



Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in M'Badon Bay (Ebrie Lagoon, Abidjan-Cote d'Ivoire)

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Abstract: Pollution of the environment by polycyclic aromatic hydrocarbons (PAHs) is of great concern because of their persistence, toxicity, mutagenic and carcinogenic nature. The distribution of 8 PAHs in water and surface sediment from M'Badon Bay (Ebrie Lagoon, Côte d'Ivoire) was investigated using high performance liquid chromatography (HPLC). The results showed that the mean PAH concentrations ranged from 0.08 to 2.70 µg/L in waters and from 0.37 to 25.9 µg/kg in sediments. It was found that pyrene and indeno[1,2,3-cd]pyrene have the highest concentrations in waters (12.35 and 4.69 µg/L, respectively) while only pyrene showed the highest concentrations in sediments (154.1 µg/kg). Furthermore, benzo[a]pyrene and indeno[1,2,3-cd]pyrene are frequently detected during the dry, wet, and flood seasons. In addition, highest PAH concentrations was detected during the wet season for both water and sediments. Diagnostic ratio revealed a petrogenic origin of PAHs contamination in M'Badon bay while sediments equivalent toxicity indicated a low toxicity of sediments for living organisms. Also, benzo[k]fluoranthene and benzo[a]pyrene concentrations exceeded in some cases the European Union Maximum Allowable concentrations for surface water (0.1 µg/L). The results of this study suggest that M'Badon Bay water may result in cancer risks to local communities who use it for fishing and domestic purposes.

Keywords: PAHs, Liquid Chromatography, Estuary, Ebrie Lagoon, Côte d'Ivoire

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), compounds resulting from natural and anthropogenic processes, pose risks to animals, plants and people at high concentrations [1, 2]. Indeed, PAHs come from anthropogenic activities (oil spills, domestic and industrial wastewater discharges, biogenic and pyrolytic formations and maritime and road traffic) or from natural activities such as natural forest fires, volcanic eruptions, etc. [3, 4]. The exposure of organisms to PAHs, due to their carcinogenic nature and their potential toxicity, can cause many diseases such as reproductive disorders, DNA mutations, leukemias and cancers [5, 6].

Thus, the presence of PAHs in the environment is a real concern for human health and the ecosystem [7, 8]. It is therefore necessary to assess the impact of PAHs on the environment and human health. Thus, the evaluation of the impact of PAHs by calculating the effect range low (ERL) and the calculation of the effect range medium (ERM), formulated by Long and MacDonald [9], proves to be very useful for researchers [10].

Although numerous studies on the presence and level of PAHs in the environment have been conducted in many developed nations [2, 11], few studies have been conducted in Côte d'Ivoire [12]. Indeed, Affian et al. [12], studied PAHs in sediments collected from Ebrié Lagoon, Côte

d'Ivoire and found the highest concentration in Bietri Bay.

In Abidjan (Côte d'Ivoire), unfortunately, any study has focused on level of PAHs in M'Badon Bay, an estuary in Ebrie lagoon although this area is a potential PAHs contamination zone. In fact, this bay receives runoff from the villages of Akouedo and M'Badon, as well as those from certain areas of Cocody [13]. So, residues of PAHs may enter in this coastal ecosystems via continental runoff, atmospheric deposition, municipal and industrial effluents, and often by direct discharge. Although the using of fossil fuels like fuel-oil (which is an important source of PAHs) has been restricted and even forbidden in developed countries [14], elsewhere including Abidjan, their use is not regulated or supervised.

The aim of the present work is to provide a comprehensive dataset on levels of PAHs analyzed in M'Badon bay. To achieve this, spatial and seasonal distribution of PAHs in water and superficial sediments were investigated. Moreover, contamination origin and potential toxicity of sediments by PAHs in M'Badon bay were studied using Diagnostic ratio

calculation and sediments equivalent toxicity respectively.

2. Material and Methods

2.1. Study Area

The study area for this research was the tropical M'Badon bay located in the Ebrie lagoon in Abidjan, Côte d'Ivoire (Figure 1). The Ebrie lagoon ecosystem is actually a complex of three small lagoons (Aghien, Potou and Ebrie lagoons). The Ebrie lagoon, the highest with an area of about 566 km², is located at the south side of Côte d'Ivoire, between 5°15' and 5°20'N and between 3°40' and 4°50'W, with a mean depth of 4,8 m [13]. This lagoon comprise three bays (Banco, Cocody and M'Badon). The M'Badon bay or Akouedo bay is located between 5°19'N and 3°55'W (Figure 1), with an area of about 1,31 km² and a mean depth of 4 m. Akouedo landfill, Akouedo and M'Badon villages and several districts of Cocody frequently discharge their waste into this water body [15], receiving diverse pollutants for many years.

