

Polychlorinated Biphenyls Content in Surface Sediments from Dakar Coast (Senegal)

Dame Cisse¹, Birame Ndiaye^{1,*}, Cheikh Tidiane Dione¹, Ibrahima Diagne¹, Momar Ndiaye¹, Maoudo Hane¹, Sitor Diouf¹, Mame Mor Dione¹, Abdoulaye Diop¹, Maurice Millet²

¹Faculty of Science and Technology, Laboratory of Organic Physical Chemistry and Environmental Analysis (LCPOAE)-UCAD, Dakar, Senegal

²Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES), University of Strasbourg, Strasbourg, France

Email address:

biramendiaye85@yahoo.fr (Birame Ndiaye)

*Corresponding author

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Abstract: Surface sediments proceeding from the coast of Dakar (Senegal) were analyzed by Gas chromatography coupled with a Mass Spectrometer (GC-MS) in order to evaluate the contamination of polychlorinated (PCB). After weighing, each mass is placed in a centrifugal tube with 10 ml of acetonitrile solvent solution (ACN) to separate the aqueous phase from the organic phase. The extraction phase with QUECHERS is followed by a purification with DSPE RESTEK salt. This salt is composed of 1.2 g MgSO₄ + 400 mg PSA + 400 mg C18 for the separation of analytes. For GC-MS kiln storage, the temperature gradient is maintained from 50 to 330°C for 40 minutes with different slopes. PCB126 displays the lowest detection and quantification limits of 0.000639 and 0.001917 ng/g, respectively. PCB18 has the highest detection and quantification limits, with values of 0.01504 and 0.04512 ng/g, respectively. The result obtained show that the PCB dioxin likes are more important in sediment. The PCB-DL ranged 5.931 (Hann) to 25.752 µg/Kg (Ngor). The PCB_i ranged 2.415 (Hann) to 4.284 µg/Kg (Soumbédioune) at the beach of Hann, the concentration of individual PCB ranged 0.007 (PCB118) to 5.073 µg/Kg (PCB167). At Soumbédioune, the individual PCB levels ranged 0.004 (PCB118) to 5.365 µg/Kg (PCB167) and at Ngor, the variation is 0.005 (PCB118) to 12.29 µg/Kg (PCB167). The analysis of principal components shows that two distinct groups which the same contamination profile whose elements have strong correlations 0.992 for PCB189-PCB101 and PCB189-PCB81.

Keywords: Sediment, Polychlorinated Biphenyls, Dakar Coast, Contamination

1. Introduction

The pollution of the sediment is still current one the worldwide. In 2006, PCB contaminated the Rhone (France) fish's and the river Pearl (Chine) sediments in 2017 are also contaminated by PCB. These PCB with their characteristics (stable, resistant) have many applications in industries and other activities [1]. Since 2011, Stockholm convention the PCB ranks among the Organics Pollutants Persistent [2]. The PCB can be bio accumulate in fish, in mussel and others aquatics organisms then they are ubiquitous pollutants. They are also toxic, cancerous, mutagen and caused many damage at human health [3, 4].

In Dakar is demographic pressure with 22.96% the national population with strong concentration of industries and firms lead to a difficult cleansing. These sanitation problems are manifested by discharges wastewater without treatment on the beaches. The wastewater transported sediments can participate in the pollution of the aquatic environment (sources of food) by PCBs.

So it's necessary to keep a close watch on such as possibility pollution on the beaches of Dakar. Therefore, sample sediments from downstream wastewater derived from Hann, Ngor and Soumbédioune of Dakar coast are analyzed to measure PCB concentrations.

2. Materials and Methods

2.1. Sampling Points

The studied stations Ngor, Hann and Soumbédioune border the Atlantic Ocean and they are seats of many activities (Figure 1). The Hann bay (SD1) is home to fishing activities, textile mills, fish processing plants and sewage from the eastern canal. The Soumbédioune beach (SD2) is a landing place for fish products and receives wastewater from the west channel (open channel IV) which passes a good part through the communes of Dakar. Ngor (SD3) bay is a tourist site is traversed by an open channel crosses the most part of this communes.



