Pollution of a Tropical Lagoon by the Determination of Organochlorine Coumpounds

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Summary

The lagoon system of Ivory Coast with 1,200 km² of area is one among the important in West Africa. In the context of national quality water assessment, study of chemicals has been carried out in the central basin and its surroundings. The samples taken in different stations have been extracted with hexane and purified on column of florisil deactivated at 5% at chemical treatment. The analysis by CPG/ECD has permitted to identify the organochlorine compound wastes such as the Lindan, Heptachlor, Dieldrin, Endrin, the metabolites of DDT (PP'DDD and PP'DDE) and PCBs. The PCA method showed the highest stations of contamination located to Abidjan, the main industrial and urban zones (PCB: 15-227 ng/g and DDT + DDD + DDE: 1.7-130 ng/g).

Résumé

Pollution chimique d'une lagune tropicale par des composés organochlorés

Le système lagunaire de Côte d'Ivoire avec 1.200 km² de superficie est l'un des plus importants de l'Afrique de l'Ouest. Dans le cadre du Réseau National de l'Observation de la qualité de l'eau, nous avons mené une étude sur le niveau de la pollution chimique. Cette étude s'est portée sur l'analyse des résidus de composés organochlorés. Les échantillons d'huîtres prélevés en différentes stations ont été extraits à l'hexane, purifiés sur colonne de florisil désactivé à 5%. L'analyse par Chromatographie en Phase Gazeuse avec Détecteur par Capture d'Electrons (CPG/ECD) a permis d'identifier des résidus de composés organochlorés tels le Lindane, l'Heptachlor, la Dieldrin, l'Endrin et les deux métabolites du DDT. La méthode de l'ACP a dégagé les stations les plus contaminées (PCB: 15-227 ng/g, DDT + DDD + DDE: 1,7-130 ng/g).

Introduction

Since about twenty years, the Ebrié lagoon of Ivory Coast (Figure 1), a West African tropical system is suffering the effect of the brutal degradation of the quality of its ecosystem. This degradation is largely caused by the drainage and the streaming of bad or non treated effluents coming from diverse origins. Recently, in august 19th 2006, 523 m³ of toxic hydrocarbon and mercaptan pollutants run in its natural surroundings.

The many studies carried out in this lagoon show its importance on economic, social and environmental field. The first studies carried out in 1974 were essentially based on its morphology, climate and taxonomic composition as well as salt distribution in that area (4, 15, 19, 20). The studies on chemical pollution started only in 1982 when the problems of sanitation of the town of Abidjan appeared (3). Later, studies showed that the lagoon of Abidjan was contaminated by chemical pollutants coming from industries, agricultural and domestics' residues (7, 10). Among the different chemical compounds, organochlorines and heavy metals have been measured with high concentrations in the sediments
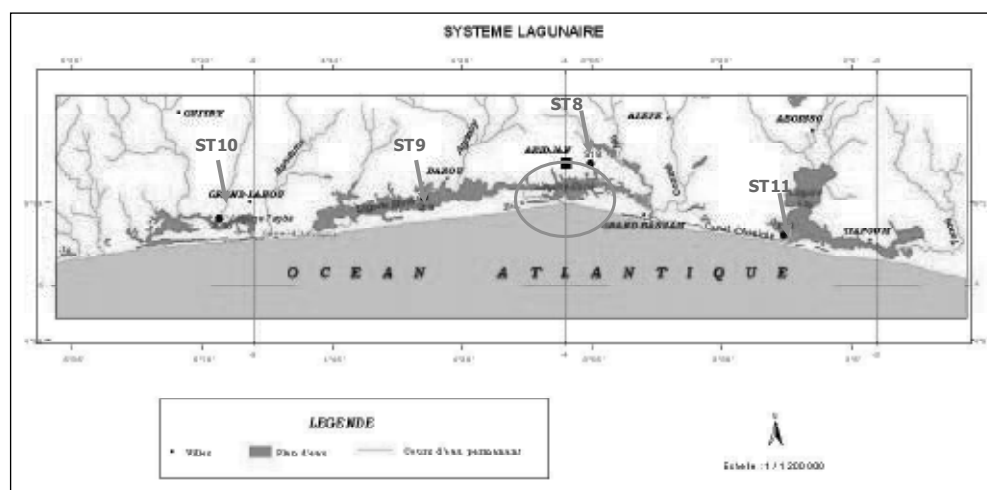
Zone of Abidjan: 7 stations (Bietry ST1, Banco ST2, Cococdy ST3, Marcory ST4, Hôtel golf ST5, Parc a bois ST6, Adiopodoumé ST7)

