



(RESEARCH ARTICLE)



## Concentration of polycyclic aromatic hydrocarbons and quality of sediments in Biétry bay (Ebrié lagoon, Côte d'Ivoire)

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GSC Advanced Research and Reviews, 2024, 20(03), 226–234

Publication history: Received on 16 August 2024; revised on 21 September 2024; accepted on 23 September 2024

Article DOI: <https://doi.org/10.30574/gscarr.2024.20.3.0322>

### Abstract

The work carried out in Biétry bay did not allow us to determine the levels of polycyclic aromatic hydrocarbons (PAHs) present in the sediments. The aim of this study is to determine the concentration of PAHs and the quality of the sediments in this bay. To achieve this, ten (10) sediment samples were taken during the low-water period. The PAH levels were obtained after the extraction of PAHs using Soxhlet and the analysis of the solutions obtained using gas chromatography coupled with a mass spectrometer (GC-MS). The PAH concentrations are distributed heterogeneously. The average values are generally between 0.003 µg/kg (acenaphthene) and 0.103 µg/kg (pyrene). Heavy PAHs are the most abundant in the sediments. Polycyclic aromatic hydrocarbons mainly come from a pyrolytic source. The sediments of stations b1, b2 and b3 are the most toxic. Correlations have highlighted common developments between certain PAHs. Stations b1, b2 and b3 are the most toxic because their TEQ value is higher than the threshold. Fluorene and fluoranthene are respectively the indicators of the level of deterioration of sediments by light PAHs and heavy PAHs.

**Keywords:** PAHs; Biétry bay; Sediments; GC-MS; Soxhlet; TEQ

### 1. Introduction

The industrial boom of recent years has largely contributed to the degradation of the quality of marine environments. It is the source of discharges of organic and inorganic pollutants into coastal water bodies. Among the organic pollutants found in this environment are polycyclic aromatic hydrocarbons (PAHs). These are hydrocarbon molecules formed from benzene rings. They are known for their ability to induce harmful effects on many living organisms and for their persistence in the environment. The sixteen (16) PAHs considered in this study are included in the list of priority pollutants [1 ;2]. These are naphthalene (N), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (P), anthracene (A), fluoranthene (Fl), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chrys), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-ed)pyrene (IdP), dibenz(a,h)anthracene (DaA) and benzo(g,h,i)perylene (BPer). The Ebrié lagoon is a coastal body of water in West Africa, located on the edge of the Atlantic Ocean. It has been facing intense human and natural pressure for several years. This situation results in the pollution of this environment by metals [3 ;4 ] and pesticides [5 ;6 ;7]. The Ebrié lagoon has several bays including the Bay of Biétry. This bay is one of the most documented bays [8 ;9 ;10 ;11]. It is used for fishing, swimming and navigation. It receives industrial and domestic wastewater without any treatment (Coulibaly et al., 2011). The work carried out in the Ebrié lagoon system indicated total hydrocarbon concentrations varying between

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57 and 1194  $\mu\text{g/g}$  in this confined environment [12]. Also, total polycyclic aromatic hydrocarbon contents ranging from 0 to 770.24  $\mu\text{g/g}$  were recorded in the sediments [13]. These different studies did not identify the types of polycyclic aromatic hydrocarbons present in the Bay of Biétry. This work aims to determine the qualitative and quantitative characteristics of polycyclic aromatic hydrocarbons and their effect on the quality of the sediments of the Bay of Biétry.

