

Residues of Organochlorine Insecticides in Fish from Polluted Water

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The organochlorine insecticides (OC) have been extensively used in Iraq over the past 25 years in malaria control program and different agricultural practices, before they were banned in 1976. A National Pesticide Monitoring Program was initiated by the Biological Research Centre/Baghdad in 1981 to determine the residue levels of these persistent compounds in the environment and biota in this country. Published works of this program indicated their presence in different food items (Al-Omar et al 1985 a & b) as well as in human milk (Al-Omar et al 1985 c).

The purpose of the present work is to find out the OC residue levels in different fish species collected from a polluted region in Diyala River (Rustamiya / Baghdad) where the largest sewage treatment plant in Baghdad discharges treated water. Al-Omar et al (1985 d) reported the presence of OC residues in the effluent water of this plant.

MATERIALS AND METHODS

Seventy fish 1-3 years old, of 11 different species were collected in 30 different collections from Oct. 1983-July 1984 from the same sampling station on the lower part of Diyala River at Rustamiya. The same muscular tissue(100-200 gm edible portions) of each sample was chopped separately and immediately after sampling. Fat was extracted with petroleum ether according to AOAC method (AOAC 1970)

All solvents used were redistilled in glass and tested by electron capture-gas chromatography so that the recorder pen deflection should be less than 1 mm from baseline for 2-45 min after injection. Florisil (60-100 mesh, PR grade, Merck, Darmstadt, W.Germany) activated and stored according to AOAC method was used for column chromatography. Standard pesticide mixture containing 13 different chlorinated pesticides at picogram level in isooctane was obtained from Supelco S.A. (Switzerland).

Subsamples of 5 gm fat were weighed out, extracted with acetonitrile which is then diluted with water, pesticide residues are extracted into petroleum ether and purified by column chromatography on florisil, eluting with mixture of petroleum and ethyl ethers (AOAC 1970). Aliquots of 5 μ l extract were injected using Hamilton microsyringe(Hamilton Bonaduz AG) into a Pye-Unicam gas chromatograph equipped with electron capture detector and a glass column (1.5 M x 4 mm i.d.) packed with 1.5% OV-17 + 1.95% OV-210 on Chromosorb W HP (Supelco S.A.). Operating temperatures were 200°,220° & 300° C for column, injector and detector respectively. Mixture of 90+10% argon/methane was used as a carrier gas at a flow rate of 30 ml/min.

Determination of OC residues was based on peak area given by a Pye-Unicam -Philips CDP-4 computing integrator coupled to the gas chromatograph. Confirmation of the results was performed by TLC according to AOAC procedure (AOAC 1970).

Recoveries from fortified samples at 1 ppm each level were in the range of 80-95% on this method, except for heptachlor 117% and heptachlor epoxide 118.2%.

RESULTS AND DISCUSSION

Among the thirty composite samples collected, 12 were consisted of only one species (one fish) which was mostly Chondrostoma regius. others consisted of 2-5 species, however only one composite consisted of 6 species. Number of fish caught for each species were as follows Chondrostoma regius 19, Liza abu 11, Barbus grypus 11, B. xanthopterus 6, B. luteus 6, B. belaweyi 4, Mystus pelusius 4, Aspius vorax 2, Heteropneustes fossilis 3, Cyprinus caprio 2, Garra ruffa 2. All are fresh water fish. Informations on the feeding behaviour for most of these native species seems to be very scarce. Remarkable differences were observed in the average percent of fat content even within the same species, the highest average value was 4.25% in Garra ruffa (muscular tissue) while the lowest was 0.47% in Mystus pelusius (muscular tissue). Higher fat contents were observed in older fish, this fact was also mentioned by Youngs et al (1972). Hence they were grouped into high fat content group (> 2%) and low fat content group (< 2%) as represented in TABLE 1 alongwith the average values for residues of total BHC, chlordane, heptachlor, aldrin and DDT reported as ppm on fat basis.

All OC residues showed high percentage of occurrance 90-100%. Concentrations detected were also high especially those of chlordane and DDT where exceptionally high average levels of these two insecticides were detected particularly in low fat content group. Generally speaking higher levels of all insecticide residues were detected in low fat content fish of all species.

Chlordane including cis-and trans-chlordane and hydroxychlordane showed the highest average residue level 73.495 ppm (fat basis) in low fat content group of the species B.xanthopterus, and 68.816 ppm (fat basis) in high fat content group of the same species, TABLE 1, and the levels in low fat content groups of all species were almost two folds higher than those of the high fat content groups. Residues of this insecticide and other related

compounds have been detected in different fish species in other countries (Johnson 1968, Castillo et al 1978, Miyazaki et al 1980, and Horii et al 1981).

