Bull. Environ. Contam. Toxicol. (2000) 64:390-397
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DOI: 10.1007/s001280000013

Bulletin of Environmental Contamination and Toxicology

Persistent Organochlorine Pesticides (POPs) in Coastal Lagoons of the Subtropical Mexican Pacific

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Received: 15 May 1999/Accepted: 6 January 2000

As is the case for most countries, chemical pollution by pesticides was not important in Mexico prior to 1945; agricultural practices were traditional with little or no use of chemicals, except for cotton; in any case, only natural extracts as quinine and inorganic pesticides were used.

However, after the second world war, organochlorine pesticides, particularly DDT, were introduced and intensively used thereafter in the country both for agricultural purposes and as part of the internationally supported campaign to eradicate malaria. Recent information by the Secretary of Health, indicates that fifty-eight of the national territory including the most productive areas and 48 million people, are potentially subject to malaria disease,

One of the more important groups of organic pollutants is the persistent organochlorine pesticides. In Mexico, their presence in the environment, food and human tissues has not been considered an important problem. Furthermore, until very recently, the production, import and use of several of these pollutants were not restricted (Restrepo 1992).

This lack of information and awareness have also contributed to the widespread use of persistent pesticides in Mexico after they were withdrawn from other markets and, in some cases, even to the transfer to Mexico of the technology to produce and use these and other hazardous chemicals (Albert 1996). Now however, Mexico is a party to a North American regional action plan to reduce the use of DDT.

On the other hand, coastal lagoons of the Subtropical Mexican Pacific are among the most productive ecosystems mainly for shrimp fisheries; however, the increase of human settlements, the agricultural wastes as organochlorine pesticides and the direct discharges of sewage into the lagoons have given rise to severe pollution jeopardizing the ecology and biodiversity of these singular areas (Toledo 1994).

Objectives of this study were to determine the current state of pesticide pollution in coastal lagoons, originated by the intensive use of agrochemicals and their accumulation in sediments and bioaccumulation in fish and shrimps employed for human consumption, and to contribute with data to observe the trends of organic pollution in these fragile ecosystems.

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MATERIALS AND METHODS.

The study includes the most important coastal lagoons in the littoral fringe of Chiapas state, in the southwest of Mexican Pacific. These are the Chantuto-Panzacola (92°45’- 92° 55’ W longitude and 15°09'-15°17’ N latitude) and Carretas-Pereira lagoons (93°06'- 93°15' W latitude and 15°23'- 15° 32' N latitude) Figure 1.

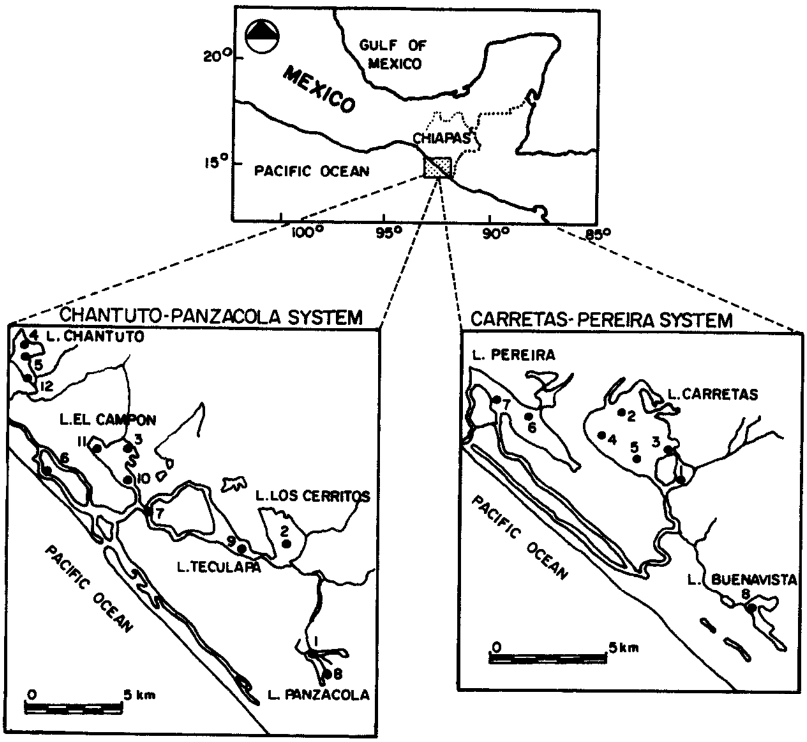


Figure 1. Sampling sites for sediments in coastal lagoons of Chiapas, Mexico.

