



Seasonal occurrence, sources and toxic potential of polycyclic aromatic hydrocarbons (PAHs) in the superficial sediments from Vridi canal (Côte d'Ivoire)

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Abstract

The seasonal dynamics of Benzo[a]Anthracene, Pyrene, Benzo[b]Fluoranthene, Benzo[k]Fluoranthene, Benzo[a]Pyrene, Benzo(g,h,i) Perylene, Fluoranthene and Indeno(1,2,3-cd) Pyrene was monitored in the superficial sediments from Vridi canal over a year (from April 2014 to March 2015). In conducting this study, monthly sampling was doing at three different stations in this estuary, a collection of 36 samples over the study period. The extracts of these hydrocarbons, obtained from these samples according to MA.400-HAP 1.1 standard, were assayed by high performance liquid chromatography (HPLC) with UV/fluorescence detectors coupled to a GC-MS mass spectrometer. The results show the absence of Benzo (g,h,i) Perylene and Indeno (1,2,3-cd) Pyrene in these entities over the entire study period. The other six polycyclic aromatic hydrocarbons, with a strong seasonal dynamics, were detected in these substrates only in a few seasons and, this with relatively high concentrations (ranging between 0.020 ± 0.001 and $123.40 \pm 6.17\text{mg/kg}$ per dry weight). As a result, significant seasonal mean values of $\Sigma_6\text{PAHs}$ (ranging between 0.020 ± 0.001 and $158.07 \pm 2.13\text{mg/Kg}$ per dry weight) with its annual mean value of $48.08 \pm 0.83\text{mg/kg}$ per dry weight, were observed on this period. Thus, the superficial sediments from Vridi Canal are heavily contaminated by polycyclic aromatic hydrocarbons. The immediate consequence of this situation is the advanced state of degradation of Vridi canal, with very high ecological risks, as illustrated by four marine sediment quality guidelines (Apparent Effect Threshold Approach, Consensus Based Sediment Quality Guidelines, Toxic BaP equivalent quotient, Hazard quotients) used in this study. This pollution is of petrogenic origin, essentially of the only and great oil-producing industrial area of Côte d'Ivoire, located near of this ecosystem.

Keywords: Côte d'Ivoire, sediment quality guidelines, pollution, polycyclic aromatic hydrocarbon, Vridi canal.

Introduction

The pollution of the entire ecosystem by the Persistent Organic Pollutants (POPs) in general, and by the Polycyclic Aromatic Hydrocarbons (PAHs) in particular, remains a global concern since the Stockholm Convention¹ and the Aarhus Protocol². Indeed, these ubiquitous substances are currently present throughout the ecosystem beyond their natural concentration. This situation is mainly due to the development and the intensification of human activities. Now, their pyrolytic source accounts for 80% of their emission sources in the environment^{3,4}. At high concentrations, these organic compounds are highly hazardous to the biotope, mainly for the human. They are at the origin of many physiological and genetic dysfunctions^{5,6}.

The ecosystems most exposed to this pollution are surface waters, especially harbor estuaries and coastal marine areas. For illustration, the studies on the pollution from marine sediments by PAHs in the Cochin estuary (India)⁷, in the Bushehr coastal zone in the Persian Gulf⁸, in the Khure-Musa estuary in the

Persian Gulf⁹, in the Suez Canal (Egypt)¹⁰ and in the harbour area of Tema (Ghana)¹¹ have all shown a high contamination of these entities by these organic compounds, with very high ecological risks.

Commonly called "the lung of the Ivorian economy", Abidjan Autonomous Harbor is due to its existence of Vridi channel. This artificial estuary is the only route between Ébrié system and Atlantic Ocean. It is a hotbed of pollutants of all kinds. So, its biodiversity is seriously threatened. For illustration, the works carried out by Yao et al.¹², Yao and Trokourey^{13,14} revealed its very high pollution by metals, punctuated by its severe ecological risks. Also, N'Da et al.¹⁵ noted an important presence of phosphorus in this ecosystem beyond its natural concentration, with a high susceptibility to its eutrophication. Therefore, it is important to conduct additional studies for a thorough diagnosis of its health status. It is in this context that the present study was carried out. Its objectives is to follow seasonal occurrence, sources and toxic potential of some PAHs in the superficial sediments from this estuary, particularly by Benzo[a] Anthracene (BaA), Pyrene (Pyr), Benzo [b]

Fluoranthene (BbF), Benzo[k]Fluoranthene (BkF), Benzo [a] Pyrene (BaP), Benzo(g,h,i)perylene (B(ghi)P), Fluoranthene (Flt) and Indeno(1,2,3-cd)Pyrene (I(1,2,3-cd)P).