Figure 1: Map of the 11 stations of oysters sampling (Centre National de Télédétection et d'Informations Géographiques de Côte d'Ivoire, CNTIG).

and in the fish. These results motivated the setting up of a monitoring program since December 1992 to October 2004. We were interested in organochlorine pesticides and polychlorobiphenyls (PCBs), because of their toxicity and their persistence in the environment. Besides, those compounds are known as persistent organic pollutants and are officially prohibited. The method used permitted to identify and quantify the organochlorine compounds such as Lindan, Heptachlor, Dieldrin, Endrin, PP'DDD, PP' DDE and aroclor 1260 (Figure 2).

Methodology

1. Sampling
The oysters, *Crassostrea gasar* populating the Ebrié lagoon are flat bivalves living on sediments. They are characterized by their capacity to accumulate and concentrate the chemical substances contained in water and suspended matters. This makes them good indicators of punctual and diffuse contamination. This is why they are used in the study of the chemical pollution of the lagoon system (1, 17).

2. Treatment of samples
The samples of oyster are freeze-dried to -8 °C and dried sample is ground and transformed in a homogeneous powder after sieving on a stainless steel sieve (0.25 mm^2 of porosity). The powder is then stocked in small glass bottles and kept in a fridge at about -4 °C.

3. Extraction of samples
Oysters' powders are extracted with hexane with soxlhet during 8 hours. The temperature of the flasks is maintained at 75 °C and 80 °C. Extracts are purified, either on column of florisil partially deactivated with 5% of water, or by treatment with sulphuric acid or sodium hydroxide (6, 9, 13, 22).

4. Analysis by gas chromatography
After purification and concentration to 1 ml, 1 μl of purified extract is analyzed by Gas Chromatography (GC) with Capture Detector (ECD). The capillary column used, is made of fused silica coated with polyamide. The stationary phase is methyl and/or phenyl siloxane which is adapted to the separation of organochlorine pesticides and PCBs (Figure 2).
Analysis conditions of GC-ECD
1- Injector (Split/Splitless): temperature 210 °C
2- Detector (ECD 63[Ni]): temperature 300 °C
3- Columns: Supelco SPB [602] (organochlorines pesticides) and SPB[5] (PCB aroclor 1260)
4- Oven: temperature max 300 °C

5- Temperature program

100 °C $\xrightarrow{\text{40 °C/mn}}$ 150 °C $\xrightarrow{\text{2 °C/mn}}$ 230 $\xrightarrow{\text{10 °C/mn}}$ 250
1 min 5 min

6- Carrier gas and injector purge: H_2 flow rate 67 ml/mn
7- Make up gas: N_2 flow rate 7,5 ml/mn
8- Sensibility (range): 0.5
9- Intensity ECD (current): 0.5 mA
10- Duration of analysis 50 min

5. Statistical analysis
Principal Component Analysis (PCA), statistical method is essentially an exploratory tool. PCA is based on the linear transformation of correlated p-response variables (measurements) to pair wise uncorrelated components (unrelated functions of de responses). In different field of sciences such as chemistry, environment ..., PCA used by many authors to analyse correlational structures between a series of measured response (2, 8).
The mathematic expression is a matrix of correlation R of p-variables obtained from pxp data. For the equation, λ refers eigenvalue, $\hat{R}$ refers to the variance - covariance matrix for the p-variables and the element of eigenvector F are scaled to satisfy F x F=1.
$\hat{R}$ is a pxp square data matrix. The solution to this equation involves solving for the terms,

$$\hat{R}\, F = \lambda F$$

the eigenvalue and the eigenvector which satisfy this equation and the derivation of linear combination of p-measured variables X_1, X_2,...
Xp to produce indices or derivated variables as Principal Components or Factors (F).

$$F_i = \sum \alpha_{ij} X_i \text{ avec } i \neq j$$

The α_{ij} terms refer to the weights or loading for each variable within those principals' components or factors. The data of table 1a and 1b are used for the implementation of PCA within statistic modeling Statisgraphics Plus4 and Sigma Plot 2000.

