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Organochlorine Pesticide Residue Concentrations in Biota and Sediments from Río Palizada, Mexico

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The Mexican State of Campeche is one of the major rice producers in Mexico, accounting for 9.3 to 20.0% of the total production during in the period of 1982-1986 (INEGI, 1990). Another important crop is sugar cane, with an average annual yield of 28,000 ton from 60,000 ha (INEGI 1990). Most of these crops come from the Palizada river basin (Figure 1). This drainage basin, with a surface area of 2,460 km^2, is the main riverine discharge into Laguna de Terminos, representing 70% of the total freshwater discharge of 6 x 10^9 m^3/year (Vera-Herrera *et al.* 1988). 20% of the basin is devoted to rice production, with an annual use of 3,000 ton of fertilizers and 37 ton of pesticides (Benítez *et al.* 1993).

Within the framework of the joint IOC/UNEP Program for Marine Pollution Assessment and Control for the Wider Caribbean (CEPPOL)(IOC 1990), a pilot study was established to assess the concentrations of organochlorine pesticide residues in recent sediments and oysters (*Crassostrea virginica*), mussels (*Brachidontes recurvus*), and juvenile shrimps (*Penaeus setiferus*) in the Palizada river. The results of previous samplings have been reported elsewhere (Gold-Bouchot *et al* 1993).

MATERIALS AND METHODS

Sediment and biota samples (where available) were collected at nine sampling stations along the Palizada river and the main lagoons close to its mouth in December, 1992, as shown in Figure 1. Sediment samples were collected with a 0.1 m^2 Van Veen grab, shrimp by trawling and bivalves (mussels and oysters) manually. Sediment samples were placed in glass jars cleaned with chromic acid and hexane. Organisms were wrapped in aluminum foil, previously cleaned with hexane and heated at 450°C for two hours. The samples were transported under refrigeration to Merida for further analysis. The solvents used were distilled twice in an all-glass still. Florisil was purified by extracting it for 8 hours with hexane in a Soxhlet apparatus. All samples were freeze-dried upon arrival at the laboratory.

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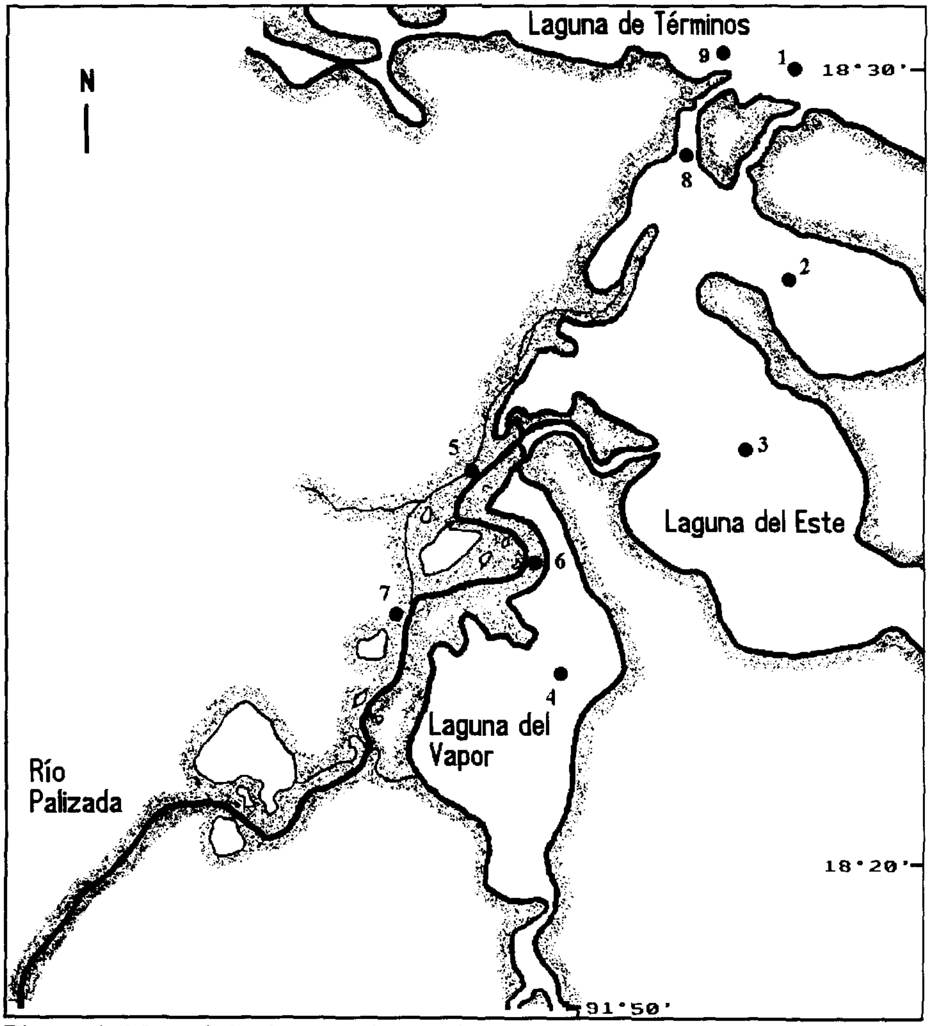