Materials and methods

Study area: Vridi canal is located in southern of Côte d'Ivoire, at exactly 4°0'50" West longitude at North latitude of 5°15'23". Well before its extension works, in progress, this canal was 2.7 km long and 370m wide, with depths ranging from 12 to 15m and pits from 10 to 25m¹⁶. Due to its position, it has an impressive hydrological network. This network consists of Ébrié system and Atlantic Ocean on the one hand, and fluvial contributions those most important are Mé, Agnéby and Comoé on other hand. These fluvial contributions in this estuary are doing through Ébrié system, Mé and Comoé to the East, Agnéby to the West. Its water seasons are characterized by five seasons: a hot season (HS) from February to April; a rainy season (RS) from May to July; a great cold season (GSC) from August to September; a flood season (FS) from October to November and; a short cold season (SCS) from December to January^{13,14}. Like the whole area from Ébrié system to Atlantic Ocean, Vridi channel has its remarkable biodiversity threatened by a severe pollution due to strong anthropic pressures. Indeed, this aquatic ecosystem is an integral part of Abidjan Autonomous Harbor, which is the fifth largest port in Africa. This port is home to the great industrial area of Côte d'Ivoire (2/3). The only and great oil-producing industrial area of this country is located on the eastern banks of this site¹². This marine estuary is currently the only true escape route for all kind of pollutants from the entire Abidjan district to Atlantic Ocean, but also by those drained by fluvial contributions¹⁷. Also, pollutants of marine origin transit there to reach Ébrié system.

So, it is therefore a hotbed of pollutants of all kinds. Its hydrological network has a strong influence on the nature and composition of its sediments, which are majority sand¹².

Samples collection and clean-up: This study was led during one year in Vridi canal, from Avri 2014 to March 2015. In its conducting, monthly sampling was doing at three different stations in this estuary, a collection of 36 samples over the study period. The sediment samples were taken 5cm below the superficial sediments using a Van-Veen grab according to AFNOR X 31-100 standard¹⁸. After their collect, the samples were coated in aluminum foil and stored at 4°C in a cooler containing an important quantity of ice. In laboratory, the samples were previously cleared of coarse elements.

It followed their cold drying by lyophilization to a constant weight in accordance with AFNOR NF EN ISO 16720 standard¹⁹. This step was continued by their reducing to diameters of less than 2mm by grinding. The crushed pieces of these samples were stored in borosilicate glass flasks doubly sealed with aluminum paper and a plastic stopper. Finally, they are kept in the freezer as prescribed by MA.400-HAP 1.1 standard²⁰.

Samples extraction and fractionation: The samples extraction and fractionation were doing following MA.400-HAP 1.1 standard²⁰.

For the samples extraction, 10g of dry sediment sample was weighed into a 150ml beaker, to which was added 10g of MgSO₄. This mixture, after a rest of 15 minutes at the room temperature, was put in a soxhlet extractor cartridge by adding 50ml of a combined standard solution of 10ng/μL recovery standard, and then extracted in a hot 500ml flat-bottomed flask containing 300ml of dichloromethane overnight at a rate of 2 to 5cycles/hour. The resulting extract was allowed to cool and all dichloromethane contained in the siphon and in the cartridge was transferred to the flask.

It is the same for the siphon rinsing water after removing the balloon. The flask was subsequently evaporated under vacuum using a rotary evaporator with ambient air until another extract of 2ml volume was obtained. The operation was repeated by adding 20ml of hexane until a new 1ml extract was obtained.

For fractionation of extracts obtained, a first 15ml conical tube was inserted under the purification column. In this tube, the extracts were deposited as close as possible to the packing surface of the column using a pasteur pipette. After this deposition, the pasteur pipette was rinsed twice consecutively with 0.5ml of pure hexane, and rinsing solutions were transferred to the purification column until their level reached that of the silica gel. This situation was shown by stopping the flow of hexane.

The solution obtained in this tube is designated "Fraction 1". This tube has been removed and stored for possible applications. A second conical tube of 15ml, pre-coated with aluminum foil, was worn instead of the first. 14ml of pure dichloromethane were decanted with great care into the column. This tube, removed after the total flow of this amount of pure dichloromethane and containing the extracts of PAHs studied, designated by "Fraction 2". The final evaporation of the purified extracts of PAHs studied was made under a jet of nitrogen until a volume of less than about 300μl was obtained. 50μl of the volumetric standard solution at 10ng/μl was added to this volume and this mixture was supplemented to 500μl with a pure isoctane solution.

