# Application of the QuECHERS method for the determination of PAHs in surface sediments along the Dakar coast

## Abstract

The bays of Dakar are a dumping ground for untreated wastewater. The beaches of Hann, Ngor and Soumbédioune constantly receive water from the canals of the city of Dakar. This wastewater is a source of pollution for the aquatic environment. Downstream of the discharges, a mass of sediment forms, which is subject to pollution, including Polycyclic Aromatic Hydrocarbons. In an aquatic environment, these hydrophobic substances can be trapped by sediments. Their toxicity is linked to mutagenic effects on the DNA or RNA of organisms. In this study, we examined the contamination of sediments on the beaches of Hann, Soumbédioune and Ngor by the 16 priority PAHs identified by the US Environmental Protection Agency (EPA). The sediment samples were taken between June and September 2018. Analyses were carried out using the GC-MS technique in tandem mode. For extraction and purification, QuECHERS and dSPE RESTEK salts were used, respectively, with recoveries ranging from 83.87 to 98.10%. For PAH repeatability, the %RSD values ranged from 0.02 to 3.08%, while those obtained for reproducibility varied from 0.01 to 1.29%. The results show that the highest levels were recorded in September: pyrene with 35.763 µg.Kg-1, benzo(a)anthracene (22.396 µg.Kg-1) and benzo(k)fluoranthene (18.678 µg.Kg-1) in Hann. At Soumbédioune, dibenzo(a,h)anthracene is at 15.782 µg.Kg-1 and at Ngor coronene has the highest content (9.030 µg.Kg-1). Analysis of the Shapiro-Wilk normality test reveals that most of the p-values for the variances of the various PAHs are above the 5% threshold. For the Levene test, apart from pyrene, the rest of the hydrocarbons satisfied the heteroscedacity hypothesis (inequality of at least two variances) with p-values below the 5% threshold.

**Key words**: contamination, sediments, Dakar, PAHs

## 1. Introduction

The presence of Polycyclic Aromatic Hydrocarbons (PAHs) in the environment is often linked to human activities, including the combustion of biomass and fossil fuels in industry (thermal power stations, oil refineries). PAHs can also come from domestic activities (individual heating, cigarette smoke, etc.) [1]. In the aquatic environment, these hydrophobic PAHs are often trapped in sediments. Shellfish can accumulate these hydrocarbons and transport them over long distances [2]. Because of their behaviour and acute or chronic toxic effects, the US Environmental Protection Agency (EPA) classifies PAHs as priority pollutants, sixteen of which are considered or suspected carcinogens. They are persistent, bioaccumulative and highly stable in the environment. Pregnant women and their foetuses may therefore be at risk from these hydrocarbons [3]. The wastewater and rainwater drainage channels of Hann, Ngor and Soumbédioune transport suspended matter, which becomes sedimented by obstacles or downstream of the discharge. These sediments can accumulate several micropollutants such as PAHs. In this study, we are seeking to determine the hydrocarbon content of sediments from beaches along the Dakar coast, which are often contaminated by wastewater discharges.

## 2. MATERIAL AND METHOD

### 2.1. Study sites

The sediment samples were taken at Ngor, Hann and Soumbédioune during the rainy season between June and September 2018. These selected sites face the Atlantic and are the scene of many activities. They are a major source of fish products. Hann Bay (SD1), which extends over 13 km, is home to fishing activities and several industries, including textile factories and fish processing plants. Hann Bay, once considered one of the most beautiful bays in the world, now receives wastewater from the East canal and has reached an advanced state of degradation. Soumbédioune beach (SD2) is a fish landing site and receives wastewater from the open West canal, which crosses a large part of Dakar's communes. Ngor (SD3), a tourist site, is also crossed by the canal, which is open and almost transformed into a rubbish dump.

*Figure 1 : Sampling points*

### 2.2. Sample processing

Sediments were collected between June and September 2018 using a hand grab at depths of between 0 and 5 cm. The samples are placed in plastic bags and then in a cooler to the laboratory [4]. In the laboratory, after extracting the coarse materials, the samples were oven-dried at 40°C for 24 hours to dry weight. The samples are then ground using an agate mortar and sieved using a sieve with a mesh size of less than 63 µm [6]. The fine fraction is used because of its high affinity with hydrophobic substances [7].

### 2.3 Extraction and purification.

For PAH analysis, we used the method developed and optimised by Dione et al [8]. After weighing, each mass was placed in a 50-mL centrifuge tube and 10 mL of an acetonitrile (ACN) solvent solution was added to separate the aqueous phase from the organic phase, then shaken and vortexed for 30 seconds. The extraction of organic pollutants is made possible by the QuECHERS extraction salt composed of 4g MgSO4; 1g NaCl; 1g trisodium citrate dihydrate; 0.5 g disodium hydrogen-citrate sesquihydrate. After adding the extraction salt, the mixture is vortexed for 10 minutes at 4000 rpm. This extraction method, which can be used to analyse other organic pollutants in different matrices, reduces analysis time and steps with less use of reagents [9]. This extraction method uses less solvent than Soxhlet, where 200 mL of mixture is used [10]. We also saved time compared with the 8-16 h Soxhlet experiment (Mzoughi et al) [11]. After this step, we recovered the supernatant in a 15 mL tube already containing the RESTEK Q-sep purification salt. QuEChERS dSPE, 1.2g MgSO4+400mg PSA+400mg C18. The extract is then vortexed for 30 seconds and centrifuged for 15 minutes at 4000 rpm. The extract is recovered in a 10 mL glass tube and then evaporated in a fume hood down to 1 mL.