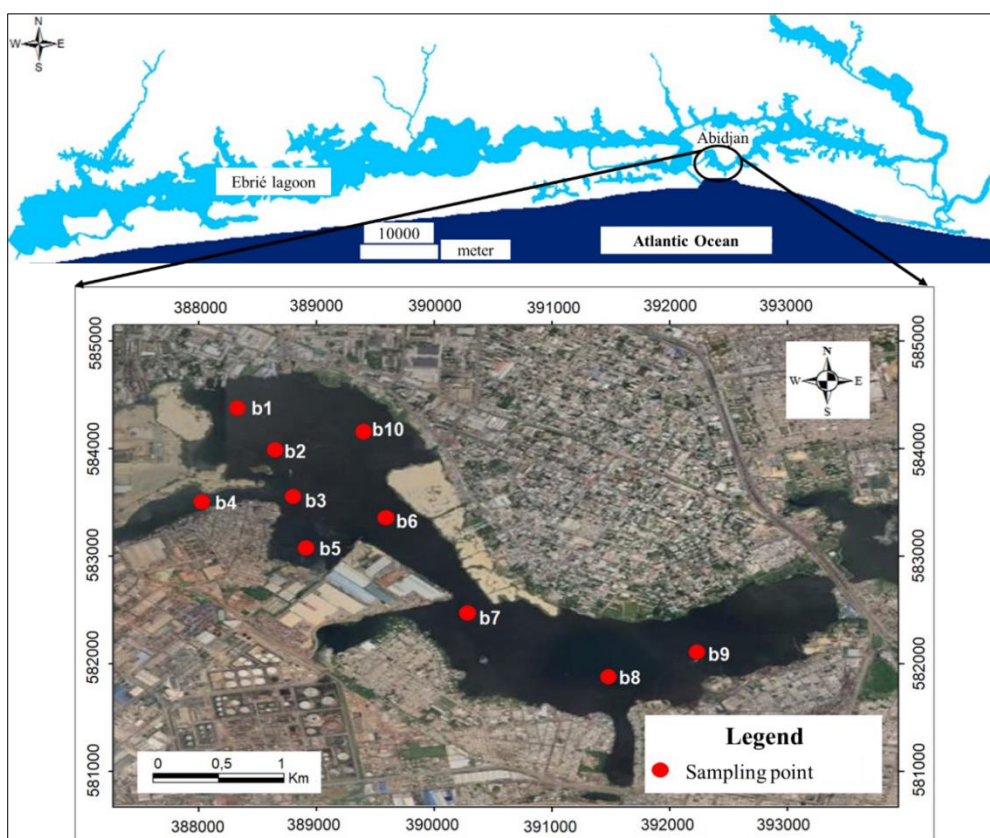
## 2. Material and methods

### 2.1. Presentation of Biétry Bay

Biétry Bay is located in the eastern part of the southern shore of the Ebrié lagoon (Figure 1). It has an area of 6  $\text{km}^2$ . Its maximum depth is 15 m [9 ;11]. This bay has been the main endpoint of the sewer network in the southern sector of Abidjan since 1984. It is bordered by industrial units (painting, refining, brewing) which discharge their wastewater there [14 ; 15].

### 2.2. Sediment sampling

A campaign organized in Biétry bay in March allowed 10 sediment samples to be collected using a Van Veen type grab (Figure 1). Representative amounts of each bottom sediment are sampled and placed in amber bottles. A sheet of aluminum foil is placed over the neck to prevent any contact between the sample and the plastic cap. These precautions are taken because of the photosensitivity of some PAHs and to avoid any contamination of the sediment.



**Figure 1** Location of Biétry bay and sampling points

### 2.3. Chemical analysis of sediments

The samples are sieved at 2 mm, crushed and freeze-dried. The sieve used is nylon. The extraction of PAHs is done in soxhlet, using a mixture of hexane and acetone as solvent. An air jet allows the evaporation of the solvent. The residue is then taken up with hexane. The purification takes place on a column of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ). The liquid obtained is analyzed by gas chromatography coupled with a mass spectrometer [16 ;17].