Analysis of HAPs studied: Eight PAHs were studied in the superficial sediments from Vridi canal over study period. These are: BaA, Pyr, BbF, BkF, BaP, B(ghi)P, Flt and I(1,2,3-cd)P. So, to determine the content of these PAHs in the samples collected, the purified extracts were analyzed by high performance liquid chromatography (HPLC) with UV/fluorescence detectors coupled to a GC-MS mass spectrometer. This method provides robust identification of these analytical compounds by retention time and the mass spectrum provides additional structural information²¹. A HPLC brand GC 2010 Shimadzu coupled with a GC-MS spectrometer brand QP-2010 Shimadzu was used for this purpose.

Control quality and assurance quality: The quality control and the assurance quality of this analysis method were done following the procedure described by Busetti et al.²², namely the solid phase extraction (SPE). The use of this procedure in this study permitted simultaneous recovery of all eight PAHs with yields superior 75% (6-14.5RSD). Previously, calibration curves were plotted from standard solutions of pure analytical quality (standard solutions brand Dr Enrhenshoffer (Merck) and Water Milli-Q brand Merck for dilutions). The statistical study of the results shows that the calibration ranges fit the linear model of 0.01 and 250mg/Kg per dry weight with correlation coefficients greater than or equal to 0.99. The limit of detection (LOD) and the limit of quantification (LOQ) were determined based on the lowest calibration standard's signal-to-noise ratio of 3 and 10 respectively. LOD and LOQ in this study were 0.021mg/Kg per dry weight and 0.069mg/Kg per dry weight, respectively.

Source of physical and chemical data used in this study: The seasonal data of pH, salinity (Sal), conductivity, redox potential (U), moisture (HR) and organic matter (OM) for the superficial sediments from Vriddi canal, from April 2014 to March 2015, were provided by Yao and Trokourey¹⁴ (Table-1). These physical and chemical parameters were used to assess the hydroclimate influence on the seasonal dynamics of PAHs studied in this estuary over this study period.

Statistical technics used: In addition to standard technics such as mean (m) and standard deviation (s), the Normalized Principal Component Analysis (NPCA) and the Student's test were used in this study. NPCA was used to study correlations

between PAHs significant (namely detected in the superficial sediments of this estuary over the study period) and the physical and chemical parameters considered in this study. This was intended to highlight common dimensions for classifying them, and to deduce their specific effects on certain groups formed from these PAHs. The correlations were considered significant at $p < .05$. As for the Student's test, it was used to assess correlations two by two between parameters used for NPCA realization. This test is performed in a 0.5 confidence interval. The correlations considered significant were also correlated for $p < .05$ for N observations with unknown mean values. In this study, the implementation of these different statistical technics was done by Statistica software version 10.0.0²³.

Assessment of ecological risks related to PAHs studied and their source in this estuary on the study period: The contamination level of the superficial sediments from this ecosystem by PAHs studied was assessed using the Apparent Effect Threshold Approach (AETA)^{24,25}, the Consensus Based Sediment Quality Guidelines (CBSQGs)^{26,27}, the toxic BaP equivalent quotient (TEQ)^{7,28-30} and the Hazard Quotients (HQ)³⁰.

Defined by Barrick et al.²⁴, AETA is the threshold value of PAH in the marine sediments above which statistically significant biological effects still occur^{24,25}. From the list of PAHs established by Barrick et al.²⁴ for this approach, six were assessed in this study (Table-2). AETA values presented are normalized for 1% Total Organic Carbon (TOC) in the marine sediments.

Table-1: Some physical and chemical characters of the superficial sediments from Vriddi canal from April 2014 to March 2015¹⁴.

| | pH | Cond | U | Sal | OM | HR |
|-------------------|------|------|--------|------|-------|------|
| Hot Season | 7.64 | 5.02 | -29.72 | 1.69 | 14.09 | 1.16 |
| Rainy Season | 7.79 | 1.59 | -31.82 | 0.74 | 11.28 | 0.63 |
| Great Cold Season | 8.07 | 2.55 | -32.43 | 1.25 | 18.74 | 0.73 |
| Flood Season | 7.51 | 5.23 | -25.70 | 0.90 | 15.18 | 0.61 |
| Small Cold Season | 7.80 | 5.72 | -29.76 | 0.62 | 15.18 | 0.70 |

Table-2: AETA values for six PAHs studied²⁴.

| HAPs | AETA (mg/kg per dry weight normalized for 1% TOC) | | | |
|--------------|---|-----------|----------------------------|--------|
| | Microtox | Amphipods | Abundance of benthic fauna | Oyster |
| BaA | > 1.60 | 2.70 | 6.50 | 1.10 |
| BaP | > 1.40 | 2.10 | > 13.00 | 0.99 |
| B(g,h,i)P | > 0.67 | 0.78 | > 12.00 | 0.31 |
| Flt | > 1.90 | 30.00 | 12.00 | 1.60 |
| I(1,2,3-cd)P | > 0.87 | 0.88 | 9.00 | 0.33 |
| Pyr | > 2.10 | 10.00 | 14.00 | > 2.10 |

