



Temporal Evolution of Marine Sediments Pollution in Dakar: Polycyclic Aromatic Hydrocarbons Determination by Gas Chromatography-Mass Spectrometry

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Marine sediments selected from the region of Dakar, Senegal and collected between year 2004 and 2008 were studied for their content on polycyclic aromatic hydrocarbons which were determined by GC-MS. The sampling sites (Port of Dakar, Hann, Soumbédioune and Mbao) were chosen according to the various commercial activities or particular situation of the given area. Thus, Dakar port is where the big tanks for storing and supplying the refined fuels to the different petrol stations around the city, ships, *etc.* are placed. Hann and Soumbédioune are the sites where urban wastewaters flow throughout the East and West canals, while Mbao is the place where the African Oil Refinery is located. A short-timed accumulation of pollutants within the sediments selected by polycyclic aromatic hydrocarbon was also noticed with their concentrations increasing from year 2004 to 2008 samples. The results show that the harbor zone has the highest level, which is followed by the sites of Soumbédioune, Mbao and Hann. These studies are an inventory of fixtures need to be carried on to provide basic scientific data to political decision makers in order to look for resolving the solution.

Keywords: Polycyclic aromatic hydrocarbons, Sediments, Pollution, CG/MS, Dakar.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are contaminants omnipresent on the marine environment because of their considerable stability and due to their many sources. The polycyclic aromatic hydrocarbons are various origins. They are associated with combustion incomplete processes (forest fires, cigarettes, barbecues *etc.*). They are also released in the environment by products which contain oil, engine oil and petroleum products^{1,2}. Polycyclic aromatic hydrocarbons may also be generated from energy production, from fossil fuels, the various metallurgical industries, but principally from the considerable amounts of hydrocarbons poured into the ocean by ships³⁻⁵.

Because of their carcinogenic and mutagenic activities with regards to the fauna and flora, these contaminants are considered priority pollutants for land as well as marine ecosystems⁶.

Their toxic properties result from the formation of metabolites (epoxies, diols) by living organisms. These metabolites link up with DNA and lead to the organism dysfunctions. Their presence can be harmful to the fauna, the flora and consequently to humans⁷. It has thus become essential to check the contents of some hydrocarbons toward off any possible population contamination. Sixteen of these compounds have been

selected by the US Environment Protection Agency (EPA) as priority pollutants to be searched for in waters, in soils and in the atmosphere⁸. Many techniques have been used of to determine polycyclic aromatic hydrocarbons in deposits to assess the presence of the contaminants and their toxicity⁹. As part of this work, a method previously used was optimized to determine polycyclic aromatic hydrocarbons contents in deposit samples coming from Dakar area coasts (Hann, Mbao, Soumbédioune and the surroundings of Dakar harbor). The polycyclic aromatic hydrocarbons isolation was performed by means of a Soxhlet extraction^{10,11} with a hexane/acetone mixture (v/v) and the purification with alumina¹². The extract was then submitted to analysis by gas chromatography coupled to a mass spectrometric detection (GC/MS)¹³.

EXPERIMENTAL

The reagents used are of analytical quality (Panréac). Alumina Al₂O₃ (150 mesh, 58 Å, Aldrich) was activated at 450 °C and then deactivated at 10 % with Millipore water. Anhydrous sodium sulphate Na₂SO₄ (Panréac) was heated at 550 °C before being used. Reference standard products mixture consisted in sixteen polycyclic aromatic hydrocarbons (Supelco). The following abbreviations were used for the polycyclic aromatic hydrocarbons: naphthalene (Nap), acenaphthylene (Aci), acenaphthene (Ace), fluorene (Flu),

phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benzo[a]anthracene (BaA), chrysene (CHry), benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP), indeno[1,2,3-c d]pyrene (Ipy), benzo[g,h,i]perylene (BghiP), dibenzo[a,h]anthracene (DahA).

Preparation of standard solutions: Standard solutions were prepared by successive dilutions of the reference standard in hexane.

Preparation of samples: Samples of marine sediments were taken at depths of 5 meters, air-dried and then freeze-dried. Evaporation losses were reduced by keeping the samples at a temperature below 0 °C. Samples were then homogenized and sieved to obtain particle diameters of about 60 µm.

Extraction of hydrocarbons: Polycyclic aromatic hydrocarbons were extracted by using a Soxhlet. 5 g of sieved samples and 2 g of anhydrous sodium sulphate were mixed in a cellulose cartridge. The extraction was made after a period of 8 h with an *n*-hexane/acetone mixture (1:1, v/v). Owing to the possible presence in the sample of sulphur compounds and in order to avoid their interferences on the separation, samples were submitted to a desulphurization step by using unoxidized copper powder which was treated with hydrochloric acid then washed with distilled water and three times with acetone. Then the copper powder was poured and left to react for 24 h on the extraction media.