Figure 1. Map of the lower Palizada river region, showing the position of the sampling stations.

Both sediments and organisms were analyzed according to established methodologies (UNEP 1982a; 1982b). Samples were extracted in hexane in a Soxhlet extractor, and the extract purified and separated into three fractions in a Florisil column. The fractions were eluted with hexane, hexane-methylene chloride 7:3 v/v, and methylene chloride (UNEP 1982a; 1982b). The fractions were evaporated in a Kuderna-Danish apparatus and the purified extracts were analyzed by capillary gas chromatography and electron capture detection (UNEP 1988), in a Hewlett-Packard 5890 Series II gas chromatgraph, connected to a personal computer equipped with Hewlett Packard 3365 Series II software.

The gas chromatograph was fitted with a split/splitless capillary injector

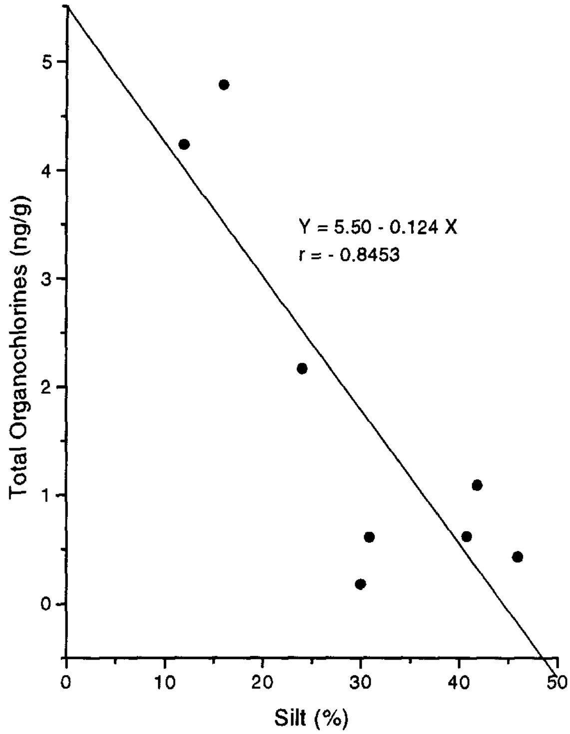

Figure 2. Relationship between the silt fraction and the concentration of total organochlorine pesticide residues in recent sediments from Palizada river, Mexico.

and a 30 m x 200 µm SE-54 capillary column. The temperature program was 70°C initial temperature for two minutes, then increased at 3°C/min to 265°C, and held there for 25 min. Some samples were spiked with 2,4,5-Toxachlorobenzene (2,4,5-TCB) as an internal standard to check the efficiency of recovery for the analytical procedure. Analytical standards provided by IAEA and Protocol Analytical Supplies, Inc. were used for identification and quantification. Some samples were fortified with standards, to confirm identification.