CBSQGs is based on the development of two empirical approaches: the approach developed by Long et al.²⁶ and that by MacDonald et al.²⁷. Both approaches are based on the definition of two threshold values:

One representing the concentration below which adverse effects of PAHs are unlikely for aquatic organisms, and above which these effects are potential for these organisms. This reference value is called "Effect Range Low (ERL)" by Long et al.²⁶ and "Probable Effect Level (PEL)" by MacDonald et al.²⁷.

The other represents the concentration in Table-3, which adverse effects are potential for aquatic organisms and, above which these effects are highly likely for these organisms. This reference value is called "Effect Range Medium (ERM)" by Long et al.²⁶ and "Threshold Effect Level (TEL)" by MacDonald et al.²⁷.

The toxic BaP equivalent quotient (TEQ) allows the assessment of the carcinogenic toxicity potential of sediments following their contamination by PAHs. It is based on the concentration of PAHs in sediments (C) and an equivalent factor of carcinogenic toxicity (TEF^{carc}). So, for a given PAH i, its TEQ_i^{carc} is obtained as follows:

$$TEQ_i^{carc} = C_i \times TEF_i^{carc} \quad (1)$$

The total toxicity coefficient equivalent to BAP is given by:

$$\text{Total TEQ}^{carc} = \sum_i C_i \times TEF_i^{carc} \quad (2)$$

TEF^{carc} is 1 for BaP, 0.1 for BaA and BbF and 0.01 for BkF^{7,28-30}.

The hazard quotients are another approach for assessing adverse effects of sediments pollution by PAHs on the biotope. They are based on the CBSQGs developed by MacDonald et al.²⁷. Two quotients are generally used: the toxicity quotient based on PEL (HQ_{PEL}) and that based on TEL (HQ_{TEL}). They are defined as follows:

$$HQ_{PEL} = \frac{C_i}{C_{PEL}} \quad (3)$$

$$HQ_{TEL} = \frac{C_i}{C_{TEL}} \quad (4)$$

Moreover, when HQ_{TEL} < 1, rare adverse ecological effects are expected. When HQ_{TEL} > 1 > HQ_{PEL}, adverse ecological effects are possible but less frequent. The HQ_{PEL} values were divided into four categories, which can be used to describe the sediment as no adverse effect (PEL < 0.1), slight adverse effect (0.1 to 0.5), moderate adverse effect (0.5 to 1.5) and heavy adverse effect (PEL > 1.5)³⁰.

The source apportionment of PAHs studied in the superficial sediments from Vridi canal over the study period was determined by the plotting of I(1,2,3-cd)P/(I(1,2,3-cd)P+BghiP) in function of Flt/(Flt+Pyr), as performed by Amine et al.³¹.

Results and discussion

Seasonal dynamic of PAHs studied: The results obtained are presented in Table-4 (1,2,3-cd)P and B(ghi)P were not detected in the superficial sediments from Vridi canal over the entire study period. Pyr was detected in these entities only in RS, where it presented the highest seasonal and annual mean values for all PAHs studied. BbF presented the lowest annual mean value over the study period. Regarding Flt, it has been present in these substrates in HS and SCS. Its highest seasonal mean was obtained in HS and the lowest in SCS; which was also the lowest of all seasonal mean values obtained in this study. BbF and BkF were also detected in these sediments only in two seasons. They were there simultaneously in HS, where BkF showed its highest seasonal mean value and, BbF its lowest seasonal mean value. In contrast, BkF was present in these entities at GCS where its lowest seasonal mean value was obtained and, BbF in RS in which its highest seasonal mean value was recorded. As for BaA, it was the most met in the different seasons over the study period, especially in FS, RS where it was noted its lowest seasonal mean value and, especially in HS where its highest seasonal mean value has been identified. The seasonal mean values Σ₈PAHs were all important, hence its annual mean value. Its highest seasonal mean value was noted in RS because of Pyr, and its lowest seasonal mean value in GCS because of Flt.

