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Abundance and Source Identification of Polycyclic Aromatic Hydrocarbons in Sediments of the Ivory Coastal Zone (Toukouzou Hozalem-Assinie)

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are strongly associated with agricultural, residential, transportation, industrial and petroleum activities. In this study, the presence of PAHs (polycyclic aromatic hydrocarbons) was investigated in sediments of the ivory coastal zone (Toukouzou Hozalem-Assinie). The main objectives of this study were to determine the abundance and to predict the source of PAHs in the sediments. Gas chromatography-mass spectrometry (GC-MS) was used to analyze sixteen priority PAHs. Total PAHs concentrations were from 1.31 to 3992.68 mg/kg in sediment with an average concentration of (307.54 ± 16.10) mg/kg. Among all PAHs, Naphthalene (Nap = 332.72 mg/kg) and Phenanthrene (Phe = 41.75 mg/kg) were found in the highest concentration, whereas Benzo (k) Fluoranthene was found in the least concentration in the range of 0 - 0.85 mg/kg (mean 0.24 mg/kg). Bassam-Modeste Lagune (BML) sampling site was the site with the highest concentration of total PAHs (all 16 PAHs) compared to the others due to their location in a highly populated estuary area that receives commercial, tourism, port, petroleum and heavy industrial activities. Diagnostic ratios were used to determine the sources of PAHs and suggested that the PAH profile in the sediments was dominated by 2 and 3 ring PAHs. The patterns of PAH compounds in sediment indicated that contamination is from mixed sources, with a strong indication of petrogenic contamination potentially from spills of fuel, oil and industrial activities.

Keywords

Polycyclic Aromatic Hydrocarbons, Sediment, Source, Abundance, Ivorian Coastal

1. Introduction

Economic development, transport and urbanization are some of the factors that are linked to environmental changes. The release of solid and liquid waste is one of the consequences of high fuel and energy consumption [1]. PAHs are formed during the incomplete combustion of coal, oil, gas, fossil fuels, wood, garbage or other organic substances, such as tobacco and charred meat [2]. The ivorian coasts have been experiencing numerous environmental problems over the last two decades. The race for economic development has led to increased exploitation and production of hydrocarbons. In ivorian coasts, the average oil production is estimated to be around 26,000 baryls of oil per day (bopd) [3] and gas production is around 220 billion cubic feet per day. Proven oil reserves are estimated at over 175 billion baryls and potential resources are estimated at about 2.500 billion baryls. Proven gas reserves are estimated at 1.190 billion cubic feet and potential resources at 6.500 billion cubic feet. These different hydrocarbons are mainly exploited within the maritime façade. This pollution often impacts tourist activities by breaking the aesthetics of the beaches. Nearly 90% of trade passes through ports and applies to all types of vessels [3]. Polycyclic aromatic hydrocarbons (PAHs) are a kind of organic environmental contaminants composed of two or more numbers of benzene rings [4]. The amount of PAHs released into the aquatic environment has increased with the intensity of industrialization, which is the main source of PAHs from anthropogenic activity [5]. They are found everywhere and are mostly hydrophobic in nature, capable of bioaccumulating in animal and human tissues. PAHs are present in soil, water, sediment and ambient air. They are ubiquitous due to bioaccumulation, degradation of refractory compounds and long-range transport. Because of these unfavorable traits, PAHs have attracted the attention of concerned agencies worldwide. PAHs in the environment typically come from a mixture consisting of natural and anthropogenic sources belonging to three categories: petrogenic, pyrogenic, and diagenetic [4]. They are released into the environment in large quantities from various human activities and may have additive or synergistic effects with other environmental contaminants [6]. Sixteen PAHs have been prioritized for control by the United States Environmental Protection Agency (USEPA) because of their carcinogenic and mutagenic properties [7]. Based on the number of benzene rings, PAHs can be classified into "light" PAHs (≤3 rings) and "heavy" PAHs (≥4 rings). The physical and chemical properties of PAHs depend on their structures and molecular weights [4]. Low molecular weight (LMW) PAHs (2 - 3 rings) are more volatile and exist in the gas phase. High molecular weight (HMW) PAHs (4 - 6 rings) exhibit insignificant vaporization and mainly in the particulate [8]. These properties condition their fate and distribution in the environment. Their hydrophobicity increases with the number of aromatic rings, while their solubility decreases. The low vapor pressures of PAHs give them low volatility that decreases with molecular weight, with the exception of naphthalene, which can volatilize from the water or soil surface [9]. The sources of PAHs are widely considered to be very important for studying their transport and use. Inputs from natural sources that include forest fires, volcanic eruptions, and natural petroleum seeps have been shown to be relatively negligible in contemporary environments [10]. In contrast, anthropogenic sources take precedence, and among them biomass (wood) and fossil fuel (coal and oil) combustion contribute much more significantly than oil spills and accidents. The input of PAHs of petroleum origin is generally punctual and locally confined. In marine sediments, a more or less significant portion of PAHs results from diagenesis processes of organic matter (phytoplankton or terrestrial plant resin). PAHs tend to increase over time as they are known to be carcinogenic, mutagenic, teratogenic and can have adverse effects on human health, fauna, flora and aquatic life. They are listed as priority substances by the European Water Framework Directive and sixteen PAHs are regulated as priority pollutants by the US Environmental Protection Agency [11]. Few studies on PAHs in this matrix in the Ivory Coastal zone have been carried out. Due to their toxic, persistent, mutagenic, and carcinogenic characteristics, PAHs are hazardous to biota and environments and are potentially detrimental to human health. Because of the toxic effect, human health risk, and their persistence in the environment, it is important to monitor their concentrations [12]. The objectives of this study were 1) to determine the abundance and the concentrations of 16 PAHs, in sediments, 2) to predict the probable sources of these compounds in the sediments of the ivory coastal zone (Toukouzou Hozalem-Assinie). Ease of Use (Heading 2).

