

Origin and Distribution of Polycyclic Aromatic Hydrocarbons in Lagoon Ecosystems of Morocco

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Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) were determined in sediments and bivalves by the Gas chromatography coupled to Mass spectrometer (GC/MS). PAHs concentrations in sediments of My Boussselham and Khnifiss, Atlantic lagoons, (expressed as Σ PAH) ranged from 31 to 82 ng/g of dry weight and from 6.6 to 34 ng/g of dry weight, respectively. Concerning organisms, PAHs levels contamination ranged from 28 to 117 ng/g of dry weight for My Boussselham (*Ruditapes Decussates*) and from 7 to 18.5 ng/g of dry weight for Khnifiss Lagoon Oyster (*Crassostrea gigas*). In the Med Lag (Nador), the results obtained showed a range varying from 6 to 126 ng/g of dry weight for sediments and from 24 to 32 ng/g of dry weight for organisms (*Mytilus Galoprovincialis*). The origin investigation of PAHs in sediment revealed, that the process of combustion was the main source in these Lagoons, while the diagenetic source, related to the high concentrations obtained of Perylene, was established only in both Atlantic Lagoons (Khnifiss and My Boussselham).

A prevalence of high molecular weight PAHs was observed, with a considerable predominance of 4-ring PAHs in sediments and organisms of the My boussselham and Nador lagoons, while, no clear predominance was observed in the compartments studied in the Khnifiss lagoon.

Correlation study of individual PAH between sediments and organisms, showed that absorption by Clams of low molecular weight PAH group, of which correlation was low, could be done through the water dissolved form, while the absorption of heavier molecular weight PAHs, which showed a high correlation of their distribution between sediments and Clams, could be the absorption from particulate matter.

Keywords: PAHs, Lagoons, Molluscs, Sediments, Molecular ratios.

1. INTRODUCTION

Polycyclic Aromatic Hydrocarbons are among the pollutants most monitored in marine environment, particularly in highly stressed areas such as harbours, estuaries, and others shallow coastal zones exposed to anthropogenic inputs and natural emissions, because are widespread class of environmental chemicals pollutants contaminants in marine environment. Among anthropogenic factors, petrogenic and pyrolytic sources are the most important. Whereas pyrolytic sources, which are largely prevalent in aquatic environment, include combustion processes (e.g., fossil fuel combustion forests fires, shrub and grass fires), the petrogenic input is closely related to petroleum products (e.g., oil spills, road construction materials) [1]. This class of compounds has been widely studied, because of its carcinogenic and mutagenic character [2]. Due to their hydrophobic character, which increases with molecular weight [3], these neutral compounds tend to rapidly adsorb to sediment particles, and therefore represent the most important reservoir of PAHs in marine environment. For that reason, sediments are of high interest in environmental assessment of aquatic ecosystems

and can represent a useful tool for monitoring inputs of PAHs in coastal areas. The fate of PAHs in water is strongly influenced by sorption mechanisms between water and the solid phase, of which physicochemical properties may play a critical role in sorption [4]. Furthermore, sources exhibit different chemical behaviours and distribution in marine sediments. In order to distinguish between these two origins, some molecular ratios of specific hydrocarbons were developed, based on the thermodynamic stability of isomers [5-8]. Also the use of marine organisms, especially, as bio-indicators of chemical pollution, was developed for pollution monitoring programs such as the "Mussel Watch" in the USA or the O.N.N (Observation Network National) in French, which use Mussels and Oysters to study spatial and temporal trends in coastal and estuaries zones [9-11].

This preliminary work focus on the presence, distribution, and origin of several PAHs (those highlighted by the US-EPA) in superficial sediments and bivalve's molluscs collected of three lagoons, which represent wetlands of particularly ecological and economic relevance in Morocco, and previously not studied. Two are located at Atlantic coast (Khnifiss and My Boussselham Lagoons) and the other one, in the Mediterranean coast (Nador Lagoon). Moreover, we have studied the processes affecting the introduction of these pollutants in these aquatic ecosystems, being an important

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aspect for different decision makers in social and economical affairs. Besides, the establishment of the referential state of contamination by these pollutants in these high vulnerable ecosystems is very important, because Coastal's areas of Morocco are highly exposed to a potential traffic of petroleum tankers, especially the Mediterranean coastline.

2. MATERIALS AND METHODOLOGY

2.1. Study Areas

The Nador Lagoon is located on the Moroccan eastern coast. It is a restricted Lagoon of 115 km² (25 × 7.5 km) and with a depth not exceeding 8 m. The island barrier is 25 km large with an average width of 300-400 m (it can come up to 2 km in some parts) and is cut by an artificial inlet. The Lagoon is nourished by several tributaries which are used today for the sewer discharge of the upstream built-up areas. There are 3 urban clusters in the surroundings and 2 saline workings on the banks of the Lagoon.

Situated on the Atlantic coast of Morocco, My bousselham Lagoon is located about 150 Km of the North of the Capital Rabat, and about 40 Km South of Larach. Its area is around 30 km², but divided into two areas by the Drader channel, Merja Kahla in the North and the Merja Zarga in the South. It's considered as an important site of biological and ecological interest.

Khnifiss Lagoon, situated in the South of the Atlantic coast of Morocco (20 Km long and 65 Km² surface area), between Tarfaya and Tantan (28° 02' 54" N - 12° 13' 66" W). This lagoon is a potential site for aquaculture and tourism, if planned with ecological awareness. It opens up to the Atlantic Ocean by a narrow inlet, about 100 m wide. The large surface area of the Lagoon and its high biological production of the avifauna, qualify it among the sites concerned by the RAMSAR convention for humid zone conservation.

