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ACCUMULATION OF ORGANOCHLORINE COMPOUNDS IN OYSTERS (CRASSOSTREA GASAR) OF AN ESTUARINE ENVIRONMENT: CASE OF A TROPICAL LAGOON IN THE GULF OF GUINEA

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As part of a pollution monitoring study, oysters (*Crassostrea gasar*) were sampled in June 1996, in order to determine the concentrations and distribution of chlorinated hydrocarbons in two stations (near Boulay Island and Riviera Golf) of the Ebrie Lagoon, in the Abidjan area.

The chromatographic analysis of the oven dried samples revealed the presence of PCBs (2.13 to 86.22 ppb or ng/g dry weight), DDE (<0.48 to 169.55 ppb), DDD (<1.04 to 60.27 ppb), DDT (1.43 to 77.81 ppb, lindane (<0.22 to 91.64 ppb), aldrin (<0.30 to 154.1 ppb), endrin (<0.23 to 293.31 ppb) and dieldrin (<0.26 to 199.74 ppb). The results indicated high concentrations in oysters sampled near Boulay Island, due to industrial, agricultural and port activities going on in this area.

Compared to DDD/ Σ DDT and DDT/ Σ DDT, the DDE/ Σ DDT ratios were high indicating old DDT inputs. The Σ DDT/PCBs ratios were higher than 1 illustrated the predominance of organochlorine inputs from agriculture activities. The presence of lindane in both stations illustrated the problem of fishing with toxic products.

Negative correlations found between dry tissue weight and organochlorine compounds concentrations showed that young oysters may concentrate more of these substances. More studies are needed in order to make any conclusions on their bioaccumulation trends.

Keywords: Pollution; coastal lagoon; organochlorine compounds; oysters; Gulf of Guinea

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INTRODUCTION

All the capital cities of the Gulf of Guinea countries are built either on the shores of lagoons connected to the Atlantic Ocean or on the seashore. Abidjan, the capital city of Côte d'Ivoire, is located on the periphery of the Ebrie Lagoon. This lagoon system is subjected, not only, to the multiple industrial and domestic waste water 'discharges without any treatment (Marchand and Martin, 1985), but also to fertilizer and pesticide runoff from agricultural lands (Broche and Pechet, 1983; Dufour, 1982; Dufour and Slepoukha, 1975; Dufour and Skubish, 1982).

Agricultural production of food for a rapidly growing population and cash crops for economic buoyancy as well as disease vector control activities over many years, represent major anthropogenic sources of organochlorine pesticide (OCP, *e.g.*, DDT and derivatives, hexachlorocyclohexane or HCH, aldrin, dieldrin, heptachlor and endosulfan) input into the aquatic environment. In 1976 about 600 tonnes of lindane were used for cocoa and 320 tonnes of DDT were applied on cotton in the Cote d'Ivoire. In 1981, 350 tonnes of lindane, dieldrin, heptachlor, and endrin were used for timber protection (Dejoux, 1988).

The persistence and bioaccumulative tendency of organochlorine compounds (OCC, including pesticides and as well as commercial and industrial chemicals such as polychlorinated biphenyls or PCBs, dioxins or PCDDs, hexachlorobenzene or HCB) their metabolites and residues in the environment allow them to remain but also instead partition between the major environmental compartments in accordance with their physico-chemical properties and may thereby become transported several kilometers from the point of their original release (Hague and Freed, 1975; Kaba, 1987). Such environmental distribution may lead to exposure of living organisms including man, that are far removed from intended targets.

As any estuarine environment, the lagoon around Abidjan serves as reproductive and nursery grounds for many continental and marine aquatic species. Therefore this is vulnerable to toxic substances such as OCC (Durand *et al.*, 1994).

In order to develop management policies and regulatory framework for the protection of the coastal environment, pollution monitoring studies based on reliable and adequate scientific data are needed. The data available on OCC in Côte d'Ivoire aquatic environment is limited. The oysters (*Crassostrea gasar*) sampled in a coastal environment were chosen as indicators for pollution by OCC.

MATERIALS AND ANALYTICAL METHODS

Sampling Environment: The Ebrie Lagoon (Fig. 1)

This is a 566 km² brackish water environment along the coast, 4.8 meters is the depth and it is connected to the sea by the Vridi Canal. It has a watershed of $94,000 \text{ km}^2$. The annual river and sea water inputs are estimated to be 8.4 km³ (Durand *et al.*, 1994), and 38 km³ (Varlet, 1978).

