

ORGANOCHLORINE PESTICIDES AND PCBS IN SEDIMENTS AND FISH (ARIOPSIS FELIS) FROM THREE COASTAL ECOSYSTEMS IN THE SOUTHERN GULF OF MEXICO AND THE YUCATAN PENINSULA

Gerardo Gold-Bouchot¹, Victor Ceja-Moreno¹, Juan Pablo Rodas-Ortíz¹, Jorge Dominguez-Maldonado¹, Dolly Espínola-Pantí¹, Paulina Ku-Chan¹ and Mario Yarto^{2*}

¹Marine Geochemistry Laboratory, Marine Resources Department, CINVESTAV, Merida, Mexico

²National Institute of Ecology (INE), Ministry of Environment and Natural Resources (SEMARNAT), Mexico

INTRODUCTION

Mexico is a signatory country of the Stockholm Convention on Persistent Organic Pollutants (POPs). As part of the activities designed for the drafting of the National Implementation Plan for this treaty, research studies have been proposed, including a survey in three coastal ecosystems in the Southern Gulf of Mexico and the Yucatan Peninsula. The selected coastal lagoons are: Laguna de Terminos, in the State of Campeche; Celestun, on the border between the states of Campeche and Yucatan, and Dzilam, in Yucatan.

Celestun is located between 20° 46' and 20° 59' North latitude, and 90° 19' and 90° 28' West longitude, with an extension of 28,400 Ha. Climate is BS1 (h') w (i') g. It is a flooded coastal depression, about 20 km long, and carbonated sediments. This lagoon is protected, with a status of Biosphere Reserve. There are artisanal fisheries, and eco-tourism activities in the lagoon.

Laguna de Terminos is located between 18° 20' y 19° 00' North latitude and 91° 10' and 92° 00' West. It is limited in the North by Isla del Carmen, which is 37.5 km long and 3 km wide. This lagoon has an extension of 196 000 Ha, and its weather is Ax' (w2) (i') gw". This lagoon is protected, with a status of Wildlife Reserve. It is a major center for workers of the oil industry and is in front of Mexico's main oil producing zone.

Dzilam is located between 21° 26' 33.4'' and 21° 24' 51.2'' North and 88° 47' 54.4'' y 88° 47' 49.7'' West, with an extension of 61,700 Ha. The lagoon is 12.9 km long, and 1.6 km wide, and a surface area of 9.4 km². This is a State of Yucatan protected area, and is considered the best preserved zone on the Yucatan Peninsula coast.

There are no antecedents for organochlorine pesticides in sediments or fish for Dzilam or Celestun, but there are a few published papers for Laguna de Terminos and its associated ecosystems, Laguna de Pom and Rio Palizada. Gold-Bouchot *et al.* (1993 and 1995) reported pesticide and PCBs concentrations in sediments and biota (oysters, clams, shrimp) of the lower Palizada river. Results were relatively low then.



Figure 1. Map showing the three coastal lagoons studied in this project.

MATERIAL AND METHODS

Recent sediments were collected at three coastal lagoons in the Atlantic coast of Mexico, Laguna de Terminos, Celestun and Dzilam (Fig. 1). A total of 20 stations were distributed in the lagoons: Celestun (8 stations), Dzilam

Levels in biota

(7 sampling stations) and Celestun (5 sampling stations). Sediments were obtained using a 0.1 m² Van Veen grab, frozen and transported to the laboratory for further analysis. Fish (catfish, *Ariopsis felis*) were caught with a net, and the liver removed immediately and frozen in liquid nitrogen. In Dzilam 19 fish were caught, 15 in Celestun and 17 in Terminos.

Chemical Analysis

Levels of hydrocarbons and organochlorine compounds in the sediments were determined according to the procedures described in Sericano *et al.* (1990) and Wade *et al.* (1993). Briefly, 30 g of freeze-dried sediments were extracted with hexane and methylene chloride for 12 hours each in a Soxhlet apparatus. Extracts were concentrated in flat-bottomed flasks equipped with three-ball Snyder column condensers and mixed. Sediment extracts were fractionated by alumina:silica column chromatography and two fractions were obtained by sequential elution: aliphatics and aromatics (chlorinated pesticides, PCBs and PAHs). Analytes were separated and quantified by gas chromatography using a Hewlett Packard 5890 Series II gas chromatograph equipped with a 30 m x 0.25 mm HP-5 capillary column and working in the splitless mode. Hydrocarbons were quantified with a flame ionization detector (FID) at 300°C. Organochlorine pesticides and PCBs were quantified with an electron capture detector (ECD) at 325°C. Individual compounds were identified and quantified using standards from Ultra Scientific®.

Fish livers were analyzed the same way, with the only exception being that lipids were removed by size-exclusion chromatography using a Beckman HPLC system. Quality assurance of the analytical procedures included the addition of internal standards and the analysis of a procedural blank for each set of samples. Recoveries were 87% on average.

Grain size of the sediments was determined by the Bouyoucos hydrometer method and percentage of organic matter in each sample was measured using the Walkley and Black wet oxidation method (Franco *et al.* 1985).