2.2. Sampling

The sampling operations took place in 2006, during the months of June, July, and August, for My Bousselham,

Khnifiss and Nador Lagoon, respectively. In each sampling station (shown in Fig. 1), superficial sediment (0-2 cm) was collected by diving, and transferred to aluminium container for all Lagoons. Nador Lagoon Mussels (*Mytilus Galoprovincialis*) and Khnifiss Oysters (*Crassostrea gigas*) were collected by diving while the My Bousselham clams (*Ruditapes Decussates*) were collected by hand. After dissection, these organisms were also transferred to aluminium containers. Both containers were put in a plastic bag and frozen at -20°C.

2.3. Samples Preparation

About 0.5 g of freeze-dried organisms and sediments sieved at 63 µm, were extracted with Methylene Chloride, using microwave assisted extraction with a Maxi-digest 350 apparatus, at 30W for 10 min. The organic extract was then reduced to a small volume using a rotary evaporator. Then the extract was purified into a micro-column containing alumina (1.5g) by eluting with Methylene Chloride. This purified extract was then fractionated on a micro column containing silica (0.8g) for organisms; and silica and activated cooper for sediment, in order to collect separately saturated and aromatic compounds, eluted with respectively pentane and a mixture of Pentane: Methylene Chloride (65:35; v:v). Activated cooper was used to eliminate the sulphur from the organic extract. The purified aromatic fraction was finally concentrated to a few µl in iso-octane and analysed by gas chromatography coupled to a mass spectrometer (GC/MS).

In these samples, the PAHs studied are: Phenanthrene (Phe), Anthracene (An), Acenaphthene (Ace), Acenaphthylene (Acy), Fluorene (F), Fluoranthene (Fl), Pyrene (Py), Chrysene (Chry), Benzo [a] Anthracene (B[a]A), Benzo [b;j;k] Fluoranthene (B[b;j;k]F), Benzo [a] Pyrene (B[a]P), Indeno [1,2,3-cd] Pyrene [IP], Benzo [ghi] Perylene (BP), Dibenzo [a,h] Anthracene (D[ah]A). This group of PAHs was identified by the U.S Environment Protection Agency (US-EPA), as priority pollutants to be monitoring in marine environments. Naphthalene was not considered because of its high volatility. [b;j;k] isomers of Benzo-Fluoranthene were grouped, because of their poor separation (coelution).

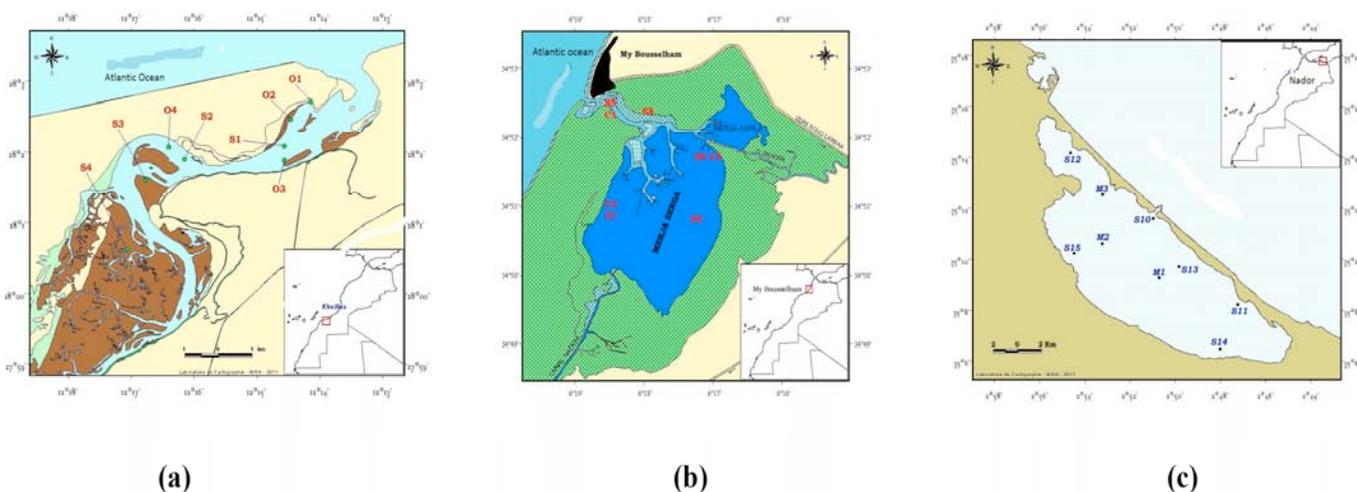


Fig. (1). Study area and location of sampling sites of sediments and organisms. (a) Khnifiss Lagoon; (b) My bousselham Lagoon; (c) Nador Lagoon.

Benzo[e]Pyrene and Perylene were also investigated but not taken into account in Σ PAHs estimated. Perylene was studied for diagenetic source investigation.

The compounds used as internal standards were perdeuterated PAHs. Phenanthrene- d_{10} , Anthracene- d_{10} , Fluoranthene- d_{12} , Chrysene- d_{12} , Benzo [a] Pyrene- d_{12} , Benzo[e] Pyrene- d_{12} , and Benzo[ghi]Perylene- d_{12} , were used for quantification (Table 5). Pyrene- d_{10} and Benzo [b] Fluoranthene- d_{10} were added to the extract injection into the chromatograph, for recovery calculation [12-14].

2.4. GC-MS Analysis

The aromatic fraction was analysed by gas chromatography coupled to mass spectrometry (HP-5890 Series II), which was operated under the Selected Ion Monitoring (SIM) mode, using the molecular ions of the studied PAHs (Table 5) (electronic impact at 70 eV, interface 290 C°). The oven temperature program used was: 50C° (2 min) to 290 C° (20 min) at 5C°/min. The carrier gas was helium at a constant flow rate of 1ml/min.