Results and discussion

1. Quantitative and qualitative assessment
Tables 1a and 1b present the concentrations measured with their standard deviations. The unit used is in ng/g of dry weight.
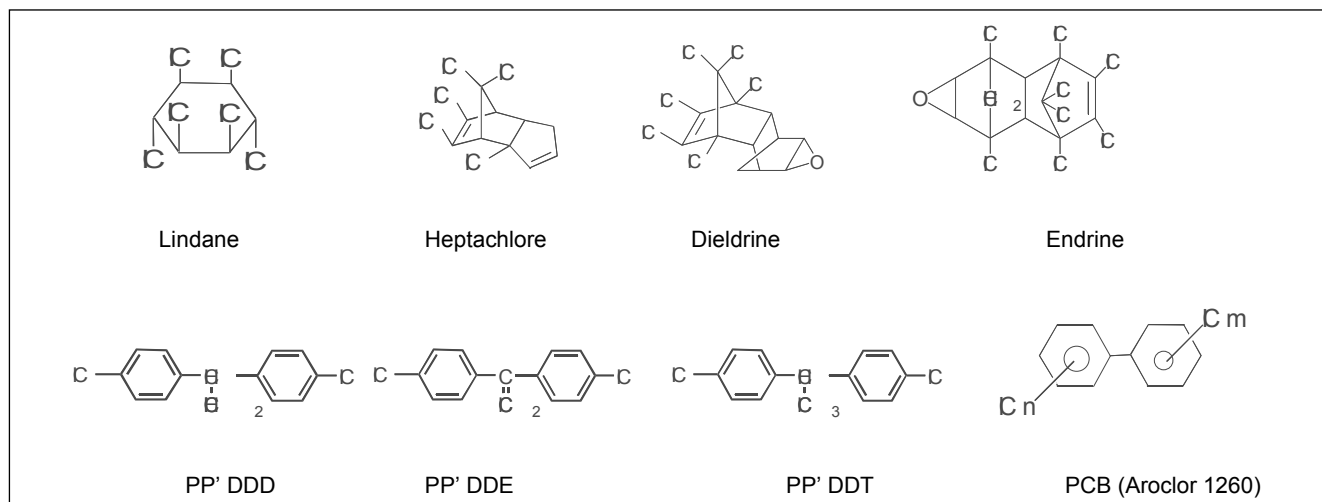

Figure 2: Formulas of organochlorine compounds studied (21).

Table 1a
Contamination by the organochlorines compounds of the oysters (December 1992 to October 2004) in the Ebrié lagoon stations,
concentration in ng/g dry weight

Stations	Code	n	Lindan				Dieldrin				Endrin			
			Min	Mean	Max	σ	Min	Mean	Max	σ	Min	mean	Max	σ
Biétry	ST1	8	1.3	1.6	1.8	0.1	1.3	3.7	15.0	4.6	1.6	2.0	4.51	1.0
Banco	ST2	8	1.3	1.5	1.7	0.2	1.0	1.0	1.0	0.0	1.0	1.3	3.7	0.9
Cocody	ST3	5	1.6	1.8	2.1	0.2	1.7	6.5	8.1	2.7	3.0	4.2	6.3	1.2
Marcory	ST4	8	1.3	2.5	8.0	2.6	1.0	3.8	6.3	1.5	1.0	1.6	2.0	0.3
Hotel du Golf	ST5	7	2.3	3.0	4.4	0.8	1.7	2.8	4.2	0.8	1.0	1.0	1.0	0.0
Parc à Bois	ST6	6	1.6	1.9	2.6	0.4	2.5	3.8	5.6	1.0	1.0	1.4	2.0	0.4
Adiopodoumé	ST7	7	1.6	2.0	3.0	0.5	1.0	2.3	3.1	0.9	1.6	2.6	3.5	0.9
Bingerville	ST8	6	1.6	2.3	3.0	0.5	1.0	1.0	1.0	0.0	2.0	4.3	10.1	3.0
Jacqueville	ST9	8	1.3	3.4	5.0	1.1	1.0	1.7	3.0	0.8	1.0	1.0	1.0	0.0
Grand Lahou	ST10	8	3.0	5.1	20.0	0.3	1.0	1.0	1.0	0.0	1.0	1.0	1.0	1.0
Assinie Mafia	ST11	8	1.3	1.3	1.3	0.0	1.0	1.0	1.0	0.0	1.0	1.0	1.0	1.0

Min: minimum, Max: maximum, σ: standard déviation.
n: number of sampling and monitoring programs of each station since December 1992 to October 2004.