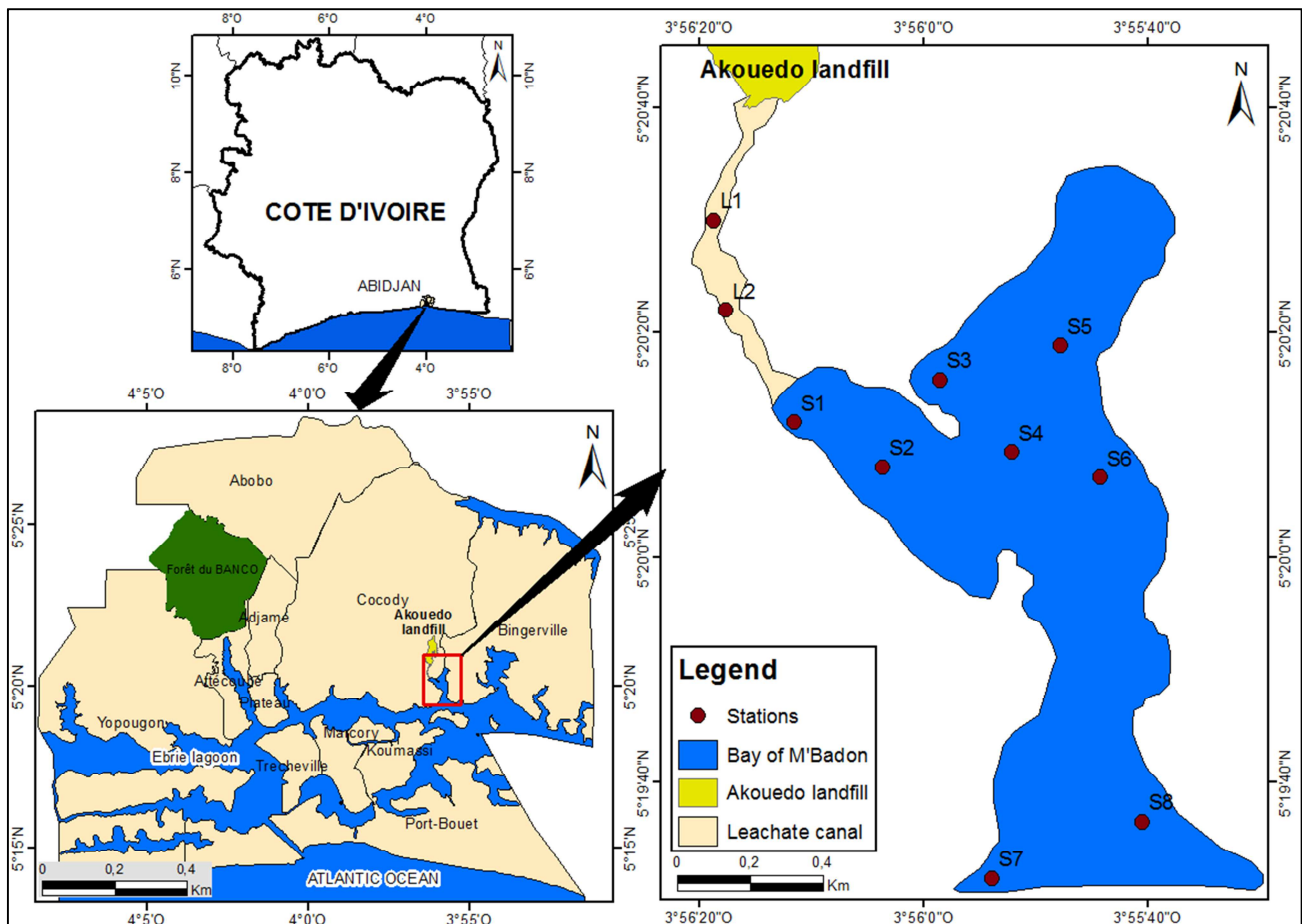


Figure 1. Sampling stations in the M'Badon bay (S_1 to S_8) [16].

2.2. Water and Sediment Sampling

In order to determine the spatial and seasonal variability of pollution by PAHs, water, leachate and sediment were sampled once a month in June, July, September, October,

December 2013 and January 2014 at several stations (Table 1 and Figure 1). Water, leachate and sediment samples were collected during the wet, flood and dry seasons and analyzed to assess eight PAHs (fluoranthene, pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene,

benzo[a]anthracene, benzo[g,h,i]perylene, and Indeno[1,2,3-c,d]pyrene) routinely detected in samples. Water samples were collected in 1 L plastic high density polyethylene bottles at regular intervals during the study period ($n=8$), at a depth of not more than 20 cm below the surface in areas free of debris and vegetation. Each bottle was rinsed with lagoon water five times prior to sample collection and filled and capped underwater to avoid headspace. Moreover, sediment samples were collected at the same times, using a Van veen grab, in an aluminium foil. All these samples were kept in an ice freezer until to the laboratory and stored at -20° for sediment samples and at 4°C for water samples and were analyzed as soon as possible after collection.

Table 1. Localization of the sampling stations.

Sampling stations	Latitude (N)	Longitude (W)
L1	$05^{\circ} 20.420'$	$003^{\circ} 56.316'$
L2	$05^{\circ} 20.320'$	$003^{\circ} 55.276'$
S1	$05^{\circ} 20.200'$	$003^{\circ} 56.193'$
S2	$05^{\circ} 20.180'$	$003^{\circ} 55.909'$
S3	$05^{\circ} 20.264'$	$003^{\circ} 55.975'$
S4	$05^{\circ} 19.859'$	$003^{\circ} 55.647'$
S5	$05^{\circ} 19.724'$	$003^{\circ} 55.821'$
S6	$05^{\circ} 20.051'$	$003^{\circ} 56.000'$
S7	$05^{\circ} 19.478'$	$003^{\circ} 55.947'$
S8	$05^{\circ} 19.629'$	$003^{\circ} 55.622'$

2.3. Chemicals and Reagents

All solvents used in this work were of analytical grade. Dichloromethane, ethyl acetate, acetone, and acetonitrile were purchased from PROLABO, France. Methanol and hexane were purchased from SCHARLAU, France, while SPE cartridge were purchased from MERCK, Germany.

2.4. Sample Extraction and Analysis

At the laboratory, PAHs were extracted and cleanup from water and sediment samples by the procedures described in detail in US-EPA Method [17]. For water samples, PAHs were extracted by dichloromethane using a liquid-liquid separation system, whereas for sediments, samples were first freeze-dried, then soxhlet extracted with dichloromethane. The extracts were reduced in volume on a rotary evaporator, solvent exchanged to hexane, and interfering compounds removed by column chromatography using SPE cartridge. PAHs were eluted with 10 mL of hexane and then transferred to 3 mL vials for High Performance Liquid Chromatography (HPLC) analysis. HPLC was a Shimadzu liquid chromatograph LC-20AT Model equipped with a getter Model DGU-20A5, a SHIMADZU UV/Visible detector, model SPD-20A and a SIL-20A injector model. The device allowed an ultraviolet detection at variable wavelengths and it allowed to obtain gradients of solvent using a pump. Also, with software (LC - solution), it could control the whole system and ensure the data acquisition. The separation was performed on an analytical column type VPODS, 154 mm length and 4.6 mm inner diameter with a degree of pre-column of 10×4.6 mm. The mobile phase consisted of a mixture of acetonitrile (A) and ultrapure water (E)

(acetonitrile/water (80/20)) with a flow rate of 0.5 mL/min and the column temperature was 40°C . The injections were performed with an automatic injector; the injection volume was 20 μL at a wavelength of 284nm and an analysis time of 15 min.

2.5. Source Identification

PAHs can be used as anthropogenic geochemical tracers and are used to identify the origins of pollutants [18]. The ratios of PAHs such as fluoranthene/(fluoranthene + pyrene) and phenanthrene/anthracene have been used to distinguish different sources in urban and rural areas [19-22]. In this study fluoranthene/(fluoranthene + pyrene) ratios were calculated for all samples [23]. Ratios below 0.4 for individual samples show some correlation with their origin or sampling time, and can be ascribed to episodic petrogenic sources (unburned petroleum). Ratios above 0.5 are characteristic of grass, wood or coal combustion, while ratios between 0.4 and 0.5 are characteristic of petroleum combustion [24].

2.6. Estimation of Carcinogenic Potencies

Knowing PAHs concentrations in the different media allows the estimation of carcinogenic exposure risk to residents of the area. Carcinogenic potencies associated with exposure of a given PAHs can be calculated using benzo[a]pyrene Toxic Equivalency Factors (BaP-TEF) as shown in the following Equation [25-26]:

$$\text{TEQ} = \sum Ci \times \text{TEF}_{i\text{carc}}$$

The TEF is expressed as a ratio of a PAHs congener to that of BaP and C_i the concentration of this congener. Adding the product of the concentration of each PAHs and its TEF produces a benzo[a]pyrene Toxic Equivalence Quotient (TEQ) for each site. TEFs for the 5 PAHs studied are listed in Table 2.