The PAHs were quantified relative to perdeuterated PAHs. The response factors of the different compounds were calculated by injecting a Standard Reference Material (NIST, SRM 2260) containing the target PAHs, at certified concentration, and spiked with perdeuterated compounds used as internal standards and those used for recoveries control). The response factor of an analyte (a) relative to internal standard (i) is given by:

$$K_a = (A_i/A_a) \times (M_a/M_i)$$

Where A_a , and A_i indicate the area of the analyte and the internal standard; and M_a , and M_i , the amount of the PAH analyte and the internal standard in the injected solution, respectively.

Recoveries were determined by adding two perdeuterated PAHs, Pyrd $_{10}$ and Chrysd $_{12}$, at a known amount to the final extract just before the injection in the chromatograph system. The amounts of the internal standards in the extract are given by:

$$M_i = K_i \times M_s \times A_i/A_s$$

Where: K_i is the instrumental response factor of the internal standards relative to perdeuterated PAHs added for recoveries control, M_s is the amount of PAHs added, and A_i , and A_s refer, respectively, to the areas of the chromatographic peak of the internal standard and the perdeuterated PAHs added for recoveries control in the final extract.

Average recoveries for all samples were $78 \pm 10\%$. The accuracy of method was estimated by analysing a Certified Reference Material (IAEA 417, Organochlorine compounds and petroleum hydrocarbons in sediment sample) at the same conditions as the sediments sampled. It was purchased at the Marine Environment Laboratory of Monaco. Results obtained were within the confidence interval (95%) (Table 3).

3. RESULTS AND DISCUSSION

3.1. PAHs in Sediments and Organisms

The results obtained for PAHs concentrations in the selected sediments stations are reported in Table 1. According to the measured levels, the lagoons studied showed a low

Table 1. Results (ng/g dry weight) Obtained in Sediments of Tree Lagoons Studied. ND: Not Detected

	S1	S2	S3	S4	S6	S5	S7	S9	S8	S10	S11	S12	S13	S14	S15
Phenathrene	7.22	3.87	3.12	2.83	1.58	19.09	5.54	3.95	4.02	8.36	17.50	18.35	7.11	ND	6.09
Anthrcene	0.49	0.21	0.28	0.17	0.90	3.10	0.97	1.52	0.79	2.40	2.05	2.92	0.95	0.47	4.49
Acenaphtylene	0.53	0.21	0.18	0.23	0.11	0.24	0.07	0.14	7.35	1.06	0.28	0.49	0.41	0.07	0.16
Acenaphtene	1.01	0.36	0.29	0.44	0.79	0.64	0.18	0.42	6.52	1.33	1.57	0.53	1.39	0.36	0.51
Fluorene	2.96	0.86	0.54	0.13	0.80	1.36	0.95	0.84	2.48	2.11	6.73	1.37	3.49	ND	2.08
Fluoranthene	2.62	2.33	0.33	0.62	2.53	9.30	2.86	2.50	4.11	13.94	6.35	10.57	3.31	0.55	2.38
Pyrene	3.28	2.39	0.42	0.81	4.42	9.02	4.04	2.20	3.32	12.82	6.33	12.88	1.43	1.52	0.06
Benzo[a]Anthracene	2.05	1.29	0.16	0.06	0.91	3.78	1.01	1.00	0.66	9.34	3.87	4.72	1.87	0.46	1.41
Chrysene	3.36	1.70	0.30	0.35	1.70	5.19	2.10	1.88	1.68	11.55	6.10	14.85	2.99	0.54	2.42
Benzo[b;k;j]Fluoranthene	5.4	2.6	0.2	0.3	2.73	9.08	4.26	3.54	3.41	25.33	14.52	17.36	5.77	1.01	5.59
Benzo[a]Pyrene	1.89	1.05	0.20	0.16	1.23	4.12	1.35	1.72	1.06	12.26	4.45	6.90	2.64	0.32	1.80
Indeno[123-cd]Perylene	1.51	0.82	0.31	0.45	1.17	3.37	1.72	1.64	1.31	13.38	7.22	7.63	3.44	0.40	2.92
Dibenzo[ah]Anthracene	0.63	0.34	0.18	0.15	0.39	0.83	0.17	0.45	ND	1.55	0.75	2.14	0.04	0.12	0.11
Benzo[ghi]Perylene	1.19	0.70	0.07	0.08	1.33	3.67	1.74	1.51	2.34	10.91	5.82	11.48	3.23	0.23	2.53
Benzo[e]Pyrene	2.21	1.11	0.03	0.15	9.13	5.54	5.43	6.11	4.20	6.57	1.91	2.47	1.05	0.18	1.01
Perylene	4.44	2.32	3.70	1.91	1.38	3.47	1.89	1.88	1.61	9.53	4.62	9.82	2.43	0.64	2.23
Σ HAP	34.10	18.7	6.6	6.8	31.09	81.79	34.27	31.30	44.86	126.34	83.53	112.20	38.08	6.07	32.57