2. Materials and Methods

2.1. Sampling

The sampling procedure was performed as described in previous works [13]. Sampling activities were carried out in six campaigns, for a total of 72 samples. The selected study area is located along the coastline which is 204 km long from Toukouzou Hozalem to Assinie. Twelve (12) sampling sites were selected and numbered as follows: Toukouzou (TKZ), Addah (ADA), Adjué (ADJU), Jacqueville (JAC), Adjouffou (ADJ), Bassam-Modeste Plage (BMP), Bassam-Modeste Lagune (BML), Azurety (AZT), Assinie-Plage (AP), Assinie-Lagune (AL), Assinie Canal Droite (ACD), Assinie Canal Gauche (ACG).

2.2. PAHs Extraction

Samples were soxhlet extracted (Grosseron, Gerhardt; France) over 24 h with 400 mL of dichloromethane (99.8% of purity)/methanol (99.9% of purity) (3/1, v/v). Then, the sediment was mixed with 5 g of anhydrous sodium sulfate (Na_2SO_4). The extracts were concentrated using a rotary evaporator (IKA, Germany) evaporated under a gentle stream of nitrogen (N50; 99.999% of purity). These extracts were further purified for analysis using 5 g of silica gel columns (silica 60; 0.063 - 0.200 mm; 5% deactivated), 2 g of alumina (aluminium oxide 90 active, 0.063 - 0.200 mm; 5% deactivated) and 2 g of Na_2SO_4, with 120 mL of hexane/dichloromethane (3:1 v/v). A solvent mixture (10 mL) hexane (99.1% purity)/dichloromethane (DCM) (4/1, v/v) was used for elution and evaporated under a stream of nitrogen to incipient dryness.

2.3. PAHs Analysis

PAHs in sediments were determined by GC - MS (Perkin Elmer Clarus 680 - Perkin Elmer Clarus 600). Calibration and quantification of PAHs were performed in SIM (Selected Ion Monitoring) mode. The identification of PAHs is carried out by acquiring the total ion current (TIC) and complete mass spectra, as well as by comparison with the chromatographic retention times determined for the standards of the pure compounds. All the operating conditions used in GC-MS are presented in Table 1.

2.4. Statistical Analysis

Pearson's correlation analysis was used to analyze the connections between PAH concentrations and external factors to identify the probable PAH sources. Statistical analyses were performed with XLSTAT (version 2017) to identify the relationships between the variables. The excel tables were performed using the office 365 proplus version.

3. Results and Discussion

3.1. Identification of PAHs in Sediments

All sediments analyzed by GC-MS had detectable concentrations of PAHs. Thus, 16 PAHs were identified (Figure 1). The average concentrations range from 0.11 to 332.72 mg/kg with an average concentration of (25.63 ± 16.10) mg/kg. Benzo (k) fluoranthene has the lowest concentration in the sediment, ranging from 0 to 0.85 mg/kg (average 0.24 mg/kg). Naphthalene (Nap) has the highest relative percentage (332.72%) of total PAHs in sediment, followed by phenanthrene (Phe = 41.75%), pyrene (Pyr = 9.42%), anthracene (Ant = 7.68%) and fluoranthene (Fla = 5.63%). The least dominant compounds are benzo (k) fluoranthene (B(k)F), benzo (a) anthracene (B(a)A) and acenaphthene (Ace). They represent 0.11%, 0.22%, and 0.28% of the sediment, respectively.

Table 1. Instrument conditions for GC-MS analysis.

