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Organochlorine Pesticide Residue Concentrations in Shrimps, Sediments, and Surface Water from Bay of Ohuira, Topolobampo, Sinaloa, Mexico

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Pesticides have a rather unique position among the chemicals that man encounters daily, in that they are deliberately added to the environment for the purpose of kiling or injuring some life form. Ideally their effect would be highly specific for undesirable target organisms and harmless to desirable nontarget organisms. Most of the chemicals used as pesticides are not highly selective but are generally toxic to other species, including man, and other desirable forms of life that share the environment.

The Mexican state of Sinaloa is characterized by a high fishing and agricultural activity. In spite of the important fishing production especially shrimp, in the last decade fluctuations and decrements were registered. Early in 1989, the shrimp yield decreased and as yet has not recovered. 1.260.019 tonnes were captured in 1994; a decrease of 19,5 % and 17,1 % compared to 1981 and 1989 respectively, the years with the highest recorded yields. This decrease was due to coastal pollution amongst other factors (SEMARNAP, 1995). The Ohuira Bay is the major lagoon of Topolobampo Lagoon System, with 125 Km at the Nortwest of the Mexican Pacific. It is located between 25° 30° and 25° 45° N, and 108° 50' y 109° 15' W and it is a Shallow lagoon with a average depth of 3 m (Phleger and Ayala-Castañares, 1969). It is connected to the Gulf of California through a shallow 3 km opening.There are freshwater inputs, waste agricultural waters and is probably the biggest source of agricultural pesticides, with respect to the other two lagoons that form the Topolobampo Lagoon System. (Phleger and Ayala Castañares, 1969).

The objective of the present work is to study the presence and the concentration of organochlorine pesticide residues in shrimp of the genus Penaeus sp, sediment and surface water in the Ohuira Bay.

MATERIALS AND METHODS

Water surface, sediments and shrimps were collected in 5 stations at the Ohuira Bay from July 1995 to June 1996. Water samples were collected in glass bottles (4 l of capacity), sediments were collected with a 0.01 m^2 Van

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Veen grab and the organisms (shrimps) were collected with a hand net, and then the samples were transported to the laboratory in Mazatlán, Sinaloa, México for further analysis.

Chlorinated organic compound concentrations were determined by the procedures described in (Holden and Marsden 1969; Elder et al. 1976; Fossato et al. 1983; APHA-AWWA-WPCF, 1992). The sediment and shrimps were freeze-dried before the analysis; approximately 30 and 20 g respectively (dry weight) were extracted with n-hexane during 8 hours in a soxhlet apparatus. The extracts were separated by alumina-silica column chromatography. The alumina was partially deactivated with 5 % distilled water (W/W) and the silica gel with 5 % distilled water (W/W). Approximately 2 cm of sodium sulfate and about 1 cm of activated granular copper (sediment samples) were added evenly over the silica gel to remove humidity and sulfur respectively. The organic compounds were separated and quantified by gas chromatography using a Shimadzu GC-14A gas chromatograph equipped with a detector of capture of electrons (ECD). A Restek RTX-5 of 30 m x 0.25 mm capillary column, and 0.33 mm film thickness 5 % dihenyl- 95 % dimethylpolisiloxane equivalent to OV-17 were used. The identification of compounds were deduced from their retention times and the quantification was based on peak height/area measurements as well as comparison with responses of reference standards. The detection limit was between 0.2 and 0.4 ng/L depending on the pesticide. Blanks were run for the entire procedure and blank corrections applied for each set of analysis.

RESULTS AND DISCUSSION

The percentage of organochlorine pesticides found in surface water is given in table 1. The highest percentages were for Endosulphane I (28 %), Lindane and Heptachlor epoxide (18 and 21 %, respectively), followed by DDT (17 %) and HHCδ (14 %) and a minor percentage of Aldrin (6.90), DDE, Dicloran and heptachlor (all 10 %).

