OCCURRENCE AND DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE WATER OF TODOS OS SANTOS BAY, BAHIA, BRAZIL

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RESUMO. Ocorrrência e distribuição de hidrocarbonetos policíclicos aromáticos em água superficial da Baía de Todos os Santos, Bahia, Brasil. Quatorze dos hidrocarbonetos policíclicos aromáticos (HPA) incluídos pelo Environmental Protection Agency (EPA) na lista de poluentes prioritários foram analisados através de cromatografia gasosa com espectrometria de massas acoplada (GC-MS). A amostragem das águas superficiais foi realizada na Baía de Todos os Santos (Bahia), norte do Brasil. Os perfis foram dominados por HPAs de alto peso molecular (quatro ou cinco anéis de componentes) em amostras de água superficial; indicativo de sua origem a partir de óleo ou contaminação residual (entrada pirogênica). Para discriminar diferenças e semelhanças entre as amostras, a análise de componente principal foi realizada utilizando uma matriz de correlação.
Palavras chave: hidrocarbonetos policíclicos aromáticos (HPA); água superficial; cromatografia à gás-espectrometria de massas (CG-EM).

ABSTRACT. In this work, 14 PAHs included in the US Environmental Protection Agency's (EPA) priority pollutant list were analyzed using gas chromatography–mass spectrometry (GC–MS). Surface water sampling was undertaken in Todos os Santos Bay, northern Brazil. The PAH profiles were dominated by high molecular weight PAHs (four- and five-ring components) in surface water samples. These indicated that PAHs in surface water might origin from oil or sewage contamination (pyrogenic input). To discriminate pattern differences and similarities among samples, principal component analysis (PCA) was performed using a correlation matrix.
Keywords: Polycyclic aromatic hydrocarbons (PAHs); Surface water; Gas chromatography–mass spectrometry (GC–MS).

INTRODUCTION

Water pollution by organic compounds, many of which are known to be toxic or carcinogenic, has caused considerable and worldwide concern. Polycyclic aromatic hydrocarbons (PAHs), hydrocarbons containing two or more fused benzene rings, are a group of ubiquitous organic pollutants of great environmental concern because of the documented carcinogenicity in experimental animals and the widespread occurrence of several of its members (Manoli et al. 2000). Due to their ubiquitous occurrence, recalcitrance and suspected carcinogenicity and mutagenicity, PAHs are included in the U.S. Environmental Protection Agency (EPA) and in the European Union priority lists of pollutants. The US EPA fixed 16 parent PAHs as priority pollutants, the latest being effective from 1997 (Baumard et al. 1997; Mastral and Call´en 2000;

Magi et al., 2002; Szolar et al. 2002; Schubert et al.. 2003), some of which are considered to be possible or probable to human carcinogens, and the endocrine disrupting activities of PAHs have been recently reported (Clemons et al. 1998; Brun et al. 2004). Therefore, their distributions in the environment and potential human health risks have become the focus of much attention.

PAHs are introduced into the environment mainly as a consequence of incomplete combustion originating from both, natural and anthropogenic processes. However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources except perylene. Anthropogenic sources include automobile exhaust and tire degradation, industrial emissions from catalytic cracking, air-blowing of asphalt, coking coal, domestic heating emissions from coal, oil, gas and wood, refuse incineration and biomass burning.

The majority of surveys worldwide were mainly focused on seawater (coastal of offshore) and estuarine water. However, few data are available for PAH contamination of the inland waters of Todos os Santos Bay, Bahia, which usually act as receptors for sewage, industrial effluents and urban or rural run off (Celino; Queiroz, 2006).

In Brazil, very limited study on surface water monitoring of PAHs is performed (CETESB, 1979; CETESB, 1981; CETESB, 1990; CETESB,2001; CRA, 2004). In order to evaluate the contamination status of PAHs in surface water from estuarine region and Todos os Santos Bay, northern Brazil, an investigation has been performed with a quantitative GC–MS method.

MATERIALS AND METHODS

Standard PAHs (16 compounds specified on EPA Method 610, each at 100, 200, 1000 or 2000µg/mL) in a mixture were obtained from Supelco (Bellefonte, PA, USA). These compounds are as follows: naphthalene (Np), metil-naphthalene (mNp), dimetil-naphthalene (dNp), acenaphthylene (Acy), acenaphthene (Ace), fluorine (F), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), chrysene (Chry), benzo[a]anthracene (BaAn), benzo[b]fluoranthene (BbFl), benzo[k]fluoranthene (BkFl), benzo[a]pyrene (BaPy), benzo[g,h,i]perylene (B[ghi]Pe) and dibenzo[a,h]anthracene (dB[ah]An). Deuterated internal standards (naphthalene-d8, acenaphthene-d10, phenanthrened10 and chrysene-d12) were obtained from Sigma–Aldrich.

