastal wetlands also possess high socioeconomic values. They play important roles in the protection of shorelines and banks from erosion and can be used to treat domestic and industrial wastewaters.

[1] Doutor, Geologia Regional – Instituto de Geociências – Universidade Federal da Bahia. Professor.
[2] Doutora, Geoquímica Ambiental – Instituto de Geociências – Universidade Federal da Bahia. Professora
[3] PHD, Geologia do Petróleo – Lenep – Universidade Estadual do Norte Fluminense. Aposentado.
[4] Doutor, Geoquímica de Manguezais - Instituto de Geociências – Universidade Federal da Bahia. Professor.
[5] Doutoranda, Geoquímica Ambiental – Instituto de Química - Universidade Federal Fluminense. Pesquisadora.

Contamination of the aquatic environment has become a serious problem in many parts of the world, with rivers and bays often seriously affected. Almost all marine coastal ecosystems have complex structural and dynamic characteristics that can be easily modified by human influence.

Oil exploration started in the early 1950s in the State of Bahia (northeastern, Brazil), when environmental issues were not relevant for coastal planning. Todos os Santos Bay (TSB) is located in Bahia State, Brazil (Fig. 1). This bay with an area of 927 km^2 is the largest on the Brazilian coast. TSB is described as a coastal body of water, strongly influenced by the masses of oceanic waters, varying in salinity from 28 to 36‰.These factors contribute to the low water residence time in the bay, minimizing the effects of the industrial effluents discharged into the bay. This region is influenced by tropical climate with a well defined rainy season from April to June.

The studied area, called DOM JOÃO, is located in the northeast portion of Todos os Santos Bay (Fig. 1). It is a shallow area with depths varying from 0.1 to 1.2 m. There was an oil production field of PETROBRAS adjacent to Dom João estuary. The Dom João river flow through zones with mangrove vegetation and carry wastes from industries and urban centers.

The sediment and physic-chemical data of the benthic environment in the northeast portion of Todos os Santos Bay, should contribute to the understanding of bottom dynamics, sedimentary processes and contaminant distribution patterns, including the content and distribution of total petroleum hydrocarbons and trace metals in the sediments.