The range of concentrations are given in the table 1. The highest concentration ranges correspond for the compounds DDT (0.018-3.75 μg/L), Endosulphane I (0.01-1.483 μg/L) and Lindane (0.009-1.26 μg/L) and the minor range of concentration for DDE (0.037-0.065 μg/L).

The concentrations of organochlorine compounds for months and station are given in the tables 2 and 3. The highest median concentration was for DDT (2.612μg./L) in July 95 and Lindane (1.260 μg/L) in November 95. The individual stations with the highest concentrations were stations 4 and 5 with 1.964 and 3.214 μg/L of DDT. The lowest concentration was found in station 2 for the pesticide Lindane (0.009 μg/L).

The highest percentages found were of Endosulphane I (60 %) and Heptachlor

with (24 %). The highest range of concentrations was 0.011-1.186 μg/g for Endosulphane I, and the lowest range of concentration was 0.0000879-0.063 μg/g for DDE (table 1).

The highest concentration found was of Endosulphane I with 0.721 μg/g in July of 95 and the lowest concentration was of DDE with 0.000132 μg/g in June of 1996. A high level of Endosulphane (0.793 μg/g) was found in the station 1, and the low level of DDE (0.00009 μg/g) was observed in the station 2 (tables 2 and 3).

Table 1. Organochlorine compound range of concentration in μg/L in surface water and in μg./g) in sediment and shrimp from Bay of Ohuira.

Surface Water			
Compound	D/A	D(%)	Range of concentration
Aldrin	2/29	6.90	BDL-0.218x10^{-3}
Lindane	5/29	17.94	0.020-0.270
δHCH	5/29	17.24	BDL-0.150
DDE	3/29	10.34	BDL-0.070
DDT	5/29	17.24	0.020-3.750
Dieldrin	4/29	13.79	0.090-0.270
Endosulphane I	8/29	27.59	0.010-1.260
Heptachlor epoxide	6/29	20.69	0.020-0.230
Heptachlor	3/29	10.34	0.010-1.480
Sediment			
δHCH	1/30	3	0.011-1.19
DDE	1/30	3	0.012-0.123
DDT	1/30	3	BDL-0.026
Endosulphane I	8/15	53	BDL-0.045
Heptachlor epoxide	2/30	7	0.020-0.132
Heptachlor	6/30	20	BDL-0.057
Shrimp			
Lindane	2/10	20	BDL-0.132
δHCH	3/10	30	0.0488-0.127
DDE	2/10	20	0.019-0.029
Endosulphane I	6/10	60	0.047-2.005
Heptachlor epoxide	1/10	10	BDL-0.058
Heptachlor	4/10	40	0.018-0.127

BDL= Below detection Limit A= Number of samples analized
D= Number of samples were the plagucide was detected

The aquatic organisms studied showed an accumulation of pesticides, the highest occurrence being for Endosulphane I (60 %) and Heptachlor (40 %) followed by DDE (20%) and Lindane (20 %). The highest levels of concentration were observed for Endosulphan I (0.0472-2.005 μg/g) and the lowest range of concentration were for DDE with 0.019-0.021 μg/g. (table 1).

Table 2. Organochlorine compounds found in surface water (μg/L), shrimp and sediment (μg/g) samples from Ohuira Bay and their concentrations. (means by station).