Working standards of PAHs were prepared by combining the standard mixture with the corresponding IS stock solution, respectively. These solutions were further diluted with dichloromethane to prepare calibration solutions in the range 0.01–10 ng μL^{-1}. All solvents used for sample processing and analyses (dichloromethane, ethyl acetate, acetone, hexane and methanol) were analytical grade and further distilled twice to remove impurities.

Todos os Santos Bay is situated on the northern of Brazil. With a population of almost 2,1 million and the surface area of the bay about 1,052 km^2, it is a huge commercial and industrial center.

Todos os Santos Bay has a hot and wet climate with distinct four seasons, sufficient sunshine and moderate rainfall. The annual mean temperature is 24 ◦C and the annual average rainfall is 2100 mm. The Todos os Santos Bay urban/industrial complex is highly polluted with the development of industry and rapid urbanization. Industry and automobiles are two major sources of pollution.

The surface water samples were collected (0–10 cm) by using cylinder samplers aboard a chartered vessel during axial surveys on july, 2007, and the (10) ten locations of sampling site of surface water are shown in Figure1. The data for the master parameters are shown in Table 1.

After returning to the laboratory, aliquots of the sample (1.0 L) were filtered through 0.45 µm microporous filter membrane under vacuum in order to remove algae, zooplankton and suspended particles and a measured aliquot of an internal standard mixture containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10 and chrysene-d12 was added to each sample. The cartridges were first conditioned with 2×5mL of methanol followed by 2×5mL of deionized water. Water samples were passed through the cartridges at a flow rate of 6 mL/min under vacuum.

Following extraction, the cartridges were eluted with 6mL of ethyl acetate, which was combined with an ethyl acetate rinse (5 mL) from the extraction glassware. After water was removed from the extracts by ashed Na_2SO_4, the volume of the extracts was reduced by N_2 blow-down in a water bath (35 ◦C) to a final volume of 1 mL.

The analysis was performed on a 50 m fused-silica column (0.32 mm i.d.) coated with CPSil5-CB (0.25 µm thickness). Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1} (pressure 0.8 kPa). The following temperature program was employed: 70 °C to 280 °C with ramping at 4 °C min^{-1}. Injector and detector temperature were held at 320 ◦C. Detection was monitored by flame ionisation detector (FID). The structure of PAHs was confirmed by gas chromatography coupled to mass spectrometry (trace 2000 GC–MS, Thermo Finnigan, USA). A fused-silica DB-5MS capillary column (30m×0.32mm i.d., 0.25µm film thickness) was used. Helium with a purity of 99.999% was used as the carrier gas at a constant flow of 1.0 mL/min. A 2µL volume was injected by applying a hot splitless injection technique. The temperature
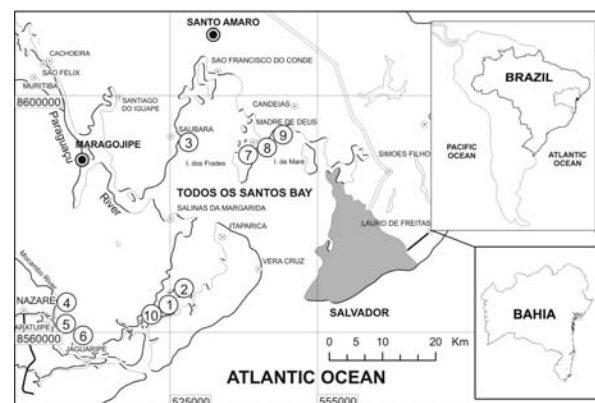

Figure 1. Map of Todos os Santos Bay, Bahia, Brazil, indicate sampling sites of surface water.

Table 1. Summary of conditions when water samples were taken and range of concentrations (ng/L) of parent PAHs in surface water from Todos os Santos Bay, Bahia, Brazil.