The lagoon area around the city of Abidjan undergoes intenser human pressure. The domestic and industrial waste water inflow in that part of the lagoon is estimated to be $1.8 \text{ m}^3 \text{s}^{-1}$ (Dufour, 1982).

The sampling was done in June 1996, corresponding to the rainy season, during which the rains and the river water level decrease the lagoon salinity to $1g^{-1}$ in the sampling stations). The temperature and water transparency also decrease (to respectively 26°C and 0.5 m with the Secchi disk in the stations). The sampling sites (Boulay Island and Riviera Golf) are less than 1 meter deep. Besides these characteristics, the two sampling sites have different settings:

- the Boulay Island station receives domestic, industrial and nearby harbour etiluents, drainage and runoff from treated farm lands.
- Riviera Golf station is near a residential area, and receives directly domestic effluents through sewer systems, drainage and runoff from treated farm lands and solid waste. Sand mining activities are going on also in this area.

The Biological Material: Oyster (Crassostera gasar)

This is a sessile bivalve living on sandy or muddy bottoms less than 3 m deep or attached stable stands (such as mangrove tree roots). It lives in water with a salinity less than 15 m^{-1} . It feeds by pumping and filtering suspended particles from the water. The speed at which the water is pumped depends on many factors including the water salinity, temperature, pH, and turbidity, and the density of organisms.



FIGURE 1 Lagoons in Côte d'Ivoire.



FIGURE 2 Variation of mean concentrations of organochlorine compounds in Riviera Golf and Boulay Island.

According to Loosanoff (1965), the oyster mutation stops during very low water salinity. According to the same author, water pumping is insignificant, at water temperatures under 3°C, it increases rapidly from 8°C to 16°C, reaching a maximum between 28°C and 32°C, that is to say $37 h^{-1}$, even 40 h⁻¹ for periods of 5 to 15 m. But suspended matter (mud, kaolin, limestone), even in small quantities, reduce the pumping rate. Relatively low pH also reduces the pumping rate which is normal at a pH of 7.75.

Sampling and Preparation of Samples

The oysters were collected by hand, using diving. The samples were immediately taken to the laboratory in a bucket containing the lagoon water. Once in the laboratory, the shells are separated and the muscles were collected, weighed, oven dried (at 105°C overnight), ground and sifted (mesh size of 0.8).

Analytical Methods

The sample reduced is extracted in a soxhlet with hexane for 8 hours. The extract collected is cooled and concentrated to a volume of about 1 ml with an rotary evaporator. The concentrated extract is then separated into 3 fractions by elution using a florisil chromatographic column with 3 different solutions:

- 70 ml of hexane which gave the fraction 1, containing aldrin, lindane, DDE, PCBs, heptachlor;
- 50 ml of a hexane/dichloromethane mixture (70:30) which gave a fraction 2, containing DDD, DDT;
- 40 ml of dichloromethane gave fraction 3 containing dieldrin, endrin.

The different fractions are concentrated with the rotary evaporator to about 1 ml, then analysed by gas chromatography with electron capture detector (VARIAN 3400) using a capillary column ($30 \text{ m} \times 0.53 \text{ mm}$ I.D. Phase DB5 with a film thickness of 1.5 micron).

The lindane, aldrin, dieldrin, endrin, DDE, DDD, DDT and PCBs were analysed in the following analytical conditions:

- column temperature: isothermal, 220°C;
- injector temperature: 180°C;
- detector temperature: 300°C;
- gas (nitrogen 99.99% pure) flow-rates: 2 ml/m in the column, 30 ml/m in the detector.

RESULTS AND DISCUSSIONS

The results of the analyses and the different calculations are presented in Tables I-VI. They represent the mean concentrations of the different organochlorine compounds analysed, standard deviations, Pearson correlation matrix and ratios between some pollutant concentrations.

The results of OCC analyses (Tabs. I and II) illustrate a state of pollution by OCC in the lagoon around this area, also observed by Marchand and Martin (1985) and Kaba (1992). This is due to the fact that this lagoon receives waste water from industries manufacturing, formulating or using OCC in their processes, drainage and runoff from treated agricultural lands, and garbage and waste dumps.