Figure 1. Location of sampling points in the Dakar coast (Senegal).

2.2. Sampling and Preparation

Surface sediments were collected between June and

September 2018. These samples were taken with hand bucket at depths between 0 and 5 cm [5]. Sample sediments were conditioned in plastics bags, placed inside cooler (4°C) and transported in laboratory. In laboratory, coarse elements whose diameter is greater than 2 mm are extracted from the sediments. These samples sediments were dried in the oven up to a constant weight. They were then crushed using an agate mortar and sieved through a sieve with smaller than 63 µm mesh. It's very interesting to study the fine fraction of sediments [6]. So, on these samples sediments we researched to quantify the concentration of PCB divided between the 12 PCB dioxin like whose PCB 81; 114; 118; 123; 126; 157; 167; 169; 189 and so-called indicators PCB.

2.3. Method of Analysis

For to analyze contents of these PCB in the sediments we have adopted Gas chromatography coupled with a Mass Spectrometer (GC-MS). In this method, there is an extraction and purification phase. The extraction salt used is QUECHERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) composed 4g MgSO₄; 1g NaCl; 1g trisodium de citrate dihydrate; 0.5 g disodium hydrogen-citrate sesquihydrate. After extraction phase, we use salt QUECHERS DSPE RESTEK for purification phase. This salt is composed 1.2g MgSO₄ + 400mg PSA + 400mg C18. After extraction and purification, the extract is vaporized to 1 mL under a hood and 500 µL of the solution is injected by the SPME, into the injection system. In this coupled technique, the separation of analytes from the mixture based on chemical and physical characteristics such as molecular weight, molecular shape and functional groups take in the chromatographic part. In Mass spectrometer, the ions detected are proportional to their number. During the analyzer relies on resolution, scanning speed m/z ratio and transmission. The detector amplifies the current of ions enabling the system electronic.

Table 1. Characteristics compounds.

Nature	compounds	Quantification of ions	Ions	Retention Time (min)	Quantification limit (µg)
PCB	PCB 18	256	186-221	19.77	0.04512
PCB	PCB31	256	186-150	20.93	0.045
PCB	PCB28	256	186-150	20.99	0.0225
PCB	PCB52	292	257-220	21.56	0.023925
PCB	PCB 44	292	257-220	21.95	0.0111
PCB	PCB 70	292	220-185	22.9	0.013716
PCB	PCB 101	326	291-254	23.31	0.01416
PCB	PCB 81	292	220-185	24.09	0.02568
PCB	PCB 123	326	256-254	24.49	0.00846
PCB	PCB 118	326	256-254	24.56	0.00531
PCB	PCB 114	326	256-235	24.73	0.023931
PCB	PCB 138	360	325-288	24.78	0.009
PCB	PCB 126	326	256-219	25.52	0.001917
PCB	PCB 167	360	290-288	25.67	0.031245
PCB	PCB 157	360	290-288-218	26.54	0.012783
PCB	PCB 180	396	361-324	26.06	0.004755
PCB	PCB 169	360	290-288-218	26.85	0.0375
PCB	PCB 189	396	326-324	26.86	0.005533

3. Result and Discussion

The chromatograms obtained with the characteristics of compounds allow us to find the PCB contents of the sediments. The PCB 28, 31, 44, 52 and PCB70 are below the limit of quantification.

Table 2. Minimums, maximums and average values of PCB.