Station	10	1	2	3	4	5	6	7	8	9
pH	6,71	6,58	6,82	7,81	6,22	6,23	6,16	8,21	8,27	8,3
Eh	41	46	36	-12	68	67	71	-35	-38	-39
Temperature (ºC)	25,1	25,1	25,1	28,0	26,2	25,5	27,6	29,4	29,4	29,6
Salinity (%o)	31	32	32	29	20	20	20	31	31	32
Dissolved Oxig. (mg/l)	5,9	5,9	5,8	7,5	2,6	1,3	5,3	7,5	7,5	7,5
Np	0,0001	0,0001	0,0002	0,0001	0,0004	0,0001	0,0001	0,0055	0,0001	0,0001
mNp	0,0001	0,0006	0,0002	nd	0,0001	0,0001	0,0000	0,0009	0,0008	0,0000
dNp	nd	0,0009	0,0002	nd	0,0000	0,0006	0,0001	0,0003	0,0010	0,0000
Acy	0,0019	0,0032	0,0077	0,0001	0,0001	0,0013	0,0061	0,0001	0,0013	0,0087
Ace	0,0002	0,0012	0,0007	0,0008	0,0003	0,0008	0,0009	0,0004	0,0015	0,0005
F	0,0001	0,0030	0,0005	0,0002	0,0271	0,0023	0,0003	0,0002	0,0032	0,0003
Ph	0,0002	0,0023	0,0010	0,0002	0,0000	0,0006	0,0002	0,0001	0,0025	0,0005
An	0,0001	nd	nd	0,0003	0,0001	0,0006	0,0001	0,0002	nd	0,0002
Fl	na	na	na	na	na	na	na	na	na	na
Py	0,0001	0,0019	0,0010	0,0003	0,0002	0,0034	0,0014	0,0001	0,0020	0,0266
BaAn	0,0001	0,0012	0,0014	0,0001	0,0001	0,0018	nd	0,0003	nd	0,0009
Chry	0,0001	0,0014	0,0007	0,0003	0,0004	0,0009	nd	0,0003	0,0019	0,0001
BbFl	0,0000	0,0006	0,0003	0,0005	0,0002	0,0004	0,0005	0,0000	0,0007	0,0011
BkFl	nd	0,0034	0,0010	0,0024	nd	0,0007	0,0019	0,0010	0,0104	0,0008
BaPy	nd	0,0064	0,0034	0,0034	nd	0,0047	0,0015	0,0016	0,0015	0,0011
Total PAH	**0,0029**	**0,0262**	**0,0184**	**0,0088**	**0,0290**	**0,0183**	**0,0132**	**0,0111**	**0,0269**	**0,0410**
PAH LMM	**0,0026**	**0,0112**	**0,0105**	**0,0017**	**0,0280**	**0,0065**	**0,0079**	**0,0078**	**0,0104**	**0,0104**
PAH HMM	**0,0003**	**0,0150**	**0,0079**	**0,0071**	**0,0009**	**0,0119**	**0,0053**	**0,0033**	**0,0166**	**0,0306**
Ph/An	**3,0487**	**nc**	**nc**	**0,6822**	**0,3812**	**0,9640**	**1,5012**	**0,5563**	**nc**	**2,0645**
BaAn/(BaAn+Chry)	**0,4724**	**0,4535**	**0,6587**	**0,2065**	**0,1942**	**0,6714**	**nc**	**0,5182**	**nc**	**0,8971**
F/(F+Py)	**0,6248**	**0,6104**	**0,3498**	**0,3988**	**0,9939**	**0,4060**	**0,1553**	**0,5363**	**0,6167**	**0,0115**
An/(An+Ph)	**0,2470**	**nc**	**nc**	**0,5944**	**0,7240**	**0,5092**	**0,3998**	**0,6425**	**nc**	**0,3263**
nd = not detected				nc = not calculated				na = not analyzed		

program of the oven was started at 70 ◦C (for 1 min) and increased at a rate 10◦C/min to 300◦C and was held for 10 min. The mass spectrometer was operated in the electronic impact (EI) mode with an ion source at 200◦C and the electron impact energy was set at 70 eV. Identification of the PAH compounds was performed by comparing GC retention time with those of authentic standards. Quantification of individual compounds was based on comparison of peak areas with those of the recovery standards.

Before sample analysis, relevant standards were analyzed to check column performance, peak height and resolution, and the limits of detection (LOD). With each set of samples to be analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times.

All data were subject to strict quality control procedures. For PAHs, deuterated IS were used to compensate for losses involved in the sample extraction and work-up. The four IS in water were determined with good precision, and their recoveries ranged from 70±5 to 93±10% for water samples. Detection limits derived from replicate procedural blanks were aproximately 1 ng/L. GC/MS data were acquired and processed by using X calibur software.