Parameter	Setting/condition	
Injection conditions of the injector	Volume injected	5 µl
	Temperature	70˚C
	Purge rate	60 mL/min
	Purge time	2.53 min
	Total flow rate	62.5 mL/min
	Pressure	30 psi
	Gas type	Helium
Oven conditions	Initial temperature	70˚C
	Initial time	2 min
	First gradient	13˚C/min to 200˚C, isothermal for 0 min
	Second gradient	5˚C/min to 290˚C, isothermal for 5 min
Conditions of the column	HP 5MS Agilent 19091S-433UI	30 m × 0.25 mm, 0.25 µm
	Carrier gas flow rate	1 mL/min, constant flow
	carrier gas	Helium (99.9995% high purity grade)
Conditions of the transfert line	Temperature	325˚C
Mass spectrometer conditions	Temperature of the SM source	230˚C
	Temperature of the SM quadrupole	180˚C
	Solvent delay	5 min
	Ionization energy	70 eV

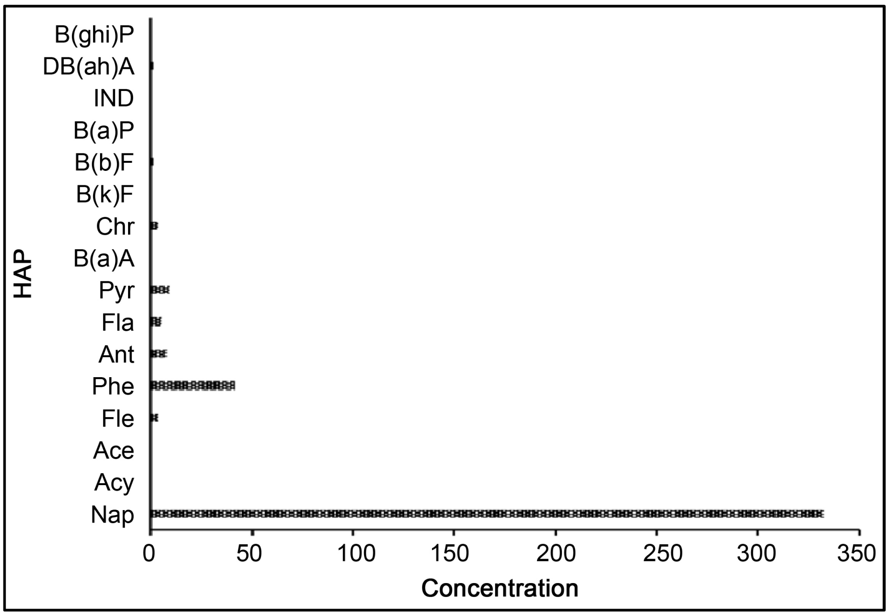

Figure 1. Content of the 16 Coastal PAHs.

This abundance of naphthalene and phenanthrene could be explained by activities such as petroleum exploitation, buffer storage of imported petroleum products, and tanker navigation. In contrast to this finding, [14] with concentrations ranging from 13 to 780 µg/kg, linked the presence of PAHs at the atlantic coast of the democratic republic of Congo to other anthropogenic activities. Indeed, these authors believe that these pollutants (PAHs) come from untreated urban, industrial and hospital effluents, agricultural runoff, solid waste, and landfills. Based on the classification adopted by [15], the level of PAH contamination is classified as low to highly contaminated. Accordingly, 16.67% of the samples were presented as low contamination (<100 ng/g); 33.33% as moderately contaminated (100 - 1000 ng/g); 41.67% as highly contaminated (1000 - 5000 ng/g), and 8.33% as very highly contaminated (>5000 ng/g). However, the level of PAH contamination in the coastal sediments of the Persian Gulf was quite low in the sediments and ranged from 3.63 to 21.75 µg/kg with an average of 6.35 µg/kg with respect to this study due to various sources such as cement complexes, fish and shrimp farming, and urban and industrial activity [16].

3.2. Distribution of PAHs in Sediments

PAHs are generally classified into two main groups: low molecular weight (LMW) PAHs (PAHs with 2 to 3 aromatic rings) and high molecular weight (HMW) PAHs (PAHs with 4 to 6 aromatic rings) [17]. Based on the benzene ring number, sixteen PAHs can be separated into three types: 2 - 3 rings (Naphthalene (Nap), acenaphtylene (Acy), acenaphtene (Ace), anthracene (Ant), phenanthrene (Phe), fluoranthene (Fla), fluorene (Fle)); 4 rings Pyrene (Pyr), benzo (a) anthracene (B(a)A, and chrysene (Chr)) and 5 - 6 rings PAHs Benzo (k) Fluoranthene (B(k)F), Benzo (b) Fluoranthene (B(b)F), Benzo(a) Pyrene (B(a)P), Dibenz (a, h) anthracene (DB(ah)A), Indeno (1, 2, 3, cd) Pyrene (IND), Benzo (g, h, i) Perylene (B(ghi)P). PAHs are mainly divided into two sources: diagenetic source and pyrogenic source. PAHs from the first source were mainly low molecular weight (LMW) PAHs, mainly exist in gaseous form and are volatile and easily degraded, while those from the second source were mainly heavy molecular weight (HMW) PAHs [4]. In this research, Naphthalene which is 2 aromatic rings is more abundant with 90.26% of total PAHs followed by 3-rings (acenaphthylene, acenaphthene, anthracene, phenanthrene, fluoranthene, fluorene) with 5.48% abundance of total PAHs, which suggest petrogenic sources [18] and also that the LMW-PAHs tend to be more conserved in the sediments [1] (**Figure 2**). 4 - 6 ring PAHs had a lower composition ratio (approximately 4.26%) than 2 - 3 ring. High ring number PAHs have a large molecular weight and are primarily found in the form of particles, which are stable and not easy to volatilize and thus can be retained in the environment for a long time [7]. Therefore, the HMW 5 - 6 ring PAHs were primarily from a pyrogenic source. This variation can be explained by the action of industrial activities, oil, gas, oil spills, pipelines and shipping off the coastal zone [17]. In addition, the highest PAH level for this study is