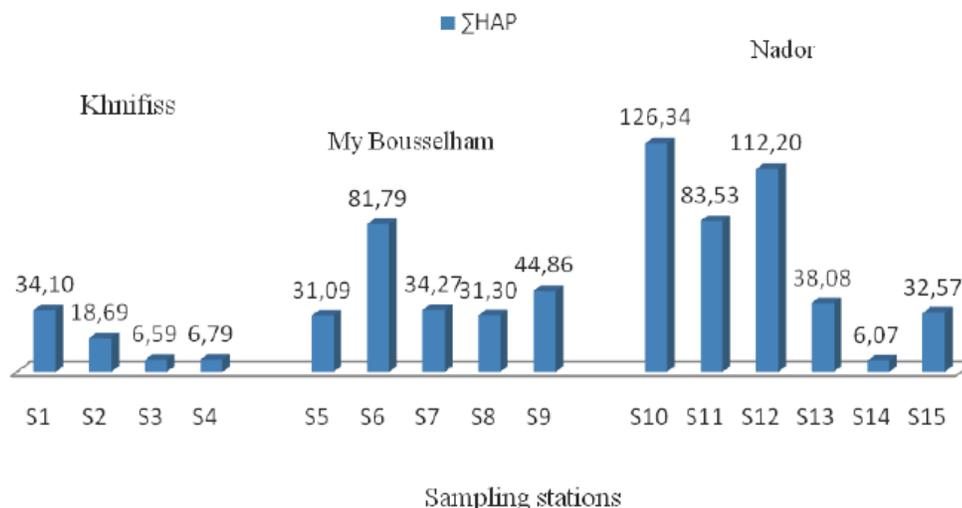


Fig. (2). Concentrations of PAHs (ng/g dry weight) in sediments, expressed as ΣPAH.

to moderate levels of contamination by PAHs. The ΣPAHs concentrations ranged from 6 to 126 ng/g dry weight, from 31 to 82 ng/g dry weight and from 6 to 34 ng/g dry weight for Nador, My Boussselhma and Khnifiss lagoon, respectively. All sampling stations located close to the open sea, exhibit the highest concentrations of PAHs (Fig. 2). A clear dominance of high molecular weight was observed (Pyrene, Chrysene, Benzo [a] Anthracene, Benzo [b;j;k] Fluoranthene, Benzo [a] Pyrene, Benzo[ghi] Perylene) in all sampling sites in respect to low molecular weight (Phenanthrene, Fluorene, Fluoranthene).

Concerning to the Organisms, levels obtained (see Table 2) showed low ΣPAHs concentrations in most samples analysed. Indeed, all Nador Mussels samples ΣPAHs concentrations were around of 30 ng/g dry weight, while the Khnifiss Oyster and My Boussselham Clams ΣPAHs concentrations ranged from 7 to 18 ng/g dry weight and from 28 to 117 ng/g dry weight. This latest moderate ΣPAHs concentration of 117 ng/g dry weight was observed in Clams of My Boussselham lagoon (C1), sampled in a site where also sediment exhibited the highest ΣPAHs concentration in this lagoon (Fig. 3).

Table 2. Concentrations (ng/g dry weight) Obtained in Organisms of Lagoons Studied. C: Clam; O: Oyster; M: Mussel, ND: Not Detected

	O1	O2	O3	O4	C2	C1	C3	M2	M1	M3
Phenanthrene	2.5	7.1	0.6	3.5	4.61	4.25	21.24	6.18	5.54	5.67
Anthracene	0.3	0.8	0.1	1.5	0.34	0.46	1.73	0.51	0.24	0.13
Acenaphtylene	0.2	0.2	0.4	0.5	0.10	0.05	1.20	0.40	0.25	0.19
Acenaphtene	ND	ND	0.5	2.0	ND	ND	8.23	3.91	ND	ND
Fluorene	1.1	ND	0.8	1.2	1.18	ND	15.25	2.75	0.72	1.23
Fluoranthene	1.8	1.3	0.8	0.6	2.73	3.41	11.19	4.14	2.23	3.28
Pyrene	3.3	3.1	1.5	1.1	5.85	4.57	50.83	8.22	3.15	6.47
Benzo[a]Anthracene	0.4	0.8	1.0	0.7	0.69	0.30	0.25	1.37	0.43	1.17
chrysene	0.6	1.4	1.2	0.9	0.75	0.94	0.32	4.79	2.85	3.34
Benzo[b;j;k]Fluoranthene	1.7	0.8	0.3	2.7	1.86	21.27	ND	3.22	13.52	2.51
Benzo[a]Pyrene	2.7	1.2	ND	1.7	6.00	6.31	2.50	6.01	6.83	7.32
Indeno[123-cd]Pyrene	0.4	0.5	0.2	4.3	0.60	0.54	ND	0.35	0.05	0.20
Dibenzo[ah]Anthracene	0.9	ND	ND	ND	ND	ND	0.09	0.53	0.21	0.15
Benzo[ghi]Perylene	1.2	ND	ND	ND	0.95	9.60	2.23	0.70	ND	0.44
Benzo[e]Pyrene	ND	0.9	0.1	0.4	2.48	1.41	ND	1.56	ND	ND
Perylene	1.0	ND	0.3	1.4	0.37	ND	2.32	0.54	ND	0.31
ΣPAH	17.10	17.2	7.41	18.50	28.50	53.12	117.39	33.47	32.45	24.45