Purification of the extracts: After evaporation of the solvent under nitrogen current in order to eliminate the solvent, the residue was dissolved in hexane and purified by passing it through an alumina column and eluted with 40 mL of hexane. The extract was then concentrated by using a rotary evaporator, at a temperature of 40 °C and under reduced pressure, until a volume of about 5 mL was reached.

Concentration: The eluate obtained was concentrated at 0.5 mL under nitrogen current. The polycyclic aromatic hydrocarbons were finally taken again in 1 mL of hexane and kept at 4 °C.

Residual traces of water were eliminated by adding anhydrous sodium sulphate into the evaporator balloon flask. The dehydrated extract is then transferred in a graduated tube. The operation had to be carried out slowly so that the sodium sulphate remained at the bottom of the balloon flask. The latter was rinsed again with 3 to 4 mL of clean solvent added into the tube. By using a flow of nitrogen the organic extract was dry evaporated. The solution was taken again with 1 to 2 mL of solvent.

Equipment: A Hewlett Packard HP 6890 series CG, fitted with a split/splitless injector (splitless time: 1 min; flow: 60 cm/s) was used. The temperature injector was maintained

at 290 °C. The CG temperature range goes from 60 °C (3 min) to 250 °C (18.33 min) then to 310 °C (33.33 min).

The carrier gas is helium with a constant output of 1 mL/min. The column used is an HP-5 MS (Hewlett - Packard, Palo Alto, California, USA): 30 m × 0.25 mm ID × 0.25 µm of film thick. The CG was coupled to an HP 5973 make mass selective detector (MSD). The mass spectrometric detector was made use of in the selected ion monitoring mode of the ions characteristic of the sought components.

RESULTS AND DISCUSSION

The efficiency of the extraction by Soxhlet was evaluated by studying the repetitiveness and percentage of recovery. To evaluate the repetitiveness of the method, three extractions of a clean sample (not contaminated) freeze-dried and homogenized, with a known quantity of standard of 16 hydrocarbons, were carried out.

The results of the repeatability, was statistically evaluated using the surface of the peaks (Table-1). The values of recovery higher than 100 % are due for a possible concentration of the compound, in the phase of solvent evaporation.

Analysis of the samples purified by CG/MS: Analysis of polycyclic aromatic hydrocarbons by GC-MS takes advantage that MS detection implies an increased confidence (selectivity) in peak identification and compound confirmation together with its ability to search and identify unknowns. Other less expensive detectors, i., FID, can be also employed,

The eluate was analyzed by gas chromatography with mass spectrometric detection.

In SIM mode the mass selective detector (MSD) is very sensitive and selective. This is the mode to be used for quantitative analyses at the state of traces of compounds previously identified in scan mode. The interface temperature is 290 °C.

The scan mode consists in scanning across several masses to get some information about the total content of the sample to be analyzed. This is the mode to be used in qualitative analysis for the identification of compounds by research, in spectra library. Also, it makes it possible to select each hydrocarbon, retention time and mass spectrum. The "fingerprint" of all the compounds is thus available.

The SIM mode makes it possible to reduce interfering products (peaks recovering) and to generally increase the detection limit. As a matter of fact, the ions trap admits only the majority of each hydrocarbon.

This is the mode to be used to conduct the quantitative analysis of elements at the state of traces already identified in scan mode. The sensitivity increases as the selected mass number goes down.

TABLE-1
PERCENTAGE OF RECOVERY AND STANDARD DEVIATION (SD)

Compounds	Recovery (%) ± SD	Compounds	Recovery (%) ± SD
Nap	42.5 ± 6.8	BaA	102.6 ± 11.9
Acl	86.0 ± 10.8	Chr	103.8 ± 5.2
Ace	57.5 ± 5.0	BbF	104.3 ± 4.9
Flu	65.7 ± 11.8	BkF	98.6 ± 9.5
Phe	87.7 ± 3.9	BaP	96.7 ± 7.1
Ant	79.8 ± 5.8	Ipy	101.2 ± 6.6
Fla	88.8 ± 13.4	DahA	98.9 ± 3.9
Pyr	92.0 ± 10.3	BghiP	99.3 ± 15.7

The polycyclic aromatic hydrocarbons chromatograms are mostly well solved. Shouldering, however, can be noticed: An and Phe, BaA and Chr, BbF and BkF, DahA and BghiP.

