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Residues of Organochlorine Pesticides in Environmental Samples from the Shatt al-Arab River, Iraq

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ABSTRACT

*Application of high resolution gas chromatography has confirmed relatively low residue levels of ΣDDT, endrin and dieldrin in the Shatt al-Arab River. Thus, average concentration of these compounds in the edible portion of the cyprinid (*Barbus xanthopetrus*) were 21, 4 and 2 μg kg*$^{-1}$ *wet weight respectively. Mean values of ΣDDT, endrin and dieldrin in surface sediments were 5, 40 and 20 μg kg*$^{-1}$ *dry weight respectively. Shrimps sampled from the Shatt al-Arab River were found to contain residues of* o, p′*-DDD only (average concentration was 2 μg kg*$^{-1}$ *wet weight). However, comparison of these samples with those from an area affected directly by a point source of organochlorine pesticides has shown that the cyprinid of the same age group contained significantly higher residue levels (average concentrations of ΣDDT, endrin and dieldrin were 166, 20 and 7 μg kg*$^{-1}$ *wet weight respectively). Thus, it may be concluded that there was no direct input of organochlorine pesticides to the Shatt al-Arab River, and transportation via the natural processes, such as drainage, appeared to be the sole source. Based upon the observation that the original compound (*p, p′*-DDT) has not been detected in this river, it has also been concluded that there was no recent contribution of DDT here.*

Relatively higher residue levels of ΣDDT, endrin and dieldrin were encountered in the muscles of the Indian shad captured from the Shatt al-Arab River (average concentrations were 163, 80 and 28 μg kg^{-1} *wet weight respectively). However, these elevated values were attributed to this fish being migratory and it being exposed to these pesticides elsewhere.*

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INTRODUCTION

The Shatt al-Arab River drains an intensively farmed area of the Tigris and Euphrates River Basins in which organochlorine pesticides have been used. Due to their relative chemical and biological stability, residues of organochlorine pesticides are expected to persist in this river for several years. At present, almost nothing is known about the existence of these pesticides, and their related compounds, in the Shatt al-Arab River.

Sensitive qualitative and quantitative methods to determine organochlorine pesticide residues in environmental samples are required in monitoring programmes. Our initial experience with the packed column chromatography has led us to suspect the existence of a whole array of compounds including; BHC, aldrin, dieldrin, heptachlor, heptachlor epoxide, endrin, chlordane and DDT. However, confirmation of the identity of most of them was not conclusive in the Shatt al-Arab River, hence, it was thought that some of these compounds were artifacts interfering with the gas chromatographic determination of the organochlorine pesticides (Oller & Cranmer, 1975). The ultimate choice for solving such an analytical problem appeared to be the use of a high performance capillary column, thus taking the advantage of high separation efficiency and also of the better accuracy of the measured retention data (Stan & Mrowetz, 1983).

Organochlorine compounds are very soluble in fatty tissues but exhibit low solubility in water. This lipophilic, hydrophobic characterstic is largely responsible for their bioaccumulation and extreme persistence in aquatic biota (Risebrough *et al.*, 1967). The present contribution describes the use of capillary gas chromatography in the determination of organochlorine pesticide residues in 'difficult samples' (i.e. those containing mixtures of these compounds) from the Shatt al-Arab River. The results are the first of their kind for the region and should provide valuable information for forthcoming studies.

EXPERIMENTAL METHODS

Materials

Pesticides grade acetone, *n*-hexane, acetonitrile and diethyl ether were obtained commercially and were used as received (supplied by Burdick & Jackson Laboratories Inc.). High-purity (>99%) standard of pesticides and their related compounds were supplied by Chrompack International B.V. and used without further purification. Florisil PR, 60–100 mesh (lot no.

307) (Supelco SA) and anhydrous, granular sodium sulphate (Fisher Scientific Company) were extracted with *n*-hexane for a minimum of 36 h in a soxhlet apparatus. Following cleanup extraction, they were oven dried at 130°C for 24 h prior to use. The amount of florisil used was determined by lauric acid titration (Mills, 1968). All non-volumetric glassware used was acetone-rinsed then oven-baked at 300°C for about 24 h prior to use. Volumetric glassware was sequentially rinsed with acetone and *n*-hexane, followed by air drying.