Compounds	SD1		SD2		SD3	
	Min-Max	Mean \pm SD	Min-Max	Mean \pm SD	Min-Max	Mean \pm SD
PCB18	0.471-0.566	0.518 \pm 0.039	0.672-0.839	0.737 \pm 0.071	0.577-0.780	0.683 \pm 0.104
PCB101	0.751-0.897	0.823 \pm 0.06	1.074-1.177	1.177 \pm 0.114	0.921-1.214	1.068 \pm 0.143
PCB 81	0.953-1.297	1.118 \pm 0.162	1.489-1.979	1.731 \pm 0.223	1.081-1.992	1.418 \pm 0.404
PCB123	0.667-0.814	0.748 \pm 0.059	0.999-1.212	1.087 \pm 0.091	0.855-1.195	0.998 \pm 0.165
PCB118	0.007-0.038	0.019 \pm 0.014	0.004-0.046	0.030 \pm 0.019	0.005-0.095	0.030 \pm 0.043
PCB114	0.018-0.101	0.052 \pm 0.039	0.015-0.112	0.071 \pm 0.043	0.021-0.249	0.081 \pm 0.112
PCB126	0.455-0.929	0.603 \pm 0.219	0.632-0.948	0.822 \pm 0.146	0.491-1.605	0.828 \pm 0.521
PCB167	0.978-5.073	2.786 \pm 1.699	1.511-5.365	3.354 \pm 1.991	1.140-12.29	4.369 \pm 5.307
PCB138	0.594-0.722	0.650 \pm 0.054	0.395-1.066	0.817 \pm 0.292	0.718-0.995	0.852 \pm 0.138
PCB157	0.891-1.433	1.094 \pm 0.245	1.252-1.557	1.410 \pm 0.147	1.084-1.554	1.296 \pm 0.231
PCB180	0.599-1.030	0.754 \pm 0.202	0.818-1.096	0.950 \pm 0.138	0.724-0.942	0.829 \pm 0.116
PCB169	0.553-1.286	0.950 \pm 0.301	0.982-1.771	1.347 \pm 0.327	0.730-1.900	1.154 \pm 0.532
PCB189	1.127-1.409	1.256 \pm 0.125	1.574-1.958	1.723 \pm 0.165	1.345-1.769	1.576 \pm 0.217

The results obtained during this study show that the contents of PCB in the sediments range according to the period and the stations studied. In Hann beach, the concentrations of individual PCB range 0.007 (PCB118) to 5.073 $\mu\text{g/Kg}$ (PCB167) and in Soumbédioune bay the variation of the concentrations for individual PCB is 0.004 (PCB118) to 5.365 $\mu\text{g/Kg}$ (PCB167). In sediments from Ngor, the minimum concentration is that of PCB118 with 0.005 and PCB167 has the maximum concentration with 12.29 $\mu\text{g/Kg}$. During this sampling period, the minimums averages obtained in Soumbédioune, Hann and Ngor are respectively 0.030; 0.019 and 0.030 $\mu\text{g/Kg}$. After this study we have remarked that sediments are more charged to PCB167 with these means 2.786; 3.354 and 4.369 $\mu\text{g/Kg}$ respectively in Hann, Soumbédioune and Ngor bay. In the Hann sediments the averages of these individuals PCB157, PCB81 and PCB189 are respectively 1.094; 1.118 and 1.256 $\mu\text{g/Kg}$. In Soumbédioune, the averages of these three PCB are respectively 1.410; 1.731 and 1.723 $\mu\text{g/Kg}$. In the sediments from Ngor station, the concentrations of the PCB157, PCB81 and PCB189 are more important respectively with 1.296, 1.418 and 1.576 $\mu\text{g/Kg}$.

In this study, the more concentrations of individual PCB in the sediments from Hann, Soumbédioune and Ngor are the PCB167, PCB81, PCB101 (1.177 $\mu\text{g/Kg}$) and PCB189. In addition to these PCB, the concentrations PCB81, PCB157 and PCB189 are compared to others concentrations found to the literature. The PCB167 whose individual concentrations are higher in the sediments from Dakar coast is not detected in the sediment of Pearl River Estuary (Pintado-Herrera *al.*, 2016), in sediment of