Table 2. Toxic Equivalency Factors for the PAHs in this study [1].

Carcinogenic PAHs	BkF	BaP	InP	BaA	BbF
$\text{TEF}_{i\text{carc}}$	0.01	1	0.1	0.1	0.1

BkF: Benzo[k]Fluorene; BaP: Benzo[a]pyrene; InP: Indeno[1,2,3-cd]pyrene; BaA: Benzo[a]anthracene; BbF: Benzo[b]fluoranthene.

3. Results

3.1. Levels of PAHs in M'Badon Bay

The concentrations of PAHs analyzed in water and sediment samples from M'Badon Bay are presented in Tables 3 and 4, respectively. From our results, it appears that pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene are the PAHs whose average concentrations were the highest in water and sediments. In the waters of the Bay of M'Badon, the concentrations of PAHs varied from not detected (nd) to $4.56 \mu\text{g/L}$, with an average of between 0.08 and $2.70 \mu\text{g/L}$ (Table 3). The lowest PAH detection frequencies in water

were obtained for benzo[a]anthracene, benzo[b]fluoranthene and benzo[g,h,i]perylene, with a detection level of less than 7%. As for the highest detection frequencies, they were obtained for fluoranthene and benzo[a]pyrene, with a frequency of 34.1% and 29.5%, respectively. The average concentrations of fluoranthene and benzo[a]pyrene in the lagoon water were 0.19 µg/L and 0.47 µg/L, respectively. The highest mean concentrations of 1.69 µg/L and 2.70 µg/L were obtained for pyrene and indeno[1,2,3-cd]pyrene respectively with detection frequencies of 9.1% for pyrene and 13.6% for Indeno[1,2,3-cd]pyrene.

In the sediments, PAHs concentrations ranged from not detected (nd) to 154.5 µg/kg, with an average ranging from 0.37 to 25.88 µg/kg (Table 4). Benzo[g,h,i]perylene was the least detected PAHs, with a frequency of 7.5%. As for benzo[k]fluoranthene and Indeno[1,2,3-cd]pyrene, they were the most detected, with a rate of 65% and 67.5% respectively and average concentrations of 0.57 µg/kg and 1.80 µg/kg, respectively.

3.2. Spatial and Seasonal Distribution of Individual PAH

The concentrations of each individual PAH in water and sediment samples in M'Badon bay and in Akouedo's dump site leachate are shown in Figure 2. For fluoranthene, the levels in leachate, water and sediments (Figures 2a and 2b) were overall weak, excepted in leachate flow (L2) and at the entry points of the bay (S₁, S₇ and S₈). In water, concentrations of fluoranthene reached a level of 1.43 µg/l at L2, S1 and S7 sites, while it reached a level of 1.81 µg/kg at L1, L2, S1 and S8 points. L1 and L2 points are situated in Akouedo's dump site leachate, S1 point is closed to the Akouedo's leachate flow, while S7 and S8 sites are situated at the entry points of the bay draining waters from others parts of Ebrie lagoon, such as Anna, Cocody... For pyrene concentrations recorded in sediments (Figure 2d) were overall higher than in water samples, where the maximum level was around 12.35 µg/l at S4, S6, L1 and L2 sites (Figure 2c). In sediments, higher concentrations of pyrene was between 44.45 and 154.15 µg/kg at S4 site, while at the others sites, including leachate and M'Badon bay, the level of pyrene was not negligible. For benzo[k]fluoranthene, the relatively low concentrations released in M'Badon bay water and in Akouedo's dump site leachate (Figure 2e) contrasted with the high concentrations released in sediments at L1 and L2 sites in leachate flow and at the entry site S₁ of the bay, where it reached up 42 µg/kg (Figure 2f). For benzo[a]pyrene, the observation was similar to that made for fluoranthene

presciently where the concentrations were higher at L1 and L2 sites in leachate flow and at entry points S₁ and S₈ in the bay (Figure 2g). However, level of benzo[a]pyrene released in water samples and sediments at M'Badon bay were globally weak, as there were lower than 2.20 µg/l and 1.50 µg/kg in waters and sediments respectively. Concentrations of in waters were higher at S4, S5 and S8 points and were weakest at L1 and L2 point in leachate flow and in S1 and S2 points in M'Badon bay (Figure 2i). S5 point is situated next to a sand extraction zone using a dredger. In the contrary of waters, concentrations of indeno[1,2,3-cd]pyrene in sediments were higher at L1, L2, S1 and S3 points and were lower at S4 and S5 points (Figure 2j). Level of benzo[g,h,i]perylene in waters and sediments were overall weak (Figure 2k and 2l), excepted at L2, S4 and S5 points respectively where it reached a level of 3.36 µg/l in waters and 1.90 µg/kg in sediments. At Akouedo's leachate points L1 and L2, level of benzo[g,h,i]perylene was important in waters and weaker in sediments, but at S1 and S2 points close to L1 and L2 concentrations are weakest. Also, it was only at L1, L2 and S8 point that level of benzo[a]anthracene was higher in water and sediments in M'Badon bay and in dump site leachate, although concentrations of benzo[a]anthracene were overall weak. In water samples, it reached a level of 2.25 µg/l and in sediments a level of 1.14 µg/kg (Figures 2m and 2n). Concentrations of benzo[a]anthracene in sediments were also higher at S1, S4 and S8 points flow. Finally, concentration of benzo[b]fluoranthene in water samples and sediments of M'Badon bay are weak. At all points in the lagoon and leachate, level of benzo[b]fluoranthene is below 0.080 µg/l in waters and below 0.32 µg/kg in sediments (Figure 2o and 2p).

Moreover, the fluctuations of PAHs concentrations in the present study indicated the influence of seasonal variation in prevailing atmospheric conditions which foster PAHs dispersion and decomposition. PAHs were detected essentially during flood and dry season, except for benzo[a]pyrene and indeno[1,2,3-cd]pyrene which were detected at all seasons (Table 5). Highest total PAHs concentrations in M'Badon water samples were detected in wet season. In sediment samples from M'Badon bay, PAHs were detected at all seasons (Table 6). Highest PAHs level in sediments was detected in wet season, while weakest level was detected in dry season. Highest level in wet season was correlated by level in lagoon water, where highest level was detected at the same season.

Table 3. Concentrations of PAHs (µg/L) in water samples collected in the M'Badon bay.