### 2.4. GC/MSMS analysis

PAHs are analysed by gas chromatography coupled with mass spectrometry (GC-MS), which is used to separate, detect and quantify these pollutants [12]. The extract solution is topped up to 20 mL with acidified water (pH 3) and then extracted using a 100 µm SPME PDMS fibre at 80°C for 40 min for the PAHs. Each fibre was then introduced into the injector maintained at 250°C in splitless mode (3 min.). The compounds were separated on an Optima XLB column (Macherey Nagel) with an internal diameter of 30 m × 0.25 mm and a film thickness of 0.25 mm. The stationary phase consists of 5% phenyl/95% dimethyl polysiloxane with sylarene groups inserted to increase its thermal stability. In the oven, a temperature gradient of 50 to 340°C was designed to separate the desired compounds as efficiently as possible, particularly those with the same characteristic ions [13]. The oven temperature was maintained at 50°C for 3 minutes and then raised to 240°C with a heating ramp of 40°C/min. The temperature reached 255°C with a slope reduced to 1.5°C/min. A slope of 20°C/min is then used to raise the temperature to 330°C for a final stage lasting 18 minutes.

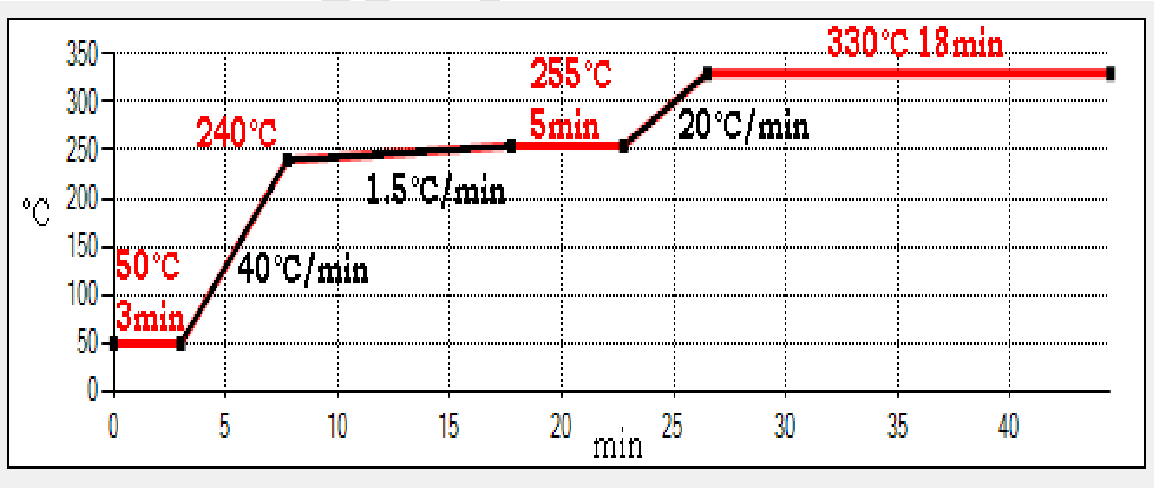

Figure 2 : Gradient de temperature

At the end of the column, the compounds pass through a transfer line maintained at 300°C and are fragmented in a 70eV electron impact source heated to 210°C. In order to avoid solvent peaks, which lead to signal saturation and premature wear of the rhenium filament (electron source), the actual signal is not acquired until 8 minutes after injection. PAHs are determined in scan mode and then in MRM (Multiple Reaction Monitoring) mode.

### 2.4.1. Scan mode

This is the mode used in qualitative analysis to identify compounds by searching the library for spectra. It can also be used for quantitative analysis. With full scan mode, you have a ‘fingerprint’ of all the compounds you are looking for. The retention time and mass spectrum of each compound can be selected (figure 3) [15] [16].

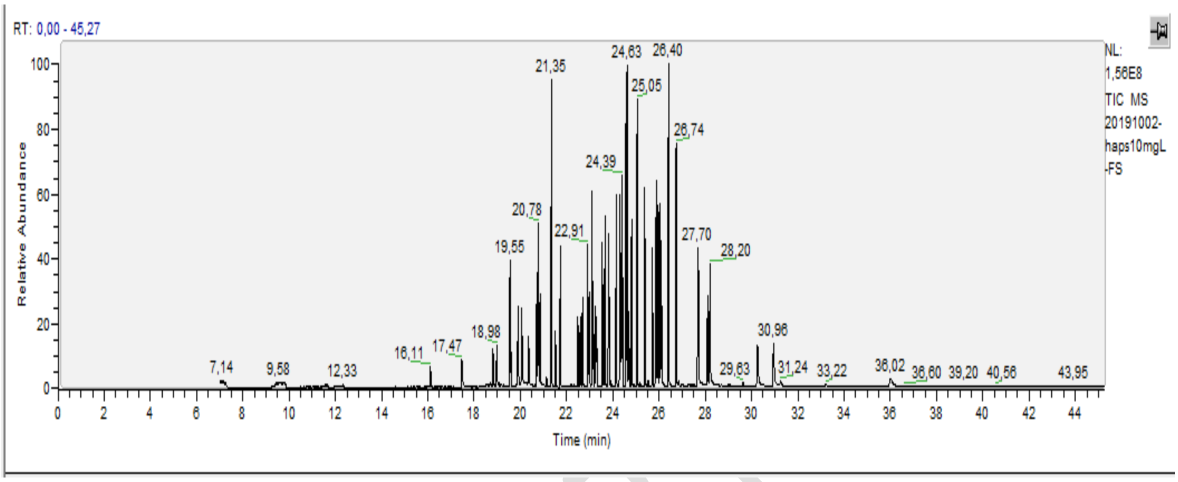

Figure 3 : PAH scan mode chromatogram

### 2.4.2. MRM mode

MRM mode is used for the quantitative analysis of trace elements already identified in scan mode. The retention times of the different molecules and the specific ions used for their quantification and identification (Table 2) [17-18].

