

## Organochlorine Compounds in Fish from a Farming Station in the Municipality of Páez, State of Zulia, Venezuela

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Optimum climatic conditions and very varied ichthic fauna provide bright prospects for the development of fish farming in Venezuela, where projects are currently under way in several regions of the country. In the basin of the Limón River, Zulia region, tests are being carried out with native species: herbivores: *Hypostomus watwata* (common name: Armadillo; Pisces *Loricariidae*), *Prochilodus reticulatus* (Bocachico; *Prochilodontidae*), *Potamorhina laticeps* (Manamana; *Curimatidae*), *Schizodon corti* (Cotí; *Anostomidae*); omnivores: *Mylossoma acanthogaster* (Pámpano de río; *Characidae*), *Petenia kraussii* (Niejita; *Cichlidae*), *Pimelodus clarias* (Bagre pintado; *Pimelodidae*); carnivores: *Hoplias malabaricus* (Guabina; *Erythrinidae*). Two other species, *Colossoma macropomum* (Cachama; *Serrasalminidae*), *Colossoma brachypomus* (Cachama, *Serrasalminidae*), have been brought in from the Venezuelan Llanos (Plains Region): as well as a hybrid obtained from *Colossoma macropomum* x *Colossoma brachypomus*.

Unfortunately, there are intense agricultural and cattle-farming activities in the Limón River basin, involving the use of pesticides, organochlorine compounds (OC) among them. This has led to the contamination of the water in the basin and, consequently, that of the ponds in which the fish are bred. Studies of the physical-chemical quality of the water and sediment in the ponds indicated the presence of:  $\alpha$ -BHC,  $\gamma$ -BHC, heptachlor,  $\beta$ -BHC, aldrin, endosulfan, DDE, dieldrin, TDE, endrin, DDT and methoxychlor (Urdaneta, 1989). These results, together with the detection of skeletal abnormalities, liver necrosis, kidney necrosis and benign and malignant tumors in the fish species being farmed (Urdaneta et al, 1987; Urdaneta, Quiñones, 1989; Aguilera, Urdaneta, 1992), have established the need for the present contribution.

### MATERIALS AND METHODS

The fish-farming lagoons are located on the north-east coast of the Lake Maracaibo Basin, specifically, in the Municipality of Páez, State of

Zulia, Venezuela. The feedwater comes from the Limón River, which rises at the confluence of the Guasare and Socuy Rivers. The fish samples were caught at random, every three months, between January, 1991 and July, 1992, from ponds chosen at random from a total of six. Ten fish were caught during each round of sampling. Each specimen was measured, weighed and identified. Each was then filleted (parietal muscles), wrapped in aluminum foil and stored at -20°C until analyzed not more than 48 hours later. 5-10g of each sample was weighed out and extraction and clean-up applied (Büther, 1990). Qualitative and quantitative analysis was done with electron-capture gas chromatography, using a Varian 3400 gas chromatograph with an electron capture detector and a Varian 4270 integrator. Optimum conditions for analysis were: Injection volume, 1 $\mu$ l; operating temperatures: injection block, 220°C; detector: 250°C; column: programmed at 200°C for 16 min and 210°C for 11 min; carrier gas was 5% argon-methane, at a pressure of 52psi and a flow rate of 32 ml/min; glass column: 2m long and 1/4" wide, with Chromosorb Q of 80-100 mesh coating, OV-17 at 2% and 1.95% of QF-1; time of analysis: 28 min.; detection limit of method: 0.001 ng.g<sup>-1</sup>.

All the solvents used in the analysis were pesticide grade, with no interfering residues. All glassware was washed with n-hexane before use. A standard solution of 11 OCs was prepared ( $\alpha$ ,  $\gamma$ ,  $\beta$ -BHC, heptachlor, aldrin, endosulfan, DDE, endrin, TDE, DDT and methoxychlor). In order to determine retention times, the following recovery percentages were obtained for each OC:  $\alpha$ -BHC, 97.8%;  $\gamma$ -BHC, 89.2%;  $\beta$ -BHC, 92.8%; heptachlor, 96.5%; aldrin, 98.1%; endosulfan 89.3%; DDE, 87.5%; endrin, 87.6%; TDE, 89.7%; DDT, 93.7%; methoxychlor, 98.7%. OC values were analyzed using the arithmetic mean ( $\bar{X}$ ).