The analysis of sediments included organochlorine pesticides (POP’s), the percentage of organic carbon and the type of sediments in 20 sampling sites, distributed in the areas of both lagoons. The sediment samples were obtained by using a Van Veen dredge of 5 kg capacity, performing three samplings during the dry seasons (April, 1997 and February, 1998) and rainy season (July, 1997).

The analytical procedures used for the extraction, purification and quantification of the chlorinated hydrocarbons in sediments were identical to those recommended by UNEP/FAO (1982). The sediments were extracted with 200 ml of bidistilled hexane for 8 hours in a soxhlet apparatus and the extracts were

reduced to 2 ml by means of a rotovapor prior to fractionation using chromatography columns (15 cm long. and 3 cm, ID) packed with fluorisil and eluted with hexane and a mixture of hexane-diethylether.
The volume was concentrated to 5 ml and analyzed by gas chromatography with capillary columns (Hewlett-Packard GC model 5890, 30 m x 0.25 mm ID x 0.25 µm bounded 5% phenyl-methylsilicone, fused silica columns). Nitrogen was the carrier gas with a flow of 1 mL/min, the oven temperature was programmed from 60°C-300°C with an increase of 8°/min and the injector temperature was 260° C.
For tissues of organisms (fishes and shrimps), the methodology used was the proposed by UNEP/FAO/IAEA, 1986. The analytical procedure is similar to the sediments one, however differences are in the use H_2SO_4 to hidrolize the lipids content, as well as the proportion of hexane-diethylether ether (3: 1 in volume) for the elution of pesticide fraction.
A mixture of 15 chlorinated hydrocarbons (Cat. 4-8858 Supelco Inc) was used as an external standard. Recovery yields were up to 92%. In order to verify the analytical performance for this study, our laboratory participated in an International Intercalibration Exercise for chlorinated hydrocarbons (IAEA, 1997) as one of the laboratories certified with acceptable analytical quality.
The grain size analysis was performed using the combined dry sieve and pipette method (Folk, 1974) and the percentage of organic matter was determined by titration using diphenylamine and 1N ferrous sulphate (Gaudette et al., 1974).

RESULTS AND DISCUSSION

Table1 shows total concentration of organochlorine pesticides in sediments for each sampling time, as well as the organic matter content and type of sediment for the systems considered in this study.

The silty sediment predominated in Chantuto-Panzacola lagoon, sandy types were only found in station **6, 7** and **10,** whereas station **4** showed clay-silt sediment. Organic matter presented a heterogeneous behavior with values ranging from 0.8 to 10.2%, the largest percentages corresponded to station **1** with 10.2% and station **11** with 8.7%. These values are relatively high for tropical coastal systems, indicative of their high productivity (Contreras, 1993).

Table 1 also summarizes the behavior of organochlorine pesticide levels for the samples collected in this lagoon. During the dry season (April 1997 and February 1998), the highest concentration were found in station **3** (317 ng g^{-1}) and station 9 (53 ng g^{-1}), whereas during the rainy season, station **7** was the one to record the highest concentration (161 ng g^{-1}).

The silty sediments also predominated in Carreteras-Pereira lagoon and the organic matter content showed an homogeneous distribution in this system (Table l), and most samples yielded high percentages, especially station **1** (9.4%), **5** (7.7%) 2 /7.3%), 3(7.2%), 4(7.5%) and 8(7.0%). Station **1,** is located in the El

Bobo system, has a low circulation that could favor concentration of organic material; besides, it is close to the location of the mouth of the Pampa del Bobo river, which in turn, receives waters from two more rivers, the Margaritas and the Progreso rivers.

Table 1. Type of sediment, % of Organic matter (%OM) and Total concentrations of persistent organochlorine pesticides (ng g^{-1}) in Chantuto-Panzacola and Carretas-Pereira lagoons, Chiapas, Mexico.