Table 1**:** Retention times and quantification ions for the PAHs studied

| Compounds | Parent ions | Son ions | Retention time (min) |
|---|---|---|---|
| Acenaphthene | 153 | 150-151 | 16.34 |
| Anthracene | 178 | 152-176 | 20.29 |
| Naphthalene | 128 | 102-126 | 11.89 |
| Fluorene | 165 | 163-139 | 17.7 |
| Phenanthrene | 178 | 152-176 | 20.13 |
| Fluoranthene | 202 | 200 | 23.2 |
| Pyrene | 202 | 200-201 | 23.74 |
| Benzo(a)anthracene | 228 | 226-202 | 26.15 |
| Benzo(k) fluoranthene | 252 | 250-226 | 27.8 |

| | | | |
|---|---|---|---|
| Benzo(b) fluoranthene | 252 | 250-226 | 28.25 |
| Benzo(a)pyrene | 252 | 250-226 | 28.35 |
| Dibenzo(a,h)anthracene | 278 | 276 | 30.55 |
| Indéno(1,2,3)pyrene | 276 | 274 | 30.47 |
| Benzo(g,h,i)perylene | 276 | 274 | 31.24 |
| Coronene | 300 | 298 | 36.48 |
| Naphtalene-d8 | 136 | 108-132 | 11.88 |
| Acénaphtene-d10 | 164 | 152-154 | 16.25 |
| Chrysene-d12 | 240 | 125- | 26.16 |
| Pérylene-d12 | 264 | 135-152 | 28.45 |
| Phénanthrene-d10 | 188 | 160-184 | 20.07 |

Extraction yields using the QuEChERS method were calculated using 250 µg/L of the PAH mixture, and the results obtained are given in Table 2. The PAH recovery rates obtained ranged from 83.87 to 98.10%. The %RSD are low and remain below 20%. In GC/MSMS, the recovery rates obtained were generally in the 70-120% range, with coefficients of variation of less than 20%, which correspond to the standards set by the European Commission.

Table 2 : Extraction yield statistics and relative standard deviation for PAHs

| Compounds | Performance ± DS | % RSD |
|---|---|---|
| Acenaphthene | 93.80± 0.21 | 0.22 |
| Anthracene | 83.87± 0.22 | 0.26 |
| Naphthalene | 86.23± 0.31 | 0.35 |
| Fluorene | 95.95± 0.13 | 0.13 |
| Phenanthrene | 85.05± 0.32 | 0.37 |
| Fluoranthene | 96.10± 0.35 | 0.36 |
| Pyrene | 98.06± 0.42 | 0.42 |
| Benzo(a)anthracene | 97.08± 0.27 | 0.28 |
| Benzo(k) fluoranthene | 97.03± 0.20 | 0.21 |
| Benzo(b) fluoranthene | 98.10± 0.25 | 0.26 |
| Benzo(a)pyrene | 93.09± 0.19 | 0.20 |
| Dibenzo(a,h)anthracene | 86.15± 0.29 | 0.33 |
| Indéno(1,2,3)pyrene | 88.00± 0.25 | 0.28 |
| Benzo(g,h,i)perylene | 86.08± 0.32 | 0.37 |
| Coronene | 84.04± 0.14 | 0.17 |

## 2.5. Calibration study.

For the calibration curves, ten points were constructed as range points using the method of least squares in the concentration range 1- 250 µg.L$^{-1}$. For all solutions, three determinations were performed. The linearity of the method was expressed by the correlation coefficient ($R^2$) of the model obtained for each analyte. The correlation coefficients for the PAHs ranged from 0.989 to 1.000. For quantification purposes, a calibration range was carried out for the compounds to be analysed with the SPME fibre. Quadratic and linear calibration lines were obtained (Figure 2).