10/10/ 1992 to 06/11/ 1992   16/08/ 1994 to 09/09/ 1994
21/07/ 1993 to 05/08/ 1993   05/12/ 1996to 04/12/ 1996
20/10/ 1993 to 26/10/ 1993   08/04/ 1999 to 30/04/ 1999
24/03/ 1994 to 07/04/ 1994   02/11/ 2004 to 10/11/ 2004

Table 1b
Contamination by the organochlorines compounds of the oysters (December 1992 to October 2004) in the Ebrié lagoon stations,
concentration in ng/g dry weight

Stations	Code	n	Heptachlor				PP' DDD + DDE				PCB 1260			
			Min	Mean	Max	σ	Min	Mean	Max	σ	Min	Mean	Max	σ
Biétry	ST1	8	1.6	3.2	8.0	2.1	3.7	53.0	64.4	20.9	173.0	215.6	250.0	23.3
Banco	ST2	8	1.3	3.8	8.0	2.1	55.4	129.8	156.0	35.8	134.0	227.0	290.0	45.8
Cocody	ST3	5	1.6	2.4	4.3	1.1	33.7	51.6	66.0	11.7	200.0	24.0	240.0	16.7
Marcory	ST4	8	1.3	2.7	4.0	0.8	22.0	47.3	76.1	15.3	117.0	187.6	260.0	40.1
Hotel du Golf	ST5	7	2.0	3.3	4.0	0.9	4.7	7.7	10.2	2.1	15.0	36.4	50.0	13.4
Parc à Bois	ST6	6	1.3	1.0	4.4	1.1	39.5	43.5	45.6	2.1	140.0	184.0	200.0	27.7
Adiopodoumé	ST7	7	1.3	1.5	2.5	0.4	1.0	6.2	8.0	2.4	13.0	30.7	57.0	14.0
Bingerville	ST8	6	1.3	1.3	1.3	0.0	5.0	9.1	20.8	5.8	13.0	35.7	88.0	27.9
Jacqueville	ST9	8	1.3	3.5	7.5	2.1	1.0	1.9	8.9	2.6	13.0	14.8	25.0	4.2
Grand Lahou	ST10	8	1.3	5.2	12.0	3.6	5.0	13.1	18.9	14.5	12.0	31.5	85.0	26.2
Assinie Mafia	ST11	8	1.3	1.3	1.3	0.0	1.0	8.9	56.5	2.0	13.0	13.0	13.0	0.0

Min: minimum, Max: maximum, σ: standard déviation.
n: number of sampling and monitoring programs of each station since December 1992 to October 2004.

10/10/ 1992 to 06/11/ 1992   16/08/ 1994 to 09/09/ 1994
21/07/ 1993 to 05/08/ 1993   05/12/ 1996to 04/12/ 1996
20/10/ 1993 to 26/10/ 1993   08/04/ 1999 to 30/04/ 1999
24/03/ 1994 to 07/04/ 1994   02/11/ 2004 to 10/11/ 2004

distinguish the most contaminated stations from the less contaminated ones.

2. Spatial distribution of the contamination

The previous results can be visualized to the help of Principal Composant Analysis (PCA). PCA is a mathematic method that has ability to provide the global description and more details information on the system (15). In our study the system is constituted by pollutants and water resource. Moreover, the figure of ACP added Radar diagram and are more usefully than different histograms.

The total results (Tables 1a, b) have been submitted to ACP modeling. For each sample, we have selected six (06) variables such as concentration of Lindan, Heptachlor, Dieldrin, Endrin, DDT and PCB of measured along the 11 stations.

Globally, we have determined 80 inputs samples and outputs results show 480 variables in PCA matrix. The results of PCA implementation within Statisgraphics Plus4 and Sigma Plot 2000 have displayed the eigenvalues and the graph with two axes (F1 and F2) which describe the chemicals data set (14).