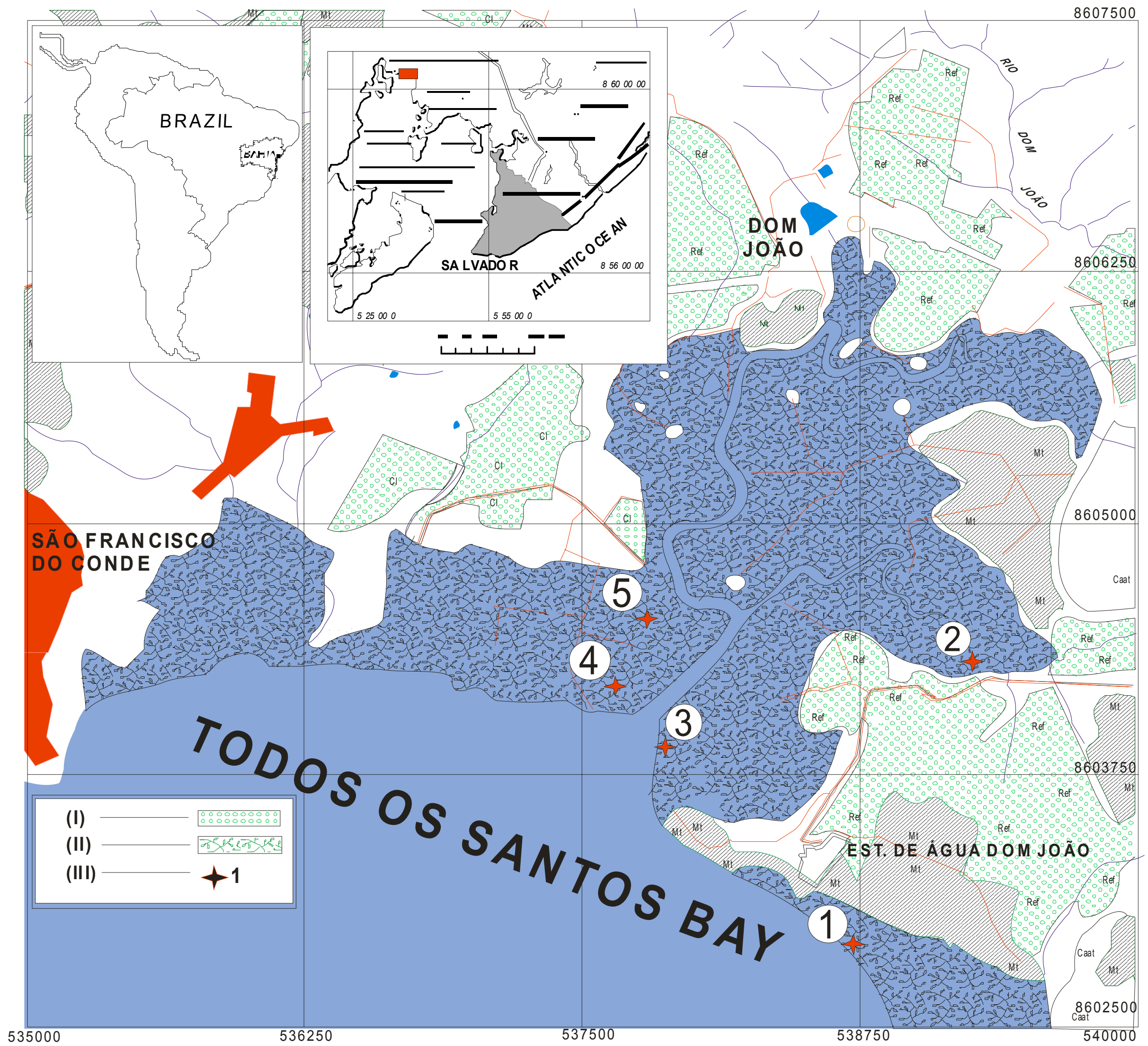

Figure 1. Location of Todos os Santos Bay, northeastern of Bahia State - Brazil - showing the sampled stations at Dom João region (Sts. 1 – 5). (I) Other vegetation; (II) mangrove and (III) stations (Sts).

2. Material and methods

Salinity, temperature, dissolved oxygen concentration, Eh and pH data of superficial water were obtained. Sediment sampling locations are shown in Fig. 1. At each station, five sediment samples were collected with a manual Kajac corer (10,0 cm internal diameter) for the following analyses: granulometric parameters, total organic matter (OM), total organic carbon (TOC), total nitrogen (N), chromium, zinc, copper, nickel, lead, cadmium and hydrocarbons.

The sediment for the analyses corresponded to the first 3 cm of the sediment column. TOC and N were determined using ca. 0.5 g of freeze dried and weighed sediment, and analysis in a LECO CNS 2000. The results are presented as percentages.

The trace metal results (Cr, Zn, Cu, Ni, Pb and Cd) correspond to mean values of duplicate analyses and are expressed in $\mu g\ g^{-1}$ dry sediment (<63 μm). The variation between duplicate analyses was always less than 5%. The superficial sediment of each core that passed through a PE-mesh of 63 μm was dried at 85°C until constant weight, prior to its homogenization with an agate mortar 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 (0.5–1.0 g) were mixed with 10 mL concentrated nitric acid and digested by microwave (Provecto DGT 100 plus) in a closed fluorocarbon vessel. Quantification was performed by ASS (Varian AA-220FS) with graphite furnace atomization (Varian GFA-4B). Quality control included procedural blanks, measurement of standards obtained from the National Institute of Standards and Technology (STSD-4 Stream Sediment Samples) and spiked samples.

For trace organic contaminants, the surface sediments were placed in pre-cleaned aluminum boxes, and then stored in a freezer at -15°C before laboratory analysis. The analytical procedure adopted for hydrocarbons analyses, including details of extraction, quantification and chromatography equipment, was that detailed by Celino & Queiroz (2006).

Procedural blanks contained a few minor contaminant peaks that did not interfere with the analyses of target compounds. A spiked-recovery experiment was conducted simultaneously with sample extraction, and the recoveries ranged 70–120% for hydrocarbons.