RESULTS AND DISCUSSION

The total PAH concentrations ranged from 0,0029 to 0,0410 ng/L in surface waters (main rivers, tributaries, ditches, etc.) with mean value of 0,0184 ng/L. The highest concentration of surface water was observed at station 9, which is situated in the mouth where Suape River merges into the Todos os Santos Bay (Figure 2). With increasingly intense urban and industrial development in Nazaré, the amount of PAHs detected there is obviously related to urban runoffs, sewage discharges, vehicular exhaust emission and intense shipping activities that were observed during the sampling. Similarly, high concentration (>0.02 ng/L) was also found at stations 4 and 8, which accumulation of sewage discharge. In addition, there were a lot of industries (e.g.

chemical, power) around the study area, many of which were discharging waste effluents; hence, there were many non-point sources in the area, contributing to the concentrations of PAHs detected.

The compositional pattern of PAH by ring size along the contamination gradient is shown in Figure 3. It is clear that two- and three-ring PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) are the most abundant PAHs, which on average occupied 90 and 20% of total PAHs in surface water. In addition, four and five-ring PAHs on average occupied 10 and 80% of total PAHs in surface water. Benzo[a]pyrene is one of the most frequently detected compounds in almost all surface water samples (except S4 and S10). Higher proportions (about 90% of benzo[a]pyrene) were observed at stations S1 and S5.

The concentrations of PAHs in waters exceeding 10,000 ng/L suggested that the water was heavily contaminated by PAHs (Who, 1998). It is clear from Figure 2 and 3 that all samples had total PAH concentrations below this value, suggesting that certain organisms in the area don't have suffered acute toxicity.
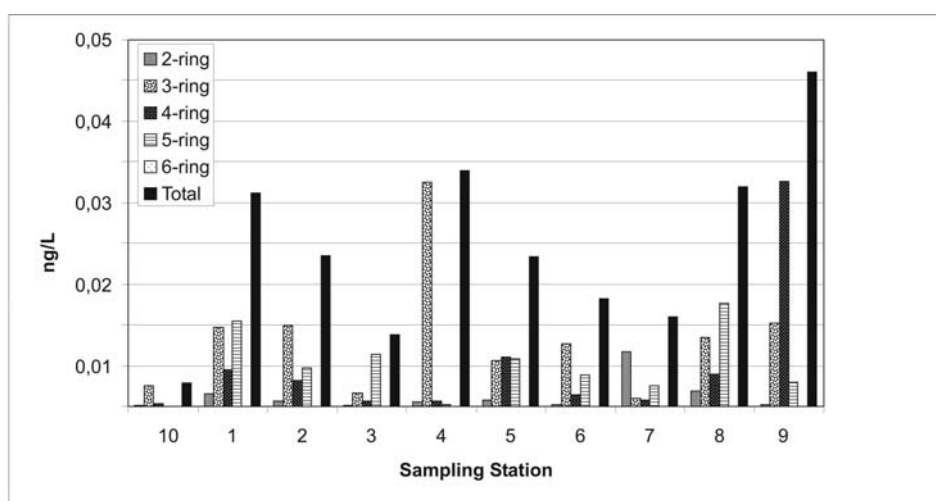
Figure 2. Concentrations of two-, three-, four-, five-, six-ring and total PAHs in the surface water column of Todos os Santos Bay. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene.
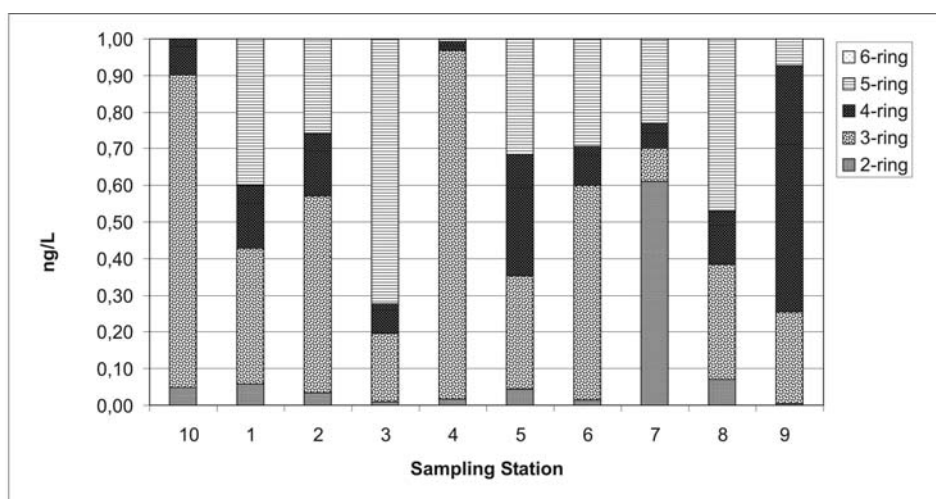
Figure 3. Composition pattern of parent PAHs in surface water of Todos os Santos Bay. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene.