Statistical Analysis

Non-parametric statistical procedures were run to evaluate seasonal differences in the levels of organic pollutants ((Mann-Whitney U test and Kruskal-Wallis ANOVA) and correlations (Spearman R), using Statistica Software (StatSoft 1991).

RESULTS AND DISCUSSION

For convenience, the pesticide concentrations were grouped according to chemical class. This also diminishes the number of zeros in the table. The results for the sediment analyzes are presented in Table 1.

Table 1. Concentrations, on a dry weight basis, of chlorinated pesticides (grouped by chemical class) and polychlorinated biphenyls (PCBs) in sediments from three coastal lagoons in Mexico.

Sample	Lagoon	Chlorobenzenes (ng/g)	HCHs (ng/g)	Drins (ng/g)	Chlordanes (ng/g)	DDTs (ng/g)	Plag totales (ng/g)	PCBs (ng/g)
C 1	Celestun	1.179	0.130	0.528	0.000	0.147	2.034	0.906
C2	Celestun	7.221	0.079	0.029	0.000	1.004	8.617	3.902
C3	Celestun	3.449	0.027	0.000	0.000	0.000	3.577	0.416
C4	Celestun	1.732	0.164	0.449	0.000	0.000	2.345	2.204
C5	Celestun	2.161	1.226	0.635	0.000	0.000	4.643	1.550
C6	Celestun	5.284	61.689	0.015	0.000	0.253	68.720	6.377
C7	Celestun	1.803	0.484	0.000	0.000	0.095	2.382	1.159
C8	Celestun	3.578	41.582	0.008	0.001	0.008	45.177	8.888
D1	Dzilam	1.099	0.392	0.000	0.007	1.966	3.929	3.209
D2	Dzilam	3.845	1.023	1.607	0.000	2.547	9.727	2.019
D3	Dzilam	1.055	0.364	0.000	0.000	2.665	4.382	1.819
D4	Dzilam	1.784	9.094	0.000	0.000	3.492	15.157	6.077
D5	Dzilam	2.817	34.741	0.000	0.000	0.149	37.707	5.431
D6	Dzilam	3.270	0.406	0.000	0.000	0.430	4.336	5.322
D7	Dzilam	1.043	0.278	0.000	0.000	0.188	1.509	1.961
T1	Terminos	18.321	4.626	1.685	5.918	70.668	105.882	21.269
T2	Terminos	22.261	9.220	2.899	5.158	12.458	54.883	10.264
T3	Terminos	9.335	3.404	2.679	12.941	39.998	69.781	1.100
T4	Terminos	3.869	2.342	1.597	0.193	7.964	19.475	0.000
T5	Terminos	4.897	1.735	4.312	0.508	10.914	29.921	3.982

The median concentrations for each lagoon, ± 1 interquartile range, are given in Fig 2.

Levels in biota

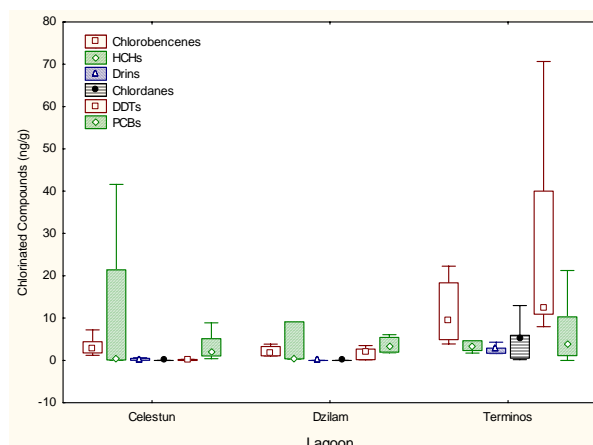


Figure 2. Median concentrations (± 1 interquartile range) for each lagoon.

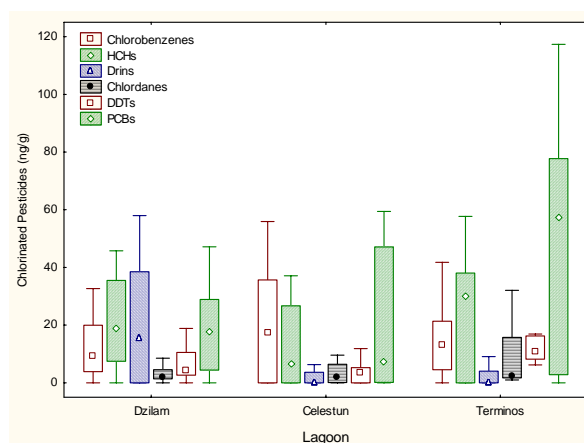
The profile of the pesticides found in each lagoon is different. Thus, in Celestun Chlorobenzenes, HCHs and PCBs predominate; In Dzilam HCHs and PCBs are the dominant compounds found, whereas in Laguna de Terminos we found in general the highest concentrations for the three lagoons studied. In particular, Chlorobenzenes and DDTs had the highest concentrations. This is the lagoon with the most agricultural influence, but DDT has been banned in Mexico since the late 1980's for agricultural use.