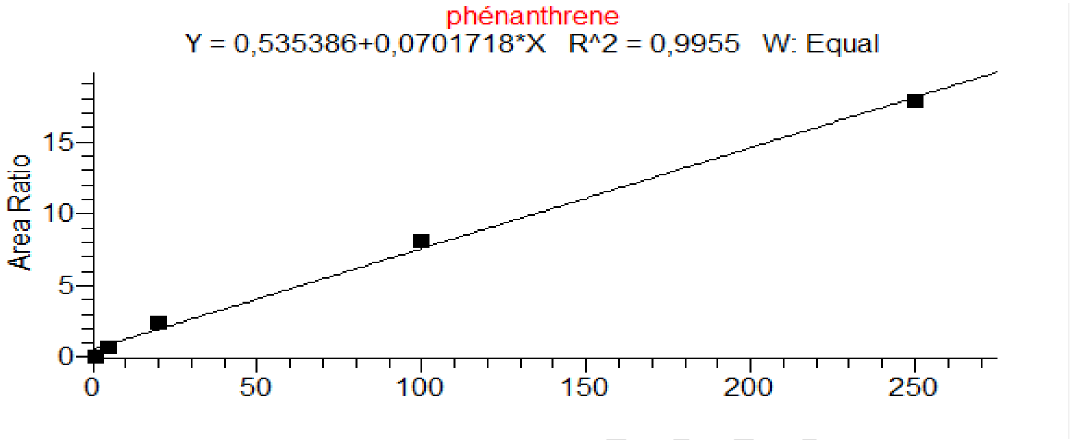

Figure 4 : Phenanthrene calibration graph

### 2.6. Study of repeatability, reproducibility and detection limit

The repeatability of the method was calculated as the relative standard deviation (RSD) of the analyte peak areas obtained after replicating (n= 5) samples of fish muscle spiked with the standard mixture at equivalent concentrations (5; 100 and 250 µg.L$^{-1}$). To ensure the reproducibility of the measuring device, we carried out a series of five injections, on three different days, of a standard solution containing the compounds to be analysed. The concentration of the most diluted compound was µg.L$^{-1}$. The mean value of each injection, carried out daily, was calculated. For PAH repeatability, the %RSD values ranged from 0.02 to 3.08%, while those obtained for reproducibility varied from 0.01 to 1.29%. Detection and quantification limits ranged from 0.003 to 0.031 ng.g$^{-1}$ and from 0.008 to 0.094 ng.g$^{-1}$ respectively (Table 3).

Table 3 : repeatability, reproducibility, LOQ and LOD statistics for PAHs

| compounds | Repeatability %RSD | Reproducibility %RSD | LOD (ng.g$^{-1}$) | LOQ (ng.g$^{-1}$) |
|---|---|---|---|---|
| Naphthalene | 0.07 | 0.03 | 0.011 | 0.032 |
| Acenaphthene | 0.12 | 0.06 | 0.031 | 0.094 |
| Fluorene | 0.09 | 0.06 | 0.009 | 0.026 |
| Phenanthrene | 0.10 | 0.05 | 0.027 | 0.080 |
| Anthracene | 0.84 | 0.15 | 0.015 | 0.045 |
| Fluoranthene | 0.02 | 0.03 | 0.004 | 0.011 |
| Pyrene | 3.08 | 1.29 | 0.015 | 0.045 |
| Benzo(a)anthracene | 0.08 | 0.01 | 0.005 | 0.014 |
| Benzo(k) fluoranthene | 0.03 | 0.05 | 0.003 | 0.008 |

| | | | | |
|---|---|---|---|---|
| Benzo(b) fluoranthène | 0.05 | 0.03 | 0.004 | 0.012 |
| Benzo(a)pyrene | 0.05 | 0.01 | 0.004 | 0.012 |
| Dibenzo(a,h)anthracene | 0.05 | 0.07 | 0.014 | 0.041 |
| Indéno(1, 2, 3)pyrene | 0.02 | 0.04 | 0.009 | 0.028 |
| Benzo(g,h,i)perylene | 0.05 | 0.04 | 0.004 | 0.013 |
| Coronene | 0.13 | 0.11 | 0.015 | 0.044 |

LOQ= Limit of quantitation  LOD = Limit of detection

## 3. Results

The results of the measurements are first given in mg.L$^{-1}$ and then expressed in dry weight in the sediments, using the expression:

$$C = [(A \times V) \div m] \times F$$

C: concentration of the substance in mg.kg$^{-1}$

A: concentration in mg/L of the metal in the assayed solution

V: volume of the solution in mL and m: sample size in g and F: dilution factor.

Nine PAHs were detected in sediments from the three Dakar sites studied. The variation in PAH levels in the sediments from the different sites are grouped by their minimum and maximum levels in Table 4. These variations are shown in Figures 5, 6 and 7.

### 3.1 Average, minimum and maximum PAH content

During this study, 9 of the 16 PAHs investigated were detected in sediments from the three sites. At Hann, the sediments were less contaminated with indenol(1,2,3)pyrene with an average of 1.320 and pyrene was more present with 12.203 µg.Kg$^{-1}$. Similarly, indenol(1,2,3)pyrene is also lower in the Soumbédioune sediments at 1.591 µg.Kg$^{-1}$. On the other hand, the highest average level was that of dibenzo(a,h)anthracene at 8.601 µg.Kg$^{-1}$. At Ngor, the average levels of PAHs detected ranged from 0.716 (pyrene) to 7.060 µg.Kg$^{-1}$ (coronene) (Table 4).

Table 4 : Average, minimum and maximum PAH content (µg.Kg$^{-1}$)