The detection and quantification limits thus obtained are relevant for the determination of the 16 polycyclic aromatic hydrocarbons in contaminated samples at low concentrations.

The equation, or graphic representation (the straight line of least square) allows the link between the two numerical variables (peak area *versus* concentration) to be studied.

The straight line equation is of the $y = ax + b$ type with $a =$ slope, b intercept. The slope of the straight line (a) shows the relation direction between the two variables. The correlation of determination coefficient R^2 allows the validity of the model to be evaluated.

In case of positive or negative linkages between the two variables regression straight line becomes a prognostic sign which enables the values of Y to be calculated as a function of the values of X (the surface as a function of the concentration). The stronger the linkage (correlation coefficient) is the more accurate and reliable the prediction is.

Starting from the straight lines it will be possible, by means of protection, to determine the polycyclic aromatic hydrocarbon concentration as the chromatogram area measured by the detector is known.

The repeatability and reproducibility of the peaks area corresponding to injections of a standard solution containing the 16 polycyclic aromatic hydrocarbons were studied.

The most diluted compound of the mixture had a concentration of 2 ppm. Table-2 brings together the statistical analysis results concerning a series of 5 successive injections, expressed by the standard deviation and the coefficient of variation. The standard deviation and variation coefficients values obtained in both cases are satisfactory. The repeatability and reproducibility can then be considered as adequate, thus showing that the system is highly stable.

Time variation of the polycyclic aromatic hydrocarbons levels in the marine sediments from the Dakar coast: The sediments samples were taken during the 2004, 2006, 2007 and 2008 periods. For the last three campaigns, samples were collected in August, in the middle of the rainy season. That of

2007 was conducted the day following a tornado night with as a result the matrix remobilization.

From these results, the total content evolution of the polycyclic aromatic hydrocarbons, in the sediments, in function of time, was established.

Fig. 1 presents a chromatogram example of the hydrocarbons detected in the Soumbédioune sediment sample, taken off in 2004.

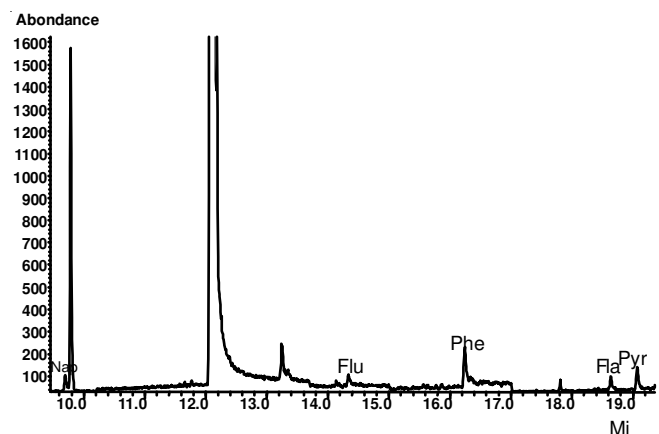


Fig. 1. Chromatogram of the sediment from Soumbédioune in 2004

The hydrocarbons identification is based on the majority ion, retention time and the three ions spectrum allocated to it. Table-3 brings together the results achieved, on the different sites, in the course of time.

Smith *et al.*¹⁴ introduced a new factor representing the toxicity limits of some aromatic compounds in marine samples (sediments, biota, *etc.*) called threshold effects levels, some of which are presented in Table-4.

The results in the Hann zone (Table-3) show the absence of high molecular weight hydrocarbons (BbF, BkF, BaP, Ipy, DahA and BghiP) in the course of the various sampling years. Yet, the low molecular weight polycyclic aromatic hydrocarbons such as the fluorene and the anthracene are not detected. Only the phenanthrene and the pyrene are present in the four periods of making up (collecting, sampling) of samples. In

TABLE-2
STATISTIC STUDIES OF THE SYSTEM'S REPEATABILITY AND REPRODUCIBILITY

Compounds	Repeatability		Reproducibility	
	Standard Deviation	Coefficient of variation	Standard Deviation	Coefficient of variation
Nap	± 5550870.85	4.31	± 14009054.50	9.67
Aci	± 8120878.97	3.03	± 12703424	3.64
Ace	± 4072974.87	4.37	± 232819.41	0.19
Flu	± 1113233.99	3.80	± 397009.74	1.07
Phe	± 449818.412	3.37	± 965728.30	6.70
Ant	± 609664.587	3.81	± 1236200.58	5.58
Fla	± 1093956.44	3.50	± 3597436.64	10.23
Pyr	± 764751.684	5.05	± 1830347.79	10.67
BaA	± 751599.451	5.68	± 368699.32	2.72
Chry	± 1064257.51	6.25	± 1871836.72	7.83
BbF	± 1938165.47	8.33	± 1065641.99	4.35
BkF	± 1226610.21	5.50	± 1996322.02	5.92
BaP	± 796656.836	5.36	± 1653738.72	9.97
BghiP	± 590580.391	5.64	± 14612521.10	6.78
DahA	± 664676.752	7.19	± 1277973.40	8.50
Ipy	± 1644255.4	5.86	± 2180800.18	7.11