## 2.4. Identification of the origin of PAHs

Source identification is based on the ratios phenanthrene/anthracene (P/A), fluoranthene/pyrene (Fl/Pyr), low molecular weight (LMW)/high molecular weight (HMW) and the diagram  $P/A = f_n(Fl/Pyr)$ . When the values of the P/A ratio ( $P/A < 10$ ) are less than 10, they characterize a petroleum source. A P/A ratio  $> 10$  designates a pyrolytic source. The Fl/Pyr ratio also makes it possible to separate the two sources. Indeed, petroleum sources are highlighted by a ratio value less than 1, on the other hand a Fl/Pyr ratio  $> 1$  is synonymous with a release by pyrolytic sources [18 ;19 ;20]. In the absence of pyrene in the sediments of stations b9 and b10, the first two indices were completed by the LMW/HMW ratio, to determine the origins of the hydrocarbons in these samples. The value of this ratio is less than 1 for PAHs from pyrolytic sources and greater than 1 for those of petroleum origin [21]. To refine the identification of the sources, the  $P/A = f_n(Fl/Pyr)$  diagram was used. It consists of two parts. One characterizes the samples from petroleum sources and the other the samples of pyrolytic origin [18]. Its interpretation is based on those of the P/A and Fl/Pyr ratios.

## 2.5. Assessment of the toxic potential of PAHs

The level of degradation of sediments by PAHs was determined using the toxic quantity equivalent to dioxin (TEQ). It was calculated by assigning each PAH an equivalent toxicity factor. Fish is a fishery product widely consumed by the Ivorian population. Also, it is fished in the Ebrié lagoon and more precisely in the Bay of Biétry, because of its proximity to the Atlantic Ocean. For these reasons, this work will use the toxic equivalence factors for fish (Fish Potency Factor : FPF), indicated in table 1. The toxic potential is determined in two steps. The first consists of multiplying the concentrations in pg/g of each PAH present in the environment by its fish equivalence factor. The second step adds up the values obtained. The TQE values are analyzed taking into account the NOEC threshold (no observed effect concentrations). It refers to the concentration below which toxic effects cannot be observed. Its threshold value is 200 pg/g [22].

$$TEQ = \sum (FPF_{HAP_i} \times [HAP_i])$$

**Table 1** Values of the toxic equivalence factor for fish of PAHs [23]

Fl	Pyr	BaA	Chrys	BbF	BkF	BaP	IdP	DaA	BPer
$2.10^{-9}$	$3.85.10^{-7}$	$2.10^{-4}$	$6.59.10^{-5}$	$1.66.10^{-4}$	$1.28.10^{-3}$	$2.44.10^{-4}$	$1.88.10^{-3}$	$2.72.10^{-4}$	$1.02.10^{-5}$

## 3. Results and discussion

### 3.1. Qualitative characteristics of PAHs

The PAHs encountered can be classified into four groups based on the number of samples in which they are identified. Group 1 includes the PAHs encountered in all sampling stations in the bay. These are acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene. They represent 37.5% of the PAHs encountered in the bay. The PAHs analyzed in seven or eight stations form group 2. There are three of them (naphthalene, pyrene and chrysene), or 18.75% of the PAHs. Naphthalene and fluorene have a half-life of 15 to 48 days and 32 to 60 days respectively [24]. The observation of these substances could suggest a recent release of hydrocarbons into the Bay of Biétry. However, the other PAHs analyzed have a longer half-life, ranging from 16 days to 5.9 years [24]. This makes it difficult to identify the period of release of hydrocarbons into the bay. The presence of chrysene in the bay would indicate an emission of PAHs into the environment by individual heating [25], waste incinerators or gasoline vehicles [26]. Group 3 is formed by benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-ed)pyrene. These PAHs are found in three or four stations. They constitute 31.25% of PAHs. In Group 4, there are 12.5% of PAHs (benzo(g,h,i)perylene and dibenz(a,h)anthracene). They were observed in one or two stations (Table 2). Benzo(g,h,i)perylene is present in samples b2 and b5. This compound is characteristic of contamination by vehicle exhaust particles [27].