Tripoli harbour, nor in sediments of Niagara River New York. Likewise, PCB167 is not detected in sediments of Niagara River New York nor in urban river sediments Huveaune, France [7]. On the other hand, certain individual PCB contents in Hann, Soumbédioune and Ngor are lower than those found in Harbour, where the levels of PCB101, PCB169 and PCB81 are respectively 3.1; 5.1 et 10.1 $\mu\text{g/Kg}$ (Merhaby *et al.*, 2015) [7]. Contrary to the sediments of Pearl River Estuary (China), where PCB with 0.1 ng/g and PCB138 with 0.1 ng/g have lower concentrations than those found at the three sites of our study [8]. The PCB138 quantified in Hann, Ngor and Soumbédioune with concentrations respectively de 0.650; 0.852 and 0.817 $\mu\text{g/Kg}$. These concentrations detected in Dakar coast are superiors than those measured in sediments from Niagara River, New York whose contents are respectively 0.50; 0.54 and 0.53 ng/g. However, stations 2; 3; 4; 6; 10 and 11 have more contaminated sediments than those of our sites with respective contents 28; 19; 5.9; 1.50; 1.00 et 1.10 ng/g (Samara *et al.*, 2006) [9]. Likewise, the sediments of Huveaune River have individual PCB contents much higher than the sediments collected in Dakar. At Huveaune River, the concentrations of PCB138 range from 3.9 (station H4) to 75.4 $\mu\text{g/Kg}$ (station H8), PCB180 ranging from 1.9 (H10) to 55.5 $\mu\text{g/Kg}$ (H6). For this same site (Huveaune River), PCB118 varying from 0.3 (H2) to 46.6 $\mu\text{g/Kg}$ (H8) against 0.019 $\mu\text{g/Kg}$ in Hann 0.030 $\mu\text{g/Kg}$ in Ngor and Soumbédioune [10].

In this study, the pollutions of each site are evaluated by total PCB concentrations regrouped between the PCB dioxin-Like and PCB indicators mentioned in the Table 3.

Table 3. Content total PCB, PCB-DL and PCB_i ($\mu\text{g/Kg}$) in dry weight of sediments.

Period	Site	Hann			Soumbédioune			Ngor		
		ΣPCB	$\Sigma\text{PCB-DL}$	ΣPCBi	ΣPCB	$\Sigma\text{PCB-DL}$	ΣPCBi	ΣPCB	$\Sigma\text{PCB-DL}$	ΣPCBi
June		13.030	10.615	2.415	16.022	13.063	2.959	10.082	7.022	3.060
July		11.768	8.804	2.964	14.288	10.004	4.284	14.551	10.688	3.863
August		12.188	9.152	3.037	13.538	9.936	3.601	10.346	7.396	2.950
September		8.494	5.931	2.563	17.172	13.291	3.881	25.752	21.897	3.856

$\Sigma\text{PCB-DL} = \text{PCB81} + \text{PCB114} + \text{PCB118} + \text{PCB123} + \text{PCB126} + \text{PCB157} + \text{PCB167} + \text{PCB169} + \text{PCB189}$

$\Sigma\text{PCBi} = \text{PCB18} + \text{PCB101} + \text{PCB138} + \text{PCB180}$