The output indicate that the first Factor F1 has the largest eigenvalue at 2.3 and account for 38.8% of data variation and the second Factor F2 has next largest eigenvalue at 1.4 and account 23.4% of data variation.

The two factors representing by axe F1 and axe F2 have been extracting with 62.2% total contribution (Figure 3).

Concerning the factor F1 representing 32.8% of the total variability of the organochlorines pollutants contamination, PCB and DDT have distinguished with coefficient α 0.90. That result means that the two pollutants are highly correlated to the factor F1.

Concerning the factor F2 representing by 23.5% of the variability, we notice morly the Heptachlor with the coefficient α 0.83.

Firstly, the previous observations show that the selective partition depending on the group of chemicals structures has been confirmed by the bioaccumulation properties of oysters. It appears two distinguished groups:

➢ The group of DDT and PCB and Heptachlor characterized by high value of factor of bioaccumulation (F_C), DDT (F_C 70.000), PCB (F_C 60.000) and Heptachlor F_C (17.500).

➢ The group constitued by Endrin (F_C 1.670-2.780), Dieldrin (F_C 2.070-5.550) and Lindan (F_C 60) is characterized by

Scatter Plot

Graphe des scores : distribution des échantillons

Biétry
Banco
Cocody
Marcory
H.Golf
P.Bois
Adiopo.
Bingerv.
Njem
G.Lahou
Assinie

Plot of Factor Loading

Graphe des coefficients : Répartition des variables
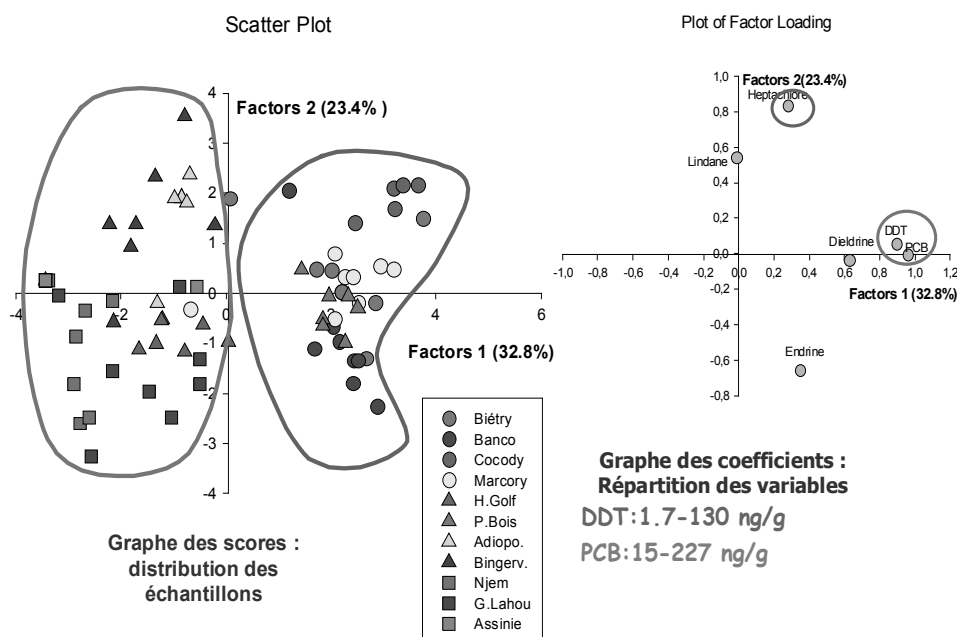
DDT: 1.7-130 ng/g
PCB: 15-227 ng/g

Figure 3: PCA score plot for Factor 1 and Factor 2 for contaminants measured in oysters taken on the bottom of lagoon system of Ivory Coast (STATISGRAPH plus4./SIGMA plot 2000).

low factor value.
Secondly these data let to interpret the graph of samples with two groups of stations which are clearly shown toward the main plan (factors F1- factors F2).

➢ The gathered points at the right side on the coordinates plan are showing stations of urban area of Abidjan that is considerably contaminated by the DDT and PCB.