### 3.2. Quantitative characteristics of PAHs

The average concentration of naphthalene is 0.04 µg/kg. Its highest concentration is obtained at station b7, located in the center of the bay. The coefficient of variation of the contents is equal to 98.98%. These high values of the coefficient would characterize the very high variability of the concentrations of hydrocarbons. The evolution of the concentrations of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene is respectively between 0.001 and 0.012 µg/g, 0.001 and 0.01 µg/g, 0.001 and 0.020 µg/g, 0.002 and 0.050 µg/g, 0.002 and 0.025 µg/g and between 0.008 and 0.088 µg/g. The coefficients of variation of the concentrations of these PAHs are between 73.4 and 121.05%.

This would indicate a heterogeneity of their concentrations. The average levels are 0.004 µg/kg for acenaphthylene, 0.005 µg/kg for fluorene, 0.027 µg/kg for fluoranthene, 0.009 µg/kg for anthracene and 0.012 µg/kg for phenanthrene. These PAHs are highly concentrated in the sediments of station b1, in the north of the bay. Pyrene and chrysene were identified in the same stations. Their respective average concentrations are 0.103 µg/kg and 0.039 µg/kg. The maximum level of pyrene (0.440 µg/g) is found at station b6, in the centre of the bay. Chrysene is highly concentrated in the sediments of station b1 (0.131 µg/g). The coefficients of variation of the pyrene and chrysene contents are very high (142.59% and 102.36%). The chrysene and pyrene contents show very high variability. Benzo(a)pyrene is identified in the sediments of three stations (b3, b5 and b6). Its average concentration is 0.013 µg/kg. With a coefficient of variation of 10.14%, its highest concentration (0.014 µg/kg) is recorded at station b6. The low value of the coefficient of variation of the benzo(a)pyrene contents would show their harmonious distribution in the bay. Benzo(b)fluoranthene and benzo(k)fluoranthene are found in the same sampling stations. Their respective average concentrations are 0.058 µg/kg and 0.094 µg/kg. The highest concentration of benzo(b)fluoranthene is identified at station b3 and that of benzo(k)fluoranthene at station b1. Their contents have high coefficients of variation. The average concentration of benzo(a)anthracene in the bay is 0.092 µg/kg. Its highest concentration (0.189 µg/kg) is observed at station b2. Indeno(1,2,3-cd)pyrene has a coefficient of variation of its contents which is 71.88%, with an average content equal to 0.051 µg/kg. Its maximum content is observed in sample b3 (Table 2 ; Figure 2). The levels of indeno(1,2,3-cd)pyrene would vary greatly from one station to another in the bay. The distribution of PAH concentrations in the Bay of Biétry would be due to the hydrodynamics, the layout of the discharge zones and their lifespan. Indeed, the distribution of anthropogenic activities around an environment is the basis of the heterogeneity of the contamination of this zone [28].

**Table 2** Characteristic values of PAHs in Biétry bay

	N assets	Mean	CI (-95-95%)	Minimum	Maximum	SD	CV (%)
N	7	0.040	0-0.08	0.001	0.106	0.04	98.98
Acy	10	0.004	0-0.01	0.001	0.012	0.00	86.15
Ace	10	0.003	0-0.01	0.001	0.010	0.00	97.68
F	10	0.005	0-0.01	0.001	0.020	0.01	102.55
P	10	0.012	0-0.02	0.002	0.050	0.01	121.05
A	10	0.009	0-0.01	0.002	0.025	0.01	73.40
Fl	10	0.027	0.01-0.04	0.008	0.088	0.02	83.25
Pyr	8	0.103	-0.02-0.23	0.019	0.440	0.15	142.59
BaA	3	0.092	-0.12-0.31	0.018	0.189	0.09	94.54
Chrys	8	0.039	0.01-0.07	0.007	0.131	0.04	102.36
BbF	4	0.058	0.03-0.09	0.036	0.077	0.02	31.58
BkF	4	0.094	-0.06-0.25	0.007	0.225	0.10	100.55
BaP	3	0.013	0.01-0.02	0.012	0.014	0.00	10.14
IdP	3	0.051	-0.04-0.14	0.010	0.080	0.04	71.88
DaA	1	0.009		0.009	0.009		0.00
BPer	2	0.020	-0.08-0.12	0.012	0.028	0.01	55.42