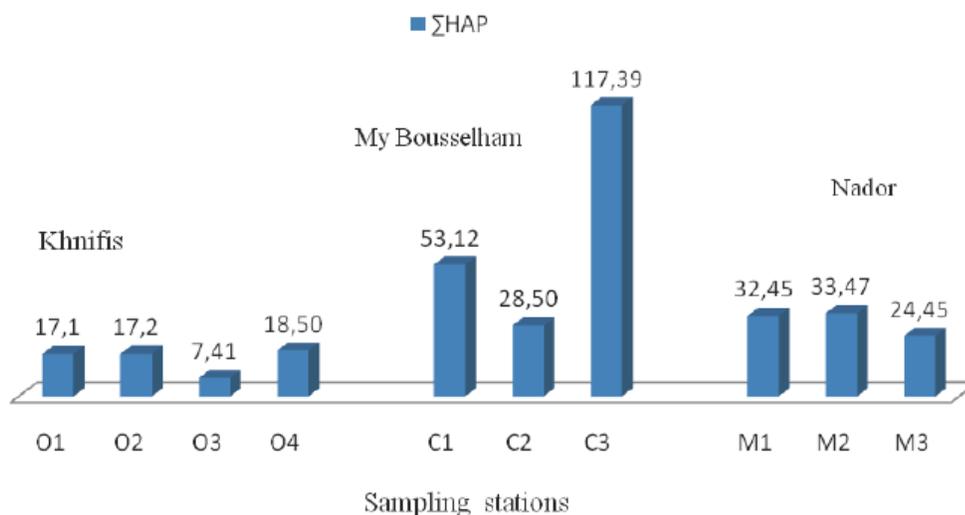


Fig. (3). Concentrations of PAHs (ng/g dry weight) in organisms, expressed as ΣPAH.

Table 3. Comparison of the Obtained (O.V.) and Certified Values (C.V.), in ng/g Dry Weight, for the Analysis of the IAEA-417 Certified Reference Material

	Phe	An	Acy	Ace	F	Fl	Pyr	B[a]A	B[b]F	B[k]F	B[e]P	B[a]P	Perylene	IP	D[ah]A	BP
O.V	626	965	41	221	297	6186	4902	3346	3959	2514	2669	3203	1520	3304	553	2599
C.V	320	630	42	180	230	7700	6000	3200	4100	200	3000	2800	2300	2700	1100	2300

Grouping polycyclic aromatics compounds into different classes depending on the number of aromatic rings present in their structure (Fig. 4), it can be observed that the PAHs with 4-rings are the most abundant in sediments of Nador lagoon and the PAHs with 4,5-rings in My Boussselham lagoon sediment, while the sediments of Khnifiss was dominated by the PAHs with 3,4-rings. This evidence suggests that PAHs sediments contamination in these ecosystems might be originated mainly from pyrolytic process [15]. When it comes to organisms, in general, these marines organisms uptake the low molecular weight HAPs and the most soluble [16, 17]. According to our study, in general, the results showed that the PAHs with 4-rings are the abundant PAHs in all organi-

sms analysed. The same result was observed concerning the profile of PAHs accumulation by clams of Ganzirri lagoon [18]. Also, as it can be observed, PAHs with 6-rings are more abundant in Clams than the others organisms (Mussels and Oysters). Indeed, all are filter feeder's and are exposed to suspended and soluble matter, but clams due to its localisation in sediments, are more exposed to PAHs from resuspended particles issues from sediment, enriched in general of heaviest aromatic compounds.

Concerning the concentrations of B[a]P, in organism samples, all of them (expressed in ng/g dry weight) are below the values established by the European Regulation,

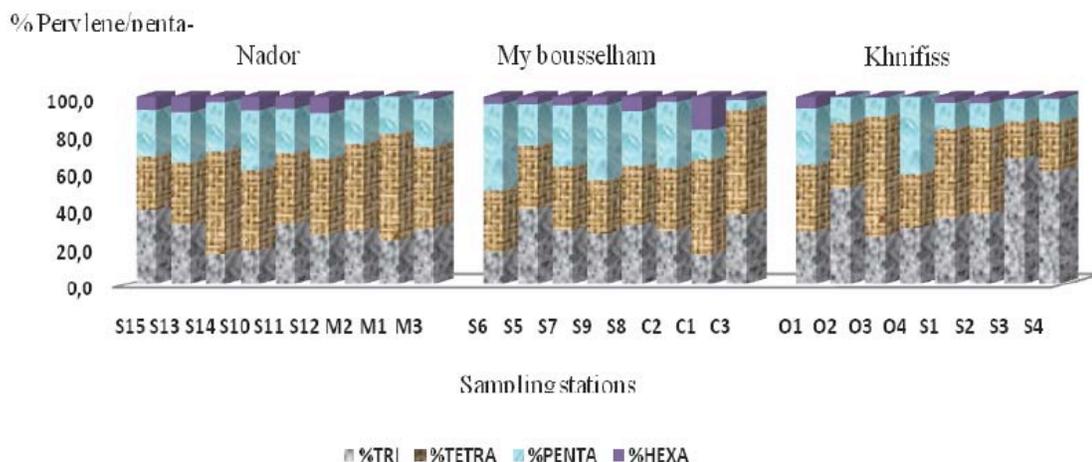


Fig. (4). Profile distribution of PAHs per group of aromaticity in sediments and organisms.

which fixed 10 $\mu\text{g}/\text{kg}$ wet weight the maximum admissible in shellfish [19].

In order to make a view of the contamination level by PAHs measured in these Moroccan's lagoons, a Comparison to other lagoons was made of by others studies [18, 20-22], showed that the Moroccan lagoons are slightly contaminated by these compounds, and our results are quiet similar to those obtained in Lessina and Varano lagoons in Italy [23].

3.2. Sources of PAHs

In an attempt to identify sources of the PAHs measured in sediments of this study, a source analysis was undertaken. Several molecular ratios, such as Phe/An, Fl/Pyr, Chrys/B[a]A have been developed for interpreting PAH composition and identifying possible sources [8, 24-27].