Sedimentary organic carbon was determined by wet oxidation with potassium dichromate, and grain size by the method of Bouyoucos (Holme and McIntyre 1982).

All concentrations are given as ng/g on a dry weight basis, and are not corrected for recovery. For simplicity, the results reported have been grouped: ΣDDT is the sum of DDT, DDD, and DDE; ΣHCB is the sum of the α-, β-, and δ- isomers; ΣHeptachlor is Heptachlor + Heptachlor epoxide; ΣEndrin is Endrin + Endrin aldehide + Endrin ketone; ΣAroclor is the sum of Aroclor 1260 + Aroclor 1254; ΣEndosulfan is the sum of the Endosulfan I and II, and Endosulfan sulfate.

RESULTS AND DISCUSSION

The organic carbon content and grain size of recent sediments are presented in Table 1, and the concentrations of organochlorine pesticides in Table 2. The average recovery using the internal standard 2,4,5 TCB was 86.6 %.

Table 1. Organic carbon content and grain size fractions of recent sediments from the Palizada river, Mexico.

Station	Organic Carbon (%)	Sand (%)	Silt (%)	Clay (%)
1	1.55	69.9	24.1	6
2	6.4	86	12	2
3	1.03	53	46	1
4	7.68	82	16	2
5	0.68	57.1	41.9	1
6	1.03	69.1	30.9	0
7	0.35	67	30	3
8	0.27	59.2	40.8	0

The concentrations of organochlorine pesticide residues in organisms are presented in Table 3. The average recovery was 88.8 %. The content in organisms are relatively low, with the exception of the oysters (*C. virginica*) in station 9, which have a concentration of total organochlorines of 246 ng/g. Endosulfan sulfate, total Chlordane, Endrin and Aroclors residues had the highest concentrations. Concentrations in sediments (Table 2) were lower and rarely exceeded 1 ng/g. More organochlorine pesticide residues were found in biota than in sediments, which is in good agreement with the results of Gold-Bouchot *et al.* (1993) in the same area. Endosulfan sulfate, Chlordane, and Aroclor residueswere not detected in the sediments analyzed, but could be detected in the organisms.

Only γ-HCB residues could be detected in all the sediment samples (Table 2), whereas in organisms only the shrimp had it in a low concentration. Most of the other pesticide residues in sediments were detected in only one or two sampling stations. Stations 1,2, and 4 presented more pesticides than the others. The highest pesticide residue values were for Endosulfan, Chlordane, and Endrin.

The concentrations obtained here for both sediments and biota are lower than those reported by Gold-Bouchot *et al.* (1993) in January 1992, probably due to the extremely wet rainy season that year. The observed

Table 2. Organochlorine pesticide residue concentrations in recent sediments of the Palizada river, Mexico. ΣDDT=DDT+DDD+DDE; ΣHCB=α-+β-+δHCB; ΣHeptachlor=Heptachlor+Hept. Epoxide; ΣEndrin=Endrin+E. aldehide+E. Ketone.

Station	ΣHCB (ng/g)	ΣHeptachlor (ng/g)	γ-HCB (ng/g)	Aldrin (ng/g)	ΣDDT (ng/g)	Dieldrin (ng/g)	ΣEndrin (ng/g)	Metoxiclor (ng/g)
1	0.21	0.26	0.40	n.d.*	n.d.	0.35	n.d.	0.95
2	0.07	n.d.	0.26	n.d.	1.23	2.29	0.39	n.d.
3	n.d.	n.d.	0.43	n.d.	n.d.	n.d.	n.d.	n.d.
4	n.d.	0.08	0.67	0.25	1.45	n.d.	2.34	n.d.
5	0.35	n.d.	0.37	n.d.	0.37	n.d.	n.d.	n.d.
6	0.04	n.d.	0.57	n.d.	n.d.	n.d.	n.d.	n.d.
7	n.d.	n.d.	0.18	n.d.	n.d.	n.d.	n.d.	n.d.
8	n.d.	n.d.	0.62	n.d.	n.d.	n.d.	n.d.	n.d.