Table-3: CBSQGs values for some PAHs studied.

| PAHs | ERL and ERM for marine sediments ²⁶ (mg/Kg per dry weight) | | PEL and TEL for marine sediments ²⁷ (mg/Kg per dry sediments) | |
|-----------|--|-------|---|-------|
| | ERL | ERM | PEL | TEL |
| BaA | 0.261 | 1.600 | 0.0748 | 0.639 |
| BaP | 0.430 | 1.600 | 0.088 | 0.763 |
| Flt | 0.063 | 5.100 | 0.113 | 1.494 |
| Pyr | 0.665 | 2.600 | 0.153 | 1.398 |
| B(g,h,i)P | 0.430 | 1.600 | - | - |
| ΣHAPs | 1.849 | 12.5 | 0.429 | 4.294 |

Table-4: Seasonal and annual mean values ($\pm s$) (in mg/Kg per dry weight) of PAHs studied and their sum (Σ_8 PAHs) in the superficial sediments from Vridi canal.

| PAHs | Water seasons of Vridi channel | | | | | |
|-----------------|--------------------------------|-------------------|-----------------|------------------|-------------------|-------------------|
| | HS | RS | GCS | FS | SCS | Moyenne |
| Flt | 0 | 9.79 \pm 0.49 | 0 | 0 | 0.020 \pm 0.001 | 4.91 \pm 0.34 |
| Pyr | 0 | 123.40 \pm 6.17 | 0 | 0 | 0 | 123.40 \pm 6.17 |
| BkF | 11.18 \pm 0.56 | 0 | 9.57 \pm 0.48 | 0 | 0 | 10.38 \pm 0.06 |
| BaP | 3.86 \pm 0.19 | 0 | 0 | 0 | 0 | 3.86 \pm 0.19 |
| I(1,2,3-cd)P | 0 | 0 | 0 | 0 | 0 | 0 |
| B(ghi)P | 0 | 0 | 0 | 0 | 0 | 0 |
| BaA | 31.93 \pm 1.60 | 21.85 \pm 1.09 | 0 | 25.07 \pm 1.25 | 0 | 26.28 \pm 0.26 |
| BbF | 0.73 \pm 0.04 | 3.02 \pm 0.15 | 0 | 0 | 0 | 1.88 \pm 0.08 |
| Σ_8 PAHs | 47.69 \pm 0.56 | 158.07 \pm 2.13 | 9.57 \pm 0.48 | 25.07 \pm 1.25 | 0.020 \pm 0.001 | 48.08 \pm 0.83 |

Influence of some physical and chemical parameters on seasonal dynamics of PAHs studied: In this study, NPCA expresses at 69.80% the information due to 12 variables (PAHs studied and the physical and chemical parameters used in this study) relating to five individuals (the five water seasons of this estuary). The first factor (F1), corresponding to the highest eigenvalue (4.89), represents 40.78% of the total variance. As for the second factor (F2), associated with the second eigenvalue (3.48), it represents the total variance at 29.02%. For variables, there is a very strong correlation of salinity (Sal), moisture (HR), organic matter (OM), Flt, Pyr, BaP, BbF and BkF with F1; while pH, redox potential, organic matter (OM), BaA and BbF are strongly correlated to F2 (Table-5). For individuals, HS and RS are strongly correlated with F1; and GCS, FS and SCS are strongly correlated with F2 (Table-6). These different typologies established by NPCA show that F1 reflects the biogeochemistry of Flt, Pyr, BaP, BbF and BkF influenced by salinity, moisture and organic matter content of these sediments in HS, RS and GCS. As for F2, it expresses the influence of redox potential, pH and organic matter content of these sediments in the biogeochemistry of BaA and BbF in HS, GCS and FS. The Student's test showed a strong positive correlation of Pyr with Flt ($r' = 1.00$), of BkF with salinity ($r' = 0.94$), and of BaP with moisture ($r' = 0.98$) in the superficial sediments of Vridi canal over the study period.

These statistical results will suggest that the relatively high presence of BaP and BkF in HS would be favored by the

relative high salinity, organic matter content and moisture of these sediments. The high presence of BaA, observed in this season in these substrates, would be favored by their reducing character; despite their basic character and relative high organic matter content, which would tend to oppose it. Also, the reducing nature of these sediments in the same season would contribute to the presence of BbF within them; phenomenon to which the other physical and chemical parameters considered in this study would be opposed. In HS, a decrease in salinity, moisture and organic matter content of these entities would be beneficial to a relatively high presence of Pyr, Flt and BbF. As for BkF, its relatively high presence in these sediments in GCS is favored by their salinity, moisture and organic matter content; the opposite of their pH and reducing character that would contribute to its inhibition in these entities. In FS, the reducing nature of these sediments would increase the concentration of BaA, whereas pH would oppose this process.