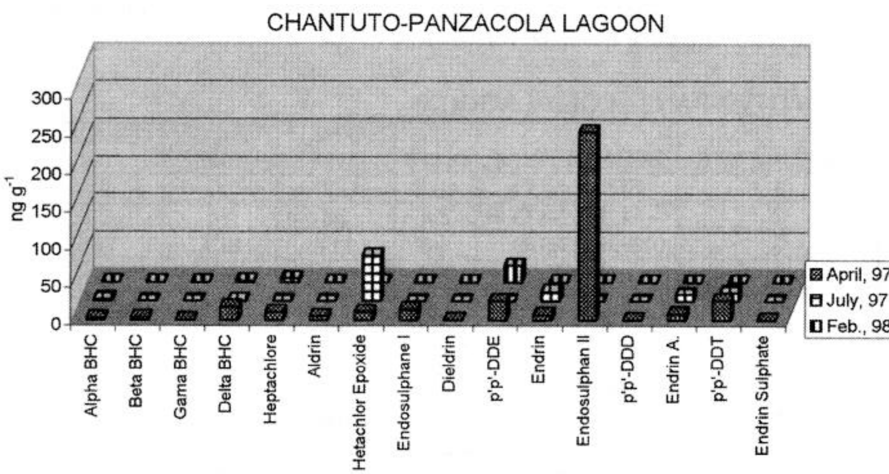
CHANTUTO-PANZACOLA LAGOON

SAMPLING SITE	SEDIMENT TYPE	% OM	APRIL, 1997	JULY, 1997	FEBRUARY, 1998
1	SLIME MUD	10.2	23	53	BDL
2	SLIME MUD	2.4	36	16	BDL
3	SLIME MUD	1.8	317	BDL	BDL
4	CLAY	7.0	14	BDL	BDL
5	SLIME MUD	7.6	17	BDL	BDL
6	SANDY MUD	0.8	34	BDL	45
7	SANDY MUD	1.5	64	162	36
8	SLIME MUD	6.0	BDL	10	18
9	SLIME MUD	2.2	BDL	102	53
10	SANDY MUD	3.2	BDL	12	22
11	SLIME MUD	8.7	BDL	4	4
12	SLIME MUD	7.2	BDL	13	4
CARRETAS-PEREIRA LAGOON					
1	SLIME MUD	9.4	18	BDL	BDL
2	SLIME MUD	7.3	190	BDL	BDL
3	SLIME MUD	7.2	224	BDL	114
4	SLIME MUD	7.5	68	15	10
5	SLIME MUD	7.7	77	16	16
6	SANDY MUD	5.0	BDL	118	22
7	SANDY MUD	2.0	BDL	138	855
8	SLIME MUD	7.0	BDL	BDL	38

BDL = BELOW DETECTION LIMIT = $<1 \times 10^{-12}$ g

The highest levels of organochlorine pesticides for the dry season was recorded at station **3** (224 ng g^{-1}) and during the rainy (July 1997) and dry (February 1998) seasons at station **7** (138 ng g^{-1} and 854 ng g^{-1}, respectively). The high values observed in station **7,** located in the Pereira estuary, are due to the hydrodynamics of the system and the high rates of evaporation that occur from January to April, which cause the agrochemical compounds to concentrate in a smaller water volume. From the studied systems, the Carretas-Pereira Lagoon was the one with the highest concentration of pesticides.

The Chantuto-Panzacola Lagoon yielded a correlation coefficient values (r) of 0.66 with sands, 0.48 with silt, and 0.33 with clay (February 1997). In the Carretas-Pereira Lagoon, r-values were 0.58 with sands, 0.54 with silt, and 0.53 with clay.



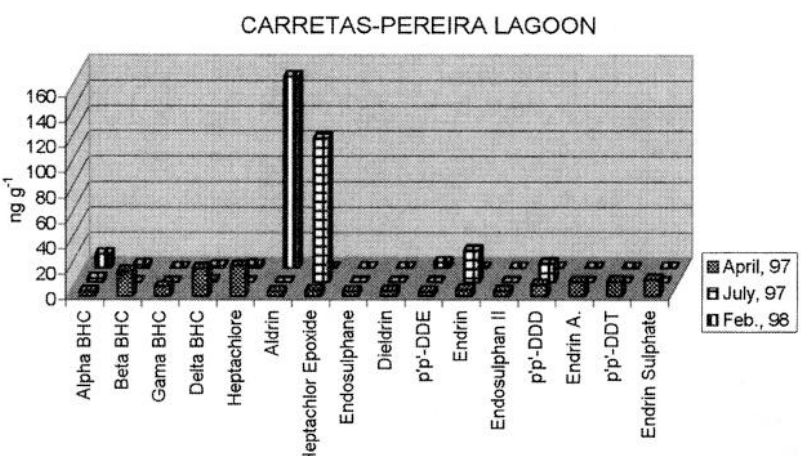


Figure 2. Individual concentrations of persistent organochlorinated pollutants in sediments from coastal lagoons in Chiapas, Mexico.

The highest correlation coefficients were evidenced with coarse material, which would indicate that the highest discharges of organochlorine pesticides occur in mainly sandy sediments and do not, necessarily reflect a relation between both parameters. Raoux and Garrigues (1991) argue that the association of organic compounds with sediments does not result from their hydrophobic properties but rather from the characteristics of the prevailing sediments in each area.