* n.d. = not detected

Table 3. Organochlorine pesticide residues in organisms from the Palizada river, Mexico. ΣDDT=DDT+DDD+DDE; ΣHCB=α-+β-+δHCB; ΣHeptachlor=Heptachlor+Hept. Epoxide; ΣEndrin=Endrin+E. aldehide+E. Ketone; ΣEndosulfan=Endosulfan I+E. II+E. sulfate; ΣAroclor=1254+1260.

Organism	ΣEndosulfan (ng/g)	ΣChlordane (ng/g)	ΣDDT (ng/g)	ΣHeptachlor (ng/g)	ΣHCB (ng/g)	ΣEndrin (ng/g)	γ-HCB (ng/g)	Aldrin (ng/g)	Dieldrin (ng/g)	Metoxiclor (ng/g)	ΣAroclor (ng/g)
Shrimp	0.94	0.54	0.25	n.d.*	1.18	0.44	0.08	n.d.	0.28	n.d.	0.74
Oysters 1	9.84	12.13	1.49	0.17	1.04	8.36	n.d.	0.54	n.d.	1.1	2.77
Oysters 9	111	104	0.39	0.63	1.97	13.35	n.d.	0.13	1.19	n.d.	12.99
Mussels	8.23	23.08	1.44	n.d.	1.68	5.32	n.d.	0.98	0.29	1.6	7.56

* n.d. = not detected

differences are not statistically significant by the non-parametric Mann-Whitney *U* test, with the exception of Heptachlor (U=15.0; P≤0.049) and Aroclor (U=4.0; P≤0.0012).

Highly significant correlations (P≤0.01) were found between the concentration of total organochlorines and the organic carbon content (r=0.97) and silt fraction (r=-0.85) of the sediments, as can be seen in Figure 2.

A comparison of our results with those of Vázquez-Botello (1990), Vázquez-Botello *et al.* (1992), and Gold-Bouchot *et al.* (1993) shows good agreement, with the exception of Aroclors and Endrin. In general, most concentrations are relatively low, and considered as not dangerous. A similar comparison for organochlorine pesticide residue concentrations in organisms is presented in Table 5, showing greater differences for sediments.

Table 4. Comparison of the concentrations of organochlorine pesticide residues in recent sediments from the Palizada river found in this study with published values in the same area. All concentrations are given as ng/g dry weight.

Compound	Vázquez-Botello 1990	Vázquez-Botello *et al.* 1992	Gold-Bouchot *et al.* 1993	This Study
Σ DDT*	10.85	27.3	11.38	0.38
Lindane	n.d.**	n.d.	0.57	0.44
Aldrin	n.d.	17.4	4.34	0.03
HCB	n.d.	n.d.	0.32	0.08
Endrin	n.d.	86.6	n.d.	0.34
PCBs	†	n.d.	48.3	n.d.

*ΣDDT=DDT+DDD+DDE ** n.d. = not detected † = not reported

Table 5. Comparison of the concentrations of organochlorine pesticides in organisms from the Palizada river found in this study with published values in the same area. All concentrations are given as ng/g dry weight.

Compound	Vázquez-Botello 1990	Vázquez-Botello *et al.* 1992	Rosales *et al.* 1979	Gold-Bouchot *et al.* 1993	This study
Lindane	†	†	†	0.89	0.02
Σ DDT*	17.88	84.8	6.0	6.0	0.89
Endrin	1110.3	796.2	†	56.7	6.87
Aldrin	269.65	119.7	†	5.91	0.41
PCBs	†	†	19.0	2.28	6.02

*ΣDDT=DDT+DDD+DDE † = not reported

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