Another way to look at sediment concentrations is to see if they exceed the Probable effects Level (PEL) (Buchman, 1999) for marine sediments. This is the level above which adverse effects are frequently expected. The following table resumes the results, giving the percentage of samples exceeding the PEL:

Lagoon	C o m p o u n d s			
	HCHs	Drins	Chlordanes	DDTs
Terminos	100 %	20 %	60 %	20 %
Celestun	38 %	0 %	0 %	0 %
Dzilam	43 %	0 %	0 %	0 %
Total	55 %	5 %	15 %	5 %

As seen from this table, Laguna de Terminos is the most impacted lagoon because results were above the PEL. On the other hand, HCHs (in particular Lindane) are the most frequent pollutant exceeding the PEL. This reinforces the request by Mexico to include this pesticide in the Stockholm Convention protocol.

Concentrations, on a dry weight basis, of chlorinated pesticides (grouped by chemical class) and polychlorinated biphenyls (PCBs) in sediments from three coastal lagoons in Mexico, were measured. The median concentrations for each lagoon, ± 1 interquartile range, are shown in Fig 3.



Levels in biota

Figure 3. Median concentrations of chlorinated pesticides and PCBs (± 1 interquartile range) in liver of catfish (*Ariopsis felis*) for each lagoon.

In this case the profiles are more similar than in the case of the sediments. Thus, it seems that differential bioaccumulation, and/or differential metabolism obscure the signal from the sediments. The high concentrations of PCBs in Terminos are notable. Also, HCHs concentrations are high for the three coastal lagoons.

A comparison with chlorinated pesticides found in liver of different fish species is presented in Table 2.

Table 2. Median concentrations found in different fish species.

Place	Species	Site	DDTs (ng/g)	Clordanos (ng/g)	HCHs (ng/g)	PCBs (ng/g)
Alina's Reef	Haemulon plumieri	Florida	33.9	24.1	1.3	N. R.
Molasses	Haemulon plumieri	Florida	128.6	42.5	8.4	N. R.
White Banks	Haemulon plumieri	Florida	28.3	5.1	0.7	N. R.
Bahía de Chetumal	Ariopsis assimilis	Mexico	28.27	26.2	7.81	83.84
Cayos Cochinos	Haemulon plumieri	MBRS	3.77	1.83	22.79	142
Puerto Barrios	Haemulon plumieri	MBRS	18	N. D.	5.3	49.08
Caulker Key	Haemulon plumieri	MBRS	20.22	N. D.	4.31	97.29
Xcalak	Haemulon plumieri	MBRS	N. D.	N. D.	N. D.	160.1
Terminos	Ariopsis felis	This study	19.82	10.83	29.15	46.50
Celestun	Ariopsis felis	This study	4.30	8.82	17.11	60.17
Dzilam	Ariopsis felis	This study	6.84	3.10	23.88	25.50

It can be seen that HCHs concentrations in Laguna de Terminos are the highest, but the other chlorinated compounds reported here are in the range of concentrations found in Florida, Bahia de Chetumal, and the Mesoamerican Barrier Reef System.

REFERENCES

1. Buchmann, M. F. 1999. NOAA Screening Quick Reference Tables. NOAA HAZMAT Report 99-1, Seattle, WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, 12 Pp.
2. Franco J, De la Cruz G, Cruz A, Rocha A, Navarrete N, Flores G, Kato E, Sánchez S, Abarca LG, Winfield I, Bedia CM (1985) Manual de Ecología. Ed. Trillas, México.
3. Gold-Bouchot, G., T. Silva-Herrera and O. Zapata-Perez. 1993. Chlorinated Pesticides in the Rio Palizada, Campeche, México. *Marine Pollution Bulletin* 26(11): 648-650.
4. Gold-Bouchot, G., T. Silva-Herrera and O. Zapata-Pérez. 1995. Organochlorine Pesticide Concentrations in Biota and Sediments from Rio Palizada, Mexico. *Bulletin of Environmental Contamination and Toxicology*. 53(4): 554-561.
5. Noreña-Barroso E.; Gerardo Gold-Bouchot; Omar Zapata-Pérez and José L. Sericano. 1999. Polynuclear Aromatic Hydrocarbons in American Oysters (*Crassostrea virginica*) from the Términos Lagoon, Campeche, México. *Marine Pollution Bulletin* 38(8): 637-645.
6. Sericano JL, Atlas EL, Wade TL, Brooks JM (1990) NOAA's Status and Trends Mussel Watch Program: Chlorinated pesticides and PCBs in oysters (*Crassostrea virginica*) and sediments from the Gulf of Mexico, 1986-1987. *Marine Environmental Research* 29: 161-203.
7. StatSoft, Inc. (1991) CSS:STATISTICA. Tulsa, Oklahoma, USA.
8. Wade TL, Brooks JL, Kennicutt II MC, McDonald TJ, Sericano JL, Jackson TJ (1993) GERG trace organic contaminant analytical techniques. In: Sampling and analytical methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch projects 1984-1992, Vol. IV. Comprehensive descriptions of trace organic analytical methods. NOAA Technical Memorandum NOS ORCA 71, pp. 121-139.