HAP	Flu	Pyr	BkF	BaP	InP	BgP	BaA	BbF
Levels range (µg/L)	nd- 0.39	nd- 4.56	nd- 0.855	nd- 1.56	nd- 4.68	nd- 3.36	nd- 0.19	nd- 0.08
Mean	0.19	1.69	0.44	0.47	2.70	1.79	0.19	0.08
N	15	4	8	13	6	3	1*	1*

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene

N: Number of individual PAHs detection in the 44 water samples analyzed. * Unique value obtained reported.

Table 4. Concentrations of PAHs ($\mu\text{g/Kg}$) in sediments collected in the M'Badon bay.

HAP	Flu	Pyr	BkF	BaP	InP	BgP	BaA	BbF
Levels range ($\mu\text{g/Kg}$)	nd- 1.03	nd- 154.5	nd- 2.37	nd- 1.39	nd-5.73	nd-1.90	nd- 1.880	nd- 0.465
Mean	0,75	25.88	0.57	0.67	1.80	1.60	0.72	0.37
N	20	15	26	22	27	3	19	13

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene

N: Number of individual PAHs detection in the 40 sediment samples analyzed.

Table 5. PAHs concentrations ($\mu\text{g/L}$) in water samples collected in the M'Badon bay during the wet, flood and dry seasons.

HAP ($\mu\text{g/L}$)	Flu	Pyr	BkF	BaP	InP	BgP	BaA	BbF	Total
Wet (T=12)	nd	nd	nd	0.21 (p=25)	3.77 (p=25)	3.36 (p=25)	Nd	nd	7.34
Flood (T=16)	0.18 (p=6)	3.04 (p=19)	0.18 (n=31)	0.81 (p=13)	0.43 (p=6)	0.22 (p=6)	Nd	0.08 (p=6)	4.94
Dry (T=16)	0.19 (p=88)	0.34 (p=6)	0.69 (p=19)	0.38 (p=50)	3.89 (p=13)	nd	0.19 (p=6)	nd	5.49

T: Total samples number analyzed during season; nd: not detected or below limit detection;

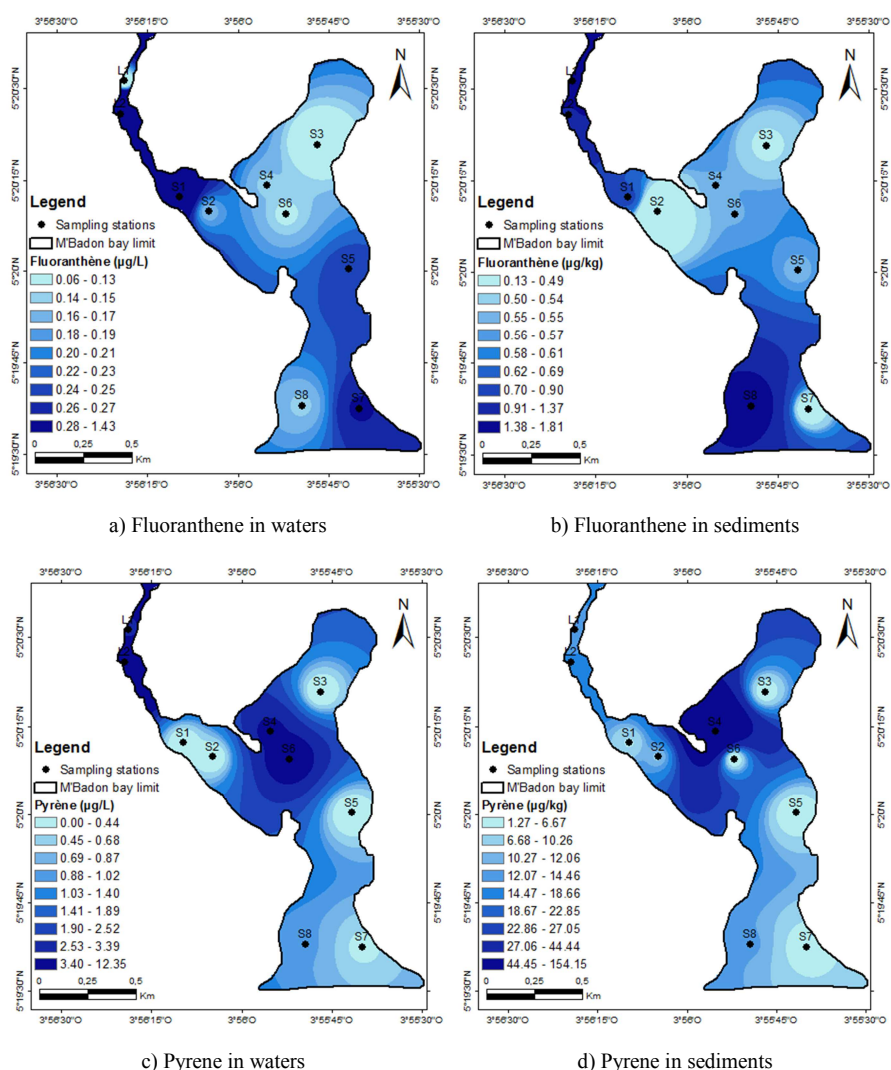
p: Appearing or detection rate of analyzed samples (%).

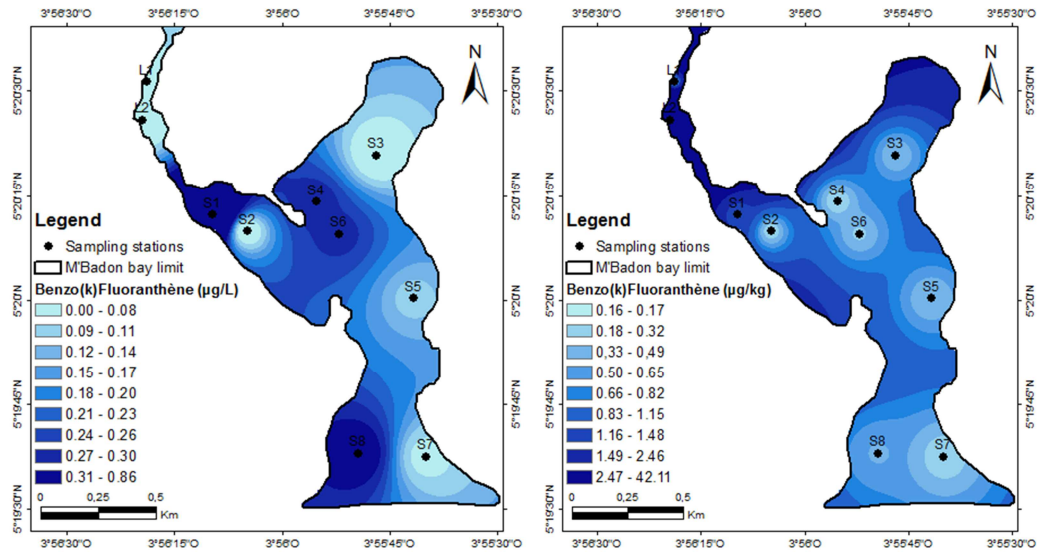
Table 6. PAHs concentrations ($\mu\text{g/L}$) in sediments samples collected in the M'Badon bay during the wet, flood and dry seasons.