Table 2. Diagnostic ratios of PAHs in sediments.

Sites	ΣLMW/ΣHMW	Fla/(Fla + Pyr)	B(a)A/(B(a)A + Chr)
TKZ	18.67	0.48	0.00
ADDA	12.61	0.43	0.02
ADJU	52.22	0.43	0.10
JAC	20.58	0.30	0.13
ADJ	2.06	0.17	0.09
BML	66.66	0.16	0.00
BMP	4.36	0.44	0.00
AZT	1.68	0.32	0.12
ACD	2.41	0.18	0.11
ACG	9.09	0.80	0.01
AL	45.85	0.57	0.01
AP	89.69	0.44	0.08

approximately 45.5 times lower than the maximum PAH concentration (78,523 μg/kg) for Guanabara Bay in Brazil, likely due to industrial activities and high population density [19]. The TKZ, ADJU, JAC, ACG, and AL stations have the highest PAH levels. This is because these are subject to oil activities, intense shipping activities, and oil spills. These high concentrations can be attributed to industrial and household wastes and oil activities on platforms upstream of these stations. The highest percentage of PAHs in sediment was found at the estuary BML station. Estuaries are characterized by receiving large amounts of organic matter and minerals from the drainage basin. This station is located not far from a main thoroughfare confirming the increased traffic intensity which is a significant source of PAH contamination [20]. It is the most urbanized and populated. Also, due to industrial, petroleum, and domestic activities related to offshore drilling activities upstream, it receives inputs of runoff from nearby landfills, atmospheric fallout from exhaust fumes from high traffic areas. There is also a wide range of economic and tourism activities along the roadside. Similar trends have been observed for river sediments in other studies. In addition, there is significant PAH pollution attributed to urban runoff and industrial activities in an industrialized region with a large anthropogenic influence [21]. The lowest concentrations at ADDA (90.67 mg/kg), AZT (50.81), ACD (40.76) stations could be attributed to the confined nature of these locations and the lesser road traffic to which they are exposed. It is shown that areas away (downstream) from industrial activities and heavy traffic have relatively low PAH concentrations. Higher concentrations are also observed near petroleum-related activities such as the oil refinery, oil terminal, and oil and gas production areas [15]. Also, residential sites affected by heavy traffic emissions have fairly high concentrations (AL: 473.72 mg/g and AP: 838.01 mg/g) [21].

3.3. Source Identification

PAH sources were predicted using conventional diagnostic ratios reported in several studies [10]. Different ratios between low and high molecular weight PAHs were used to analyze the main sources of emission of this compound in soils and sediments (**Table 2**). The diagnostic ratio of PAH components can be used to determine the contributions from different PAHs sources. Different diagnosis ratios indicate specific emission sources.

All sediment samples analyzed show ∑LMW/∑HMW ratios greater than 1 (**Table 2**) with a predominance of low molecular weight species over high molecular weight PAHs. This suggesting similar source for all samples and that the low weight species tend to be more conserved in the sediments [1]. Thus, the primary source of PAHs is petrogenic [1]. This is confirmed by the value of the Fla/Pyr ratio of 0.60 less than 1 [21]. The main source of low molecular weight (LMW) PAHs is mainly due to anthropogenic activities involving low temperature combustion process of coal and biomass [21]. Other sources include industrial activities, urban wastewater, chemicals, spills, oil leaks from drilling near oil installations, ships, discharges from oil exploration and exploitation, discharges from fuels (diesel, super), lubricating oils or tire debris and shipping [10]. However, high molecular weight PAHs (HMW; 4 - 6 rings) were low, this may reflect the presence of high combustion from pyrogenic sources [20]. The BaA/(BaA + Chr) ratio is more appropriate for identifying pyrolytic sources [22]. All nearshore samples have BaA/(BaA + Chr) ratios below 0.2, suggesting petroleum contamination (Yunker *et al*., 2002). 25% of the samples have BaA/(BaA + Chr) ratios greater than 0.1, indicating inputs from pyrogenic sources [18]. The value of IND/(IND + B(ghi)P) ratio [23] of value 0.5 between (0.2 - 0.5) corresponds to a petroleum combustion source [8]. The same is true for the Ant/(Ant + Phe) ratio with an average value of 0.2 greater than 0.1 which therefore confirms the source of oil combustion. Fla/(Fla + Pyr) ratio values less than 0.4 indicate petrogenic sources [24] subject to liquid petroleum, and chemical contamination. These are the JAC, ADJ, BML, AZT, and ACD sites, which are major shipping lanes with the presence of a BML estuarine area [25]. For TKZ, ADDA, ADJU, BMP and AP where oil exploration is undertaken, the Fla/(Fla + Pyr) values are between 0.4 and 0.5. This implies that these sites are polluted by fossil fuels [24]. There are large freight and tourist ships along the coastline that could account for the source of fossil fuels. These stations are located where there is frequent traffic from oil and shipping activities. Fla/(Fla + Pyr) values above 0.5 are obtained at the ACG and AL sites. The samples from these sites are far from the action of wastewater discharges, industrial, oil and shipping activities, which explains their low PAH content. Mixed sources of PAHs in these areas may be due to transport of pollutants from other areas via the tidal current to local pollution sources. It is clearer that these sources are a mixture of oil and combustion sources (fossil fuels and biomass) but suggest that oil sources are the primary and fossil fuel sources and biomass combustion are the secondary sources of