Statistical analyses, including Pearson's Product-Moment correlations between all the sediment variables studied, were performed in order to determine the degree of relationship. The variables were analysed for normality using Kolmogorov–Smirnov test and when this analysis failed to meet assumptions for parametric statistics, transformations were applied to give the best approximation to normality. An ''environmental variable · sampling sites''
(variables previously standardized) matrix was constructed to perform a principal components analysis (PCA). The PCA was used in order to characterize spatial aggregation within the study area on an environmental basis.

3. Results and discussion

In the inner region of Todos os Santos Bay, sediment grain size distribution, organic carbon and nitrogen contents (Table 1) were consistent with those previously reported by other authors (Lessa *et al.*, 2001; Celino *et al.* 2005; Hadlich *et al*., 2007). It would appear that, at least potentially, the supply of particulate matter has been derived from riverine inputs. The dominance of fine sand with an important contribution of mud (Table 1) shows that the area can be characterized as a low energy environment.

Total organic matter (TOM) showed lowest values at those stations located in front of river mouths (Table 1). Total organic carbon (TOC) and TOM showed the same distribution pattern and were highly correlated (Table 2). Total nitrogen showed the same distribution pattern as TOC, and presented the highest correlation between the variables analyzed ($r = 0.659$, $p < 0.0005$). Concerning the source of sedimentary organic matter, C/N ratios suggested a mixed origin of the sedimentary organic matter (Jaffé *et al*., 2001).

In general, metal contents were low (Tab. 1, Fig. 2), but some stations were highlighted for their Cu and Cr values, such St. 1 and 3 for Cr and St. 1 for Zn. In all cases Zn, Cr and Cu were low at St. 5 and Cr was low only at St. 2. These late sites are the most remote from contaminant sources and are more influenced by incoming shelf-waters. Conversely, the most outermost stations, located in the mouth of the Dom João river (Fig. 1), presented the highest concentrations of the studied trace metals, particularly St. 1 (for Cu and Cr) and St. 3 (for Cr). The three metals (Cu, Ni and Cr) analyzed showed strong positive correlations with each other, and with TOM and TOC content (Tab. 2). The lack of correlation between the metal contents and the sediment fractions suggests that their distribution is not dependent on granulometry, exception to Zn, but is dependent on the organic load. Furthermore, a high degree of association among the metals was observed, as previously reported for different urbanised and developing urban areas (Ruiz, 2001; Muniz *et al*., 2004). The similarity of Cu and Zn values at St. 1 and 3 could be related to the incipient tourism development of the region during the last decade. According to the EPA criteria (Anonymous, 1977), only Sts.

1 and 3 were classified as moderately polluted (MP) by Cu (Fig. 2). There are no apparent adverse biological effects caused by Zn, and toxicity is rarely threatened by Cr, only at St. 3 (Anonymous, 2000).

Table 1. Physico-chemical and sedimentological variables, percentages of organic matter constituents, total petroleum hydrocarbons and metal concentration in surface sediments at five sampling stations from Dom João estuary.

Station	1	2	3	4	5
pH	7.3	6.8	8.0	6.9	7.7
Eh (mV)	-20	29	-34	27	-18
T (ºC)	28.7	28.6	35.7	34.6	31
Sal (%o)	39	37	30	40	41
DO (mg L^{-1})	14.7	6.1	7	5.8	7.3
Sand (%)	77	78	79	69	78
Silt (%)	5	9	6	8	11
Clay (%)	18	13	15	23	11
Cu (µg g^{-1})	25.47	18.42	27.33	20.08	16.09
Ni (µg g^{-1})	12.86	5.65	19.66	16.70	8.00
Pb (µg g^{-1})	< 1.0	< 1.0	< 1.0	20.03	9.27
Cr (µg g^{-1})	15.59	5.60	24.60	20.03	11.60
Cd (µg g^{-1})	0.30	0.56	< 0.1	< 0.1	< 0.1
Zn (µg g^{-1})	40.47	29.46	39.92	52.22	27.99
TPH (µg g^{-1})	9.00	10.60	1.60	5.10	4.70
TOM (%)	5.17	4.13	4.46	2.99	1.80
TOC (%)	3.00	2.39	2.59	1.73	1.04
N (%)	0.27	0.19	0.18	0.23	0.14
C/N	11.2	12.6	14.7	7.7	7.3