Parent PAHs have both natural sources (oil seeps, bitumen, coal, plant debris and forest and prairie fires) and anthropogenic sources (fossil fuels and combustion). Since the PAH compositions of the two sources overlap, the significance of anthropogenic PAHs in the environment must be evaluated against a dynamic background of natural PAHs.

However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources except perylene. Anthropogenic sources include both high and low temperature combustion of fossil fuels and the direct release of oil and its products.

The ratios of Ph/An within the two-ring PAH group were used to differentiate PAHs of different origins. Ph is more thermochemically stable than An, and therefore at low maturation temperatures much higher molar fraction of Ph is produced compared to An. These molar ratios of Ph/An at petroleum maturation temperatures lead to higher values. These can be as high as 50 at 373 K. To the contrary, high temperature processes (800–1000 K), such as the incomplete combustion of organic materials (coal burning, wood burning, vehicular exhaust emission, waste crankcase oil and asphalt roofing material), are characterized by low Ph/An ratio value (4–10).

Thus, Ph/An > 15 for petrogenic sources and Ph/An < 10 for pyrolytic sources. Due to the wide range of values for this index found in the literature, values between 10 and 15 are considered indeterminate relative to source (Tam et al., 2001; Sanders et al., 2002).

In order to explore more latent relationships among all the stations investigated, the principal component analysis (PCA) was applied to the results obtained.

The two principal components selected are able to account for 53.23% of total variance of the original data. The first and second PCs in surface water represented 29.62 and 23.61% of the variability, respectively.

There are three groups discriminated on the factor loading plot (Figure 4A). Group A clusters samples of stations 4, 5, 6 and 10; group B, samples collected from stations 1, 2 and 8; group C contains samples collected from stations 3, 7 and 9. The discrimination in three groups was confirmed by hierarchical clustering analysis (HCA), using complete linkage and Euclidean distances (Figure 5).

From Figure 2, we can see the samples of stations 1, 2 and 8 collected from the Jaguaripe River and Madre de Deus, probably contain similar contaminants, so they constitute the group B. As shown in Figure 4A, group C is characterized by the negative axes of both principal components; on the other hand, from Figure 4B, this quadrant is dominated by pyrene. This indicated that pyrene contributed significantly to the samples in group C, and the contribution of phenanthrene over the contribution of the other PAHs notability.