N Assets : number of samples in which PAH was detected ; CI : Confidence Interval ; SD : Standard Deviation ; CV: Coefficient of Variation

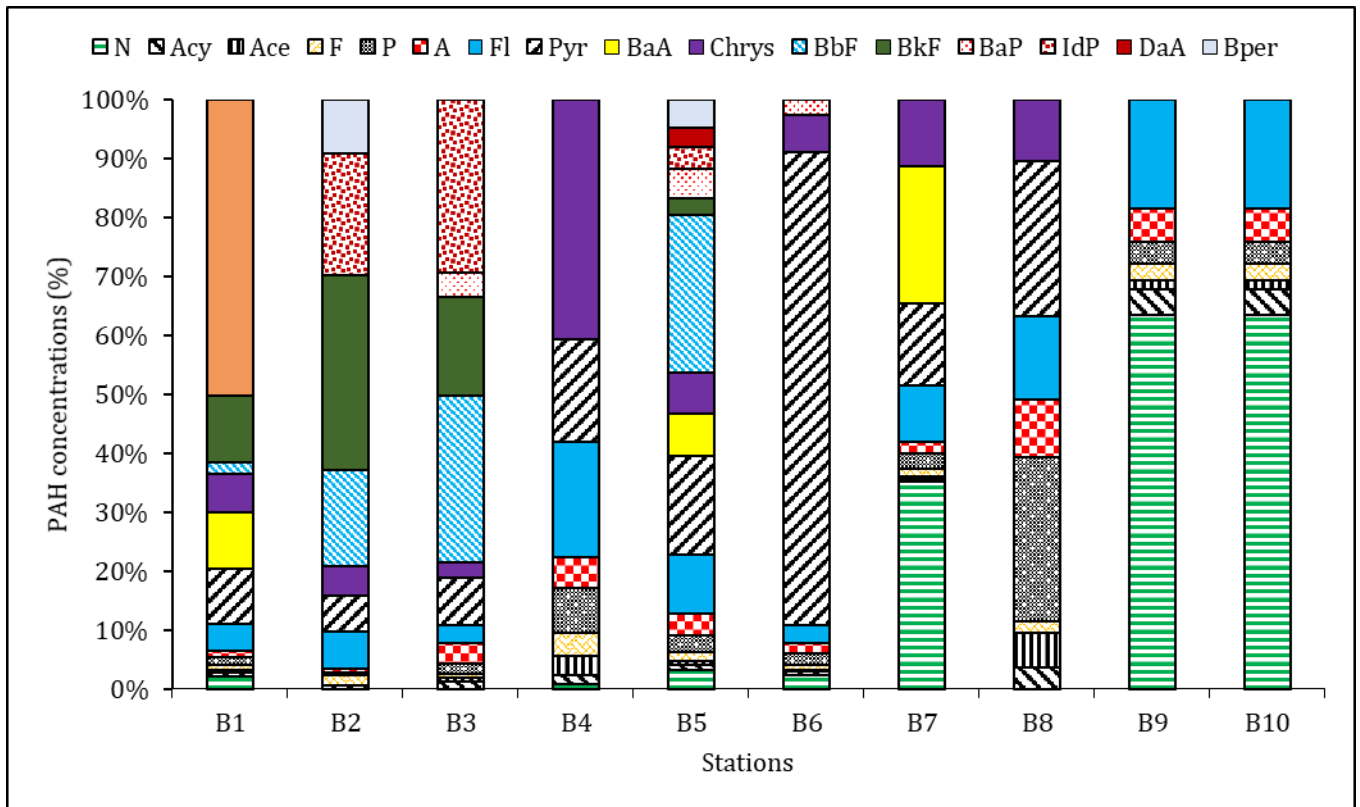