PAHs. The ratios of the different PAH isomers are usually plotted in a cross plot to determine the types and source of PAHs in the environment. Thus, the graphs of the diagnostic ratio (LMW/HMW and Fla/Pyr); IND/(IND + B(g h i)P) and Fla/(Fla + Pyr) (**Figure 2** and **Figure 3**) consolidate the results obtained by the previous table and other integrated diagnostic ratios and indicate the sources.

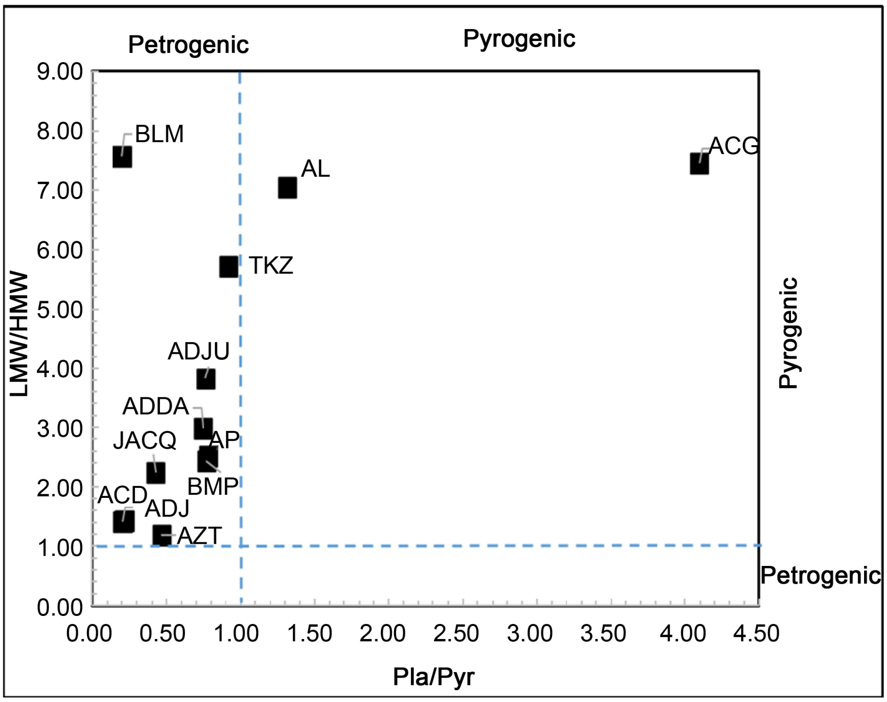

Figure 2. Diagram of molecular index ratios (LMW/HMW) vs. (Fla/Pyr).