Eh = redox potential, T = Temperature, Sal = salinity, DO = dissolved oxygen in bottom water, TPH = Total petroleum hydrocarbons, TOM = total organic matter, TOC = total organic carbon, N = total nitrogen

Table 2. Pearson correlation matrix for the variable analyzed.

	pH	Eh	T	Sal	DO	Sand	Silt	Clay	Cu	Ni	Cr	Zn	TPH	TOM	TOC	ON
pH	**1.0**															
Eh	-0.9	**1.0**														
T	0.4	-0.2	**1.0**													
Sal	-0.5	0.4	-0.5	**1.0**												
DO	0.1	-0.5	-0.5	0.2	**1.0**											
Sand	0.6	-0.6	-0.4	-0.5	0.2	**1.0**										
Silt	-0.1	0.4	-0.1	0.5	-0.6	0.0	**1.0**									
Clay	-0.4	0.3	0.4	0.1	0.1	-0.9	-0.5	**1.0**								
Cu	0.4	-0.6	0.3	-0.7	0.5	0.2	-0.9	0.3	**1.0**							
Ni	0.4	-0.4	**0.8**	-0.5	0.0	-0.3	-0.6	0.6	0.7	**1.0**						
Cr	0.5	-0.5	**0.9**	-0.5	0.0	-0.3	-0.6	0.5	0.7	**1.0**	**1.0**					
Zn	-0.2	0.2	0.6	0.0	0.0	-0.8	-0.5	**1.0**	0.4	0.8	0.7	**1.0**				
TPH	-0.8	0.5	-0.9	0.5	0.3	0.0	0.0	0.0	-0.3	-0.7	-0.8	-0.3	**1.0**			
TOM	-0.1	-0.2	-0.2	-0.5	0.6	0.3	-0.9	0.2	**0.8**	0.3	0.2	0.2	0.3	**1.0**		
TOC	-0.1	-0.2	-0.2	-0.5	0.6	0.3	-0.9	0.2	**0.8**	0.3	0.2	0.2	0.3	**1.0**	**1.0**	
ON	-0.5	0.2	-0.2	0.2	0.7	-0.4	-0.7	0.7	0.5	0.3	0.2	0.6	0.5	0.7	0.7	**1.0**

Total petroleum hydrocarbons levels ranged between 1.60 and 10.60 µg g^{-1}dry weight (Table 2). The low positive correlation with TOM, TOC and total nitrogen content of the sediments could be explained by the input of by human activities.