Sample collection

Composite samples of the cyprinid (*Barbus xanthopetrus*) (lean fish, residental species) and the Indian shad (*Tenualosa ilisha*) (medium fatty, migratory species) have been collected from the Shatt al-Arab River (Station I) in order to establish the 'background' residue levels of organochlorine pesticides. Comparison with that influenced directly by a point source was made possible by analysing the cyprinid of the same age group obtained from Hor al-Hammar Lake (Station II) Fig. 1. Between the 1950s and 1976 this lake was sprayed with DDT and aldrin–dieldrin. Endrin was also applied to the lake on a few occasions. Generally, each composite sample consisted of 25 uniform-sized adult fish of the species. Shrimp (*Metapenaeus affinis*) samples, of at least 1000 individuals, were obtained from the Shatt al-Arab River. Finally, superficial sediments were collected from the river by means of a previously-cleaned grab sampler. Only the top layer (about 5 cm) was taken, wrapped in aluminium foil and stored at −20°C until analysis.

Extraction

The extraction procedure employed in the present study was based upon that of the Draught Method of the Standing Committee of Analysis for the determination of organochlorine insecticides and PCB in fish tissue, and is outlined in the following paragraph.

Fish or shrimp samples (edible portions only) were pooled and then macerated in a food mixer from which at least 10 replicates of about 100 g were freeze-dried, ground and sieved through 1 mm metal sieve. Sediment samples were treated similarly. Exactly 10 g of the dried biota, or 20 g of sediment, were placed in a pre-extracted cellulose thimble and soxhlet-extracted with *n*-hexane for about 24 h. At the end of this period, the extract was transferred to a storage flask and the sample was further extracted with fresh solvent. The combined extracts were reduced in volume to *ca.* 10 ml by a rotary evaporator.

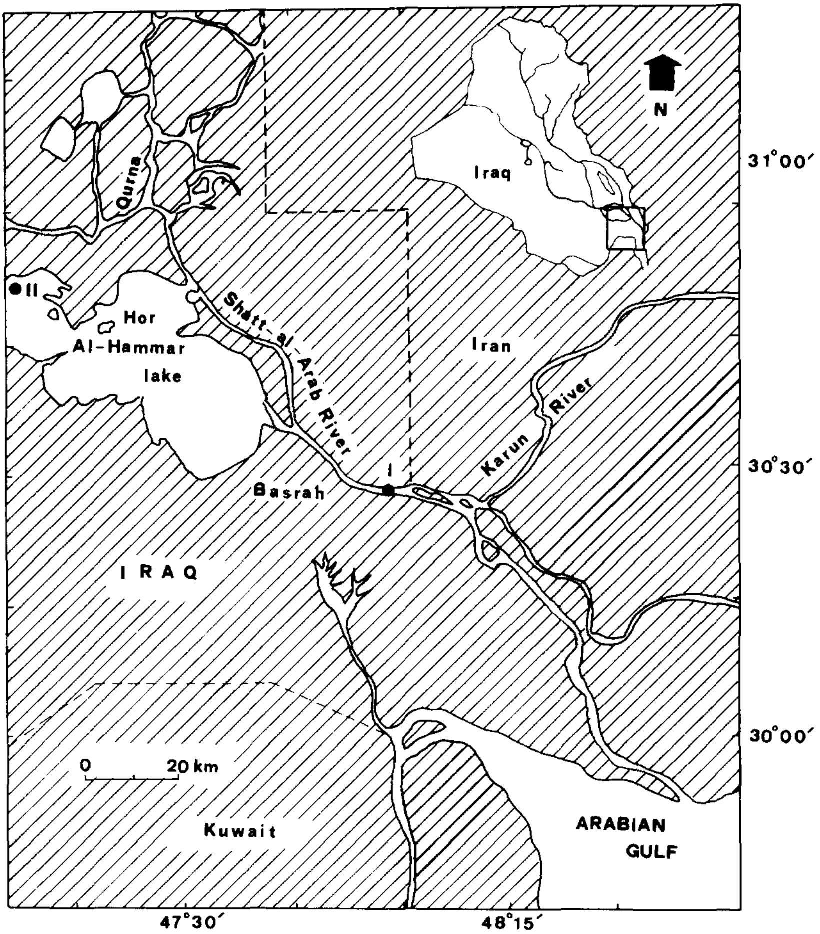

Fig. 1. Map of the Shatt al-Arab River showing the location of sampling stations.