Bicego [28] used the following four PAHs isomer pair ratios to identify possible sources in sediments of the Santos

and Sao Vicente Estuary of Sao Paulo (Brazil): An/An+Phe; Fl/Fl+Pyr; B[a]A/B[a]A+chry; IP/IP+BP [28]. According to Yunker [8]. When the ratio of An /An+Phe < 0.1 , the PAHs were mainly from petroleum contamination, while it is > 0.1 , PAHs were from combustion source. PAHs with Fl/Fl+Pyr < 0.40 were from petroleum contamination, while a PAHs with $0.4 < \text{Fl/Fl+Pyr} < 0.5$ were mainly from oil combustion, and PAHs with Fl/Fl+Pyr > 0.5 were from a combustion of coal, wood and grassed matter [8].

Concerning to the B[a]A/B[a]A+chry ratio, PAHs with $0.2 < \text{B[a]A/B[a]A+chry} < 0.35$ could be related to a mixed origin. PAHs with B[a]A/B[a]A+chry < 0.2 were mainly from petroleum contamination, while PAHs with B[a]A/B[a]A+chry > 0.35 were from combustion source. Finally, PAHs with IP/IP+BP < 0.2 were from petroleum origin input, while PAHs with $0.2 < \text{IP/IP+BP} < 0.5$ were mainly from oil combustion, and IP/IP+BP > 0.5 were typical of the combustion of coal, wood and grassed matter.

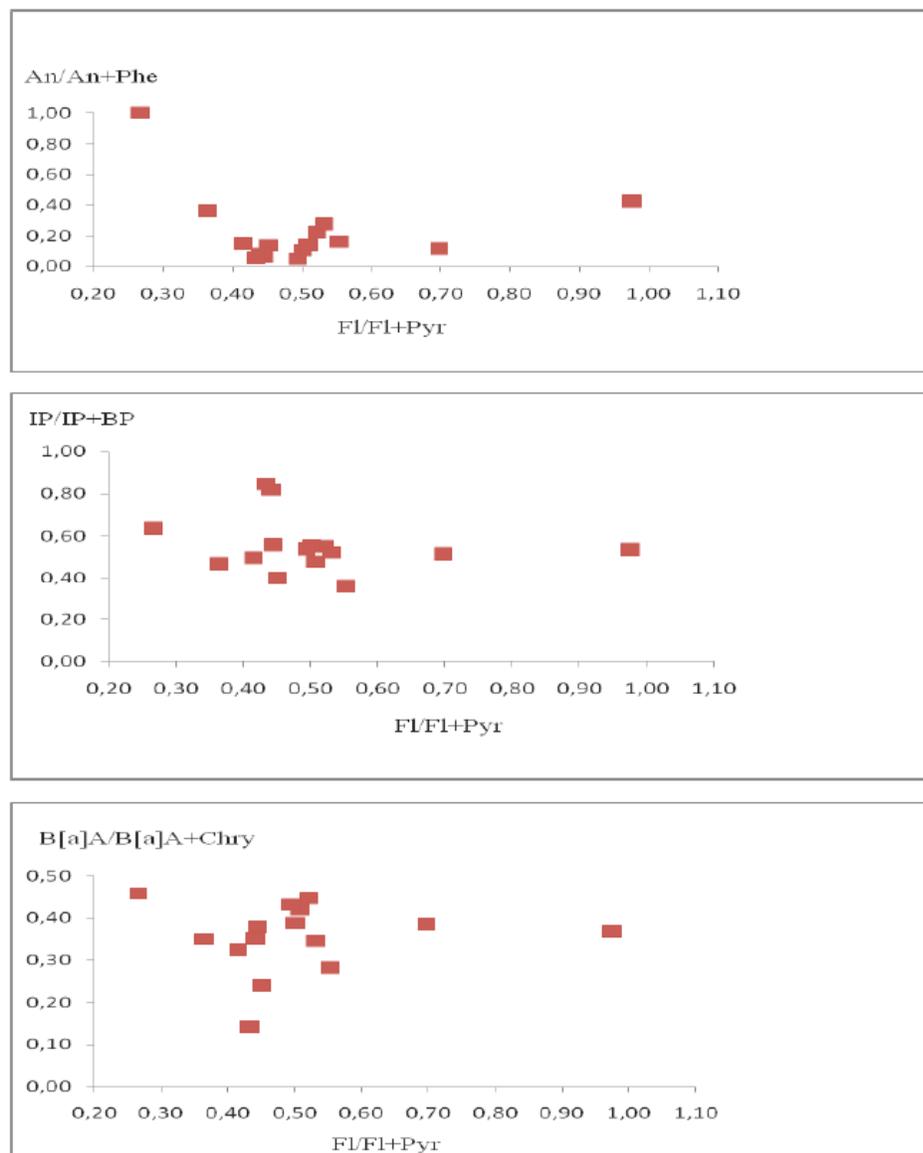


Fig. (5). PAHs cross plots for sediments. Figures show ratios of: (a) IP/IP+B[ghi]P vs.F/F+Pyr; (b) An/An+Phe vs. Fl/Fl+Pyr; (c) vB[a]A/B[a]A +Chry vs. Fl/Fl+Pyr.

These ratios were determined only for sediments lagoons, but organisms weren't concerned by the source study. Indeed, origin study must be limited to sediments, because of possible biotransformation ability of pollutants by organisms, and the PAHs content does not reflect the really fraction that was accumulated [29]. The isomers ratios An/An+Phe, B[a]A/B(a)A+Chry; IP/IP+BP have been plotted against Fl/Fl+Pyr to show how PAHs are distributed relative to their source (Fig. 5).

PAHs An/An+Phe values were > 0.1 for Nador and My bousselham sediments, while it were < 0.1 for PAHs Khnifiss sediments, showing that PAHs were introduced by combustion and petroleum sources respectively.

PAHs IP/IP+BP values were > 0.5 for Nador and Khnifiss sediments lagoons, while the ratios values were between 0.2 and 0.5 for Moulay Bousselham sediments lagoon, indicating that the input of PAHs were mainly from coal, wood and grasses and petroleum combustion respectively.