Figure 2 Proportions of PAHs in the samples

### 3.3. Origins of PAHs

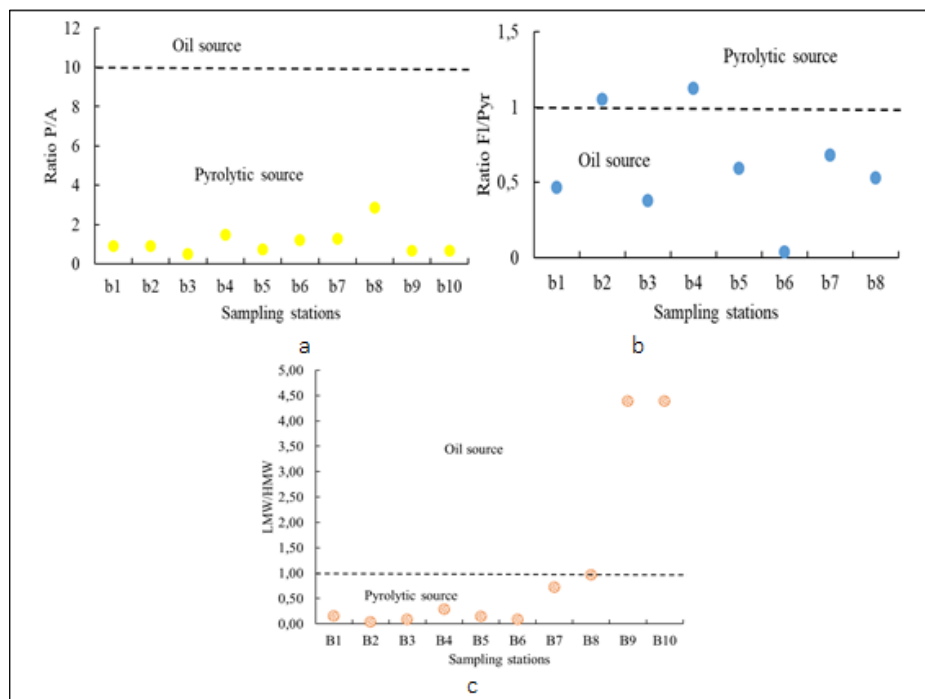
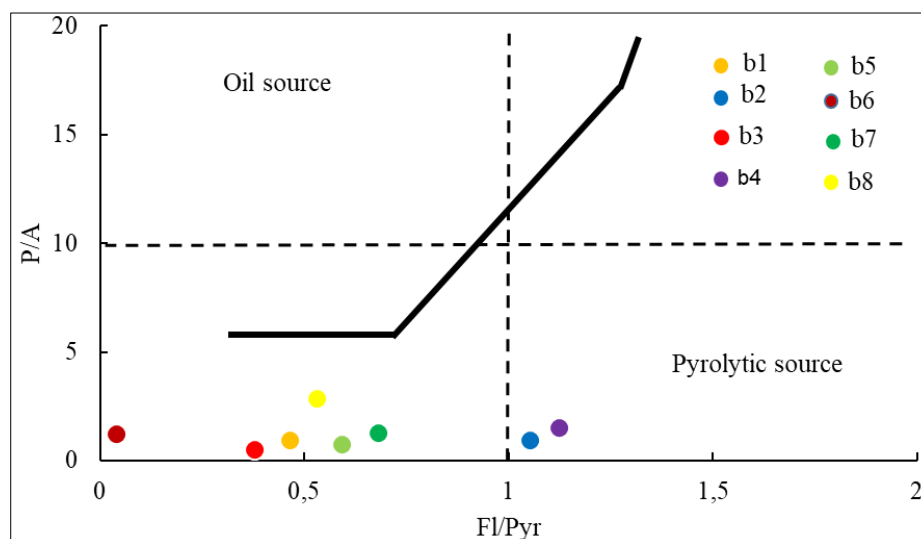