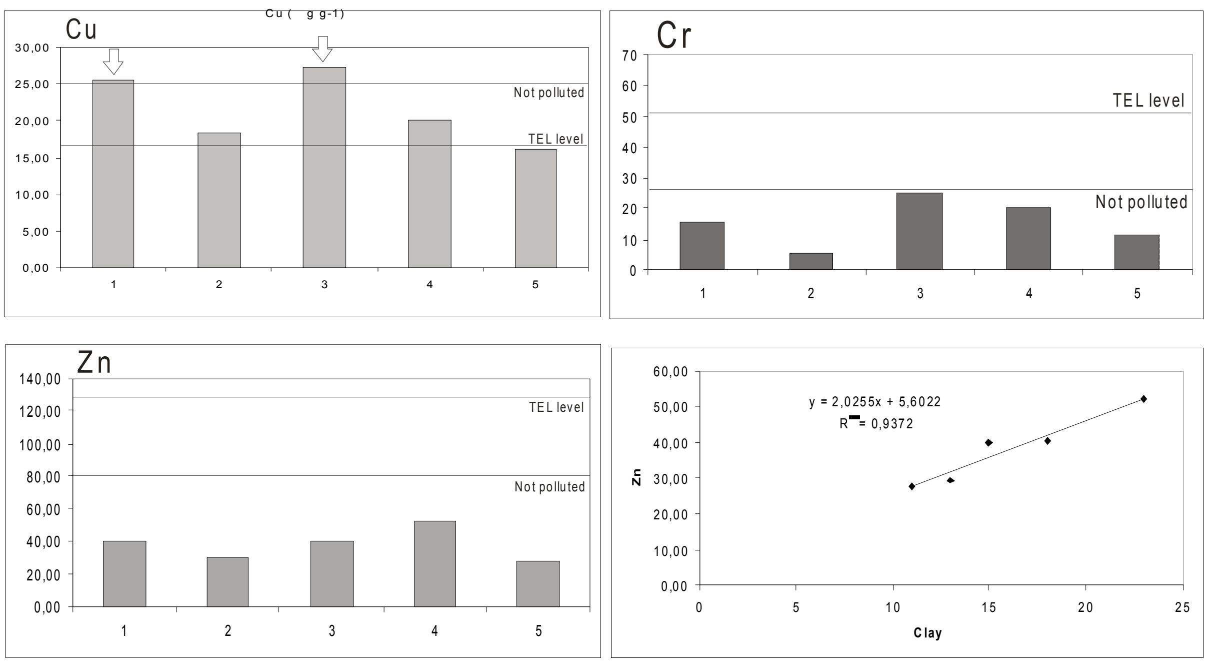

Figure 2. Concentration (µg g^{-1} dry weight in sediment fraction < 63µm) of copper (Cu), chromium (Cr), zinc (Zn) at the five stations of the Dom João Estuary, Bahia - Brazil. TEL level and not-polluted level, as considered in the Environmental Protection Agency (EPA) (Anonymous, 1977, 2000), are also shown.

The principal component analysis results showed the formation of four groups of stations (Fig. 3). The first and second components together explained 68% of the total variance; the first component alone explained 40%. Granulometric influence appeared as an important primary discriminative variable. PH influence appeared as an important secundary discriminative variable since its contribution to the explained variance was only important in axis II. The first group, formed by St. 2, was characterized by high content of TPH. Conversely, groups II (St. 5), III (St. 3) and IV (Sts. 1 and 4) showed the opposite characteristic. Discrimination between these three groups is reinforced by group III which is characterized by high Cr content and low TPH values (Fig. 3). Groups I and II are under the direct influence of riverine inputs that introduce to the bay domestic sewage and terrestrial material.

4. Conclusions

Findings obtained in this investigation showed that the spatial distribution of sedimentary trace metals and organic compounds in the Dom João region were clearly affected by riverine input. The Dom João river is mainly responsible for the quality of bottom sediments, which are affected by domestic sewage, city runoff and urban activities in São Francisco do Conde city. Increasing tourism and the lack of sewage treatment systems may be responsible for the entrance of metals and TPH into the bay's water and their subsequent deposition in bottom sediments. Sts. 1 and 3, located near the mouths of the river, are the most affected locations. The clockwise water circulation pattern in the bay may contribute to the observed distribution of sediments and associated particles.

On the other hand, those stations located more distant from the river plume presented a clear contribution of oil production field to the TPH. The higher TPH and metal contents observed suggest that the expansion of a local village due to increasing tourism activities could be affecting the environmental quality.

5. Acknowledgements

This research project was supported by the financial help of the Brazilian Science and Technology Ministry Project FINEP - CT-PETRO no. 640002700.