According to the PAHs Fl/Fl+Pyr ratio, PAHs were introduced by the combustion of petrol coal, wood and grasses for both sediments of Nador and Moulay bousselham lagoons, while the combustion of petrol was the main source of PAHs in Khnifiss lagoon sediments.

PAHs B[a]A/B[a]A+Chry exhibit values > 0.35 for most sediments samples of Nador and Khnifiss, while most sediments of Moulay Bousselhma PAHs B[a]A/B[a]A+Chry were between 0.20 and 0.35. These results show that PAHs were mainly from combustion source for Nador and Khnifiss lagoons, but were from a mixed source (combustion and petroleum) for Moulay Bousselham lagoon.

As it can be observed, most ratios used in this study pointed to combustion source (oil, coal, grasses and wood), while the petroleum emission source accounts only for Khnifiss lagoon related to An/An+Phe values. Moreover, restriction to the Fl/Fl+Pyr and IP/IP+BP ratios, showed that PAHs in Nador lagoon were typically from the combustion of coal, grasses and wood, while in case of the others lagoons, PAHs were from petroleum combustion and the

combustion of coal, grasses and wood. This could be easily justified by the fact that, the surrounding areas of Nador lagoon are more urbanised, with untreated urban waters wastes discharged directly.

Concerning others lagoons less urbanised, where the petroleum combustion is also a prevalent source, the traffic of motors boats often contributes to the pollution lead of these areas.

Moreover, in this study, Perylene was observed to be present at high concentrations in most of the sediments analysed. This compound could be introduced in the aquatic environment by pyrolytic and fossil fuel such as petroleum and by degradation of biogenic precursors (diagenetic origin). This latter source can be predominant in older core sections of anoxic sediment [30], and Perylene is probably the most important diagenetic PAH encountered in sediments. To investigate this diagenetic source, calculations of relative concentration of this compound, relative to the concentration of the penta-aromatic were done, and ranged from 43 to 75%, from 51 to 69 %, and from 8.5 to 15% for Khnifiss, My Bousselham and Nador lagoons, respectively were done (Fig. 6). This high occurrence of Perylene, especially in sediments of Khnifiss and My Bousselham, the atlantic lagoons, could be attributed to natural source (diagenetic source).

4. COMPARISON BETWEEN SEDIMENTS AND ORGANISMS: CASE OF MY BOUSSELHAM LAGOON

In order to make a comparison between PAHs accumulated by organisms and sediments, we have chosen only the case of My Bousselham Lagoon, where organisms and sediments were sampled at the same locations. \sum PAHs concentrations in clams has been plotted versus the \sum PAHs concentrations in sediments, showing a very low correlation ($R^2 = 0.038$). PAHs are hydrophobic compound, and as for the others hydrophobic contaminants (PCB, Pesticides), their accumulation by organisms has been shown to be governed by several factors, such as the lipids content [31], physicals and chemicals parameters of the environment (Turbidity,

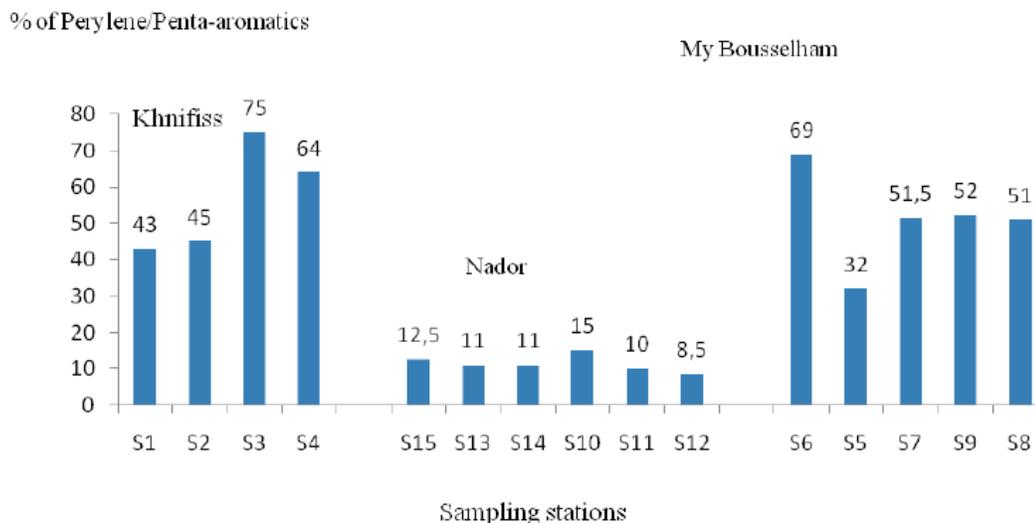


Fig. (6). % of concentrations of Perylene relative to Penta-aromatics PAHs.

Salinity, Temperature...), localisation of the organism (column water, bottom), and the bioavailability of the contaminant [30]. Concerning to the sediments or particles, the concentration of the organic matter could help to determine the characteristics of the hydrocarbons adsorption [32], so that we could predict their availability in column water. High concentration of organic carbon in the sediments is known to reduce the bioavailability of PAHs adsorbed on particles [33].

