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Organochlorine Pesticide Residues in Fish from the Shatt al-Arab River, Iraq

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Organochlorine pesticides are a class of toxic compounds characterized by their relative chemical and biological stability, hence persistence in the environment. Furthermore, these compounds have a high lipid/water partition coefficient resulting in biomagnification (Risebrough *et al.* 1967). Consequently organochlorine pesticides have been placed on "the top of the list" of potential environmental hazards. The wide-spread occurrence of these compounds as environmemtal pollutants have been well documented for all major terrestial, fresh water and marine environments. At present almost nothing is known about the existence of these pesticides and their related compounds in the Shatt al-Arab River which drains an intensively farmed areas of the Tigris and the Euphrates River Basins. However, relatively low levels of DDE residues were detected in the oyster, *Pinctada margaratifera*, collected from the coast of Kuwait, an area influenced by the discharge of the Shatt al-Arab River (Anderlini *et al.* 1981). The work described in this paper was conducted in order to establish the background residue levels of organochlorine pesticides in two commercially important fish species from the Shatt al-Arab River. The cyprinid (*Barbus xanthopterus*)(lean fish, residental species) and the indian shad (*Tenualosa ilisha*)(medium fatty, migratory species).

MATERIALS AND METHODS

Analytical standards for organochlorine pesticides were obtained from Supelco Inc. (Supelco S.A.). All solvents were redistilled in an all-glass-still prior to use and tested by EC-GLC. Florisil was supplied by Merck (Merck, Darmstadt, W-Germany) activated and stored according to the procedure described in the "Analysis of Pesticide Residues in Human and Environmental Samples" (U.S. Environmental Protection Agency 1980).

Six composite samples of the cyprinid have been collected from the Shatt al-Arab River (Station I) during April 1984. Comparison with that immediately influenced by pesticides source was achieved by analyzing the cyprinid of the same age group obtained from Hor al-Hammar Lake (Figure 1). At least five composite samples of the indian shad were also captured from Station I in

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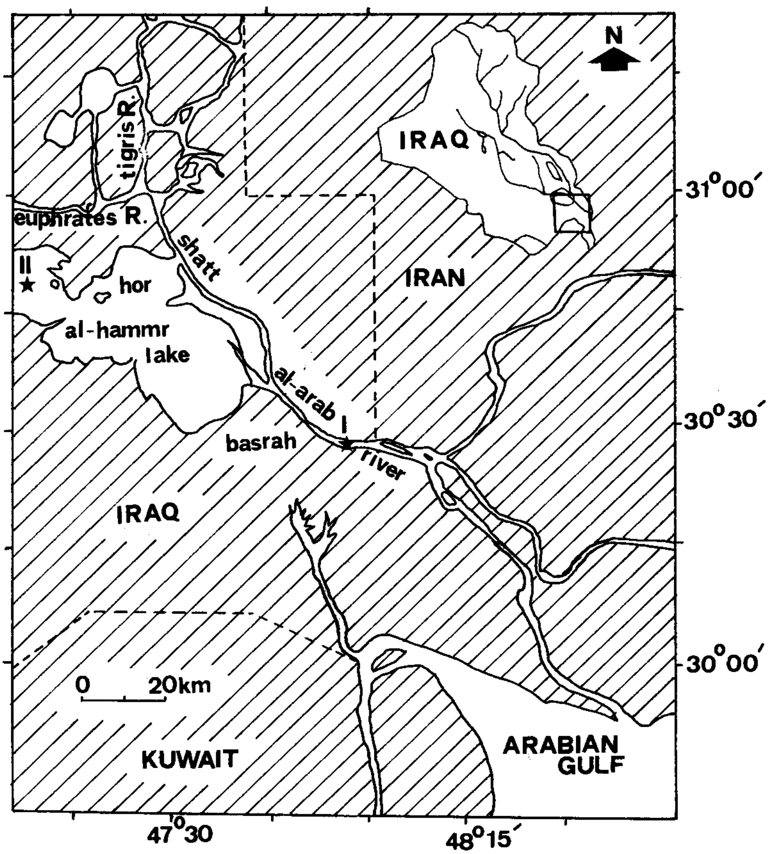

Figure 1. Map of the Shatt al-Arab River showing position of stations.

three occassions (spring, summer and autumn 1984) in order to gain some knowledge about the seasonal variations of organochlorine pesticide residues in these fishes. Gerenrally, each composite cosisted of at least 10 uniform-size adult fish of the same species. Fish samples (edible portion only) were pooled and then macerated in a food chopper from which at least 6 replicates of 150g of the cyprinid and 60g of the indian shad were taken. Pesticide residues were extracted according to AOAC Mills procedure (AOAC 1975). Exactly 1µl was injected into a Pye-Unicam model GCV gas chromatograph (Pye-Unicam, Cambridge, England) equipped with a constant current Ni-63 electron capture detector and a glass column (1.5m X 4mm i.d.) packed with 1.5% OV-17 + 1.9% OV-210 chromosorbW HP (Supelco S.A.). Operating temperatures were 200, 220 and 300°C for column, injector and detector respectively. A mixture of 90+10% argon/methane was used as a carrier gas at a flow rate of 30ml/min. Ouantification of peaks and identification of pesticides in chromatograms were achieved by direct comparison with a standard calibration graph plotted against peak area given by a Pye-Unicam-Phillips CDP-4 computing integrator coupled to the gas chromatograph.