| **HAPs** | **Hann (SD1)** | | **Soumbédioune (SD2)** | | **Ngor (SD3)** | |
|---|---|---|---|---|---|---|
| | Min-Max | Moy ± DS | Min-Max | Moy± DS | Min-Max | Moy ± DS |
| pyrene | 1.310-35.763 | 12,203±16.220 | 0.0004-4.823 | 1.611±2.195 | 0.188-1.668 | 0.716± 0.826 |
| benzo(a)anthracene | 1.156-22.396 | 7.483±8.637 | 1.9264-4.953 | 3.379±1.238 | 1.544-3.049 | 2.117± 0.690 |
| benzo(k)fluoranthene | 0.752-18.678 | 5.775±1.150 | 1.9467-2.556 | 2.274±0.269 | 1.052-2.026 | 1.379±0.442 |
| benzo(b)fluoranthene | 1.023-3.445 | 2.191± 3.210 | 1.7119-2.913 | 2.230±0.500 | 0.990-1.723 | 1.427± 0.310 |
| benzo(a)pyrene | 0.625-7.504 | 2.778±0.668 | 1.5098-2.230 | 1.866±0.294 | 0.747-1.313 | 1.081± 0.257 |
| dibenzo(a,h)anthracene | 9.655-11.024 | 10.025±0.392 | 3.0046-15.782 | 8.601±6.504 | 1.540-2.452 | 1.959± 0.384 |
| indénol(1,2,3)pyrene | 0.811-1.711 | 1.320±1.436 | 0.4129-2.180 | 1.591±0.821 | 1.452-2.102 | 1.671± 0.294 |
| benzo(g,h,i)perylene | 1.134-4.217 | 2.080±1.436 | 1.5557-1.980 | 1.723±0.183 | 1.264-2.156 | 1.629± 0.376 |
| coronène | 4.763-6.498 | 5.263±0.828 | 5.608-10.127 | 8.106±1.877 | 5.781-9.030 | 7.060±1.484 |

### 3.2. Variation in PAH levels in sediments from the three sites

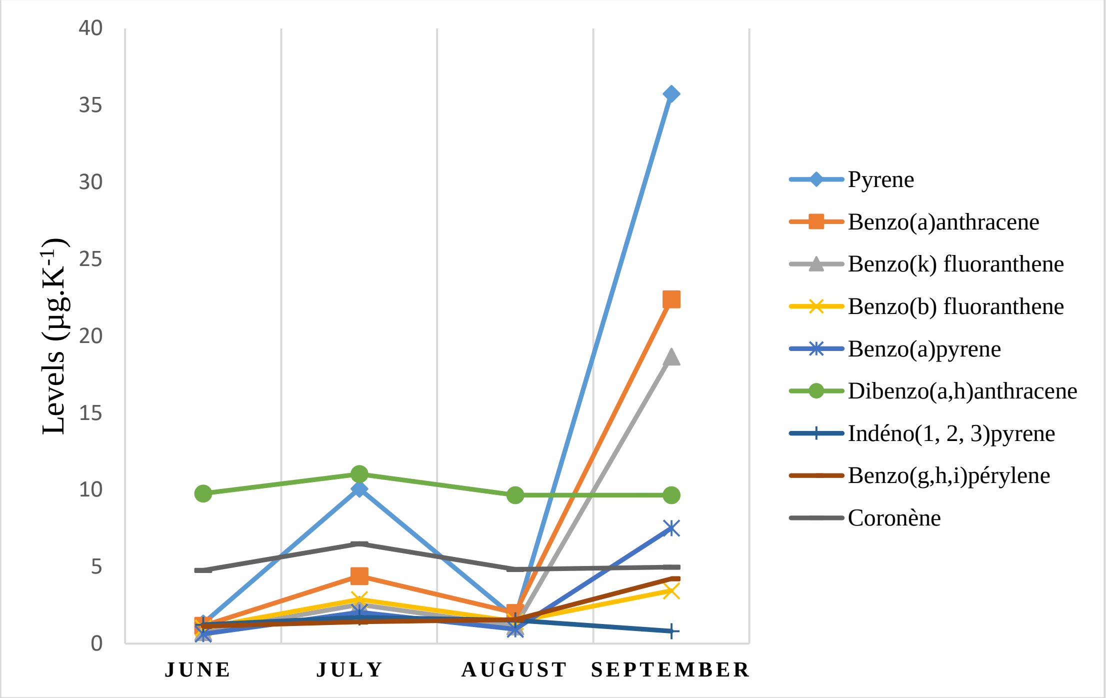

Figure 5 : Variations of PAH content in Hann sediment

At Hann, the highest levels of most PAHs were recorded in September. The concentration of pyrene dominated (35.763 µg.Kg$^{-1}$), followed in that order by benzo(a)anthracene (22.396 µg.Kg$^{-1}$), benzo(k)fluoranthene (18.678 µg.Kg$^{-1}$), dibenzo(a,h)anthracene (9.655 µg.Kg$^{-1}$) and benzo(a)pyrene (7.504 µg.Kg$^{-1}$). These relatively high levels may be due to accidental pollution. In August, with the exception of dibenzo(a,h)anthracene, coronene and benzo(a)pyrene, which had levels of 4.8213 and 9.6608 µg.Kg$^{-1}$ respectively, the other PAHs had levels of between 0.9331 (benzo(a)pyrene) and 1.6699 µg.Kg$^{-1}$ (pyrene). In July, anthracene was the lowest at 0.4455 µg/Kg and the highest level was 11.024 µg.Kg$^{-1}$ for dibenzo(a,h)anthracene (Figure 5).