Table 4. Correlations Values of PAHs between Sediments and Organisms of My Bousseham Lagoon

Compound	R ²	Correlation
Phenanthrene	0.101761	Low
Anthracene	0.164836	Low
Acenaphthylene	0.5041	Moderate
Acenaphthene	0.944784	High
Fluorene	0.105625	Low
Fluoranthene	0.157609	Low
Pyrene	0.334084	Low
Benzo[a]Anthracene	0.189225	Low
Chrysene	0.436921	Moderate
Benzo[b;k;j]Fluoranthene	0.906304	High
Benzo[a]Pyrene	0.281961	Low
Indeno[123-cd]Pyrene	0.035721	Low
Dibenzo[a,h]Anthracene	0.571536	Moderate
B[ghi]Perylene	1	High
Perylene	0.702244	High
B(e)Pyrene	0.178929	Low

For a better understanding of the factors affecting PAHs distribution in Clams of this lagoon, we have considered each PAH individually, and have determined the correlation of each PAH between the two matrices studied, using PCA correlation statistical results obtained with ADE-4 statistical program [34], clams and sediments for the tree stations. Tree levels of correlation were obtained (Table 4). The low correlation obtained for Phenanthrene, Anthracene, Fluorene and the Fluoranthene, considered as the most soluble PAHs in water, means that there is no correlation between the distribution of these PAHs in sediments and Clams.

Clams are filter feeder's organisms and live in sediment compartment, but remain close to the surface that the tips of their siphons are exposed. Water and food particles are drawn in through one siphon to the gills where tiny, hair-like cilia move the water, and the food is caught in mucus on the gills. From there, the food-mucus mixture is transported along a groove to the palps which push it into the clam's mouth. The second siphon carries away the water. The gills also draw oxygen from the water flow. Consequently they are submitted to the pollution adsorbed on particles and also to the dissolved pollution in water column. The lack of correlation between sediments and clams of these compounds, suppose that were assimilated through the gills, the

principal way for the absorption of dissolved compounds, while the high correlation of the distribution of Benzo [ghi] Perylene, Perylene, the Benzo [b;j;k] Fluoranthene, the heavier molecular weight and the less soluble PAHs, could suggest that were absorbed through the digestive system.

Table 5. Studied PAHs and the Corresponding Molecular Ions and Internals Standards Used for Quantification

PAH studied	m/z	Relative internal standard	m/z
Acenaphthene	154	Phenanthrene-d ₁₀	188
Acenaphthylene	156	Phenanthrene-d ₁₀	188
Fluorene	166	Phenanthrene-d ₁₀	188
Phenanthrene	178	Phenanthrene-d ₁₀	188
Anthracene	178	Anthracene-d ₁₀	188
Fluoranthene	202	Fluoranthene-d ₁₂	212
Pyrene	202	Fluoranthene-d ₁₂	212
Chrysene	228	Chrysene-d ₁₂	240
Benzo[a]Anthracene	228	Chrysene-d ₁₂	240
Benzo[b;k;j]Pyrene	252	Benzo[e]Pyrene-d ₁₂	264
Benzo[a]Pyrene	252	Benzo[e]Pyrene-d ₁₂	264
Perylene	252	Benzo[e]Pyrene-d ₁₂	264
Indeno[1.2.3-cd]Pyrene	276	Benzo[ghi]Perylene-d ₁₂	288
Dibenzo[ah]Anthracene	278	Benzo[ghi]Perylene-d ₁₂	288
Benzo[ghi]Perylene	276	Benzo[ghi]Perylene-d ₁₂	288

The high correlation obtained for Perylene could be explained also by the fact that, the major fraction is introduced by diagenetic process in sediments, and the fraction accumulated of this PAH by Clams was probably absorbed from sediment. The low correlation also obtained for Benzo[e] Pyrene, could be explained, as reported by Baumard *et al.*, [29], this PAH could be obtained by a partial depletion of its isomer the Benzo[a] Pyrene in Mussels, due to metabolic biotransformation. The metabolite obtained is more hydrophilic. Baumard *et al.*, studied the correlation distribution between sediments and Mussels sampled of a Mediterranean French coastal zones, and a moderate correlation (< to 0.6) for heavier PAHs was observed [29], while in our case, correlation was high and reached a value of R² around 0.9. This could be explained by the difference location of Mussels (Rocks) and Clams (Bottom). Indeed, organisms living in or near by bottom sediments, could be more exposed to particles matter, enriched in general by heavier molecular weight organics xenobiotics.

CONCLUSIONS

The results of this study have confirmed the presence of these compounds in sediments and organisms analysed of these tree coastal ecosystems. The high concentrations of PAHs in sediments and organisms were observed in My Bousseham Lagoon, but could remain, from an eco-toxicological point of view, as low levels of pollution comparing to others lagoons investigations. The PAHs detected are originating mainly from the combustion process at higher temperature of the organic matter for My Bousseham and Nador Lagoons, while the combustion of petroleum products

were the main source of these compounds in Khnifiss Lagoon. Some diagenetic source of Perylene was observed, especially in both Atlantic Lagoons.

The PAHs distribution patterns were different for sediments and similar for organisms. In Atlantic Lagoons, the 4-rings and the 5-rings, the 4-ring and the tri-rings were the dominant groups in sediment respectively of My Boussselham and Khnifiss Lagoons, while the 4-ring compounds were dominant in the other Mediterranean Lagoon sediments. Concerning organisms, the 4-ring compounds were dominant in My Boussselham and Nador Lagoons, but in Khnifiss Lagoon there was no obvious dominance.

Correlation study between sediments and Clams of My Boussselham Lagoon, showed low correlation for low molecular weight and most soluble PAHs (Phenanthrene, Anthracene, Fluorene and Fluoranthene), suggesting that they were absorbed as dissolved compounds. A high correlation was observed concerning the heavier molecular weight and the less soluble PAHs (Benzo[ghi]Perylene, Perylene, the Benzo [b,j;k]Fluoranthene), suggesting their absorption via particulate matter.

CONFLICT OF INTEREST

None declared.

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