Stat.	Aldrin	Lindane	δHCH	DDE	DDT	Dichloran	Endosulphane	Endosulphane I	Heptachlor epoxide	Heptachlor
Surface water										
1	Nd	[2]0.2 (±0.024)	Nd	*0.07	*0.02	Nq	Nq	[2]1.28 (±0.29)	*0.14	Nq
2	Nd	*0.01	*0.16	*0.04	*1.52	Nd	Nd	*0.27	*0.12	Nq
3	Nd	[2]0.64 (±0.09)	Nd	Nd	*3.75	Nd	Nd	[2]0.27 (±0.02)	*0.23	*0.06
4	Nq	*0.03	*0.27	Nd	*1.96	Nd	Nd	[2]0.12 (±0.03)	[2]0.11 (±0.01)	[2]0.15 (±0.02)
5	Nd	Nd	[2]0.15 (±0.09)	*0.04	*3.21	*0.15	Nq	*0.11	*0.08	Nq
Sediment										
1	Nd	Nd	Nd	Nq	Nd	Nq	Nd	[4]0.79 (±0.05)	Nd	[2]0.09 (±0.004)
2	Nd	Nd	Nd	Nq	Nd	Nd	Nq	[3]0.41 (±0.03)	Nd	*0.02
3	Nq	Nq	Nq	Nq	Nd	Nd	Nd	[3]0.04 (±0.01)	Nd	*0.01
4	Nq	*0.03	*0.05	Nd	Nd	Nq	Nd	[3]0.08 (±0.04)	*0.02	*0.03
5	Nd	Nd	Nd	*0.06	*0.06	Nd	Nd	[3]0.02 (±0.01)	*0.13	Nd
Shrimp										
2	Nq	*0.08	[2]0.09 (±0.006)	*0.03	Nd	Nd	Nd	[2]0.4 (±0.03)	Nd	*0.12
5	Nd	*0.13	*0.05	*0.02	Nd	Nq	*0.05	[2]1.27 (±0.95)	*0.06	*0.10 (±0.01)

*= one value
2= Mean of two values
3= Mean of three values
4= Mean of four values
Nq= Not quantified
Nd= Not detected

Table 3. Organochlorine compounds found in surface water (μg/L), shrimp and sediment (μg/g) samples from Ohuira Bay and their concentrations (means by month).

Month	Aldrin	Lindane	δHCH	DDE	DDT	Dicloran	Endosulphan	Endosulphan I	Heptachlor epoxide	Heptachlor
Surface water										
Jul/95	Nd	Nd	Nd	Nd	^{4}2.61(±1.05)	Nd	Nd	Nd	*0.23	Nd
Sep/95	Nd	Nd	Nd	Nd	Nd	Nd	Nd	^{4}0.35(±0.05)	Nd	Nd
Nov/95	Nd	*1.26	Nd	Nd	Nd	Nd	Nd	^{4}0.57(±0.06)	Nd	Nd
Jan/96	Nd	Nd	*0.21	Nd	Nq	Nd	Nd	Nd	Nd	Nd
Apr/96	Nd	^{3}0.02(±0.006)	Nd	Nd	Nd	Nd	Nd	Nd	*0.02	*0.02
Jun/96	Nd	^{2}0.02(±0.003)	^{3}0.17(±0.09)	^{3}0.05(±0.01)	*0.02	*0.15	Nd	Nd	^{4}0.13(±0.05)	*0.17
Sediment										
Jul/95	Nd	Nd	Nd	Nd	Nd	Nd	Nd	^{3}0.35(±0.05)	Nd	Nd
Sep/95	Nd	Nd	Nd	Nd	Nd	Nd	Nd	^{5}0.32(±0.05)	Nd	^{2}0.04(±0.01)
Nov/95	Nd	Nd	Nd	Nd	Nd	Nd	Nd	^{4}0.21(±0.04)	Nd	*0.02
Jan/96	Nd	Nq	Nq	Nd	Nd	Nd	Nd	Nq	Nq	Nq
Apr/96	Nd	*0.26	*0.05	*0.06	*0.06	Nd	Nd	^{3}0.43(±0.06)	^{2}0.08(±0.08)	^{2}0.08(±0.02)
Jun/96	*0.0002	Nd	Nd	$^{3}10^{-2}(\pm 4x10^{-3})$	Nd	Nd	Nd	Nd	Nd	Nd
Shrimp										
Jul/95	Nd	Nq	Nq	Nd	Nd	Nd	Nd	Nd	Nq	Nq
Sep/95	Nd	Nd	Nd	^{2}0.02(±0.006)	Nd	Nd	Nd	^{2}1.11(±0.13)	Nd	*0.13
Nov/95	Nd	Nd	^{2}0.09(±0.03)	Nd	Nd	Nd	Nd	^{2}1.26(±0.96)	Nd	^{2}0.04(±0.02)
Jan/96	Nd	*0.13	Nd	Nd	Nd	Nd	Nd	*0.10	*0.06	^{2}0.06(±0.02)
Apr/96	Nd	*0.26	*0.05	Nd	*0.06	Nd	Nd	Nd	Nd	Nd
Jun/96	Nd	Nd	Nd	Nd	Nd	Nd	*0.05	Nd	Nd	Nd