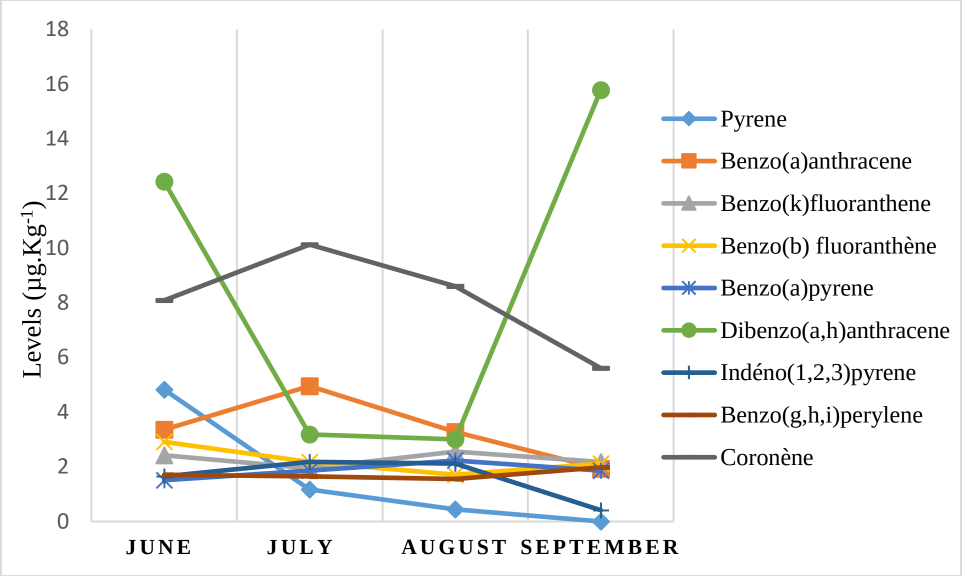

Figure 6 : Variations of PAH content in Soumbedioune sediments

At Soumbédioune, the results show that most of the PAHs have levels below 4 µg.Kg$^{-1}$ dry weight. Only coronene was present in all the sediments, with higher concentrations varying between 5.6082 (September) and 10.1267 µg.Kg$^{-1}$ (July). There was also a slight variation in benzo(g,h,i)perylene, with concentrations ranging from 1.5557 (July) to 1.980 (September). Indenol(1,2,3)pyrene was recorded at concentrations ranging from 1.6487 µg.Kg$^{-1}$ (June). Benzo(b)fluoranthene concentrations ranged from 1.7119 (August) to 2.9165 µg.Kg$^{-1}$ (June) and the variation in indenol(1,2,3)pyrene levels ranged from 0.41287 to 2.1803 µg.Kg$^{-1}$ (Figure 6).

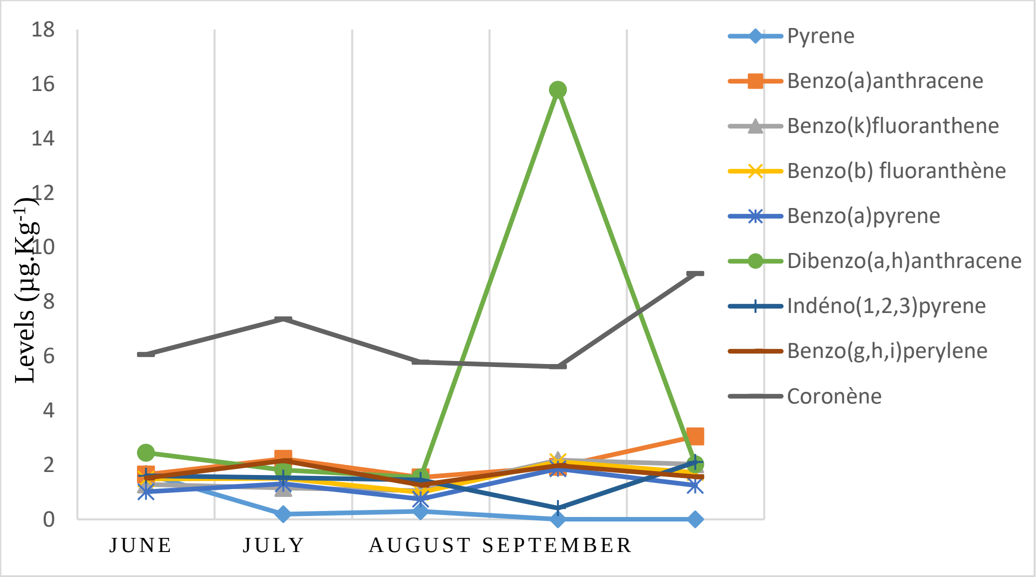

Figure 7 : Variations of PAH content in Ngor sediments

At Ngor, anthracene is below the limit of quantification. Levels of benzo(g,h,i)perylene ranged from 1.2644 to 2.1562 µg.Kg$^{-1}$. Similarly, benzo(k)fluoranthene levels varied between 1.0523 and 2.0264 µg.Kg$^{-1}$. Apart from the concentrations of benzo(a)anthracene in September with 3.0492 µg.Kg$^{-1}$ and in July (2.223 µg.Kg$^{-1}$), dibenzo(a, h)anthracene in June (2.4515 µg.Kg$^{-1}$)

and in September (2.0275 µg. Kg-1), benzo(g,h,i)pyrene in July (2.1562 µg.Kg$^{-1}$) and indenol(1,2,3)pyrene (2.102 µg.Kg$^{-1}$), the rest of the other concentrations obtained being less than 2 µg.Kg-1. Coronene had the highest levels, varying from 5.7807 to 9.0303 µg.Kg$^{-1}$ (Figure 7).

### 3.3. Overall PAH content

The results obtained show a contamination of sediments, with overall PAH levels higher in Hann. In September, the levels obtained in Hann (107.437 µg.Kg$^{-1}$) were much higher than those in Soumbédioune and Ngor (31.867 and 22.781 µg.Kg$^{-1}$ respectively). Similarly, Hann sediments in July were more contaminated than the other sites, with an overall content of 42.567 µg.Kg$^{-1}$ compared with 29.246 and 19.251 µg.Kg$^{-1}$ for Soumbédioune and Ngor. In June and August, the sediments at Soumbédioune were higher in PAHs, with total concentrations of 38.902 and 25.507 µg.Kg$^{-1}$ respectively (Table 5).