Source and assessment of the contamination level of these entities by PAHs studied: Referring to CBSQGs criteria and the hazard quotients (Table-7) used in this study, BaA has a severe toxicity to the biotope of this ecosystem in HS, RS and FS. This is also the case for Pyr in RS and, BaP in HS. As for Flt, its toxicity to these aquatic organisms is very pronounced in RS, but relatively very low in SCS. For Σ_8 PAHs, its toxicity based on these five PAHs mentioned above and referred to CBSQGs used, shows a severe toxicity of all these PAHs for biotope in all seasons, except in SCS.

The carcinogenic toxicity of BkF towards the biotope of this canal is very important in RS and GCS, having regard to its high TEQ_i^{carc} values in these seasons. This is also the case of BaP in HS; BaA in HS, RS and FS; BbF in HS and RS. In general, the total carcinogenic potential (Total TEQ_i^{carc}) of this ecosystem is very important in all seasons, except in SCS (Table-8). By complying with AETA criteria and the seasonal mean values normalized for 1% TOC of PAHs studied (Table-9), BaA would be specifically very toxic and carcinogenic to microtox, amphipods and oysters in HS, RS and FS. In general, it would affect the abundance of aquatic fauna. That is the same case for Pyr in RS.

Table-5: Factorial coordinates variables based on correlations.

| PAHs | F1 | F2 |
|------|-----------|-----------|
| Flt | -0.790658 | 0.015150 |
| Pyr | -0.790199 | 0.015580 |
| BkF | 0.833813 | -0.222266 |
| BaP | 0.723338 | 0.449629 |
| BaA | 0.044849 | 0.873828 |
| BbF | -0.738163 | 0.524789 |
| pH | 0.031265 | -0.981357 |
| Cond | 0.486771 | 0.475229 |
| U | 0.040586 | 0.763481 |
| Sal | 0.824049 | 0.128981 |
| MO | 0.542306 | -0.580837 |
| HR | 0.815773 | 0.256991 |

Table 6: Factorial coordinates individuals based on correlations.

| PAHs | F1 | F2 |
|------|----------|----------|
| SC | 2.86226 | 1.50106 |
| SP | -3.12683 | 0.05201 |
| GSF | 1.05898 | -2.74376 |
| SCr | -0.68520 | 1.90655 |
| PSF | -0.10921 | -0.71587 |

Discussion: The seasonal mean values of Flt in RS and SCS; Pyr in HS; BkF in HS and GCS; BaP in HS; BaA in HS, RS and FS; BbF in HS and RS show their relatively high presence in the superficial sediments from Vridi canal in these seasons over the study period. This fact is especially for Pyr and BaP, which have their seasonal mean values higher than their ubiquitous value in marine sediments (0.5mg/Kg per dry weight for Pyr³² and 0.001mg/Kg per dry weight³³). The contamination of these substrates by PAHs should be very important if we consider the different seasonal mean values of Σ_8 PAHs and its annual mean value, obtained with only six PAHs in this study. In addition, seasonal and annual mean values of Σ_8 PAHs obtained in this study are greater than the mean values of Σ PAHs obtained in the sediments from the Cochin Estuary (India) (ranging from 0.194 to 14.149mg/Kg per dry weight) by Ramzi et al.⁷, from the Bushehr coastal zone in the Persian Gulf (between 0.042 and 0.0228mg/Kg dry sediments) by Mirza et al.⁸, from the Khure-Musa estuary in the Persian Gulf (between 0.703 and 3.302 mg/Kg per dry weight) by Mirza et al.⁹ and from the Suez Canal (Egypt) (0.103 and 0.239mg/Kg per dry weight) by Al-Agroudy et al.¹⁰. Thus, Vridi Canal is one of the most polluted marine estuaries in Africa, as is Tema harbour (Ghana), where Σ HAPs obtained by Gorleku et al.¹¹ is between (28.60 and 190.30mg /Kg per dry weight).

Table-7: Hazard quotients of four PAHs studied in the superficial sediments of Vridi canal on over the study period.

| PAHs | Seasonal water of Vridi canal | | | | | | | | | |
|-------|-------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| | HS | | RS | | GCS | | FS | | SCS | |
| | HQ _{PEL} | HQ _{TEL} | HQ _{PEL} | HQ _{TEL} | HQ _{PEL} | HQ _{TEL} | HQ _{PEL} | HQ _{TEL} | HQ _{PEL} | HQ _{TEL} |
| Flt | 0 | 0 | 86.637 | 6.553 | 0 | 0 | 0 | 0 | 0.177 | 0.0134 |
| Pyr | 0 | 0 | 806.536 | 88.269 | 0 | 0 | 0 | 0 | 0 | 0 |
| B[a]P | 43.864 | 5.059 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| BaA | 426.872 | 49.969 | 292.112 | 34.194 | 0 | 0 | 335.160 | 39.233 | 0 | 0 |