Organoci compoun	hlorine ds											
Sample		LIN		ALDRIN			DIELDRIN			ENDRIN		
p.sec(g)		М	SD N	/ M	t S	D N	М	SD	N	М	SD	N
0.3		< 0.22*		17.	62 1.	02 3	39.86	0.58	3	10.4	9 0.49	3
0.8		< 0.22*		0.	87 0.	56 3	38.53	0.76	3	33.5	3 1.4	3
1		24.72	0.84 3	0.	47 0.	19 3	85.18	0.77	3	118.8	2 1.68	3
1.1		27.78	2.6 3	18.	70 1.	12 3	104.76	0.79	3	293.3	1 2.13	3
1.4		13.86	0.61 3	1.	67 0.	11 3	13.78	0.27	3	8.8	4 0.42	3
1.7		< 0.22*		2.	19 0.	08 3	3.94	0.09	3	8.4	6 0.43	3
1.8		< 0.22*		26.	7 0.	17 3	30.74	1.5	3	13.0	4 0.77	3
2.2		22.67	0.20 3	1.	25 0.	11 3	32.46	0.58	3	71.0	1 1.17	3
2.4		< 0.22*		< 0.	30* -		4.16	0.24	3	6.3	1 0.24	. 3
3.5		1.87	0.21 3	0.	31 0.	3 3	9.05	0.24	3	< 0.2	3* -	-
	DDE			DDD			DDT			I	PCBs	
Μ	SD	N	М	SD	Ν	М	SD	N		М	SD	N
< 0.48*			11.60	0.62	3	19.50	0.67	3	8	6.22	0.90	3
< 0.48*	-	_	< 1.04*	_		2.68	0.23	3	1	8.22	0.57	3
52.35	1.36	3	85.60	1.15	3	18.56	0.32	3		4.60	0.70	3
< 0.48*	_	-	19.45	0.62	3	15.3	0.3	3	1	7.60	0.71	3
102.81	1.37	3	< 1.04*	-	_	4.92	0.98	3	1	5.77	0.56	3
4.31	0.30	3	6.7	0.56	3	62.6	0.63	3	20	6.40	0.55	3
4.47	0.12	3	12.53	0.69	3	1.53	0.55	3		5.32	0.16	3
27.7	1.14	3	< 1.04*	_	-	5.75	0.35	3		3.37	0.08	3
< 0.48*	-		5.1	0.18	3	14.92	0.20	3		3.51	0.18	3
44.68	0.44	3	< 1.04*			7.65	0.33	3	9	9.1	0.23	3

TABLE I Riviera Golf. dry weight (DW in g), mean concentrations (m in ppb or ng/g), standard deviations (SD) and number of analysis for each sample (N)

M: Arithmetical mean calculated for each sample;

* not detected. Concentration less than the detection limits calculated.

The OCC concentrations in the oysters depend on the level of contamination at the sampling site (Focardi *et al.*, 1984). We observe in Table III that except for the DDD and DDT, lindane, aldrin, dieldrin, endrin, DDE and PCBs residue mean values are higher in Boulay Island samples than in Riviera Golf samples. The Boulay Island area is more contaminated by OCC than the Riviera Golf area. Boulay Island is near the important Abidjan which is an important shipping port, and has big industrial plantations, and receives waste water from shipping and industries manufacturing or using OCC in their manufacture processes; while Riviera Golf station receives essentially domestic waste water.

From the comparison of DDT, DDD and DDE mean values (Tab. IV), it is shown that DDE mean values are higher than those of