Results were semiconfirmed in about 10% of the samples by injection into a second glass column packed with 10% DC-200 on Gas Chrom Q (80-100)(Chrompack, Holland). Data of gas chromatographic analysis were further confirmed by TLC following AOAC procedure. Procedural blanks, consisting of all reagents and glassware used during the analysis, were periodically determined. For fish tissues, no compound that interferred with organochlorine pesticides was detected, therefore, the sample values were not corrected for procedural blank. Recovery studies with fortified samples have indicated that recovery efficiency exceeded 85% for all compounds measured except βBHC(65%), lindane (45%) and heptachlor (70%). Results were not adjusted for percent recovery.

RESULTS AND DISCUSSION

Mean concentrations of endrin, ΣDDT(DDE+DDD), dieldrin (+aldrin) and heptachlor(+heptachlor epoxide) residues in the cyprinid from the Shatt al-Arab River are given in Table-1.

Table-1. Average concentrations (ppb wet weight) of organochlorine pesticide residues in *Barbus xanthopterus* (muscle tissues) collected from the Shatt al-Arab River, and comparison with those from Hor al-Hammar Lake.

Composite number	% Fat	Dieldrin[1]	Heptachlor[2]	Endrin	Chlordane[3]	ΣDDT[4]
The Shatt al-Arab River (Station I)						
1	2.8	2	2	35	nd	6
2	3.1	2	2	24	nd	17
3	3.3	nd	nd	1	nd	13
4	2.9	nd	4	2	nd	18
5	3.0	nd	8	27	nd	13
6	3.0	2	4	5	nd	13
Mean*	3.0	2	3	16	nd	13
Range	(2.8-3.3)	(nd-2)	(nd-8)	(1-35)		(6-18)
Hor al-Hammar Lake (Station II)						
1	2.8	3	5	13	15	34
2	2.8	13	2	355	20	31
3	2.9	12	nd	276	64	18
4	3.1	10	13	148	141	125
5	3.2	nd	5	40	93	177
6	3.1	10	nd	287	47	33
7	3.0	7	nd	96	30	11
8	3.1	4	nd	20	49	33
Mean*	3.0	8	6	154	58	57
Range	(2.8-3.1)	(nd-13)	(nd-13)	(13-141)	(15-355)	(11-177)

1. Sum of aldrin and dieldrin; 2. Sum of hepatachlor and heptachlor epoxide; 3. Sum of *cis*-and *trans*- chlordane; 4. Sum of DDE and TDE only in Station I, or DDE+TDE+DDT in Station II; nd = None detected; * = Means of detectable values only.

However, the present study has shown that residues of βBHC, lindane and chlordane were below the detection limit of 1ppb wet weight in these fishes.

Endrin is considered to be the most toxic of all commercial organochlorine insecticides (Johnson and Finley 1980) and was the most prevalent compound in the cyprinid from the Shatt al-Arab River. Thus residue levels ranged from 1 to 35ppb wet weight with an average concentration of 16ppb.

Both *p,p'*-DDT and *o,p'*-DDT were below the detection limit of 1ppb wet weight which suggest that there was no recent input of DDT (Aguilar 1984). Apparently transported DDT undergoes both metabolic conversion (Bridges *et al.* 1963) and dehydrochlorination (Hannon *et al.* 1970) in the warm, rather alkaline waters of the Shatt al-Arab River. These phenomena may be account for the proportion of DDT and its metabolites encountered in the cyprinid (ΣDDT comprised the two isomeres *p,p'*-DDE and *p,p'*-DDD only; DDE:TDE ratio was 1:4).

Aldrin and dieldrin were both officially banned in Iraq in 1976, nevertheless dieldrin residues were expected to persist due to its long use for agricultural and public health purposes. However, occurrence of dieldrin in the cyprinid from the Shatt al-Arab River was approximately 50%, with residue levels at or near the detection threshold (average concentration was 2ppb wet weight). It is interesting to note that aldrin residues were not detected in any of the samples, which may be due to active conversion of aldrin to dieldrin (Ludke *et al.* 1972).

In approximately 15% of the analyzed cyprinid from Station I, heptachlor residues were below the detection limit of 1ppb wet weight. However, in the remainder 85% residue levels were relatively low ranged from 1 to 8ppb wet weight with an average concentration of 3ppb. Heptachlor has never been used in Iraq, however, the detection of heptachlor residues in these fishes may be attributed to chlordane formulations which are known to contain heptachlor to an extent of 10-11% (Braun and Frank 1980).