TABLE-3
CONCENTRATION ($\mu\text{g}/\text{kg}$) OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) PER ZONE, IN 2004, 2006, 2007 AND 2008

PAHs	Hann				Mbao				Dakar Port				Soubédioune			
	2004	2006	2007	2008	2004	2006	2007	2008	2004	2006	2007	2008	2004	2006	2007	2008
Nap	ND	ND	220.86	180.31	ND	ND	19.82	170.62	ND	4.57	12.43	168.68	ND	ND	16.58	166.77
Acl	ND	ND	465.28	346.76	ND	163.26	156.50	360.10	ND	ND	156.74	355.56	ND	151.95	157.62	350.78
Ace	ND	ND	275.27	224.54	ND	ND	111.01	209.22	ND	82.02	247.40	207.05	ND	ND	256.87	206.89
Flu	ND	ND	ND	ND	4.9	ND	ND	69.64	3.9	ND	33.45	70.67	ND	ND	ND	66.52
Phe	6.4	33.35	66.37	53.02	ND	28.26	41.41	52.69	12	107.02	85.54	117.14	4.9	72.17	112.06	76.56
Ant	ND	19.7	ND	ND	5.4	ND	ND	ND	ND	46.07	94.82	46.14	ND	11.67	ND	41.86
Fla	ND	59.25	42.36	30.36	8.7	49.41	36.91	141.74	15.6	220.97	213.29	204.67	ND	145.82	241.16	98.19
Pyr	5.5	36.18	20.17	14.28	ND	25.11	26.39	92.55	15.7	183.02	126.23	175.66	6.8	116.47	111.37	73.32
BaA	ND	ND	ND	150.05	ND	ND	ND	76.65	ND	154.73	120.54	135.25	ND	ND	ND	90.96
Chry	ND	32.06	ND	145.87	ND	ND	55.24	64.53	ND	152.9	178.65	226.52	ND	ND	ND	76.89
BbF	ND	ND	ND	ND	ND	ND	ND	ND	ND	133.36	156.78	199.46	ND	ND	ND	88.71
BkF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	123.36	204.11	ND	ND	ND	86.40
BaP	ND	ND	ND	ND	ND	ND	ND	ND	ND	334	264.57	401.98	ND	ND	ND	115.04
Ipy	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	36.08	ND	ND	ND	137.22
DahA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	179.67	ND	ND	ND	147.38
BghiP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	95.44	ND	ND	ND	91.04
Total	11.9	180.54	1090.30	1145.19	19	266.04	447.27	1237.74	47.2	1418.66	1813.80	2824.07	11.7	498.08	895.66	1914.53

TABLE-4
THRESHOLD EFFECTS LEVEL (TEL) IN SEDIMENT¹⁵

Polycyclic aromatic hydrocarbons	TEL ($\mu\text{g kg}^{-1}$)
Naphthalene	40
Acenaphthylene	10
Acenaphthene	10
Fluorene	20
Phenanthrene	90
Anthracene	50
Fluoranthene	110
Pyrene	150
Chrysene	110

the same way, the contents of the polycyclic aromatic hydrocarbons found in this zone are lower than the threshold effect levels, in the 2004 and 2006 campaigns. On the other hand, in 2007 and 2008, the naphthalene, the acenaphthylene and the acenaphthene show contents which can disrupt the evolution of species living in these environments.

The results found in Mbao (Table-3) show the absence of high molecular weight hydrocarbons (BbF, BkF, BaP, Ipy, DahA and BghiP) in the course of the different sampling years. The anthracene, however, with a low molecular weight, could not be detected in the last 3 years. The pyrene, absent in 2004, is detected between 2006 and 2008. Except for the acenaphthylene, in 2006 and 2007, the polycyclic aromatic hydrocarbons contents are lower than the threshold effect levels, in the first three campaigns. On the other hand, in 2008, the naphthalene, the acenaphthylene and the fluorine show contents higher than the threshold effect levels.