## RESULTS AND DISCUSSION

During the sampling period, 210 fish were caught, 70 from each pond. Most abundant were *Colossoma* (hybrid), 62; *Petenia kraussi*, 37; *Pimelodus clarias*, 25; *Hypostomus watwata*, 23; *Schizodon corti*, 20 and *Prochilodus reticulatus*, 15. The greatest variety of specimens (13) was caught in Pond I, and the smallest (5) in Pond IV. Of the fourteen (14) species caught, five (5) are not farmed in the ponds, but were introduced by the pumps that provide the feedwater for the lagoons. These were: herbivores: *Astianox* sp (Sardina; *Characidae*), *Dasylicaria filamentosa* (Corroncho, *Loricariidae*); omnivores: *Aequidens pulcher* (Niejita, *Cichlidae*), *Rhamdia quelen* (Bagre negro, *Pimelodidae*); carnivores: *Roeboides* sp. (Manamana dientona, *Characidae*).

Tables 1, 2 and 3 present mean sizes, weights, and concentration of each OC per pond,  $\Sigma$ -BHC ( $\alpha$ -BHC +  $\gamma$ -BHC +  $\beta$ -BHC), heptachlor, aldrin, endosulfan, endrin,  $\Sigma$ -DDT (DDT + TDE + DDE) and methoxychlor.

Table 1. Muscular tissue, wet-weight concentrations ( $\mu\text{g.g}^{-1}$ ) of organochlorine compounds in fish from Pond I. January 1991-July 1992

Species	N	Size ( $\bar{X}$ ) (cm)	Weight ( $\bar{X}$ ) (g)	$\Sigma$ -BHC	Heptachlor	Aldrin	Endosulfan	Erdrin	$\Sigma$ -DDT	Methoxychlor
Schizodon corti	4	23.9	151.3	0.079	0.012	N.D.	0.023	0.023	0.057	0.369
Prochilodus reticulatus	15	22.8	201.4	0.081	0.030	N.D.	0.009	0.015	0.037	0.341
Colossoma (hybrid)	18	26.5	349.4	0.473	0.141	0.013	0.026	N.D.	0.758	1.186
Pimelodus clarias	10	18.8	47.8	0.305	0.014	0.006	0.029	0.019	0.192	1.079
Petenia kraussii	7	18.9	143.0	0.245	0.022	N.D.	0.093	N.D.	0.170	1.079
Hypostomus watwata	4	26.3	117.8	0.201	0.026	0.044	0.099	0.083	0.140	0.166
Hoplias malabaricus	3	38.1	814.0	0.831	0.047	N.D.	N.D.	N.D.	0.600	2.191
Roeboides sp.	4	35.5	621.3	0.584	0.064	N.D.	N.D.	N.D.	1.315	2.873
Potamorhina laticeps	3	26.8	295.1	0.178	0.047	0.198	N.D.	N.D.	0.161	0.171
Astianax sp.	2	11.0	12.5	0.499	0.029	0.064	N.D.	0.007	0.058	0.125
$\bar{X}$ TOTAL				0.347	0.043	0.033	0.052	0.017	0.349	0.958

$$\Sigma\text{-BHC} = \alpha\text{-BHC} + \gamma\text{-BHC} + \beta\text{-BHC}$$

$$\Sigma\text{-DDT} = \text{TDE} + \text{DDE} + \text{DDT}$$

Table 2. Muscular tissue, wet-weight concentrations ( $\mu\text{g/g}$ -1) of organochlorine compounds in fish from Pond III. January 1991-July 1992

Species	N	Size ( $\bar{X}$ ) (cm)	Weight ( $\bar{X}$ ) (g)	$\Sigma$ -BHC	Heptachlor	Aldrin	Endosulfan	Erdrin	$\Sigma$ -DDT	Methoxychlor
Schizodon corti	13	30.2	272.0	0.081	0.034	0.017	0.017	0.025	0.022	0.158
Colossoma (hybrid)	6	16.4	70.7	0.327	0.033	N.D.	0.022	N.D.	0.229	0.390
Pimelodus clarias	13	29.2	291.6	0.249	0.034	0.010	0.029	N.D.	0.185	0.149
Petenia kraussli	12	12.9	72.2	0.205	0.081	0.014	0.126	0.033	0.152	0.633
Hypostomus watwata	12	22.3	72.3	0.055	0.041	N.D.	0.092	0.007	0.040	0.151
Hoplias malabaricus	2	37.2	776.3	0.560	0.037	N.D.	N.D.	N.D.	0.758	1.783
Roeboidea sp.	3	32.1	335.4	0.897	0.044	N.D.	N.D.	N.D.	0.974	1.489
Potamorhina laticeps	3	32.5	614.2	0.279	0.095	N.D.	N.D.	N.D.	0.043	0.442
Astianax sp.	2	9.9	22.5	0.146	0.041	0.033	0.044	0.086	0.149	0.319
Aequidens pulcher	2	9.1	13.3	0.290	0.025	N.D.	0.023	0.062	0.312	0.261
Dasylicaria filamentosa	2	32.7	166.7	0.110	N.D.	N.D.	N.D.	N.D.	0.077	0.451
$\bar{X}$ TOTAL				0.291	0.042	0.068	0.032	0.019	0.267	0.659