Cleanup and fractionation

Cleanup of the extracts prior to gas chromatographic analysis eliminates, *inter alia*, the many volatile constituents of the samples, thus improving resolution and prolonging column life. Therefore, our extracts were cleaned by transferring to a separating funnel and apportioning between acetonitrile/*n*-hexane (Mills, 1961). Then, the acetonitrile was diluted with water and the residues were extracted with *n*-hexane which was dried over a column of sodium sulphate. However, in order to remove the unsaponified lipids, extracts were further cleaned and fractioned on active florisil. The extract was charged to the column, and elution took place with 6% and 15% diethyl ether in *n*-hexane. The combined elutants were evaporated to about 10 ml by a rotary evaporator, then to exactly 1 ml by a stream of purified nitrogen. In the case of the sediment extracts, the combined elutants were treated with activated copper in order to remove elemental sulphur.

Fat content

Since organochlorine pesticides are lipophilic, an accurate determination of the fat content in the samples to be analysed is desirable. In order to achieve this, 5 g of each freeze-dried sample was soxhlet-extracted with a 2:1 mixture of *n*-hexane and acetone for about 24 h. The extracts were reduced in volume by a rotary evaporator, and subsequently to exactly 1 ml by a stream of purified nitrogen. 10 μl of the concentrated extracts were taken quantitatively by a Hamilton syringe and weighed after evaporation of the solvent in a CAHN 29 Automatic Electrobalance.

Gas–liquid chromatography

Two Pye Unicam gas chromatographs model 304, equipped with constant current Ni^{63} electron-capture detectors and split/splitless mode injection ports, were used. Quantification of peaks and identification of pesticides in chromatograms were achieved by a Spectra-Physics computing integrator (model SP-4100). Abate was used as an internal standard. A wall-coated open tubular (WCOT) fused silica capillary column (30 × 0·25 mm i.d.) with 0·22 μ film thickness coated with SE-30 (methylsilicone) (Supelco SA) was used. Operating temperatures were 220, 270 and 300°C for column, injector and detector respectively. A mixture of 95 + 5% argon/methane was used as a carrier gas with a linear velocity of 75 cm s^{-1} and split ratio of 10/1. An argon/methane mixture was also used as a make-up gas to boost the flow into the detector to 60 ml min^{-1}. A second WCOT glass capillary column, 60 m long, 0·2 mm i.d. with 0·25 μ film thickness coated with SE-54 (phenyl polymethylphenylsiloxane) was employed to determine the proportion of DDT and its metabolites. This column was operated under temperature programmed conditions (1°C min^{-1}) from 200 to 250°C with an isothermal period (10 min) at the end. Argon was used as a carrier gas with a linear velocity of 80 cm s^{-1}, with a 95 + 5% argon/methane mixture as a make-up gas to increase the flow in the detector to 65 ml min^{-1}. Exactly 0·5 μl of the concentrated extracts were injected splitless (60 s splitless period 'hot needle') with the injection port at 250°C and the electron-capture detector at 300°C. Results were compared by injection into a glass column (1·5 m × 4 mm diameter) packed with 1·5% Ov-17 + 1·9% OV-210 on chromosorb W HP (Supelco SA). 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 30 ml min^{-1}.

Blanks

Procedural blanks, consisting of all reagents and glassware used during the analysis, were periodically determined. Only a single interfering compound, which possesses the same retention time of that of heptachlor, was detected in the blank of both biota and sediment. Therefore, apart from that, the sample values were not corrected for procedural blanks.