compound	ls													
Samples		LINDANE			Ŀ	ALDRIN			DIELDRIN			ENDRIN		
P.sec(g)		M	SD	N	M	SL	N	M	SD	Ν	M	SD	N	
1.3		< 0.22*	_	.	154.1	1.5	3 3	166.51	1.53	3	45.8	7 1.6	53	
1.5		91.64	1.20	3	< 0.30	*		69.71	0.79	3	21.2	6 1.32	2 3	
1.6		63.87	1.47	3	82.77	0.74	43	69.65	0.79	3	65.2	2 1.69	93	
1.8		< 0.22*			< 0.30	* _	-	199.74	3.1	3	173.5	6 1.00) 3	
2.1		8.92	0.60	3	< 0.30	* -	-	150.37	1.38	3	67.1	7 2.10	63	
3.4		< 0.22*	-	_	5.36	5 0.6	33	< 0.26*	-	-	52.1	6 1.12	23	
3.6		30.84	1.33	3	142.55	5 1.9	13	96.7	0.85	3	73.8	0 0.24	43	
4		< 0.22*	-		< 0.30	* -	-	< 0.26*	-		< 0.2	3* –	-	
4.5		34.41	1.93	3	< 0.30	*		67.62	2.40	3	151.1	0 1.6	33	
5.2		7	1.20	3	< 0.30	* -	_	< 0.26*	·	-	< 0.2	3* –	-	
	DDE				DDD			DDT			ŀ	CBs		
М	SD	Ν	<u>N</u>	1	SD	N	M	SD	N		M	SD	N	
< 0.48*	_	_	8.4	1 7	0.417	3	34.11	0.40	3	38	3.12	0.72	3	
< 0.48*	-	-	5.6	58	0.1	3	2.82	0.67	3	1().73 (0.14	3	
64.52	0.83	3	12.5	56	1.32	3	18.31	0.60	3	10	0.30	0.16	3	
1114.14	0.60	3	<1.()4*	÷	-	77.81	1.40	3	51	1.34 (0.82	3	
94.67	1.80	3	42.0)9	0.70	3	3.09	0.36	3	ç	9.90	0.40	3	
132.20	1.62	3	6.0)2	0.30	3	4.87	0.26	3	35	5.98	1.22	3	
169.55	1.06	3	60.2	27	3.58	3	8.37	1.05	3	42	2.26	1.78	3	
9.33	0.60	3	< 1.()4*	-		1.43	0.77	3	2	2.65	0.60	3	
< 0.48*	_	_	3.9	98	0.21	3	3.77	0.20	3	29	9.77	0.81	3	
6.90	0.27	3	1.9	93	0.56	3	5.14	0.17	3	2	2.13	0.27	3	

TABLE II Boulay Island

M: Arithmetical mean calculated for each sample;

* not detected. Concentration less than the detection limits calculated.

DDT and DDD, showing that in the sampling environment the DDE is more available. DDE is a DDT degradation product and is the most abundant metabolite in the environment (Cliath and Spencer, 1972). The ratio DDE/ Σ DDT is higher than the ratios DDD/ Σ DDT and DDT/ Σ DDT. According to Marchand and Martin (1985), it can be concluded that the DDT present in the environment comes from old inputs. The ratios Σ DDT/PCBs in both stations are higher than 1. If we suppose the DDTs are essentially brought by farm activity, we could conclude that the organochlorine inputs from agricultural activities are predominant. As for the lindane, which is banned, its presence could be explained by fishing practices with toxic compounds such as lindane (Marchand and Martin, 1985; Colcanap and Dufour, 1982).

The Pearson correlation matrix with the level of confidence 95% (Tabs. V and VI) show some significant and positive correlations

Organochloring

Organochlorine compounds	Station	Mean	SD	Number of samples
Lindane	Boulay Island	54.40	26.87	11
	Riviera Golf	23.02	5.10	11
Aldrin	Boulay Island	131.94	30.84	8
	Riviera Golf	21.01	4.36	9
Dieldrin	Boulay Island	96.54	40.04	15
	Riviera Golf	37.50	20.12	17
Endrin	Boulay Island	55.63	16.89	16
	Riviera Golf	13.47	9.79	17
DDE	Boulay Island	114.75	34.63	12
	Riviera Golf	56.89	29.24	12
DDD	Boulay Island	7.79	2.72	11
	Riviera Golf	14.53	3.76	9
DDT	Boulay Island	9.70	5.63	8
	Riviera Golf	14.95	4.39	14
PCBs	Boulay Island	27.01	13.60	22
	Riviera Golf	15.29	3.92	12

TABLE III Mean concentration values for each compound in each sampling station

TABLE IV Ratios between total DDT and its metabolites. Ratios between total DDT and PCBs

	Boulay island	Riviera golf
DDE	114.75	57
DDD	7.8	14.53
DDT	9.7	14.94
$\Sigma DDT = DDE + DDD + DDT$	132.25	86.47
PCBs	27	15.3
DDE/SDDT	0.86	0.66
DDD/EDDT	0.06	0.17
DDT/SDDT	0.08	0.17
ΣDDT/PCBs	4.9	5.65

TABLE V Pearson correlation matrix (Riviera Golf)

Riviera Golf	Lindane	Aldrin	Dieldrin	Endrin	DDE	DDD	DDT	PCB
Weight Lindane Aldrin Dieldrin Endrin DDE	-0.202 1	-0.336**- -0.0467 1	-0.506** 0.734 ** 0.359 1	-0.277** 0.791** 0.278 0.892** 1	$\begin{array}{r} -0.0572\\ 0.349\\ -0.417\\ -0.114\\ -0.143\\ 1\end{array}$	-0.325** 0.501 -0.020 0.641 ** 0.387 0.162	$\begin{array}{r} -0.0899 \\ -0.155 \\ -0.146 \\ -0.149 \\ -0.0392 \\ -0.253 \\ 0.104 \end{array}$	$\begin{array}{r} -0.578 \\ -0.305 \\ 0.346 \\ 0.0229 \\ -0.138 \\ -0.256 \\ 0.122 \end{array}$
DDD DDT PCBs						L	0.104 1	-0.122 0.262 1