$$\Sigma\text{-BHC} = \alpha\text{-BHC} + \gamma\text{-BHC} + \beta\text{-BHC}$$

$$\Sigma\text{-DDT} = \text{TDE} + \text{DDE} + \text{DDT}$$

Table 3. Muscular tissue, wet-weight concentrations ( $\mu\text{g/g}$ -1) of organochlorine compounds in fish from Pond IV. January 1991-July 1992

Species	N	Size ( $\bar{X}$ ) (cm)	Weight ( $\bar{X}$ ) (g)	$\Sigma$ -BHC	Heptachlor	Aldrin	Endosulfan	Endrin	$\Sigma$ -DDT	Methoxychlor
Schizodon corti	3	30.2	288.9	0.122	0.065	0.033	0.018	N.D.	0.043	0.230
Colossoma (hybrid)	38	22.8	228.1	0.267	0.065	0.033	0.134	N.D.	0.286	0.882
Petenia kraussii	18	17.2	111.9	0.192	0.105	0.085	0.232	0.019	0.192	0.523
Hypostomus watwata	7	37.4	268.5	0.068	0.044	0.019	0.054	0.008	0.039	0.117
Mylossoma acanthogaster	4	28.4	397.0	0.248	0.019	0.014	0.031	0.029	0.014	0.935
$\bar{X}$ TOTAL				0.179	0.040	0.037	0.094	0.011	0.115	0.538

$$\Sigma\text{-BHC} = \alpha\text{-BHC} + \gamma\text{-BHC} + \beta\text{-BHC}$$

$$\Sigma\text{-DDT} = \text{TDE} + \text{DDE} + \text{DDT}$$

In fish from Pond I, methoxychlor reached the highest total mean accumulation,  $0.958 \text{ ug.g}^{-1}$ , followed by  $\Sigma$ -DDT,  $0.349 \text{ ug.g}^{-1}$  and  $\Sigma$ -BHC,  $0.347 \text{ ug.g}^{-1}$ . Methoxychlor concentrations were highest in *Roeboides sp.* ( $2.873 \text{ ug.g}^{-1}$ ) and *Hoplias malabaricus*, ( $2.191 \text{ ug.g}^{-1}$ );  $\Sigma$ -DDT in *Roeboides sp.* was  $1.315 \text{ ug.g}^{-1}$ , with DDT predominating. ND was taken as zero for calculating the arithmetical mean, represented by aldrin at the level of the following species: *Schizodon corti*, *Prochilodus reticulatus*, *Petenia kraussii*, *Hoplias malabaricus*, and *Roboides sp.*; endosulfan in the following species: *Hoplias malabaricus*, *Roeboides sp.*, *Potamorhina laticeps* and *Astianax sp.*; and endrin in *Colossoma* (hybrid), *Petenia kraussii*, *Hoplias malabaricus*, *Roboides sp.* and *Potamorhina laticeps*.