In Hor al-Hammar Lake (Station II) pesticides have been applied close to or over water, causing fairly direct contamination of fishes (Johnson 1968). Comparison of organochlorine pesticide residue levels in the cyprinid sampled from the Shatt al-Arab River with those from Hor al-Hammar Lake (Table-1) have shown that:

1] Significantly higher concentrations were detected in the fishes from Hor al-Hammar Lake. Thus average concentrations of endrin, ΣDDT, dieldrin and heptachlor were 154, 57, 8 and 6ppb wet weight respectively.

2] In addition to DDE and TDE; *p,p'*-DDT has also been detected in approximately 50% of the fishes here reflecting continuing inputs (Frank *et al.* 1974).

3] Chlordane residues were also confirmed in the cyprinid from Station II, residue levels ranged from 15 to 141ppb wet weight with an average concentration of 58ppb.

Relatively higher concentrations of endrin, ΣDDT, dieldrin and heptachlor were detected in the indian shad, moreover, residues of βBHC, lindane , *cis-* and *trans*--chlordane and *p,p'*-DDT were also confirmed in these fishes. Thus average values of endrin, ΣDDT, dieldrin, heptachlor, chlordane, βBHC and lindane were 90, 92, 26, 17, 31, 12 and 5ppb wet weight respectively (Table-2). The rather elevated concentrations may be due to the fact that the indian shad muscle tissues contain higher fat content than that of the cyprinid. It has been well established that maximum occurrence of organochlorine pesticides coincide with the high lipid content (Rickard and Dulley 1983). Furthermore, migratory indian shad might have been exposed to pesticides from additional source/s where they are still used in agriculture.

Table-2. Seasonal average concentrations (ppb wet weight) of organochlorine pesticide residues in *Tenualosa ilisha* (muscle tissues) captured from the Shatt al-Arab River.

Composite number	% Fat	βBHC	Lindane	Dieldrin[1]	Heptachlor[2]	Endrin	Chlordane[3]	ΣDDT[4]
Spring 1984:								
1	6.2	nd	7	126	18	18	46	114
2	6.2	nd	15	5	26	15	34	144
3	6.1	nd	9	44	30	225	50	99
4	6.2	11	3	13	nd	191	18	60
5	6.2	16	6	10	16	11	41	69
6	6.2	33	11	31	33	34	46	82
Mean*	6.2	20	9	38	25	82	39	95
Range	(6.1-6.2)	(nd-33)	(3-15)	(5-126)	(nd-33)	(11-225)	(18-50)	(60-144)
Summer 1984:								
1	6.0	nd	2	30	3	50	13	187
2	6.0	nd	3	6	nd	18	26	64
3	5.9	nd	6	31	13	48	36	140
4	5.8	2	3	21	4	31	26	113
5	6.0	29	7	44	nd	58	39	149
Mean*	6.0	16	4	26	7	41	28	131
Range	(5.8-6.0)	(nd-29)	(2-7)	(6-44)	(nd-13)	(18-58)	(13-39)	(64-187)
Autumn 1984:								
1	6.3	nd	nd	6	nd	83	50	23
2	6.2	nd	nd	11	nd	213	17	11
3	6.4	nd	3	28	13	236	29	136
4	6.3	nd	nd	11	19	56	15	23
5	6.3	nd	3	16	29	nd	16	60
Mean*	6.3	nd	3	14	20	147	25	51
Range	(6.2-6.4)		(nd-3)	(6-28)	(nd-29)	(nd-236)	(15-50)	(11-136)

1. Sum of aldrin and dieldrin; 2. Sum of heptachlor and heptachlor epoxide; 3. Sum of *cis*-and *trans*-chlordane; 4. Sum of DDE, TDE and DDT in both spring and summer, or DDE and TDE only in autumn;nd=None detected;*=Means of detectable values.

The present data have indicated that maximum ΣDDT levels (average concentration 131ppb wet weight) were detected in summer, while minimum (average concentration 51ppb) in autumn. Seasonal variations in ΣDDT residues have earlier been described for fishes reaching their highest levels in summer (Edgren *et al.* 1981). Contrarily, endrin residue levels were higher in autumn (average concentration was 147ppb wet weight) corresponding to the fat content. However, it has been demonstrated that there was a trend toward a reduction in endrin levels in fishes which were exposed to both DDT and endrin concurrently (Denison *et al.* 1985). The remaining organochlorine pesticides did not exhibit a definit trend of variations with respect to seasons.

Comparison of organochlorine pesticide residue levels detected in fishes from the Shatt al-Arab River have indicated that they were below the range of values reported for *Epinephelus tauvina* and *Lethrinus nebuluosus* sampled from the Arabian Gulf (Burns *et al.* 1982).

In the light of the above reasoning we may thus conclude that there was no direct input of organochlorine pesticides to the Shatt al-Arab River. Transportation via natural processes appreared to be the sole source for these contaminants.

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