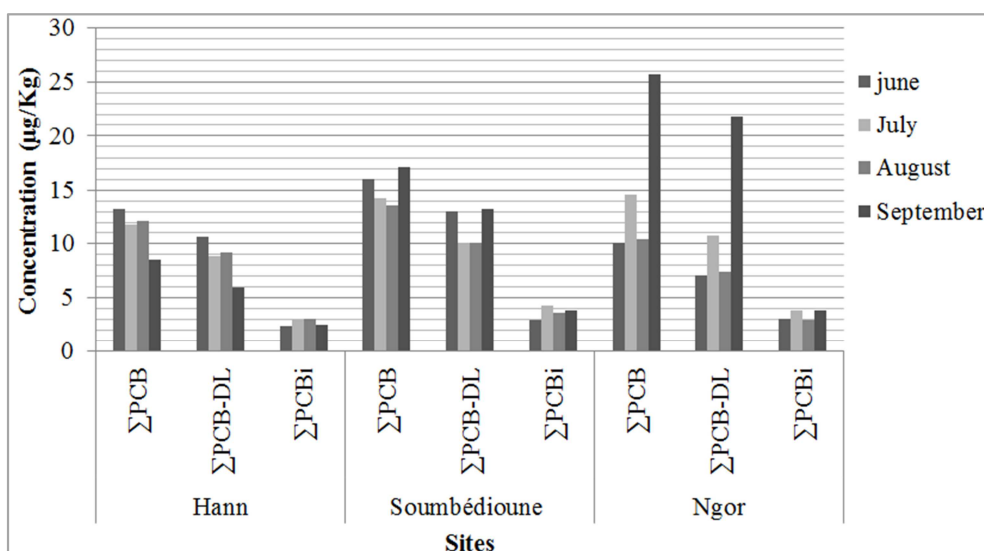


Figure 2. Variation of Σ PCB, Σ PCB-DL and Σ PCBi in sediments from sampling points.

During this campaign the concentrations of total PCB are more important into September in the sediments from Ngor and Soumbédioune respectively with 25.752 and 17.172 $\mu\text{g/Kg}$. Their lowest contents are respectively 10.082 (June) and 13.538 $\mu\text{g/Kg}$ (August). Concentrations of total PCB in sediments from Hann range 8.494 (September) 13.030 $\mu\text{g/Kg}$ (June) (Table 3, Figure 2). These concentrations of total PCBs at the different sites are much lower than those found in marine sediments of the Toronto golf course ranging from 54 to 1780 $\mu\text{g/Kg}$ except for stations 1 and 2 where PCBs were not detected (Annicchiarico et al., 2011). Also these concentrations of total PCBs are inferior to the concentration of 7 PCBs measured at seven out of from Huveaune River (38.6; 195.3; 435.0; 200.3; 416.3 and 134.9 $\mu\text{g/Kg}$ respectively to stations (H3, H5, H6, H7, H8 and H9). On the other hand, the station of H2 recorded a sum of 2.8 $\mu\text{g/Kg}$ lower than those found in the study sites (Kanzari et al., 2014). These contents obtained during this campaign are as well inferior to the for sediments quality guideline values (SQG ERL-ERM) 23-180 mg/Kg [11, 12]. Despite the relatively low levels compared to other sites in other countries, this contamination could become increasingly important as the food chain increases by bioaccumulation. These concentrations can be redistributed in the nearest waters then filtered and accumulated by aquatic animals. These levels often biomagnified in the adipose tissues of fish, mussels and shrimp could disrupt the endocrine system (Mc Kinney and Waller, 1994), reduce the number of eggs generated in fish species (Black and al. 1998) [13]. The total levels of dioxin-like PCBs (Σ PCB-DL) which the 12 congeners of have toxicities similar to dioxins and indicator or marker PCBs (PCBi) which are 6 congeners, vary according to the site and the period [14]. The PCB-DL concentrations of sediments from bay of Hann range 5.931 (September) and 10.615 $\mu\text{g/Kg}$ (June). For PCBi, the concentrations obtained in Hann range 2.415 (June) to 3.037 $\mu\text{g/Kg}$ (August). In Soumbédioune, the variation of PCB-DL contents is from 9.936 $\mu\text{g/Kg}$ (August) to 13.291 $\mu\text{g/Kg}$

(September) and for PCBi, the lowest content is obtained in June with 2.959 $\mu\text{g/Kg}$. The highest concentration in Soumbédioune sediment is recorded in July with 4.284 (Figure 2). For these, polychlorinated biphenyls contamination of the sites is dominated by the presence of PCB-DL (of the Dioxin Like type) considered to be the most toxic. In Hann, PCB-DL concentrations constituted 69.8 to 81.4% of PCB contamination; in Soumbédioune they are present from 70 to 81.5% of this pollution and from 69.6 to 85% in Ngor. However, total PCBi represent relatively low proportions in these sediments. Their total concentrations vary between 2.415 and 3.037 $\mu\text{g/Kg}$ in Hann, between 2.959 and 4.284 $\mu\text{g/Kg}$ in Soumbédioune and Ngor the minimum content is 2.950 and the maximum obtained is 3.863 $\mu\text{g/Kg}$. During this study, the PCBi contamination is less significant than that found in the majority of surface lake sediments of Lemán (Switzerland), the contents of which in sum of 7 PCBi range 1.23 to 17.58 $\mu\text{g/Kg}$. These concentrations remain much lower than that found in the sediments of the Bay of Vidy, the sum of which is 79.07 $\mu\text{g/Kg}$, and even remain below the quality guide value for freshwater sediments 34.1 $\mu\text{g/Kg}$ and the concentration threshold to effect (TEC), 59.8 $\mu\text{g/Kg}$ (McDonald et al., 2000) [15, 16].