In the fish from Pond III, methoxychlor reached the highest total mean accumulation,  $0.659 \text{ ug.g}^{-1}$ , followed by  $\Sigma$ -BHC,  $0.291 \text{ ug.g}^{-1}$  and  $\Sigma$ -DDT,  $0.267 \text{ ug.g}^{-1}$ ; methoxychlor was highest in *Hoplias malabaricus*, ( $1.783 \text{ ug.g}^{-1}$ ), *Roeboides sp.*, ( $1.489 \text{ ug.g}^{-1}$ ); *Pimelodus clarias*, ( $1.149 \text{ ug.g}^{-1}$ ), this was followed by  $\Sigma$ -DDT, in *Roeboides sp.*,  $0.974 \text{ ug.g}^{-1}$ , with the highest contribution coming from DDT;  $\Sigma$ -BHC in *Roeboides sp.*,  $0.897 \text{ ug.g}^{-1}$ ; with the isomer  $\alpha$ -BHC predominating; likewise, endrin evidenced the smallest mean total concentration in the fish from Pond III,  $0.019 \text{ ug.g}^{-1}$ ; ND was also the smallest mean concentration per species, in aldrin: *Colossoma* (hybrid), *Hypostomus watwata*; *Hoplias malabaricus*, *Roeboides sp.* and *Potamorhina laticeps*; in endosulfan: *Hoplias malabaricus*, *Roeboides sp.* and *Potamorhina laticeps*; the same was observed for endrin in *Colossoma* (hybrid), *Pimelodus clarias*, *Hoplias malabaricus*, *Roboides sp.*, and *Potamorhina laticeps*.

The results from Pond IV showed that the behavior of total mean OC accumulation in fishes was similar to the one evidenced by OC in the fishes of Pond III. Methoxychlor showed the highest mean concentration in *Mylossoma acanthogaster*,  $0.935 \text{ ug.g}^{-1}$ ; *Colossoma* (hybrid),  $0.882 \text{ ug.g}^{-1}$ ; and *Petenia kraussii*,  $0.523 \text{ ug.g}^{-1}$ ; this was followed by  $\Sigma$ -DDT in *Colossoma* (hybrid),  $0.267 \text{ ug.g}^{-1}$ , with DDE predominating;  $\Sigma$ -BHC in *Mylossoma acanthogaster*,  $0.248 \text{ ug.g}^{-1}$ , with  $\alpha$ -BHC predominating; and endosulfan in *Petenia kraussii*,  $0.232 \text{ ug.g}^{-1}$ . The smallest total mean concentration per species was shown by endrin,  $0.011$ ; as before, ND was the smallest total mean accumulation per species in endrin for *Schizodon corti* and *Colossoma* (hybrid).

In general, methoxychlor,  $\Sigma$ -DDT through DDT and its metabolites TDE and DDE and  $\Sigma$ -BHC, represented by the isomers  $\alpha$ -BHC,  $\gamma$ -BHC and  $\beta$ -BHC, presented the highest total mean concentrations. It was also observed that the highest mean OC concentrations were presented by the carnivores, *Roeboides sp.* and *Hoplias malabaricus* followed by omnivores, *Pimelodus clarias*, *Mylossoma acanthogaster*, *Colossoma* (hybrid) and *Petenia kraussii*. However, it should also be pointed out that (ND) was not detected in some fish. The analytic method used did not detect (ND) the presence of aldrin, endosulfan and endrin in some species, carnivores, omnivores and herbivores among them.

In 1987 and 1988, Urdaneta (1989) determined levels of organochlorine compounds in water and sediments from fish-farming ponds in the Municipality of Páez. A comparison of those results with those of the present contribution shows the identification of the same type of OC. As expected, there was greater concentration in the muscular tissue of the fishes. It was thus observed that at least the same types of OCs are still being used in the area, because they were identified in the young fish caught in the farming lagoons. Such is the case of the presence of DDT as DDT and not only as metabolites (DDE; TDE). Regulation No. 4 of the Environmental Act (MARNR, 1977) establishes the limits stipulated in Venezuela for OC concentrations in seas, estuaries and fresh water dedicated to farming of molluscs and fish. A comparison of the concentrations found in the lagoons shows that all values >ND went over the legal limits since the regulation establishes that the presence of OCs should not be detected.

Not only is it important to point out that the levels found confirmed OC contamination, but also that compounds such as Endosulfan and DDT cause internal necrosis in fish (Sinderman, 1979). Likewise, BHC, heptachlor, aldrin, DDT and their metabolites produce tumors in laboratory animals. (O.P.S. and O.M.S., 1982; IMCO et al., 1989; IMCO et al., 1991). It has also been determined that under certain environmental conditions, DDT can be transformed into polychlorinated biphenyls (O.P.S. and O.M.S., 1982). These may trigger off the fish's cytochrome P450 system, the one responsible for activating the carcinogenic system in the presence of certain compounds (Miyauchi, Uematsu, 1987). McCain et al., (1991) also found adverse biological side effects in fish after they were exposed to OCs in estuarian ecosystems.

The evidence indicates that there exist potential conditions for producing sublethal effects on the fish being bred in the fish-farming lagoons.

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