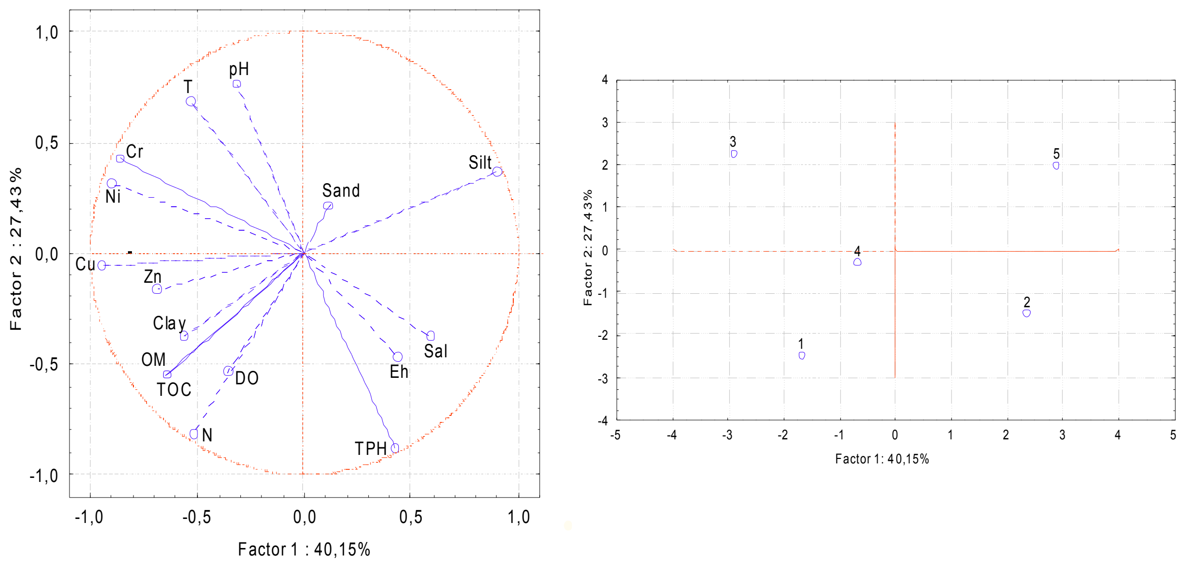

Figure 3. Principal component analysis (PCA) diagrams for environmental and contamination variables, showing their contribution for the first two axes. Axis 1 (40,15%) correlated positively with silt, salinity (sal), Eh and total petroleum hydrocarbon (TPH). Axis 2 (27,43%) correlated positively with pH, T, chromium (Cr), nickel (Ni) and sand. Sampling stations are represented by numbers 1-5.

6. Referências

ANONYMOUS. Implementation Manual for Section 103 of Public Law 92- 532: Marine Protection, Research and Sanctuaries Act of 1972. July 1977. U.S. Army Corps of Engineers, Environmental Effects Laboratory, Waterways Experiment Section, Vicksburg, MS; 1977.

ANONYMOUS. Microwave assisted acid digestion of aqueous samples and extracts. SW-846. Method 3015 and 3051. Test methods for evaluating solid waste. Washington, DC: U.S. Environment Protection Agency (EPA). 1990.

CELINO, J.J. e QUEIROZ, A. F. de S. Fonte e grau da contaminação por hidrocarbonetos policíclicos aromáticos (HPAs) de baixa massa molecular em sedimentos da baía de Todos os Santos, Bahia. *R. Esc. Minas*. v 59, n. 3, p. 265-270. 2006.

CELINO, J. J. ; QUEIROZ, A. F. S. ; SANTOS, J. B. Heavy Metals and Petroleum Hydrocarbons in Sediments of the Mangrove from São Francisco do Conde Region, Todos os Santos Bay, Bahia.. *In*: 3º Congresso Brasileiro de P & D em Petróleo e Gás, 2005, Salvador. Boletim de Resumos do 3º Congresso Brasileiro de P & D em Petróleo e Gás. Salvador : Mundo Virtual, 2005. v. 1. CD-ROM

HADLICH, G. M. ; CELINO, J. J. ; UCHA, J. M. ; SANTIAGO, J. S. . Geoquímica de Metais Traços em Apicuns (Planícies Hipersalinas) do Campo de Produção de Petróleo Dom João, São Francisco do Conde, Bahia.. *In*: XI Congresso Brasileiro de Geoquímica, 2007, Atibaia. Anais XI Congresso Brasileiro de Geoquímica. Rio de Janeiro : Sociedade Brasileira de Geoquímica, 2007. v. 1. p. 1-3. CD-ROM.

JAFFÉ, R., MEAD, R., HERNÁNDEZ, M.E., PERALBA, M.C., DIGUIDA, O.A. Origin and transport of sedimentary organic matter in two subtropical estuaries: a comparative biomarker-based study. *Organic Geochemistry*. v. 32, p. 507–526. 2001.

LESSA, G.C.; DOMINGUEZ, J.M.; BITTENCOURT, A. C. S. P.; BRICHTA, A. The tides and tidal circulation of Todos os Santos Bay, Northeast Brazil: a general characterization. *An. Acad. Bras. Cienc*., v. 73, no. 2, p. 245 – 261. 2001.

MUNIZ, P., DANULAT, E., YANNICELLI, B., GARCÍA-ALONSO, J., MEDINA, G., BÍCEGO, M.C., Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). *Environment International*. v. 29, p. 1019–1028. 2004.

RUIZ, F., Trace metals in estuarine sediments from the Southwestern Spanish coast. *Marine Pollution Bulletin*. v. 42, p. 482–490. 2001.