HAP ($\mu\text{g/L}$)	Flu	Pyr	BkF	BaP	InP	BgP	BaA	BbF	Total
Wet (T=12)	1.07 (p=50)	67.70 (p=42)	0.96 (p=67)	1.01 (p=75)	1.65 (p=67)	Nd	1.46 (p=42)	0.44 (p=50)	74.28
Flood (T=14)	1.02 (p=29)	6.51 (p=29)	0.52 (p=43)	0.57 (p=29)	1.94 (p=50)	0.42 (p=7)	0.57 (p=71)	0.26 (p=21)	11.80
Dry (T=14)	0.47 (p=71)	3.94 (p=43)	0.33 (p=86)	0.39 (p=64)	1.81 (p=85)	2.19 (p=14)	0.18 (p=29)	0.35 (p=29)	9.66

T: Total samples number analyzed during season; nd: not detected or below limit detection;

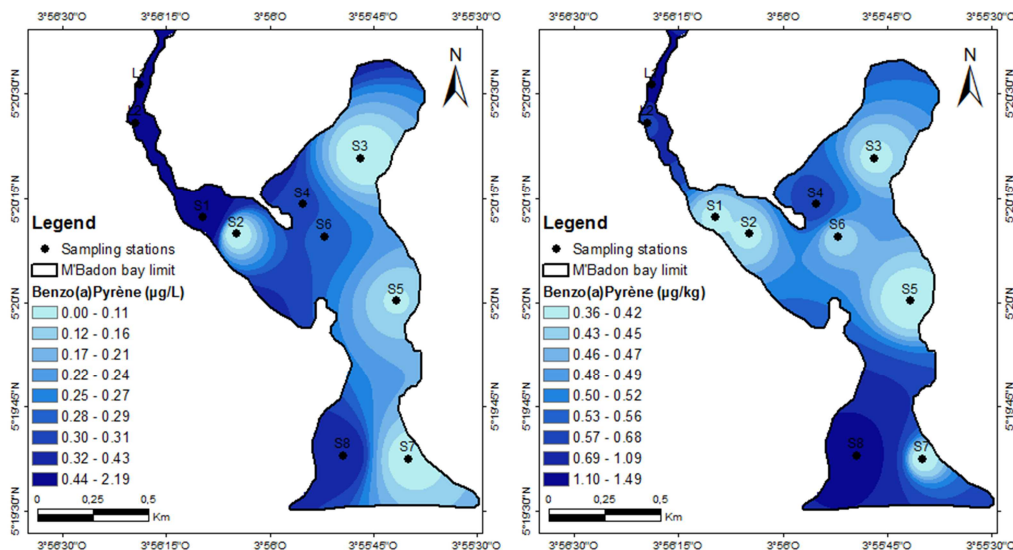
p: Appearing or detection rate of analyzed samples (%).