Confirmatory tests

Results of the capillary gas chromatographic analysis were confirmed by thin-layer chromatography (TLC) according to the AOAC procedure (AOAC, 1975). Furthermore, the peak identified as *p,p'*-DDT was shifted upon saponification of the extracts to a position with a retention time of the ethylene derivative (Risebrough *et al.*, 1969), whereas that of endrin was isomerised by acid-catalyst to ketone and aldehyde (Chau & Cochrane, 1969), thus providing confirmation of their identity.

Recovery

Recovery studies with fortified samples indicated that the recovery efficiency exceeded 85% for all compounds measured except—BHC (65%), HCB (45%) and heptachlor (70%). In general, recoveries from sediments were somewhat lower at 70 to 75%, while those from biota ranged between 80 and 90%. Results were not adjusted for per cent recovery.

RESULTS

The multi-residue extraction procedure employed in the present study, followed by gas chromatographic determination, should screen most of the common organochlorine pesticides. High resolution gas chromatography has confirmed the residues of: *p,p'*-DDE; *o,p'*-DDD; *p,p'*-DDT; and endrin and dieldrin in the Shatt al-Arab River. The mean values and ranges of these compounds in fishes, shrimps and sediments are given in Table 1. Average concentrations of ΣDDT, endrin and dieldrin in the cyprinid were 21, 4 and 2 $\mu\text{g kg}^{-1}$ wet weight. Relatively higher levels of these compounds were detected in the Indian shad (average concentrations were 163, 80 and

28 $\mu g\,kg^{-1}$ respectively). Only *o,p′*-DDD residues were detected in the shrimps (average concentration was 2 $\mu g\,kg^{-1}$ wet weight). In the sediment extracts *o,p′*-DDE; endrin and dieldrin were observed with averages of 5, 40 and 20 $\mu g\,kg^{-1}$ dry weight. These findings are consistent with the fact that DDT, endrin and dieldrin have been used in southern Iraq. In addition to organochlorine pesticides, lipid content is reported as percentage by weight, muscle tissue or sediment (Table 1). All samples showing no response, or less than the detection limit, are reported as nd = none detected and are averaged as 0·7 × limit of detection following the method of Nicholson (1980). On the other hand, α-BHC, HCB, β-BHC, heptachlor, aldrin, heptachlor epoxide, α-endosulfan, α-chlordane, γ-chlordane, *o,p′*-DDT, and β-endosulfan were below the detection limit of 1 $\mu g\,kg^{-1}$ wet weight.

DISCUSSION AND CONCLUSIONS

DDT and its metabolites

The present study has shown that biota and sediments sampled from the Shatt al-Arab River were contaminated to some extent with DDT. Conversion of DDT into its metabolites is initiated by soil microorganisms immediately after it enters the environment. Other factors, such as high pH, light, or heat may also produce chemical changes in the original DDT molecule. Thus accurate determination of both the original compound and its metabolites and degradation products should give an insight into the fate of DDT in the environment (Siewiérski & Helrich, 1967). Aguilar (1984) has demonstrated that the rate of DDE to ΣDDT can tentatively be used to assess the chronology of pollutant input. However, one of the problems encountered in pesticides analysis by gas chromatography has been the on-column decomposition of DDT. A phenomenon that was found to be associated with the column wall and solid support (Radomski & Rey, 1970), or to the build-up of irreversibly bound substances on the column (Brodtmann & Koffskey, 1979). In order to overcome this disadvantage, it has been proposed to use a glass column and glass inlets and to replace the PTFE-faced septa, clean the injection system and take-away the first 10 cm or so of the column regularly (Snochik & Walker, 1979). Utilising an SE-54 glass capillary column and following these instructions, we observed that both *p,p′*-DDT and *o,p′*-DDT were below the detection limit in the cyprinid from the Shatt al-Arab River, which suggest that there has been no recent input of DDT (Frank *et al.*, 1974). This view is further supported by the fact that only *o,p′*-DDD was detected in the shrimps, and only *p,p′*-DDE in the sediments of this river