DDT (the sum of o,p'- and p,p'-isomers of DDT,DDE and DDD) is the second highest level to be detected in fish from this area, again higher levels were found in low fat content group, where 26.629ppm (fat basis) in *Mystus pelusius*,25.417ppm in *Aspius vorax*,and 20.334 ppm in *B.xanthopterus*were reached in the low fat content group and 17.325 ppm in *H. fossilis*, 12.097 ppm in *Liza abu* and 10.102 ppm in *B.luteus*were detected in high fat content group. This insecticide has been widely investigated being the most common residue in fish as well as other biota and environmental samples, and extensive work can be fond in this respect (Edward 1976).

BHC (the sum of α -, β - and δ -isomers) was foud also at higher levels in low fat content fish of the species H.fossilis and B.luteus where an average values of 7.083 ppm and 6.103 ppm respectively were reached.

Heptachlor(including its epoxidation product heptachlor epoxide) and aldrin were found at lower levels which were also showing higher values in low fat content fish of all species, TABLE 1. Dieldrin as an insecticide and a metabolite of aldrin could not be detected in any of the samples examined.

Henderson et al (1971) were unable to correlate OC residue levels with different species of fish. Youngs et al (1972) stated that older fish could built up higher residue levels.

The purpose of this survey was to determine the background levels of OC compounds in different fish species collected from a river which was previously considered as an extensively polluted area with chlorinated hydrocarbon insecticides due to the discharge of large quantities of treated water containing residues of these compounds, from sewage treatment plant (Al-Omar et al 1985 d). They were considered as relatively low concentrations particularly after the dilution given by Diyala River, except in Mach and April when a special condition of zero dilution might occur because the Tigris is at high level in this time can back up the Diyala(Edgles and Allen 1981) thus exposing aquatic life in this way to higher concentrations of these compounds which will be accumulated in fish both by the bioaccumulation through food chain and through direct absorption from water (Bevenue 1976).

It is known that OC compounds in water are taken up very rapidly by living organisms. Holden(1962) and Marth (1965) demonstrated that fish can take up 80-90% of the DDT from water by gills and since the exposure to OC residues in this case , in our study, is the same for both low and high fat content groups, thus, build up of high residue levels in low fat content group could most likely be due to the direct absorption from water and sediments rather than by the bioaccumulation through food chains, taking into considerations the absence of definite informations on the feeding behaviour of most of these native species.

Table 1:Organochlorine Residue Levels in Different Fish Species Collected from Diyala River/Baghdad-1984.

Species of	Aver. of fat	Average	levels in ppm (μ g/gm fat of edible portions) \pm 5.b.	/gm tat ot edit	ie portions) ±	S.D.	Group of fat
fish	cont %	внс1	Chlordane ²	Heptachlor ³	Aldrin	Total DDT	content
Chondrostoma	3.84	1.547±0.802	20.432±16.212	1.353±1.266	0.876±0.720	6.467± 3.811	~
regius	1.06	4.884±4.571	44.465±38.354	2.465±1.214	2.284±1.078	14.286±10.805	~ 2
Liza abu	2.40	5.026±2.346	21.889± 7.590	1.401±0.635	2.217±1.097	12.097± 5.982	>5
	0.94	5.938±5.682	29.982±19.983	3.846 ± 3.623	1.806±1.453	13.003± 4.862	<2 <2
Barbus grypus	3.03	1.005±0.476	10.478± 6.443	0.333 ± 0.316	0.925 ± 0.616	3.768± 2.621	75
	0.89	4.233±2.887	20.892±10.601	1.194 ± 0.494	0.807±0.801	9.034± 2.793	< 2
B. xanthopterus	3.05	2.011±0.292	13.462± 4.191		0.805 ± 0.825	7.072± 1.009	>5
	1.44	2.644±1.284	73.495±40.272	2.303±1.713	1.449±1.505	20.334±13.302	~
B. Luteus	2.10*	1.231	16.550	0.970	0.711	10.102	>2
	09.0	$ 6.103\pm5.039 $	27.516 ± 12.201	_	0.752 ± 0.689	14.235± 9.613	42
B.belaweyi	1.36	1.553±1.214	46.532±11.395	2.707±0.794	2.342±0.111	10.042± 3.628	\$
Mystus pelusius	0.47	3.468 ± 3.210	25.451 ± 6.851	1.367 ± 0.234	0.468±0.662	26.629±19.269	< 2
Aspius vorax 1.76	1.76	2.956±1.798	41.521± 8.461	1.765 ± 0.567	1.879±0.619	25.417±15.462	<2 -
Heteropneustes	2.58*	4.372	68.816	5.205	0.426	17.325	75
fossilis 1.80*	1.80*	7.083	57.657	4.012	3.760	10,490	<2 -
Cyprinus caprio	3.67	1.832±0.831	36.384±16.044	1.370±0.051	1.747±1.153	10.195±1.086	>2
Garra ruffa 4.25	4.25	1.189±0.277	5.975± 1.376	1.085±1.207	1.061±0.596	6.607±3.450	75

^{1.}Sum of α' , β - and α -isomers; 2. Sum of cis-, trans- chlordane and hydroxychlordane; 3.Sum of heptachlor and heptachlor epoxide; 4. Sum of o,p'- and p,p'-isomers of DDT, DDE and DDD. (*) Results of only one sample.

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