In order to obtain a better interpretation of the results obtained from polychlorinated biphenyls in the surface sediments of the sites studied, principal component analysis was applied. The graphical representation of the two main extracted components is shown in Figure 3.

The variance of the initial eigenvalues show that the components (axes) 1 and 2 contain 88.266% of the information and that the PCBs are well represented in the axes, except the PCB169 whose extraction value is 0.211. The matrix, outputs high positive correlations (≥ 0.9) such as PCB81/PCB101 (0.993), PCB189/PCB81 (0.992), PCB123/PCB18 (0.989), PCB123/PCB101 (0.972), PCB157/PCB180 (0.944). Moderate correlations are also observed between PCB118/PCB81 (0.503), PCB180/PCB81 (0.578), PCB126/PCB123 (0.555) and PCB180/PCB138 (0.572)

(Table 4). The orientation of the PCBs along the axes indicates the existence of two groups. The first group formed by PCB189, PCB189, PCB101, PCB18, PCB123, PCB157, PCB81 and PCB138 are well represented on axis 1 and they have high positives correlations (Table 4). This first group of PCBs seems to have the same contamination profiles at these sites. These strong correlations may indicate a homogeneous

distribution of PCBs in the different sites. They also suggest common sources of pollution such as industrial or domestic activities. On the other hand, the second group, whose contamination profiles are similar, consists of PCB114, PCB118, PCB167 and PCB126. They are well represented in axis 2 also have strong positive correlations between these PCBs.