➢ The scattered points on the left side of plan are mostly representing stations situated outside urban area of Abidjan. These areas are less contaminated by DDT and PCB and give prominence to significant concentration with Heptachlor (Adiopodoumé) and Endrin (Grand-lahou).

In partial conclusion, the use of the ACP has permitted to highlight the highest contaminated stations that are those of Abidjan, the main industrial and urban zones (PCB: 15-227 ng/g, DDT + DDD+DDE: 1.7-130 ng/g). These stations contain essentially PCB and metabolites DDD and DDE held simultaneously with the concentration relatively raised. The four stations situated out of Abidjan are less contaminated. The results observed would confirm that the lagoon of Abidjan area would be more vulnerable in reason of its geomorphology situation on one hand, and its urbanization and its industrialization degree on the other hand. However, this contamination appears less alarming in comparison with the rates of PCB, observed in Europe and in America (10).

It appears that the Lindan, the Heptachlor, the Dieldrin, and the Endrin are distributed in all stations. Their presence is marked in stations situated in the areas located out of Abidjan. The contamination by these organochlorines pesticides can be explained by molecule used in the agricultural farm situated in the catchment areas of the streams that communicate directly with the lagoon. About the lagoon of Abidjan the level of contamination would be caused essentially by the draining water from three rivers such as Comoé, Mé and Agnébi.

3. Impact of the contamination by organochlorine residues on the aquatic live

The previous studies about the lagoon contamination have brought out some case of depth and physiological trouble of aquatics organisms: regular observation of death of many fishes and size of some fishes species become more wittered in these bays. Interesting by oysters, the investigations showed that an individual consumes like a melt on average between 100 and 1000 g of oysters per day.

We have compared the values measured in oysters and waters with some value of MRLs FAO/WHO in melt (5, 11). The examanination of data from table 2 indicates that the levels of concentration measured in oysters are under the MRLs values for each pollutant.

However according to waters, we notice high level concentration for heptachlor: 0.034 µg/l and PCB: 0.436 µg/l. In comparison to ecotoxicology data (20), the concentration of 0.1 µg/l would be harmful to the growth of algae and concentration between 0.10- 0.32 µg/l would product the same effect on young fishes and alevins. Regarding the effect of relationship between the concentrations of these compounds relatively high in some stations of the field of Abidjan, the persistence and the bioaccumulation properties of oysters, the consumption of the oysters appears to be critical.

Conclusion

This work shows the presence of organochlorine compounds (pesticides and PCB) in the Ebrié lagoon system with variable concentrations. Stations from the area of Abidjan are the most contaminated ones. Although the use of these compounds is forbidden, their residues are detected with significant concentrations that fluctuate and that are increased in the oysters populating this lagoon. These results, as well as those of works made on sediments, confirm the chemical stability and the persistence of these compounds in the aquatic systems (17, 18). This study shows that the tendency of this contamination would also be decreasing in general way. It appears again the consumption of the oysters must be controlled in order to prevent important doses susceptible to cause a food poisoning.

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AVIS

Nous rappelons à tous nos lecteurs, particulièrement ceux résidant dans les pays en voie de développement, que TROPICULTURA est destiné à tous ceux qui œuvrent dans le domaine rural pris au sens large.

Pour cette raison, il serait utile que vous nous fassiez connaître des Institutions, Ecoles, Facultés, Centres ou Stations de recherche en agriculture du pays ou de la région où vous vous trouvez. Nous pourrions les abonner si ce n'est déjà fait.

Nous pensons ainsi, grâce à votre aide, pouvoir rendre un grand service à la communauté pour laquelle vous travaillez.

Merci.

BERICHT

Wij herrineren al onze lezers eraan, vooral diegenen in de ontwikkelingslanden, dat TROPICULTURA bestemd is voor ieder die werk verricht op het gebied van het platteland en dit in de meest ruime zin van het woord.

Daarom zou het nuttig zijn dat u ons de adressen zou geven van de Instellingen, Scholen, Faculteiten, Centra of Stations voor landbouwonderzoekvan het land of de streek waar U zich bevindt. Wij zouden ze kunnen abonneren, zo dit niet reeds gebeurd is.

Met uw hulp denken we dus een grote dienst te kunnen bewijzen aan de gemeenschap waarvoor u werkt.

Dank U.