The samples of stations 1, 2 and 8 were collected from the places nearby different interchanges, so they cluster together. However, the characteristic of the sample from station 9, is similar to that of those samples in group C. The similarity may be caused by their complicated origins of contamination. Nevertheless, the sample of station 7 has some characteristics different from that of the other samples in group C. Contrary to the other samples in group C, the sample of station 7 is characterized by positive loading in the first principal component, so it got more contribution from the naphthalene than the other samples.
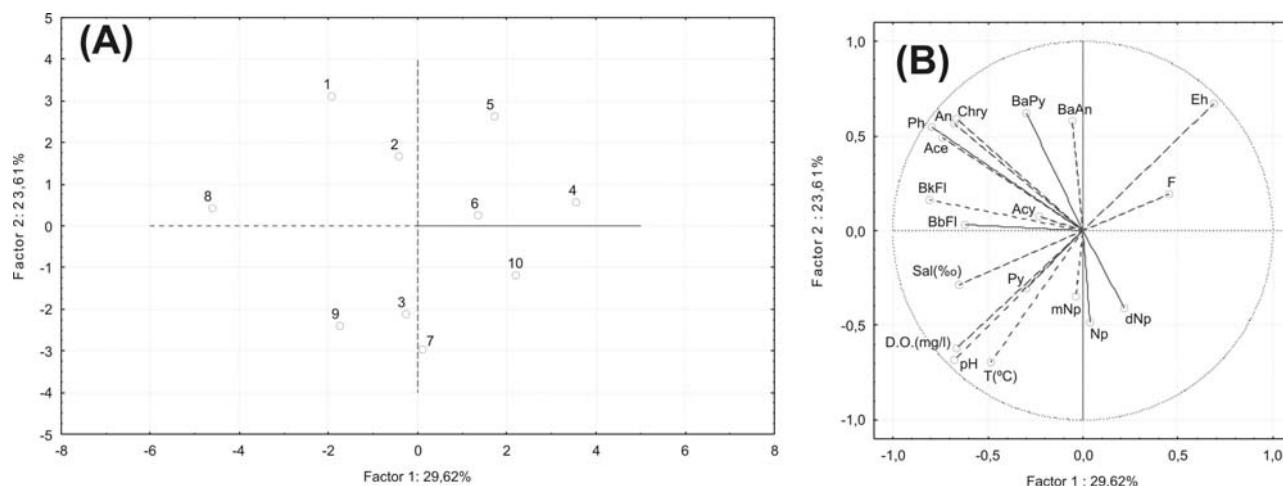
Figure 4. PCA showing the pattern of PAHs in the surface water: (A) factor loading plot and (B) factor score plot—(Np) naphthalene, (Acy) acenaphthylene, (Ace) acenaphthene, (F) fluorene, (Ph) phenanthrene, (An) anthracene, (Fl) fluoranthene, (Py) pyrene, (Ba) benzo[a]anthracene, (Chy) chrysene, (BbFl) benzo[b]fluoranthene, (BkFl) benzo[k]fluoranthene, (BaP) benzo[a]pyrene and (dAn) dibenzo[a,h]anthracene.
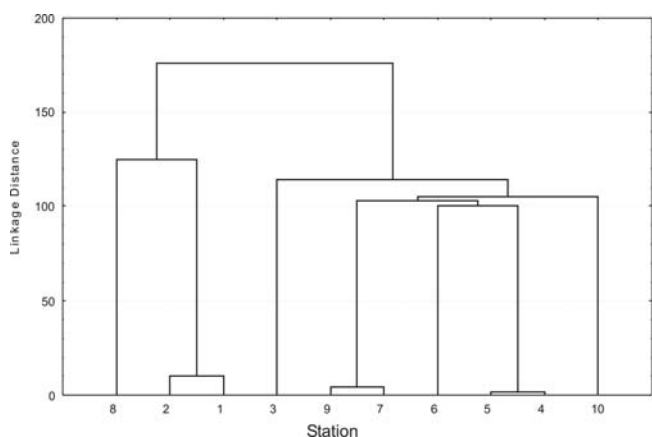
Figure 5. Hierarchical clustering of the surface water stations (complete linkage, Euclidean distances).

The samples in group B got the contribution from phenanthrene mostly among all the PAHs. However, compared with group A, the samples in group B gave a relatively low contribution to factor 1, so they got less contribution from phenanthrene than group A. This conclusion can be confirmed by Figure 4.

The sample of station 3 was collected from Saubara, so the characteristic of this sample may be different from the others. As shown in Figure 4A, the station 3 has a low value of factor 2 and it can be assumed that it is able to get the contribution from something with a low score value of factor 2, which seems to be the metilnaphthalene, gave the mostly contribution among these PAHs.

CONCLUSIONS

The PAH profiles of water samples revealed that the dominant PAHs were high molecular weight (four- and five ring) PAHs in surface water of Todos os Santos Bay, Brazil including (Py) pyrene, (Ba) benzo[a]anthracene, (Chy) chrysene, (BbFl) benzo[b]fluoranthene, (BkFl) benzo[k]fluoranthene, (BaP) benzo[a]pyrene.

The PAHs in surface water samples originated mainly from pyrogenic inputs based on the high proportion of four-ring and five ring PAHs (benzo[a]pyrene). Although the calculated ratios of Ph/An and principal component analysis are usually performed to analyze the origin of PAHs in sediments, we attempted to apply the ratio and PCA to the surface water in this study. The analysis results showed that the ratios and PCA could be applied to the surface water investigation to some extent.

Oil spill and leakage from boats and ships, vehicular exhaust emission, discharge from municipal and industrial wastewater and runoff might be important sources. These indicate that surface water received anthropogenic PAHs from different sources and although specific sources are known to be responsible for the presence of PAHs in surface waters, their occurrence cannot always be related to a particular source. This indicates that the studied area doesn't show any modern environmental impact and that it can be used as background in order to identify typical geochemical signature of non-impacted ecosystems in Todos os Santos Bay, Brazil.

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