Figure 3 Source of PAHs according to aromatic indices

The P/A ratio values vary between 0.49 and 2.85. They are all less than 10. The PAHs identified in Biétry bay are of pyrolytic origin (Figure 3a). In the case of the Fl/Pyr ratio, the values oscillate between 0.04 and 1.12. The aromatic indices of stations b2 and b4 (20% of the stations) are greater than 1. The PAHs of these stations are of pyrolytic origin. Stations b1, b3, b5, b6, b7 and b8 (60% of the stations) have index values less than 1. The PAHs of these stations come from an oil source. The Fl/Pyr ratio was not calculated in stations B9 and B10 (Figure 3b). The LMW/HMW ratio values

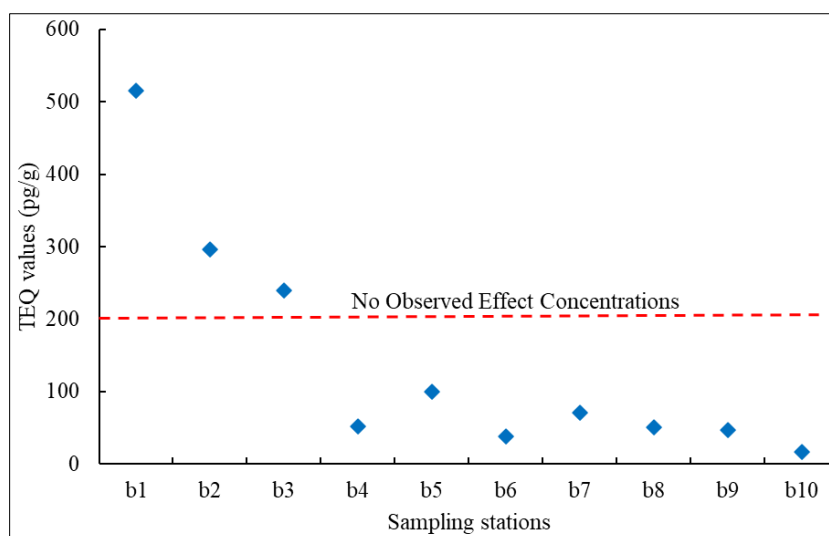
are between 0.03 and 4.39. Samples from stations b1 to b8 (80% of stations) have LMW/HMW values lower than 1. PAHs from stations b1 to b8 come from a pyrolytic source. Heavy PAHs have high levels in stations b1 to b8. This trend could be explained by their less soluble and more lipophilic nature [28], which would make their degradation difficult. Stations b9 and b10 have the same aromatic index values (4.39). This value is higher than 1. PAHs from stations b9 and b10 are of petroleum origin (Figure 3c). The results highlight a difference between the sources of PAHs determined in the samples by the different ratios used (P/A, Fl/Pyr and LMW/HMW). This difference could be explained by the specific nature of each method but also by a mixture of PAHs coming from several sources by floods or rainwater. Indeed, land erosion by rainwater runoff promotes the mixing of sources. This complicates the identification of the origin of PAHs in the samples [28]. The diagram shows that the PAHs at stations b2 and b4 (20%) are of pyrolytic origin. However, it does not allow the origin of the PAHs at stations b1, b3, b5, b6, b7 and b8 to be determined (Figure 4). This observation confirms the results given by the characteristic ratios. The PAHs would therefore come from a mixed source (mixture of PAHs of different origin).