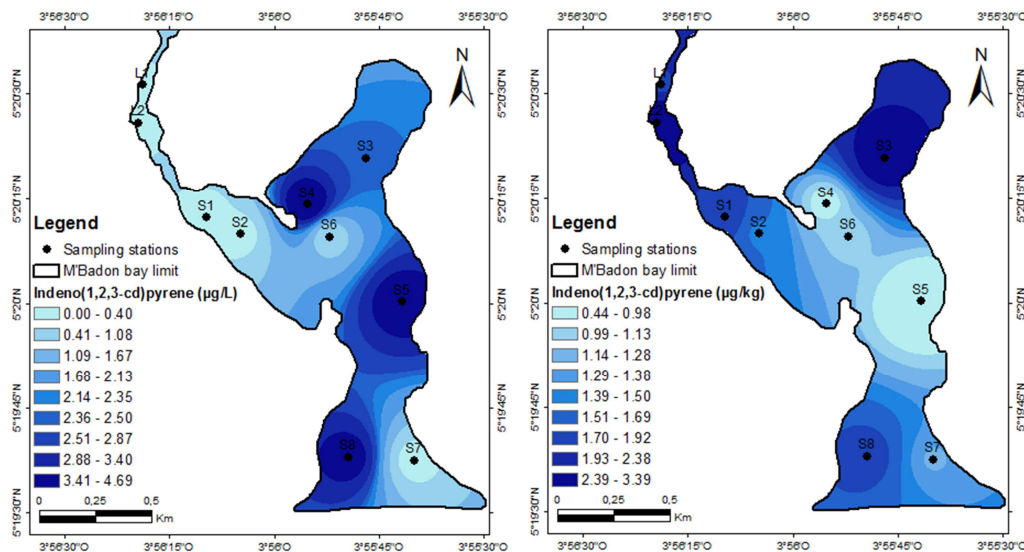
e) Benzo[k]fluoranthene in waters

f) Benzo[k]fluoranthene in sediments



g) Benzo[a]pyrene in waters

h) Benzo[a]pyrene in sediments



i) Indeno[1,2,3-cd]pyrene in waters

j) Indeno[1,2,3-cd]pyrene in sediments

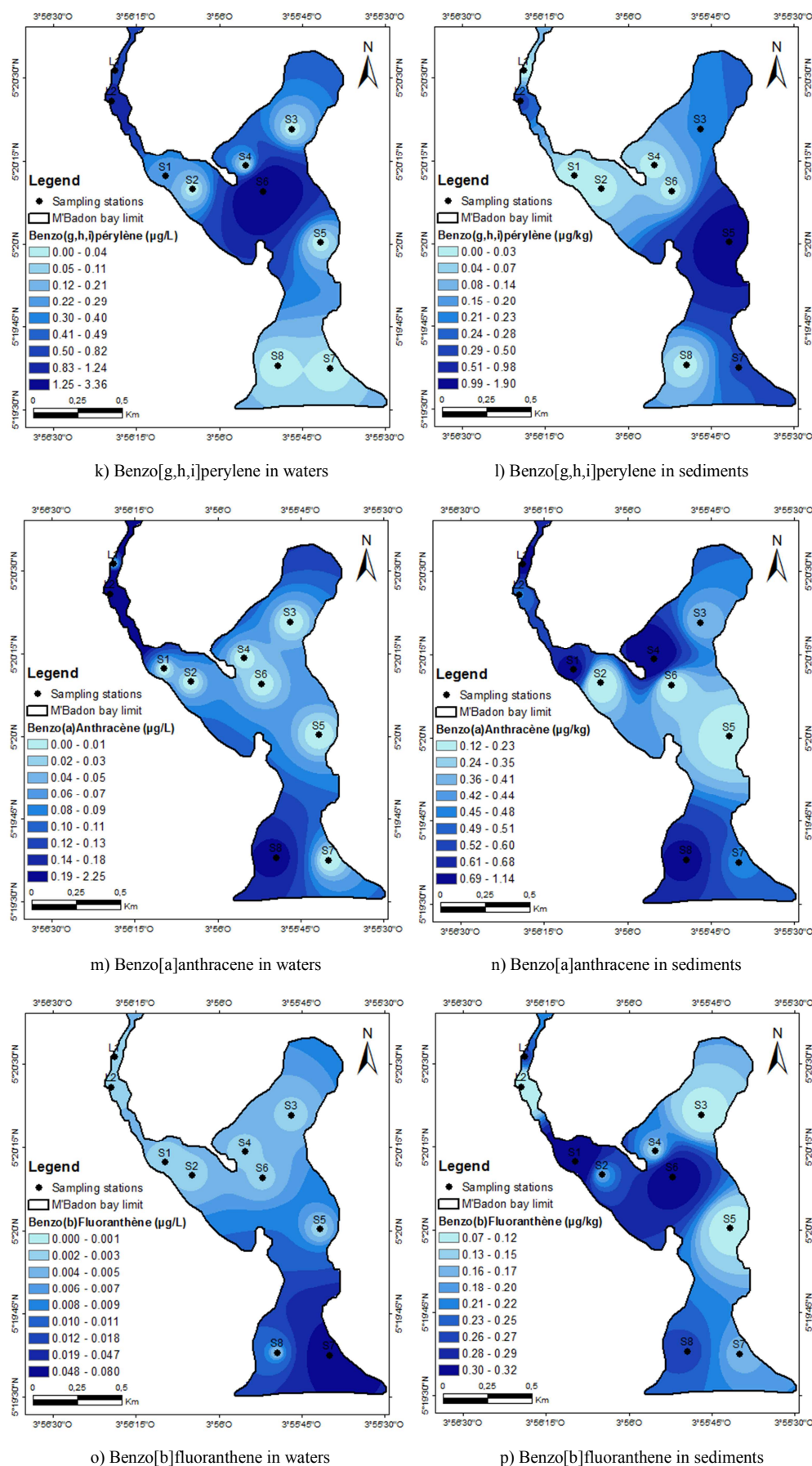


Figure 2. Mean distribution of each PAH in water and sediments of M'Badon lagoon at all stations.

4. Discussion

4.1. Levels of Pahs in M'Badon Bay

The PAHs concentrations in M'Badon Bay water for different sites were in good agreement with studies by Essumang [27] in the Ghanaian coast (nd-2.2 µg/L) but were higher than that reported by Jaward et al. [14], (nd-26.2 ng/L). In sediments, concentrations of each PAH at all stations were higher than those obtained in water of M'Badon Bay. The higher concentrations of each PAH at all stations in sediments were a proof of the deposit of PAHs in sediments. Higher values released in sediments than in water samples, could be explain by PAHs deposit in sediments. Generally, PAHs levels in sediments were weaker than that reported by Affian et al. [12] in Ebrie lagoon, Wagener et al. [28] in Todos os Santos bay in Brazzilia and Nekhavhambe et al. [24] in South-Africa. The higher concentrations of PAHs in these sediments than in water samples were consistent with the high traffic density of boats in this lagoon, the Akouedo's leachate runoff in this lagoon and waste waters coming from village nearby. However, the European Union directive stated a maximum acceptable PAHs value of 0.1 µg/l in water [29] and of 4000 µg/kg in sediments [30]. In sediments, the level of PAHs reported in this studies was weaker than EU maximum acceptable value, but in water it was above the EU maximum acceptable PAHs value excepting for benzo[b]fluoranthene. This data suggests that the lagoon water samples of M'Badon are not suitable for human consumption. In fact, people living around M'Badon bay use this water for many activities such as fishing, agriculture, thereby exposing themselves to dangers and risks, like a risk of cancer [31-32].

Moreover, in this study fluoranthene/(fluoranthene + pyrene) ratios [23] were calculated for all the samples. Ratios obtained in this study ranged between 0.05 and 0.36 for water and between 0.02 and 0.11 for sediments. These obtained ratios (below 0.4) indicated that PAHs in water and

sediments in the M'Badon bay site were mostly of petrogenic origin [24]. This result suggests that PAHs in sediments come from water above which is in agreement with Akouedo's leachate upstream of the site, that enters in lagoon water without treatment, and other commercial activities in the vicinity, such as fluvial transport and sand drudging.

4.2. Sediments Negative Toxic Effects and Carcinogenic Potencies

Calculation of carcinogenic potencies (TEQs) associated with exposure of a given PAH using benzo[a]pyrene Toxic Equivalency Factors (BaP-TEF) are listed in Table 7. TEQs mean values by season ranged from 0.27 to 0.95 µg/Kg with mean of 0.57 ± 0.35 µg/Kg. Comparison of these data with standards such as the Dutch soil standards [33] showed that the TEQ in M'Badon bay sediments were weaker than that of Dutch standard. This data showed the weakest carcinogenic potencies of sediments for living species in M'Badon bay. Sediments from this bay may be used without carcinogenic risk by the population living around.

In addition, the ERL (effect range low) and ERM (effect range median) values, presented in Table 8, highlight the negative toxic effects of the PAHs contained in the sediments on the species living in M'Badon. Indeed, PAH concentrations below the ERL values indicate that no negative effects are to be expected for PAHs [34]. Concentrations of PAHs that fall between the ERL and ERM values imply a mild toxic effect [9] while concentrations above the ERM values indicate a high probability of occurrence of a high negative toxic effect on the species. In our study, all the PAHs analyzed are below the ERL value (Table 8), so there is a very low probability of risk for the organisms living in the bay of M'Badon. Thus, there is a low probability of the occurrence of possible biological effects (cancer, physiological and reproductive disorders, etc.) in species living in and around the bay of M'Badon.

Table 7. PAHs mean Toxic Equivalence Quotient (TEQ) in M'Badon bay sediments (µg/Kg).

TEQ (µg/Kg)	wet	Flood	Dry	Moyenne
sediments	0.95	0.27	0.49	0.57 ± 0.35

Table 8. Concentrations of PAHs in M'Badon bay sediment and toxicity guidelines.