*= One value 2= Mean of two values 3= Mean of three values
4= Mean of four values Nq= Not quantified Nd= Not detected

The month that levels of pesticide seems to increase in animals was November (Endosulphane I with 1.260 μg/g) and the lowest concentration was found in June (Endosulphane I with 0.047 μg/g) (table 3).

Due to the variations in pesticide residue concentrations found, it was impossible to conduct a statistical analysis of the spacial and time differences of the most prominent pesticides.

Recently the Ministry of environment and agriculture of México introduced some regulations on the use of pesticides. It is known by several research works on concentrations of organochlorine compounds that pesticides prohibited and/or restricted are being found in aquatic media of the country. Some of the concentrations of these compounds are above legally permitted levels in the water of the coastal system like the values reported by other authors: for example DDT (0.0003-4 ppm) Lindane (0.0003-0.75 ppm), Endosulphane (1.0 ppm) Endrin (1.5 ppm) Metoxichlore (1.4 ppm), Chlordane (2.1 ppm), and Isodrin(0.024-0.3 ppm) (Galindo 1987;1989; Galindo et al. 1992;1997; Rosales et al. 1985; SRH, 1974; Albert and Armenta, 1975; Vejar 1986; Vergara, 1986; CNA.CESA, 1992; De La Lanza, 1986; Hernández et al. 1994; Secretaria de Marina, 1987).

Our results agree with other authors (Galindo et al. 1999) that reported values of Endosulphane I (<0.20-73.20 ng/L in water; 10.0-118.5 ng/g in sediment and 57.93-210.01 ng/g in shrimp); Heptachlor (11.0-60.0 ng/g in sediment and 17.05-126.04 ng/g in shrimp); Lindane (0.20-1.60 ng/L in water and 48.02-132.05 ng/g in shrimp); Aldrin (0.95 ng/g in sediment); Dieldrin (2.06 ng/l/gin sediment); DDT (<0.4.0-1.57 ng/L in water); and DDE (19.0-29.03 ng//L in shrimp), who studied at a nearly location in different periods of time.

According to the results obtained in the present work, it can be seen that the number of pesticides in surface water and sediment are similar in appearance with the compounds observed in the *Penaeus sp* shrimp. The compound Endosulphane I had the highest occurrence in all matrixes, probably due to the fact that is an insecticide and acaricide widely used in agricultural activities (Barberá, 1989) and is a pesticide authorized in Mexico (Albert, 1996); and similar results have been reported for Botello et al. (2000).

It was also observed that the compounds Endosulphane I and Heptachlor had the highest occurrence in sediment and shrimps and the pesticides found in the surface water were Endosulphane I, Epoxide Heptachlor and Lindane. This can be related to the bentonic habitats of the shrimps, by ingestion and absorbption through of the organic and inorganic material particles.

In general no relation was found between the highest pesticide concentrations in the stations near to the source of agricultural waste (stations 1 and 2) where the sediment was finer (slimemud-Caly), and the stations away from the connection to the California Gulf, where the sediment is sandy and with

presence of bioclasts. Raoux and Garrigues, 1991 (cited in Botello et al., 2000) argue that the association of the organic compounds with sediments is not due to the result from their hydrophobic properties but rather from the characteristics of the prevaling sediments in each geographycal area.

Our study showed that in Ohuira Bay an important level of pollution by pesticides exists, and some of them were present in concentrations above legally permited levels and they are classified as forbiden and/or restricted to use. In conclusion, we suggest that it is imperative to implement stricter environmental controls in the bay in oder to minimise potential risks to other life forms including humans.

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