**Figure 4** Origin of PAHs according to the  $P/A = \text{fn}(\text{Fluo}/\text{Pyr})$  diagram

### 3.4. Quality of sediments in Biétry bay

The values of the toxic equivalent quantity (TEQ) vary from 16.31 to 515.54  $\mu\text{g/g}$ . The maximum and minimum values were recorded at stations b1 and b10 respectively. Stations b1, b2 and b3 have toxic equivalent quantities above the threshold of 200  $\mu\text{g/g}$  (NOEC). These stations could represent a danger for fish. The other stations have TEQ values below the threshold (Figure 5). They would not represent a danger for fish.



**Figure 5** Potential toxicity of sediments from Biétry bay

### 3.5. Correlations between parameters

The correlations are good and positive between the TEQ values and the concentrations of fluorene ( $r = 0.76$ ) and fluoranthene ( $r = 0.71$ ). They reveal an affinity between TEQ and the two compounds that are representative of light (fluorene) and heavy (fluoranthene) PAHs. These two compounds could be considered respectively as indicators of the degradation of sediment quality by light PAHs and heavy PAHs. The correlations are also good and positive with the sum of heavy PAHs and the total PAH content. A good positive correlation is observed between the sum of heavy PAHs and the sum of all PAHs, TEQ, acenaphthylene, fluorene, fluoranthene and chrysene. The total PAH content has good positive correlations with fluorene, acenaphthylene, fluorene, fluoranthene and chrysene. Good positive correlations are also noted between certain PAHs: Acy/F ( $r=0.85$ ), Acy/A ( $r=0.96$ ), Acy/Fl ( $r=0.85$ ), Acy/Chrys ( $r=0.79$ ), Ace/P ( $r=0.96$ ), Ace/A ( $r=0.75$ ), F/Fl ( $r=0.97$ ), F/Chrys ( $r=0.96$ ) and Fl/Chrys ( $r=0.95$ ) (Table 3). They would suggest a common evolution of the contents or a common source of these PAHs.

**Table 3** Correlations between chemical parameters

	$\Sigma$ LMW	$\Sigma$ HMW	$\Sigma$ HAP	TEQ	Acy	Ace	F	P	A	Fl	Pyr	Chrys
$\Sigma$ LMW	1											
$\Sigma$ HMW	0.37	1										
$\Sigma$ HAP	0.51	0.99	1									
TEQ	0.23	0.75	0.73	1								
Acy	0.61	0.72	0.77	0.66	1							
Ace	0.44	0.01	0.08	0.04	0.67	1						
F	0.59	0.87	0.90	0.76	0.85	0.30	1					
P	0.48	0.03	0.06	-0.08	0.60	0.96	0.20	1				
A	0.63	0.58	0.64	0.48	0.96	0.75	0.72	0.69	1			
Fl	0.69	0.76	0.82	0.71	0.85	0.39	0.97	0.28	0.76	1		
Pyr	0.12	0.61	0.59	-0.03	0.26	-0.07	0.32	0.03	0.22	0.17	1	
Chrys	0.61	0.77	0.82	0.63	0.79	0.32	0.96	0.18	0.69	0.95	0.30	1

$\Sigma$ LMW: light HAP sum;  $\Sigma$ HMW: heavy HAP sum,  $\Sigma$ HAP: HAP sum

## 4. Conclusion

The present study aimed to know the concentration status of polycyclic aromatic hydrocarbons and the quality of the sediments of the Bay of Biétry. The concentrations of PAHs show a very large variability in the Bay of Biétry. These PAHs. Pyrene has the highest average content in the sediments of the Bay of Biétry. Heavy PAHs are the most abundant in the majority of sediments because they are less soluble and more lipophilic. PAHs come from mixed sources. Stations b1 to b3 have the highest toxic equivalence quantities. The other stations have TEQs below the threshold. Fluorene is an indicator of contamination by light PAHs in the bay, while fluoranthene is an indicator of contamination by heavy PAHs. The correlations highlighted common developments between certain PAHs.

## Compliance with ethical standards

### Disclosure of conflict of interest

No conflict of interest to be disclosed.

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