HAP	Flu	Pyr	BkF	BaP	InP	BgP	BaA	BbF
Levels range (µg/Kg)	nd- 1.03	nd- 154.5	nd- 2.37	nd- 1.39	nd-5.73	nd-1.90	nd- 1.88	nd- 0.46
Mean (µg/Kg)	0.75	25.88	0.57	0.67	1.80	1.60	0.72	0.37
ERL (µg/Kg)	600	665	na	430	na	na	261	na
ERM (µg/Kg)	5100	2600	na	2800	na	na	1600	na

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene

ERL: Effect Range Low, ERM: Effect Range Median, na: data not available

4.3. Spatial and Seasonal Distribution of Individual PAH

The distribution of almost all analyzed PAHs at the stations close to the leachate flow (S1, S2, S4 or S6) were in

the same order of the leachate contamination level at points L1 and L2. This distribution highlighted the influence of leachate and therefore the Akouedo dump site on PAHs contamination in M'Badon Bay. This high concentration of

some PAHs at entry sites in M'Badon Bay suggests a contamination by petrogenic sources such as combustion of fossil fuels and vehicle exhausts. Indeed, the entry sites of M'Badon bay (S7 and S8) are the road of many boats that release a significant amount of PAH in the waters of the bay. This is confirmed to some extent by the individual + fluoranthene/(fluoranthene + pyrene) ratios calculated for all the samples [23]. Moreover, the high variability of the most contaminated sites for each individual PAH (Figure 2) is evidence of the influence of external conditions, other than tidal and lagoon currents on M'Badon contamination. Contrary to the other studied PAHs, the distribution of pyrene was higher at stations S4 and S6 and weak at the entry points of M'Badon. This difference in the distribution of pyrene could be explained by the influence of the tide, the lagoon currents and the easy deposition and adsorption of this PAH in the sediments. Also, for some PAHs, the weak concentrations recorded inside the bay, in the contrary of the entry points of the bay, proved the effect of dilution and lagoon currents on the movement of pollution in the M'Badon Bay. The report of the distribution of pyrene in sediments which was similar to those in water, higher than the distribution of other PAHs and weaker at the entry points (S1, S7 and S8) of the M'Badon bay highlighted the negative influence of the leachate and thus the dump site of Akouedo upstream on the qualities of the waters of M'Badon Bay. It is therefore imperative to draw the attention of the public and the public authorities to the treatment of Akouedo leachate before its release into M'Badon bay. Also, the weak distribution of some PAHs in sediments at the entry points (S7 and S8) of the bay could be explained by the strong current recorded during the sampling campaign which makes it difficult to deposit these substances in the sediments. This strong current could also be responsible for the leaching of sediments and thus the release of PAHs in the water column.

Furthermore, an evaluation of the PAHs distribution between water, sediments and Total Organic Compound (TOC) could provide useful information to understand the transport and fates of PAHs. So, the distribution coefficients between water and sediment (K_d) were determined as the ratio of each PAH concentration measured in sediment to that in water [35]. Those of the distribution coefficients between Organic Carbon and water (K_{oc}) were determined as the ratio of K_d obtained for various PAH compounds by sediment Total Organic Carbon (TOC) [35]. Values of K_d and K_{oc} obtained for each analysed PAH are shown in Table 9 and Table 10, respectively. The distribution coefficients for the eight PAHs at each station ranged between 0.11 and 42.02 L/kg for K_d (Table 9) and between 11.05 and 1616.15 L/kg for K_{oc} . The obtained values for K_d in this study are under the range found by Van Hattum *et al.* [36] in netherlands and by Marini and Frapiccini [37] in Lesina lagoon, Italy for each analysed PAH (Table 11). Our results for K_d are almost in the same order of results found by offshore Ravenna harbor [37], Italy for each analysed PAH (Table 11). Also, the obtained values of K_d for total PAH (Σ HAP) are also under the range found by Yuyun *et al.* [38]

and Wei *et al.* [39] in China (Table 11). Between the eight PAHs analysed in that study, benzo[g,h,i]perylene, benzo[a]anthracene and benzo[b]fluoranthene were those with the weakest distribution coefficients K_d . So, benzo[g,h,i]perylene, benzo[a]anthracene and benzo[b]fluoranthene were weakly adsorbed from water to sediment at each station in leachate and in M'Badon bay. Fluoranthene were the better distributed at each station, with distribution coefficients ranged between 0.87 and 30.17 L/kg. The higher distribution coefficients K_d were obtained for pyrene at station S4. This result means that pyrene is very adsorbed by the sediments at this station. Moreover, adsorption of pyrene at this station have given the highest rate of adsorption. In M'Badon bay, the distribution coefficients K_d were overall weak at the stations S1, S2 and S5. In leachate flow, the distribution coefficients K_d were globally higher at L1 station than those at L2 station. This result tends to prove that PAHs were adsorbed throughout the flow of the leachate towards M'Badon bay. The adsorption rate at L1 station, furthest away from the leachate, was higher than the rate at L2 station, nearer to the bay. S4 station where the distribution coefficient K_d of pyrene was of 42.02 L/kg, the distribution coefficients of the studied PAH were higher in leachate (L1 and L2 station). These results show the impact of Akouedo's leachate contamination on M'Badon sediments contamination.

For K_{oc} , values obtained in this study were under the range found by Van Hattum *et al.* [36] for each PAH analysed in netherlands and under those found by Bouloubassi and Salot [40] and Fernandes *et al.* [41] in France for fluoranthene, pyrene, benzo[a]pyrene and benzo[a]anthracene (Table 12). Comparatively to the distribution coefficients K_d , benzo[g,h,i]perylene, benzo[a]anthracene and benzo[b]fluoranthene were PAHs with the weakest distribution coefficients K_{oc} . Moreover, fluoranthene, pyrene and Indeno[1,2,3-cd]Pyrene, were PAHs with the highest distribution coefficients K_{oc} . These results shows that PAHs sorption on sediments could be affected by both organic matter content when sediment TOC values are weak [38]. The observations and interpretations drawn from the values of obtained distribution coefficients K_d were also confirmed by the values of obtained distribution coefficients K_{oc} . Indeed, the higher distribution coefficients K_{oc} were obtained for pyrene at S4 station, the distribution coefficients K_{oc} were overall weak at the stations S1, S2 and S5 in M'Badon bay and in leachate flow, the distribution coefficients K_d were globally higher at L1 and L2 stations.

All statistical analyses were carried out using ANOVA. Statistical analyse tests by ANOVA ($p < 0.05$) indicated any statistical significance at the seasonal factor level of PAHs in M'Badon waters. The results also indicated that the detection frequencies of these PAHs were higher in the flood and the dry months than wet months. This was likely due to increased input via Comoe River in flood season and atmospheric deposit, via bush fire and garbage incineration in dry season. Moreover, higher PAHs concentrations in lagoon

water in wet season may be explained by polluted rain, surface runoff and leachate from Akouedo's landfill. In fact, high level in sediment at wet season was likely due to increase input via deposit from water column. In sediments

also, PAHs were more frequently detected in dry season and less in flood season. Statistical analyse tests by ANOVA ($p < 0.05$) indicated any statistical significance at the seasonal factor level of PAHs in M'Badon sediments.