TABLE 1

Mean Concentrations ($\mu g\,kg^{-1}$ Wet Weight, Muscle Tissue or Dry Weight Sediment) and ranges of Organochlorine Pesticides in Environmental Samples from the Shatt al-Arab River and Comparison with the Cyprinid from Hor al-Hammar Lake

Sample	*Sample number*	% *Fat*	*Dieldrin*	*Endrin*	p,p'-*DDE*	o,p'-*DDD*	p,p'-*DDT*	Σ*DDT*
The Shatt al-Arab River (Station I)								
Barbus xanthopetrus (cyprinid)	1	3·0 (2·9–3·2)	3 (nd–8)	5 (nd–9)	4 (nd–6)	12 (8–15)	nd	16
	2	3·0 (2·9–3·1)	2 (nd–7)	3 (nd–5)	4 (nd–7)	22 (18–30)	nd	26
Average for the cyprinid		3·0	3	4	4	6n 17	nd	21
Tenualosa ilisha (Indian shad)	1	6·2 (6·1–6·2)	23 (16–34)	70 (57–98)	41 (37–46)	89 (69–109)	8 (nd–13)	138
	2	6·3 (6·2–6·4)	32 (23–41)	90 (80–108)	64 (43–80)	115 (89–125)	10 (nd–13)	188
Average for the Indian shad		6·2	28	80	53	102	9	163

Metapenaeus affinis (shrimp)	1	1·1 (1·0–1·1)	nd	nd	nd	2 (nd–3)	nd	2
	2	1·1 (1·0–1·2)	nd	nd	nd	2 (nd–4)	nd	2
Average for the shrimp		1·1	nd	nd	nd	2	nd	2
Superficial sediment	1	0·08 (0·07–0·09)	13 (8–16)	37 (35–46)	6 (2–7)	nd	nd	6
	2	0·08 (0·07–0·08)	27 (20–40)	43 (35–50)	4 (2–5)	nd	nd	4
Average for sediment		0·08	20	40	5	nd	nd	5
Hor al-Hammar Lake (Station II)								
Barbus xanthopetrus (cyprinid)	1	2·9 (2·8–3·1)	5 (3–8)	16 (11–21)	19 (8–29)	127 (113–141)	8 (nd–12)	154
	2	3·0 (2·8–3·1)	8 (5–10)	24 (19–27)	33 (21–42)	135 (119–145)	10 (nd–13)	178
Average for the cyprinid		3·0	7	20	26	131	9	166

Bracketed figure underneath the mean is the range.
nd = None detected.

(Table 1). Similarly, residues of only DDE were confirmed in the oyster, *Pinctada margratifera*, collected from the coast of Kuwait, and attributed to the discharge of the Shatt al-Arab (Anderlini *et al.*, 1981). We may thus conclude that transportation, via natural processes, seems to be the sole source of DDT, and this has apparently suffered both metabolic conversion (Bridges *et al.*, 1963) and/or intensive dehydrochlorination (Hannon *et al.*, 1970) in the warm, rather alkaline waters of the Shatt al-Arab River. These phenomena may account for the observed proportions of DDT and its metabolites in the cyprinid (ΣDDT comprised the two isomers *p,p*-DDE and *p,p*′-DDD only; DDE:DDD ratio was 1:4).

Significantly higher levels of ΣDDT were detected in the cyprinid from Hor al-Hammar Lake (Station II) (residue levels ranged from 154 to 178 $\mu g\,kg^{-1}$ wet weight). At this location DDT has been applied close to or over water, causing direct contamination of fish (Johnson, 1968). In addition to *p,p*′-DDE and *o,p*′-DDD, *p,p*′-DDT has also been detected in approximately 50% of the fishes here, reflecting continuing inputs (Aguillar, 1984). The DDE:DDD ratio in the cyprinid obtained from Station II was 1:5 probably reflecting conditions which were more anaerobic than those in Station I (Ware & Roan, 1970).