The harbor zone (Table-3) is characterized by the absence of all the polycyclic aromatic hydrocarbons, in 2004, except for the fluorene, the phenanthrene, the fluoranthene and the pyrene. However, in 2008 all the hydrocarbons are detected. In 2006 and 2007, high molecular weight hydrocarbons like Ipy, DahA and BghiP, are seen to be absent. During the latter campaigns the naphthalene presents values lower than the threshold effect level, whereas in 2004 all the hydrocarbons detected have the same trend.

In the Soubédioune zone (Table-3), only the phenanthrene and the pyrene are detected in 2004. Both compounds are, however, present in the different campaigns. In 2008, all the polycyclic aromatic hydrocarbons were detected and quantified. In 2006 and 2007 the high molecular weight compounds (BaA, Chr, BbF, BaP, Ipy, DahA and BghiP) could not be detected. The hydrocarbons analyzed in 2004 and 2006 show contents lower than the threshold effect level, with the exception of acenaphthylene, fluoranthene and pyrene for the latest campaign. In 2007 naphthalene and pyrene are below the threshold effect level.

Evolution of the total content of the polycyclic aromatic hydrocarbons in the different sites: The histograms analysis (Fig. 2) shows an accumulation of the polycyclic aromatic hydrocarbons in function of time. The years 2007 and 2008 present the highest contents of the four sites. The year 2004 concentrates fewer hydrocarbons.

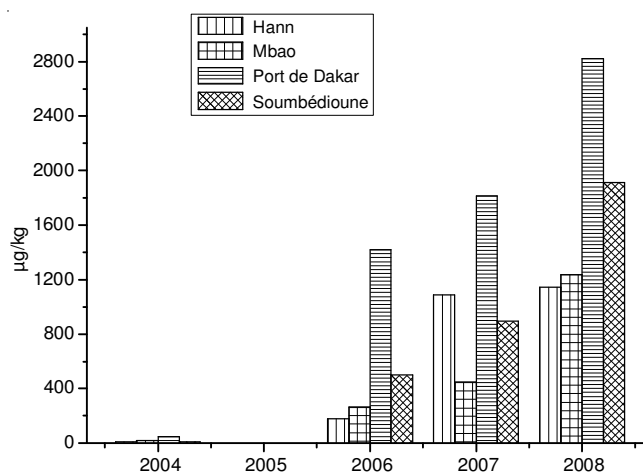


Fig. 2. Temporal evolution of the total content of polycyclic aromatic hydrocarbons following the sites

The strong concentrations are observed in the deposits taken during the year 2008.

The harbor zone, which shelters the fuel storage warehouses intended to supply the different service stations of the capital, thus concentrates the maximum values, with 2824.07 µg/kg.

The Soumbédioune site, which receives the town evacuation waters through the West canal, follows a cumulative total of 1.914.53 µg/kg.

The Mbao zone concentrates a low content (1237.74 µg/kg) compared with the other sites, despite the presence of a refining plant. The Hann zone, with harbor halieutic, products manufacturing plants and the town water evacuation East canal, has the lowest concentration with 1145.19 µg/kg.

However, in the different sites studied, the polycyclic aromatic hydrocarbons total content follows an increasing evolution, *versus* of time, starting from 2004. These indicate the accumulation phenomenon of these pollutants in our coasts.

Conclusion

In this research work, a gas chromatograph coupled to a mass spectrometer (CG/MS) was used to study the marine sediment contamination profile in Dakar by polycyclic aromatic hydrocarbons. An analysis method was developed, with the help of the Soxhlet to extract the polycyclic aromatic hydrocarbons with hexane/acetone mixture as a solvent. The measurement device detection limit varies between 0.23 and 38.66 ppb. This technique made it possible to determine the concentrations of the 16 hydrocarbons recommended by the American Agency for the environment protection.

The results obtained show that the total amount of hydrocarbons varies between 2824.07 and 1145.19 µg/kg. The Dakar harbor area presents the maximum values, then that of Soumbédioune, Mbao and finally Hann place. In the same way, an increasing evolution of pollutants was observed from 2004 to 2008.

Some polycyclic aromatic hydrocarbons contents, however, are lower than the threshold effect level. Nevertheless, it is necessary to regularly check the pollution time evolution as the accumulation of hydrocarbons can cause serious problems for the environment and public health.

The presence of polycyclic aromatic hydrocarbons in the marine sediments of the region of Dakar has been confirmed.

Thus, to better determine this phenomenon it would be interesting to study the origins of polycyclic aromatic hydrocarbons, the contents of these compounds adsorbed on the particulate phase but also their impact on the population.

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