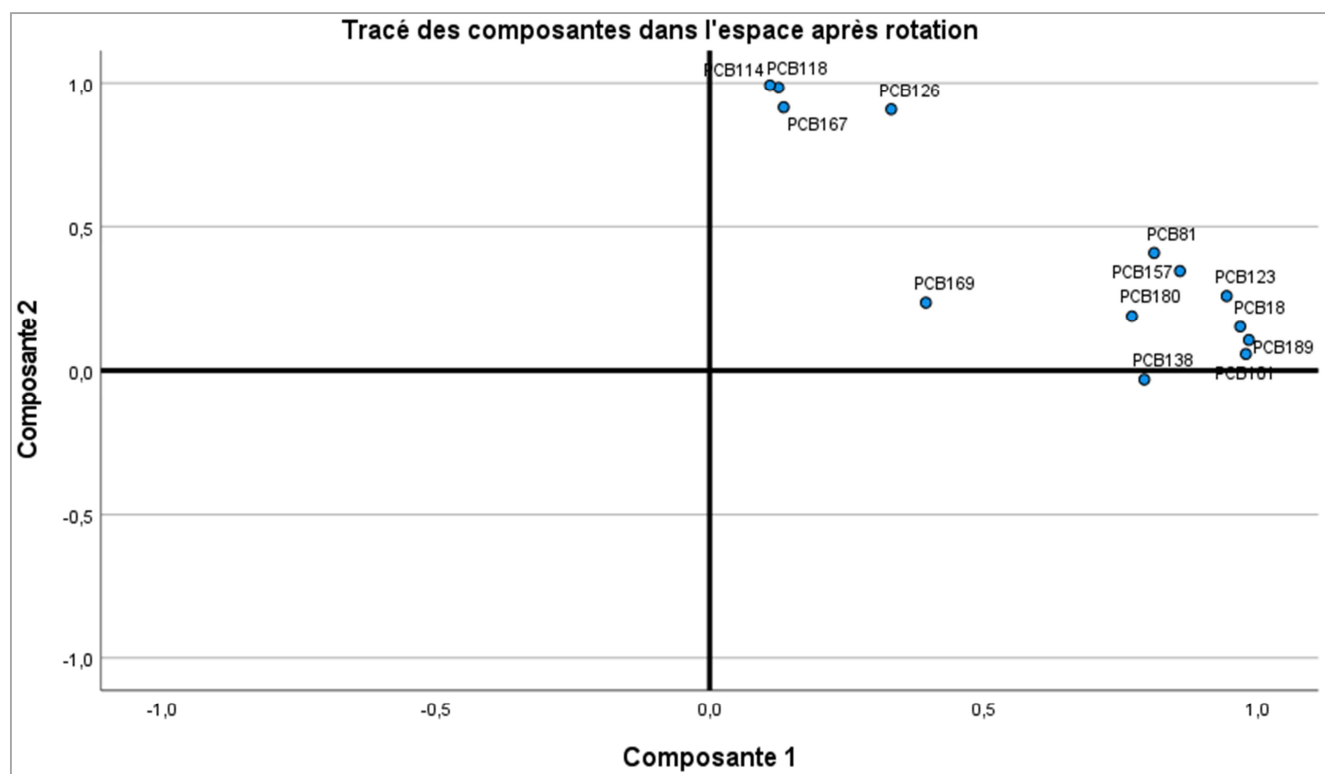


Figure 3. Distribution of PCB in sediments from Hann, Ngor and Soumbédioune at PAC plane.

Table 4. Correlation between polychlorinated biphenyls in the surface sediments.

Corrélation	PCB18	PCB101	PCB81	PCB123	PCB118	PCB114	PCB126	PCB167	PCB138	PCB157	PCB180	PCB189
PCB18	1											
PCB101	0.993	1										
PCB81	0.858	0.828	1									
PCB123	0.989	0.972	0.910	1								
PCB118	0.266	0.177	0.503	0.370	1							
PCB114	0.253	0.158	0.481	0.356	0.992	1						
PCB126	0.450	0.364	0.681	0.555	0.935	0.942	1					
PCB167	0.299	0.204	0.420	0.373	0.901	0.920	0.800	1				
PCB138	0.745	0.724	0.586	0.721	0.073	0.081	0.240	0.179	1			
PCB157	0.826	0.807	0.760	0.834	0.459	0.449	0.613	0.374	0.669	1		
PCB180	0.678	0.685	0.578	0.669	0.306	0.287	0.417	0.206	0.572	0.944	1	
PCB189	0.992	0.992	0.852	0.975	0.224	0.207	0.406	0.250	0.739	0.85	0.732	1

4. Conclusion

At the end of this study, 13 out of the 18 PCBs sought are present in the sediments with significant total PCB contents of up to 25.752 $\mu\text{g/Kg}$ recorded in Ngor (September). These concentrations remain at the guide values for the quality of the sediments (SQG ERL-ERM 23 and 180 $\mu\text{g/Kg}$). This contamination is dominated by DL-PCBs with respective maximum levels of 10.615 and 21.897 $\mu\text{g/Kg}$. Among the

PCBs detected, PCB167 is the most present with levels of 2.786 $\mu\text{g/Kg}$ in Hann, 3.354 $\mu\text{g/Kg}$ Soumbédioune and 4.369 $\mu\text{g/Kg}$ in Ngor. However, the less toxic PCBs are relatively lower with 2.786; 3.354 and 4.369 $\mu\text{g/Kg}$ respectively in Hann, Soumbédioune and Ngor. The statistical study by the ACP shows two distinct groups which seem to have the same contamination profiles with strong positive correlations of up to 0.993 between PCB18 and PCB101 and 0.992 for PCB114/PCB118. Given this significant contamination of the sediments, it is also necessary to monitor the possibility of

the presence of PCBs in the aquatic organism in pelagic and benthic species.

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