** Significatively correlated.

Boulay island	Lindane	Aldrin	Dieldrin	Endrin	DDE	DDD	DDT	PCB
Weight	-0.327**	-0.316**	-0.734**	-0.252**	-0.0996	-0.0683	-0.503**	-0.286
Lindane	1	0.0320	-0.0943	-0.0728	-0.202	0.0531	-0.277	-0.279
Aldrin		1	0.332	-0.0535	0.203	0.472	0.136	0.385
Dieldrin			1	0.598	0.227	0.274	0.718**	0.557
Endrin				1	0.338	0.0384	0.609	0.695**
DDE					1	0.639**	-0.218	0.537
DDD						1	-0.232	0.164
DDT							1	0.635**
PCIBs								1

TABLE VI Pearson correlation matrix (Boulay Island)

** Significatively correlated.

between different pollutants and negative and significant correlations between pollutants and oyster dry weights. The significative and positive correlations between pollutants indicate joint inputs. PCBs are only industrial and commercial chemicals, so being positively correlated to the DDT and the endrin in Boulay Island station, indicates the sources of these substances into this aquatic environment may have been industrial effluents.

We observe that the levels of OCC residues decrease when the oyster muscle dry weights increase (negative correlations between them, Tabs. V and VI). It is the indication that the OCC accumulation in oysters is inversely proportional to their weight and that the youngest (low muscle) accumulate most of the OCC. For many authors (Marchand and Cabane, 1980; Fossato, 1975; Butler, 1971; Goldberg *et al.*, 1978), the accumulation of OCC in bivalves is a function of physico-chemical parameters (such as salinity, temperature, turbidity) of the environment, their physiological cycle and the stress they undergo.

The sampling was done in June, corresponding to the end of the adult oyster reproduction cycle (May, April, June), during which they lose some lipids (Marchand *et al.*, 1976). It is known that the OCC are lipophilic; so, when adults lose lipids, they also lose OCC. This could be the explanation that the fact that OCC accumulation in oysters in inversely proportional to the weight.

According to Yonge (1960), during the reproduction cycle, the activity of lateral filaments (used by oysters to feed) is at its minimum. So, during that time, adult oysters intake of polluted particles is also

low. That could also lead to the OCC accumulation in oysters being inversely proportional to the weight.

Levels of OCC in oysters from this tropical lagoon in the Gulf of Guinea are relatively low compared to values from other parts of the world and similar to results obtained in other countries of the Gulf of Guinea (Osibanjo *et al.*, 1994; COI/FAO/PNUE, 1989), except in a few cases around pollution hot spots. Levels found are much lower than the permissible limits for OCC in fish and fish products for human consumption (Nauen, 1983; FAO, 1989).

CONCLUSION

The uptake of OCC by oysters (*Crassostrea gasar*) depends not only on external (such as salinity, temperature, turbidity) and internal parameters (physiological state of the animal), but also on the levels of contamination of the sites by OCC.

The high levels of OCC observed at Boulay Island station could be due to the nearby harbour, and the industrial zones which discharge untreated effluents. DDT found in the lagoon environment may come from old inputs.

The data available is limited to enable us to conclude on the accumulation trends of OCC in oysters, But the oysters (*Crassostrea gasar*) in this estuarine environment are qualitative pollution indicators. It forms a good basis for further monitoring work. More studies are needed on the OCC uptake by these shellfish which is dependent on hydro-climate parameters (such as temperature, pH, salinity, turbidity, dissolved oxygen) and physiological parameters (growth, reproduction cycle).

Although the levels of contamination are not alarming, the occurrence of OCC in these organisms, even at trace levels, should be a cause its concern. Long-term exposure to sub-lethal concentrations of these substances through various pathways in the aquatic environment may cause far reaching ecological damages and health problems in man.

The regulatory framework and control on the use of these chemicals should be put in place in the countries of the region as well as enforcing the International Code of Conduct on the Distribution and Use of Pesticides, adopted by FAO Conference in 1985 and amended in 1989 (FAO, 1990).

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