As mentioned already, the Indian shad muscles retained relatively higher ΣDDT residues compared to the cyprinid, which may be due to the fact that the former has a higher fat content. It has been well established that maximum occurrence of ΣDDT coincides with high lipid content (Rickard & Dulley, 1983). In the Indian shad *o,p*′-DDD was also the major constituent, followed by *p,p*′-DDE. However, *p,p*′-DDT has also been detected in approximately 50% of the samples. These migratory fishes may have accumulated *p,p*′-DDT from additional sources where it is still used in agriculture.

Comparison of ΣDDT concentrations in fishes sampled from the Shatt al-Arab River show that they are within the range of values reported for *Epinephelus tauvina* and *Lethrinus nebuluosus* captured from the Arabian Gulf (average concentrations were 117 and 268 $\mu g\,kg^{-1}$ wet weight respectively) (Burns *et al.*, 1982).

Endrin

Endrin is considered to be the most toxic of all commercial insecticides to fish (Johnson & Finley, 1980) and this was the second most prevalent compound in the cyprinid. Appreciably higher residue levels were detected at Station II compared to the Shatt al-Arab River (Station I). Hence, endrin followed a similar distribution pattern described earlier for ΣDDT, and may thus be explained accordingly. Generally speaking, endrin concentrations in the cyprinid were low (average 12 $\mu g\,kg^{-1}$ wet weight) which may be due to the fact that this insecticide is relatively short-lived and has been used on few occasions in Hor al-Hammar Lake. Moreover, it has been demonstrated that there tends to be a reduction in endrin levels in fishes which are exposed to both DDT and endrin concurrently (Denison *et al.*, 1985). Endrin residues were confirmed in the sediments of the Shatt al-Arab River (average concentration was 40 $\mu g\,kg^{-1}$ dry weight) which may thus act as a reservoir giving traces of endrin to the water. Endrin concentrations were an order of magnitude higher in the Indian shad than in the cyprinid. This may be due to the migratory Indian shad being subjected to additional sources of endrin.

Dieldrin

Although dieldrin has been officially banned in Iraq since 1976, its residues are expected to persist, owing to its long use for agricultural and public health purposes. However, residue levels of dieldrin in the cyprinid collected from the Shatt al-Arab River were at, or near, the detection threshold (1 $\mu g\,kg^{-1}$ wet weight). Relatively higher concentrations were observed at Station II (average concentration was 7 $\mu g\,kg^{-1}$) which may be due to the fact that aldrin and/or dieldrin have been used in this location. Analysis has shown that the Shatt al-Arab River sediments contained appreciable amounts of dieldrin (average concentration was 20 $\mu g\,kg^{-1}$ dry weight). Thus, dieldrin may have been adsorbed to suspended particulate matter carried by the Tigris and Euphrates Rivers, which is subsequently deposited in the Shatt al-Arab River in considerable amounts. Dawson and Riley (1977) showed that elevated dieldrin levels in the water are associated with high levels of suspended particulates. Again, the Indian shad muscles contained higher concentrations of dieldrin (average 28 $\mu g\,kg^{-1}$). Despite the fact that dieldrin is a metabolite of aldrin, it is interesting to note that residues of the latter were below the detection limit, which may be due to active conversion of aldrin to dieldrin (Ludke *et al.*, 1972).

In the light of the above, the following conclusions may be drawn:

(1) Concentrations of most persistent organochlorine pesticides, even those used in southern Iraq, were relatively low in both biota and sediments from the Shatt al-Arab River.

(2) There are no direct inputs of organochlorine pesticides to the Shatt al-Arab River, and transportation via the natural processes seems to be the sole source. This conclusion was further supported when considering the significant correlations between ΣDDT, endrin and dieldrin which are related to patterns of use, and are reflected in the

presence of relatively higher concentrations in the Hor al-Hammar Lake.

(3) ΣDDT mainly comprised the two isomers *p,p'*-DDE and *o,p'*-DDD, which are attributed to metabolic conversion and/dehydrochlorination of DDT.

(4) Low endrin levels were detected in the cyprinid, and this is attributed to both limited application of this insecticide and the presence of DDT. In the Indian shad, however, endrin was the principal contaminant.

(5) Dieldrin concentrations were relatively high in the sediment of the Shatt al-Arab River and is probably adsorbed onto suspended particulates.

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