Table-8: Toxic BaP equivalent quotient (mg/Kg per dry weight) of four PAHs studied in the superficial sediments on over the study period.

| PAHs | Water seasons of Vridi channel | | | | |
|--|--------------------------------|-------|-------|-------|-----|
| | HS | RS | GCS | FS | SCS |
| TEQ ₁ ^{carc} | | | | | |
| BkF | 0.112 | 0 | 0.096 | 0 | 0 |
| BaP | 3.860 | 0 | 0 | 0 | 0 |
| BaA | 3.193 | 2.185 | 0 | 2.507 | 0 |
| BbF | 0.073 | 0.302 | 0 | 0 | 0 |
| Total TEQ ₁ ^{carc} | 7.238 | 2.487 | 0.096 | 2.507 | 0 |

Table-9: Seasonal and annual mean values normalized for 1% TOC of PAHs studied on over the study period.

| PAHs | HS | RS | GCS | FS | SCS | Mean |
|---------------------|-------|--------|-------|-------|-------|--------|
| Flt | 0 | 1.501 | 0 | 0 | 0.002 | 0.570 |
| Pyr | 0 | 18.926 | 0 | 0 | 0 | 14.333 |
| BkF | 1.373 | 0 | 0.883 | 0 | 0 | 1.205 |
| BaP | 0.474 | 0 | 0 | 0 | 0 | 0.448 |
| I(1,2,3-cd)P | 0 | 0 | 0 | 0 | 0 | 0 |
| BghiP | 0 | 0 | 0 | 0 | 0 | 0 |
| BaA | 3.920 | 3.351 | 0 | 2.857 | 0 | 3.053 |
| BbF | 0.090 | 0.463 | 0 | 0 | 0 | 0.218 |
| Σ ₈ PAHs | 5.855 | 24.243 | 0.883 | 2.857 | 0.002 | 5.585 |

As shown in Figure-1, all PAHs studied in the superficial sediments of Vridi canal are of petrogenic origin over the study period. The high contamination of these superficial sediments by PAHs in general, and by some PAHs studied in particular, is mainly due to accidental or unintentional releases of petroleum products^{3,4,34} from only and great oil-producing industrial area of Côte d'Ivoire, installed on the banks of this canal. This situation is illustrated by the petrogenic source of PAHs detected in these substrates over the study period, as evidenced by the plot of I(1,2,3-cd)P/(I(1,2,3-cd)P+BghiP) in function of Flt/(Flt+Pyr).

The presence of PAHs in the superficial sediments from this estuary is a function of their quantity released. It is also depend to the seasonal nature of the waters and the strong hydrodynamics of this estuary, which condition the different biogeochemical and photochemical reactions.

In HC, the meteorite waters contribution in Ébrié system are negligible. Thus, the waters of Vridi canal are essentially those of Atlantic Ocean. Their circulation would favor the formation of an important mud plug, translated by the importance of these sediments moisture (the most important over the study period)¹⁴. This phenomenon would partially favor the organic particulate deposition of PAHs^{35,36}, particularly BkF and BaP, on its superficial sediments.

Also, the high salinity of the waters and sediments from this ecosystem in this season would partially inhibit the proliferation of microorganisms responsible for the biodegradation of PAHs in marine environments^{37,38}. This process would particularly favor the presence of BkF and BaP in its superficial sediments in this season. This would explain the favorable contribution of salinity, organic matter and moisture in the relatively high presence of these two PAHs in these substrates, as reported by the results of NPCA.

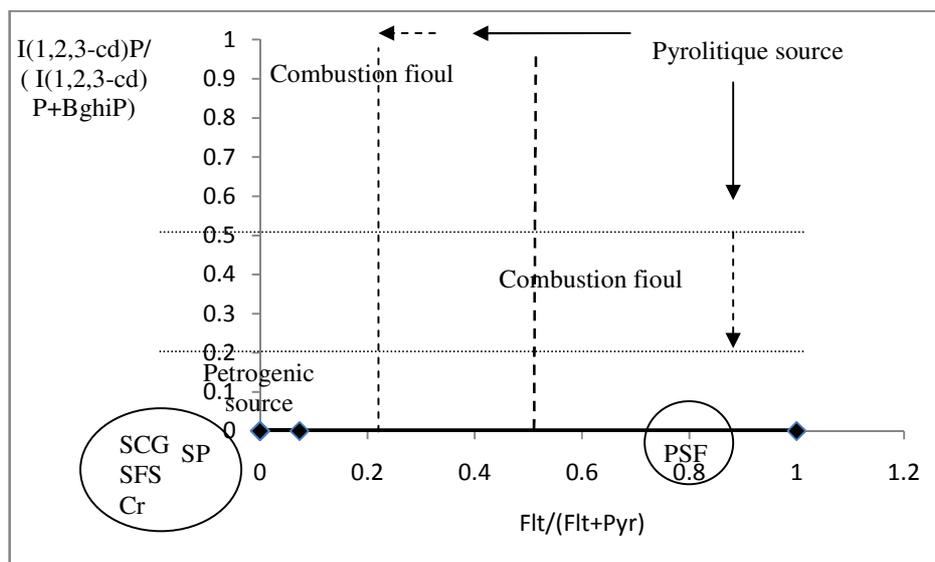


Figure-1: Petrogenic source of PAHs studied in the Vridi Canal over the study period.