Table 9. Distribution coefficient K_d (L/kg) in the M'Badon bay.

Station	Flt	Py	BkF	BaP	InP	BgP	BaA	BbF	Σ HAP
L ₁	30.17	1.45	9.40	1.49	5.2	na	na	na	2,71
L ₂	0.94	1.17	na	0.29	19.94	0.25	0.21	na	3,49
S ₁	1.82	na	1.36	1.43	na	na	na	na	13,54
S ₂	0.87	na	na	3.08	na	na	na	na	18.25
S ₃	7.83	na	na	1.08	1.27	na	na	na	3.66
S ₄	3.93	42.02	0.55	na	0.18	na	na	na	18.41
S ₅	2.35	na	3.3	3	0.11	na	na	na	1.63
S ₆	4.58	0.28	1.04	0.27	2.39	na	na	na	1.04
S ₈	2.93	4.19	0.57	0.44	0.32	na	2.3	na	1.92

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]Perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene. na: data not available

Table 10. Distribution coefficient K_{oc} (L/kg) and Total Organic Carbon (TOC) in the M'Badon bay.

Station	Flt (l/kg)	Py (l/kg)	BkF (l/kg)	BaP (l/kg)	InP (l/kg)	BgP (l/kg)	BaA (l/kg)	BbF (l/kg)	Σ HAP
L ₁	1473.86	70.84	459.21	72.79	254.03	na	na	na	132,39
L ₂	49.47	61.58	na	15.26	1049.47	13.16	11.05	na	183,68
S ₁	57.59	na	43.04	45.25	na	na	na	na	428,48
S ₂	43.28	na	na	153.23	na	na	na	na	907,96
S ₃	352.70	na	na	na	57.21	na	na	na	164,86
S ₄	151.15	1616.15	21.15	na	6.92	na	na	na	708,08
S ₅	97.11	na	136.36	123.97	4.55	na	na	na	67,36
S ₆	206.31	12.61	46.85	na	107.66	na	na	na	46,85
S ₈	116.73	166.93	22.71	17.53	12.75	na	91.63	na	76,49

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]Perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene. na: data not available

Table 11. Distribution coefficient K_d ranges values of PAHs in the world Distribution.

Locations	Flt (10 ³ l/kg)	Py (10 ³ l/kg)	BkF, (10 ³ l/kg)	BaP (10 ³ l/kg)	InP (10 ³ l/kg)	BgP (10 ³ l/kg)	BaA (10 ³ l/kg)	BbF (10 ³ l/kg)	Σ HAP (10 ³ l/kg)	References
Weihe River, China	na	na	na	na	na	na	na	na	684 - 7390	[37]
Eight water systems, Netherlands	12.59 - 1000	25.12 - 1584.89	31.62 - 15848.93	10.00 - 19952.62	1.58 - 1000	1.99 - 2511.89	31.62 - 7943.28	25.12 - 12589.25	na	[35]
Lake Baiyangdian, China	na	na	na	na	na	na	na	na	173 - 4700	[38]
Lesina lagoon, Italy	0.050 - 0.054	0.048 - 0.055	0.105 - 0.133	0.106 - 0.121	0.120 - 0.141	0.130 - 0.137	0.087 - 0.089	0.094 - 0.113	na	[36]
Ravenna harbour, Italy	0.010	0.012	0.017	0.017	0.015	0.019	0.016	0.014	na	[36]

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]Perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene. na: data not available

Table 12. Distribution coefficient K_{oc} ranges and mean values of PAHs in the world Distribution.

Locations	Flt (10 ⁶ l/kg)	Py (10 ⁶ l/kg)	BkF (10 ⁶ l/kg)	BaP (10 ⁶ l/kg)	InP (10 ⁶ l/kg)	BgP (10 ⁶ l/kg)	BaA (10 ⁶ l/kg)	BbF (10 ⁶ l/kg)	Total PAHs	References
delta du Rhône, France	1.05	1.20	na	19.50	na	na	10.96	na	na	[39]
Eight water systems, Netherlands	0.79 - 15.85	0.63 - 19.95	2.51 - 158.49	1.00 - 251.19	0.16 - 15.85	0.20 - 39.81	2.00 - 100.00	2.51 - 158.49	na	[35]
Seine River, France	3.24	2.51	na	na	na	na	10.23	na	na	[40]

Flu: Fluoranthene, Pyr: Pyrene, BkF: Benzo[k]fluoranthene, BaP: Benzo[a]pyrene, InP: Indeno[1,2,3-cd]Pyrene, BgP: Benzo[g,h,i]Perylene, BaA: Benzo[a]anthracene, BbF: Benzo[b]fluoranthene. na: data not available

5. Conclusion

In This study, the spatial distribution maps of PAHs in both water and sediments of M'Badon Bay has revealed that the uncontrolled urban landfill of Abidjan, sediment dredging

activities within the lagoon, boat transport and domestic combustion were probable sources of PAHs in M'Badon Bay. The concomitant analysis of PAH distribution maps in water and sediment was an important tool in the identification of the PAH sources in water systems. Water flow, difference in the PAHs deposition rate in sediment and seasonality control

PAH distributions in waters and sediments. The PAH concentration ratios (Flu/(Flu + Pyr)) indicated a petrogenic origin in the bay. The carcinogenic potencies associated (TEQs) calculation indicated low carcinogenic potencies of M'Badon Bay sediments for living organisms. On the contrary, the PAH concentration levels in waters, especially for Benzo[k]fluoranthene and Benzo[a]pyrene exceeded often the limit set by the European Union Maximum Allowable concentration for surface waters (0.1 µg/L), suggesting a potential cancer risks for local communities.

Statements and Declarations

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Conflicts Of Interest/Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors' Contributions

Koffi Marcellin Yao and Albert Trokourey conceptualized, supervised and administrated the projet. Urbain Paul Gnonsoo, Naminata Soumahoro Sangaré and Koffi Martin N'Goran realized sampling and investigation. Urbain Paul Gnonsoo realized the Data curation, the Formal analysis and wrote the original draft of the manuscript. Koffi Marcellin Yao, N'Guessan Louis Bérenger Kouassi and Naminata Soumahoro Sangaré revised the manuscript critically. Koffi Martin N'Goran found the Software, realized, reviewed and edited all figures in the manuscript. All authors read and approved the final manuscript.

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