Figure 2 shows the single compounds most often found in the Chantuto-Panzacola lagoons during 1997-98. These were endosulphan II (250 ng g^{-1}) and p,p'-DDE (22 ng g^{-1}), both ocurred lagunar during the dry season (April 1997 and February 1998) and heptachlor epoxide (61 ng g^{-1}) during the rainy season (July 1997). Predominance of endosulphan can be explained since it is one of the authorized agrochemicals being used in Mexico (Albert, 1996). Its presence in the form of endosulfan II metabolite can be attributed to its higher octanol-water partition coefficient than endosulphan I, indicating a higher tendency to attach to sediments, especially colloids (Peterson and Batley, 1993). Also, some of the predominant metabolites, such as heptachlor epoxide, once incorporated by aquatic organisms, are more noxious than the original compounds (Kirk, et al., 1994).

In Carretas-Pereira Lagoon, the most evident compounds in sediments during the dry season were heptachlor (23 ng g^{-1}) and delta HCH (22 ng g^{-1}) during April 1997, and Aldrin (151 ng g^{-1}) in February 1998, whereas heptachlor epoxide was most abundant (113 ng g^{-1}) during the rainy season (July 1997). The high concentration of this agrochemical compound can be explained if we consider that cotton was one of the most important crops in Chiapas, for which organochlorine compounds, mainly heptachlor, were widely used (March et al., 1994). Although it has not been used for a couple of decades, traces of this compound can still be detected due to its high persistence in nature.

It is worthwhile to note that the highest pesticide levels were found during the dry season when high evaporation rates favored the concentration of these agrochemical compounds.

In general, the highest levels of organochlorine pesticides in sediments were recorded in the Carretas-Pereira Lagoon; discrepancies were also found regarding the type of predominating pesticides in the lagunar systems studied. Heptachlor, heptachlor epoxide, and Aldrin were the dominant compounds found in the Carretas-Pereira system, whereas endosulfan II, p,p'-DDE and heptachlor epoxide were the most abundant compounds in the Chantuto-Panzacola system. It should be noted that the use of most of these compounds has been restricted and even prohibited due to their high toxicity (Albert, 1996).

The observed differences can also be accounted for the different agrochemical compounds used for diverse agricultural purposes according to the type of crops cultivated around the lagoons and to the amount of pesticides applied.

In comparison with previous studies conducted in the Mexican Pacific, the total concentrations recorded in the sediments of Chantuto-Panzacola (14-262 ng g^{-1}) and Carretas-Pereira (18-993 ng g^{-1}) lagoons are extremely higher than those reported 15 years ago by Rosales et al. (1985) in the Yavaros Lagoon, state of Sonora, (1.85-10.45 ng g^{-1}) and the Huizache-Caimanero system (5.1-16.4 ng g^{-1}) both located in Sonora state.

Finally, because of their economic importance to the region, the concentrations of organochlorine pesticides were determined in white shrimp *(Penaeus vannamei)* and in the brown porgy *(Lutjanus novemfasciatus)* from both lagoons, using a set of 50 shrimps and 20 fishes from each lagoon.

In the Chantuto-Panzacola Lagoon, the concentrations were greater (94 ng g^{-1}) in muscle of the dark porgy *(L. novemfasciatus)* than those found in muscle (not detectable) and exoskeleton (21 ng g^{-1}) of the white shrimp *(P.vannamei).* The high amount of fat present in the fish could favor accumulation of these compounds due to the lipophilic character of these pesticides (Connell, 1988). Thus, the high pesticide levels found in these fishes can be explained by considering that crabs, shrimps, and small fishes are their main sources of food and pesticide traces present in these organisms can be bioconcentrated through one or various trophic levels of the food chain (Clark et al., 1988).

In the white shrimp *(P. vannamei)* muscle from the Carretas-Pereira Lagoon only heptachlor and p,p'-DDE were detected (5 and 2 ng g^{-1} respectively), whereas the exoskeleton only showed low delta HCH (2 ng g^{-1}) and p,p'-DDE (0.5 ng g^{-1}) values. The organochlorine pesticide concentrations in *Penaeus vannamei* muscle (7 ng g^{-1}) might result mainly from the feeding habits of these organisms, which allow them to ingest sediment particles with associated pollutants, such as organochlorine pesticides that accumulate in muscles due to their lipophilic properties.

Concentrations of pesticides in the white shrimp *(P. vannamei)* muscle from the Carretas-Pereyia Lagoon (9 ng g^{-1}) are higher than those reported by Rosales and Escalona (1983) for the same species from the Caimanero (1.02 ng g^{-1}) and the Moroncarit (1.4 ng g^{-1}) Lagoons in the state of Sinaloa.

In both species *(P. vannamei* and *L. novemfasciatus),* the organochlorine compounds were degraded at concentrations below the allowed limits for human consumption according to the standards established by international agencies (USFDA, 1984).

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