Table 5 : Total PAH content at various sites

| | **Hann** | **Ngor** | **Soumbedioune** |
|---|---|---|---|
| **June** | 21.757 | 18.742 | 38.902 |
| **July** | 42.567 | 19.251 | 29.246 |
| **August** | 24.703 | 14.663 | 25.507 |
| **September** | 107.437 | 22.781 | 31.867 |
| **∑ PAHs** | 196.464 | 75.437 | 125.522 |

### 3.4. Statistical studies of PAH contamination in sediments

To gain a better understanding of the distribution of the various PAHs within the sediments, the Shapiro-Wilk normality test and the Levene homogeneity test under SPSS were used.

Table 6 : Levene's test of homogeneity of variance based on the mean.

| | **Statistique de Levene** | **ddl1** | **ddl2** | **Signification** |
|---|---|---|---|---|
| benzo(g,h,i)perylene | 5.183 | 2 | 9 | 0.032 |
| coronene | 0.671 | 2 | 9 | 0.535 |
| pyrene | 5.789 | 2 | 9 | 0.024 |
| benzo(a)anthracene | 6.762 | 2 | 9 | 0.016 |
| benzo(k)fluoranthene | 7.981 | 2 | 9 | 0.010 |
| benzo(b)fluoranthene | 9.069 | 2 | 9 | 0.007 |
| benzo(a)pyrene | 6.485 | 2 | 9 | 0.018 |
| dibenzo(a,h)anthracene | 51.622 | 2 | 9 | 0.000 |
| indénol(1,2,3)pyrene | 1.705 | 2 | 9 | 0.236 |

Table 7 : Shapiro-Wilk test for normality

| Sites | | Shapiro-Wilk | | |
|---|---|---|---|---|
| | | Statistique | ddl | Signification |
| pyrene | Hann | 0.797 | 4 | 0,096 |
| | Ngor | 0.774 | 4 | 0,064 |
| | Soumbédioune | 0.816 | 4 | 0,134 |
| benzo(a)anthracene | Hann | 0.744 | 4 | 0.034 |
| | Ngor | 0.895 | 4 | 0.405 |
| | Soumbédioune | 0.953 | 4 | 0.736 |
| benzo(k)fluoranthene | Hann | 0.705 | 4 | 0.013 |
| | Ngor | 0.815 | 4 | 0.132 |
| | Soumbédioune | 0.972 | 4 | 0.852 |
| benzo(b)fluoranthene | Hann | 0.913 | 4 | 0.498 |
| | Ngor | 0.895 | 4 | 0.405 |
| | Soumbédioune | 0.928 | 4 | 0.582 |
| benzo(a)pyrene | Hann | 0.781 | 4 | 0.072 |
| | Ngor | 0.924 | 4 | 0.558 |
| | Soumbédioune | 0.946 | 4 | 0.690 |
| dibenzo(a,h)anthracene | Hann | 0.684 | 4 | 0.007 |
| | Ngor | 0.988 | 4 | 0.946 |
| | Soumbédioune | 0.839 | 4 | 0.193 |
| indénol(1,2,3)pyrene | Hann | 0.965 | 4 | 0.807 |
| | Ngor | 0.813 | 4 | 0.127 |
| | Soumbédioune | 0.828 | 4 | 0.163 |
| benzo(g,h,i)perylene | Hann | 0.742 | 4 | 0.032 |
| | Ngor | 0.907 | 4 | 0.464 |
| | Soumbédioune | 0.911 | 4 | 0.487 |
| coronene | Hann | 0.720 | 4 | 0.019 |
| | Ngor | 0.909 | 4 | 0.476 |
| | Soumbédioune | 0.963 | 4 | 0.799 |

## 4. Discussion

According to these results, there were slight variations in the levels of dibenzo(a,h)anthracene, benzo(a)pyrene and coronene, with the smallest deviations around the mean being 0.392, 0.668 and 0.828 respectively. Similarly, the smallest variations at Soumbédioune were obtained for benzo(g,h,i)perylene (0.183), benzo(a)pyrene (0.294) and benzo(k)fluoranthene (0.269). These low variations at Soumbédioune can also be justified by this homogeneous continuity. At Ngor, PAH levels varied more evenly (0.257- 0.690) than at the two sites with more industrial activity. At these two sites the variations in the other PAHs are relatively large (Table 4). These levels of benzo(g,h,i)perylene, indenol(1,2,3)pyrene and benzo(b)fluoranthene are lower than the minimum levels recorded in the sediments of Lake Geneva, which are 16, 14 and 17 µg.Kg$^{-1}$ respectively [19]. The risk of chemical contamination by PAHs could be considered an environmental risk, especially in the aquatic environment in contact with sediments. They can also cause cancer and cardiovascular disease [20,21]. Contaminated sediments also contribute to the contamination of aquatic species. Laboratory studies by Cheikh et al show the presence of these same PAHs in fish species such as Cephalopholus taeniops, Scomber japonicus, Lagocephalus laevigatus, Pagellus bellottii and Pagrus caeruleostictus. Sediments, which are considered to be contaminant sinks, are therefore vectors of this pollution in the marine environment [22].