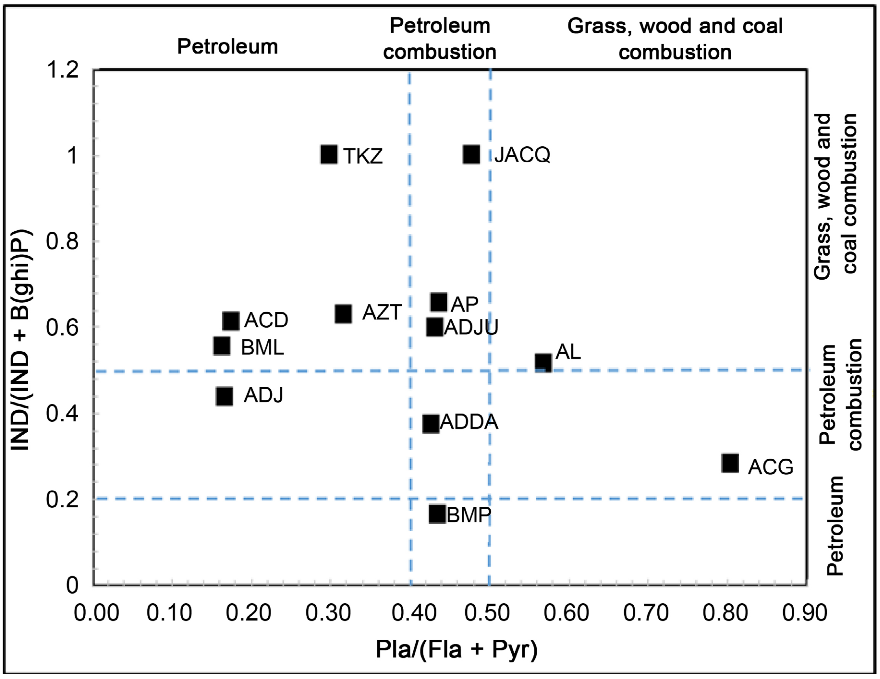

Figure 3. Diagram of molecular index ratios IND/(IND + B(ghi)P) vs. Fla/(Fla + Pyr).

3.4. Source Analysis via Statistical Analysis

The statistical analysis carried out on the data of the 16 detected hydrocarbons allowed to obtain the table of the eigenvalues (**Table 3**). Of the 11 factors obtained only 6 were retained to do the principal component analysis (**Table 2**) [20]. Indeed, a factor is chosen when its eigenvalue is ≥1. Of the 6 factors, F1, F2, F3 and F4 were selected because the correlations between certain parameters and these factors are significant. These factors combined two by two resulted in the correlation circles. According to **Table 4**, the hydrocarbons Ace, Phe, Ant, Chr, B(a)P and IND have significant correlations with the factor F1. These correlations are 0.744, 0.878, 0.817, 0.700, 0.731 and 0.726, respectively. As for the Fle and Fla hydrocarbons, they admit significant correlations of 0.795 and 0.763 respectively with the F2 factor. Like the F2 factor, the F3 factor is correlated with two hydrocarbons (Pyr; r = 0.758) and (B(k)F; r = 0.700). The F4 factor is correlated only with the hydrocarbon B(ghi)P.

Table 3. Distribution of eigenvalue, total variance and correlation between physical and chemical parameters.

	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**	**F9**	**F10**	**F11**
Eigenvalue	4.582	2.791	2.686	1.897	1.319	1.115	0.793	0.397	0.298	0.093	0.028
Variability (%)	28.639	17.442	16.787	11.858	8.248	6.967	4.957	2.479	1.863	0.582	0.178
% cumulative	28.639	46.081	62.868	74.726	82.974	89.941	94.898	97.377	99.240	99.822	100.000

Table 4. Correlation between variables and d factors.

Variables	F1	F2	F3	F4	F5	F6
Nap	0.608	−0.653	−0.047	−0.188	0.001	0.143
Acy	0.220	0.040	−0.209	0.291	−0.435	0.675
Ace	**0.744**	−0.001	0.453	0.451	−0.060	−0.003
Fle	0.082	**0.795**	−0.487	0.072	−0.166	0.011
Phe	**0.878**	0.132	−0.179	−0.289	−0.031	−0.114
Ant	**0.817**	−0.363	−0.096	−0.293	0.173	−0.137
Fla	0.121	**0.763**	−0.418	0.026	0.064	0.110
Pyr	0.338	0.494	**0.758**	−0.195	−0.011	−0.052
B(a)A	−0.248	0.205	0.501	−0.306	0.444	0.558
Chr	**0.700**	0.293	0.007	−0.095	0.592	0.132
B(k)F	0.159	0.611	**0.700**	−0.136	−0.159	−0.092
B(b)F	0.565	−0.072	0.477	−0.073	−0.554	−0.062
B(a)P	**0.731**	−0.274	0.048	0.428	0.034	0.195
IND	**−0.726**	−0.192	0.507	−0.152	−0.213	0.075
DB(ah)A	−0.310	−0.287	0.407	0.476	0.342	0.056
B(ghi)P	0.045	0.235	0.122	**0.895**	0.139	−0.242

The hydrocarbons differ on the one hand by the number of carbon they contain. The statistical study carried out allows us to see a link between certain hydrocarbons by observing the correlation table (Table 5). Ant is significantly correlated to Nap and Phe with respective correlations of r = 0.76 and 0.73. B(a)P and Ace with a correlation r = 0.70 are significantly correlated. Like B(a)P, B(b)F is moderately correlated with Ace with a correlation of r = 0.61. Also, Fle is correlated to Fla with a significant correlation of r = 0.79. With a highly significant correlation of r = 0.94, B(k)F is related to Pyr. However, if Ant is significantly correlated to Phe, it is not so for Chr which is moderately correlated with a correlation of r = 0.62.

Table 5. Corrélation entre différents hydrocarbures.