In RS, the meteorite waters runoff and the fluvial waters of Mé and Agnéby (in their flood season) transit this channel to reach Atlantic Ocean. These two coastal rivers, the most important for Ébrié system, are weakly acidic to neutral, desalted, oxidizing and weakly mineralized^{39,40}. These waters, with the meteorite waters runoff, cause a dilution of the marine waters in this canal. As a result, there is a slight decrease in salinity, conductivity and organic matter content, but slight increases in pH and reducing character of these sediments. The modification of the waters circulation that they induce also leads to a reduction of the mud plug formation, translated by the decrease of these sediments moisture in this season¹⁴. The simultaneous increase of the reducing character with the decrease of the salinity and organic matter content of these entities would be very favorable to the organic particulate deposition of some PAHs, particularly Flt, Pyr, BaA and BbF, which have their highest seasonal content in this season; what would be shown in this study by results of NPCA.

In GCS, the upwelling of deep and cold marine waters in Vridi canal during the great upwelling season of Atlantic Ocean leads to an increase in pH, salinity, conductivity, reducing character and organic matter content of these sediments¹⁴. The simultaneous decrease in temperature with the increase of salinity in this aquatic ecosystem would favor the adsorption of PAHs on the dissolved fraction of humic substances⁴¹. This would justify the absence of all PAHs studied in the superficial sediments from this estuary; except partially to BaF, which would be deposited mainly on the surface of these sediments by organic particles. This situation would be favored by the muddy plug formation induced by the waters circulation; phenomenon translated by the increase of the moisture of these sediments in this season. However, the basic and reducing characters of the waters and sediments from this canal, which are more pronounced at this period, tend to partially inhibit this process, as results of NPCA.

In FS, the fluvial waters of Comoé, which are acidic, oxidizing, anoxic and have low organic matter content⁴², are fully established in Vridi canal. The presence of these fluvial waters has the same effects as contributions to the meteorite waters in RS, but with a more pronounced character. This situation results in a significant drop in pH, salinity, reducing and moisture in the superficial sediments from this estuary, as well as an increase in their organic matter content. This modification of the physical and chemical characters of this ecosystem by these fluvial waters would be favorable to the bacterial degradation of PAHs and their transport in organic dissolved form in general^{3,4,31}; except partially for BaA. For this PAH, some physical and chemical conditions of this environment, particularly its pH, would favor their deposition on the surface of these sediments, in spite of their reducing character which would partially inhibit this process, as the results of NPCA would show.

In SCS, the rise of deep and cold marine in the presence of Comoé during the short upwelling season of Atlantic Ocean leads to the presence of the brackish waters in this estuary¹⁴. As cold and deep marine waters in the great upwelling season of Atlantic Ocean, the physical and chemical characters of these waters and sediments in this season would be favorable for the bacterial degradation of PAHs and their transport in organic dissolved form in general; except very partially Flt in this study.

The use of different international criteria for the assessment of these sediments contamination by PAHs and ecological risks has once again confirmed the very advanced ecological degradation of this estuary, with very high ecological risks. This situation, already mentioned by Yao et al.¹², Yao and Trokourey^{13,14} and N'Da et al.¹⁵, is the result of the very strong anthropic pressures on this aquatic ecosystem.

Conclusion

The superficial sediments from the Vridi canal are heavily contaminated by PAHs in general. This fact is essentially linked to the accidental or unintentional releases of petroleum products from the only and great oil industry in Côte d'Ivoire, installed near this ecosystem. PAHs in general, and those detected in the superficial sediments from this estuary in particular, know an important seasonal dynamics. This phenomenon is due to the physical and chemical characters of this estuary, strongly influenced by meteorite (Mé, Agnéby, Comoé and meteorite waters runoff) and marine contributions. The strong hydrodynamics of this estuary, biological activities and photochemical reactions also contribute to this. This ecosystem presents a state of very high ecological risks. The results obtained in this study could serve as a base for eventual actions aimed at the rehabilitation and the protection of this marine ecosystem as part of its sustainable development.

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