During this campaign, the highest average pyrene content (12.203 µg.Kg-1) was found in Hann, where there is more industry and heavy road traffic. This high level may be due to soot and smoke from all sources (industry, exhaust fumes, tar, etc.). This level is relatively low compared with the highest values found in 2021 at Aube (465 µg.Kg-1) and Port-la-Nouvelle (216 µg.Kg-1). On the other hand, the average levels recorded at Ngor and Soumbédioune are lower than those obtained at Emb. Hérault (1.9) and Montpellier (2.1 µg.Kg-1) [23]. The PAH levels measured during this campaign were below the interpretation threshold values, ranging from 85 µg.Kg-1 for Benzo(g,h,i)perylene to 665 µg.Kg-1 (Effects Range Low (ERL)) for Pyrene [24]. The levels obtained for benzo(a)pyrene (highly toxic to aquatic organisms) are below the threshold effect concentration (TEC 0.15 mg.Kg-1) and probable effect concentration (PEC 1.45 mg/Kg) established by Mac Donald et al. 2000 [25]. These benzo(a)pyrene levels are also below the threshold concentrations for minor effects (Lowest Effect Level; 0.32 mg.Kg-1) and severe effects (Severe Effect Level; 1480 mg.Kg-1) for continental sediments. Overall, sediment pollution at the various sites is dominated by the heavier hydrocarbons pyrene and benzo(a)pyrene. On the other hand, the light PAHs (naphthalene, acenaphthene, fluorene, phenanthrene and anthracene, fluoranthene) are below their limits of quantification (LOQ). These three-ring hydrocarbons (light hydrocarbons) degrade 90% after 6 months. Overall levels at Ngor (18,742 - 22,781 µg.Kg-1) between June and September are the lowest of the three sites. There is less industrial activity in the area, so the majority of these levels may come from rainwater run-off, the canal of which runs through several districts [26]. For the Hann and Soumbédioune sites, the sediments are more contaminated than those studied in 2006, 2007 and 2008 by Ndiaye. The sediments from the sites studied are less contaminated than those from the five Saguenay fjord stations sampled in May 2002, the Port of Saint Elm (France), Lac du Bourget (France) and Bizerte (Tunisia). The overall levels in the three sites studied also remain lower than the levels found in the three samples of sediment from the Bonpas canal in January

2022, with respective values of 357, 358 and 393 µg.Kg-1 [27]. For each of the sites studied, the total concentrations of PAHs were below the tolerable concentration (ER-L) of 4000 µg.Kg-1 but also below the limit (45,000 µg.Kg-1) not to be exceeded in marine sediments [28, 29]. For the entire Canadian Arctic archipelago, the sum of the concentrations in surface marine sediments of the 16 PAHs listed as priorities by the US Environmental Protection Agency varies between 7.8 and 247.7 ng.g-1 (dry mass) with an average value of 56.8 ng g-1 [30]. These overall PAH levels are also lower than the significant concentrations of up to 600 ng/g of PAHs in the sediments of the motorway basin studied by Honge Y et al [31].

The results of the Levene variance homogeneity test (Table 6) based on the average PAH content show that only coronene and indenol(1,2,3)pyrene have homogeneous variances (equality of variances) within the sediments of the sites studied, with p-values of 0.535 and 0.236 respectively and Levene indices of 0.671 and 1.705 respectively. The rest of the hydrocarbons satisfied the heteroscedacity hypothesis (inequality of at least two variances) with p-values below the 5% threshold. Dibenzo(a,h)anthracene had a p-value <0.001, indicating that the variances of this hydrocarbon were not homogeneous within the sediment samples. The same applies to benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)anthracene, with significant values of 0.018, 0.007, 0.010 and 0.016 respectively. It is therefore accepted that at least two of the PAH variances are different (Table 6).

Analysis of the Shapiro-Wilk normality test reveals that the majority of the p-values for the variances of the various PAHs are above the 5% threshold. At Hann, benzo(a)anthracene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and coronene have p-values between 0.007 and 0.034. Thus, the hypothesis of an abnormal distribution of the variance of these PAHs in the various Hann sediments is accepted. However, the rest of the PAHs showed normal distributions of variance in the Hann sediments, with p-values ranging from 0.072 (benzo(a)pyrene) to 0.807 (indenol(1,2,3)pyrene). At Soumbédioune, the p-values ranged from 0.134 (pyrene) to 0.799 (coronene) (Table 7) [32] [33].

## Conclusion

At the end of the study, the low molecular weight PAHs were found to be below their limits of quantification. The study shows contamination of the various sediments, with the greatest variations in content noted in September: pyrene (35,763), benzo(a)anthracene (22,396) and benzo(k)fluoranthene (18,678 µg.Kg-1) in Hann, dibenzo(a,h)anthracene (15,782 µg/Kg) in Soumbédioune and coronene (9,030 µg/Kg) in Ngor. For this sediment campaign, the Hann sediments may contribute to the pollution of this bay with a discharge greater than or equal to 196.464 µg.Kg-1. On the other hand, sediments at Ngor contributed less to the contamination of the marine environment and were able to transport at least 75.437 µg.Kg-1 of PAHs. These average hydrocarbon levels obtained at the three study sites are below the tolerable limit (TLV) of 4,000 µg/Kg. They are also below the standard for marine sediments of 45,000 µg/Kg. These levels are also lower than the PAH levels found in the literature for various localities. Similar studies with aquatic species undoubtedly show that sediments are part of the chain of contamination of the marine environment and aquatic species. The authorities have a duty to clean up the canals regularly, install treatment plants and prevent any contact between the sediment and the environment.

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