Variables	Nap	Acy	Ace	Fle	Phe	Ant	Fla	Pyr	B(a)A	Chr	B(k)F	B(b)F	B(a)P	IND	DB(ah)A	B(ghi)P
Nap	**1**															
Acy	0.19	**1**														
Ace	0.39	0.24	**1**													
Fle	−0.42	0.22	−0.13	**1**												
Phe	0.55	0.06	0.43	0.32	**1**											
Ant	**0.76**	−0.05	0.44	−0.28	**0.73**	**1**										
Fla	−0.31	0.22	−0.05	**0.79**	0.26	−0,09	**1**									
Pyr	−0.09	−0.15	0.51	0.02	0.29	0,08	0.09	1								
B(a)A	−0.24	−0.01	−0.15	−0.20	−0.29	−0,24	−0.07	0.41	**1**							
Chr	0.19	−0.04	0.40	0.20	**0.62**	0,57	0.31	0.35	0.29	**1**						
B(k)F	−0.24	−0.10	0.42	0.17	0.17	−0,14	0.19	0.94	0.32	0.14	**1**					
B(b)F	0.27	0.17	**0.61**	−0.16	0.41	0,40	−0.22	0.49	−0.14	0.12	0.39	**1**				
B(a)P	0.50	0.34	**0.70**	−0.11	0.48	0,47	−0.19	0.05	−0.17	0.46	−0.15	0.43	**1**			
IND	−0.29	−0.21	−0.39	−0.36	**−0.66**	**−0,59**	−0.42	0.04	0.38	**−0.61**	0.13	0.03	−0.46	**1**		
DB(ah)A	0.08	−0.13	0.19	−0.41	−0.44	−0,27	−0.19	−0.03	0.15	−0.19	−0.00	−0.24	0.01	0.42	**1**	
B(ghi)P	−0.41	0.01	0.47	0.14	−0.22	−0,25	0.06	0.05	−0.21	0.09	0.08	−0.03	0.33	−0.23	0.32	**1**

According to [18] a correlation is considered strong when it is equal or higher than 0.70. The principal component analysis carried out according to the factors F1 and F2 resulted in the distribution circle in **Figure 4**. From this figure, it can be seen that the detected hydrocarbons are divided into 4 groups. Fle, B(ghi)P and B(a)A form one group. Also, Fla, B(k)F, Pyr, Acy, Phe, Ace, Chr and Acr formed another group. A third group is formed by B(b)F, B(a)P, Ant and Nap. The fourth group is formed by IND and DB (ab)A. According to [18], these groups formed could indicate a common origin for the elements belonging to the same group.

However, considering the factors F1 and F3 (**Figure 5**), which total 46% variance, the distribution circle (**Figure 5**) shows that some hydrocarbons although considered to belong to a group are not. Instead of four groups for the factors F1 and F2 considered, we obtain three groups for the factors F1 and F3 considered. The IND and DB(ab)A which formed the fourth group are associated with DB(ab)A to form a group. The B(ghi)P, B(k)F, Pyr, Acy, B(b)F, B(a)P, Ace and Chr form a second group that is full of the most hydrocarbons. More than 90% of the elements belonging to this second group belonged to the second group when considering the F1 and F2 factors and in the same quadrant (**Figure 5**). This allows us,

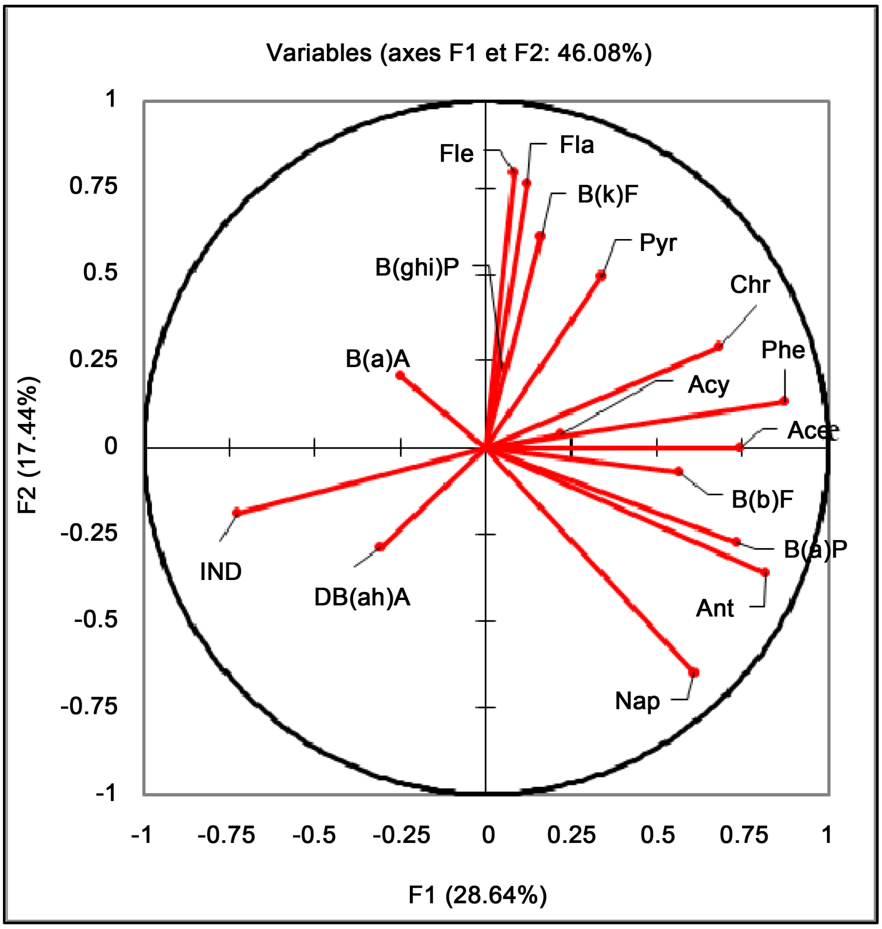

Figure 4. Distribution of hydrocarbons according to the factors F1 and F2.

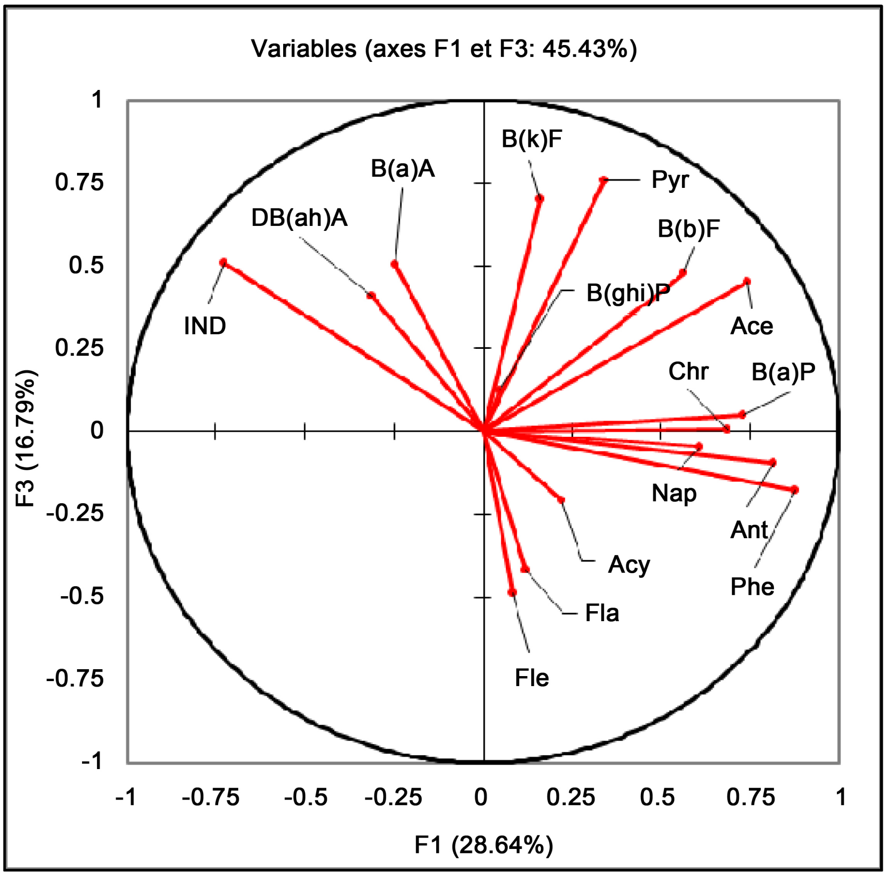

Figure 5. Distribution of hydrocarbons according to the factors F1 and F3.

in accordance with [26] to affirm that these hydrocarbons are indeed of common origin. The third group formed in this figure (**Figure 5**) contains Fle, Fla, Acy, Nap, Ant and phe. Only Nap and Ant did not leave the quarter circle. This suggests that these two elements could indeed be of common origin.

4. Conclusion

In this study, 16 priority listed PAHs were analyzed in GC-MS and all sediments tested had detectable concentrations of PAHs. The general distribution of PAHs in descending order in the nearshore samples is as follows: Nap > Phe > Pyr > Ant > Fla > Fle > Chr > B(b)F > DB(ah)A > INP > B(ghi)P > B(a)P; Ace > Acy > B(a)A > B(k)F. Naphthalene showed the highest relative percentage (332.72%) of total PAHs in the sediment, followed by phenanthrene (41.75%), pyrene (9.42%), anthracene (7.68%) and fluoranthene (5.63%). Based on the adopted classification, the level of PAH contamination is classified as low to very high. Naphthalene is the most abundant with 90.26% of total PAHs followed by 3-ring PAHs (acenaphthylene, acenaphthene, anthracene, phenanthrene, fluoranthene and fluorene) with an abundance of 5.48% of total PAHs. The diagnostic ratios and statistical analysis suggested that sediment PAHs were mainly emitted by petrogenic sources with combustion sources (vehicle emissions, coal and biomass combustion).

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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