RESIDUES OF ORGANOCHLORINE PESTICIDES IN FISH FROM THE ARABIAN GULF

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Abstract. High-resolution electron capture gas chromatography was used to determine residue levels of organochlorine pesticides in 13 commercially important fish species collected from the NW Arabian Gulf. While most of the residues were below the detection limit of 1 $\mu g\,kg^{-1}$ wet weight, relatively low concentrations of ΣDDT, endrin and dieldrin were detected in the edbile tissue of these fishes. The ΣDDT residue levels ranged from 2 to 11 $\mu g\,kg^{-1}$ wet weight, endrin ranged from none detected (nd) to 45 $\mu g\,kg^{-1}$ and dieldrin from nd to 5 $\mu g\,kg^{-1}$. A definite correlation was established between total organochlorine pesticide residues and lipid content ($r = 0.6$) for the NW Arabian Gulf fishes. Comparison with fish from Hor-al-Hammar Lake (an area that used to be sprayed with pesticides) has shown that the latter contained significantly higher residue levels. The ΣDDT residue levels ranged from 5 to 45 $\mu g\,kg^{-1}$ wet weight, endrin from 3 to 83 $\mu g\,kg^{-1}$ and dieldrin from nd to 4 $\mu g\,kg^{-1}$. Based upon the observation that the original DDT (p, p'-DDT) was identified in the NW Arabian Gulf fishes, it has been concluded that there was a recent input of DDT to this region. Since DDT application has been banned in Iraq, consequently it was assumed that DDT must originate from a more remote source.

1. Introduction

The Arabian Gulf is a semi-enclosed sea situated both downstream and down-wind of the Shatt al-Arab Delta and the Tigris-Euphrates River Basin. This latter area is a well established agricultural region in which various pesticides such as DDT, aldrin-dieldrin, ..., etc. have been used. These compounds are characterized by their relative chemical and biological stability, and hence persistence in the environment. Organochlorine pesticides could enter the Arabian Gulf either as a run-off or through atmospheric deposition. Damage to marine environment by these chemicals is well documented. However, up to this time of writing, only sparse data concerning the distribution of organochlorine pesticides in the Arabian Gulf have been available (Burns *et al.*, 1982). A preliminary survey of marine samples revealed the presence of DDT derivatives in the oysters (*Pinctada margaratifera*) collected from Kuwaiti waters (Anderlini *et al.*, 1981). These findings indicate that inputs from the Tigris-Euphrates Basin may indeed be taking place. It has also been observed that at a certain times, dust fall-out is associated with shirmp-larval kills in culture ponds (Farmer, 1984). Although speculative, it may be possible that at these times, airborne dust from Tigris-Euphrates carries pesticides and/or their chlorinated extenders. The work described in this paper was conducted in order to establish the background residue levels of organochlorine pesticides in 13 commercially significant fish species from the NW Arabian Gulf.

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2. Materials and Methods

2.1. Materials

Pesticides grade acetone, *n*-hexane, acetonitrile, and diethyl ether were obtained commercially from Burdick and Jackson and were used as received. High purity (99 + %) analytical standards of pesticides and their related compounds as well as the remaining chromatographic supplies were provided by Supelco S.A. FlorisilPR, 60 to 100 mesh (lot No. 307) and anhydrous, granular sodium sulphate (Fisher Scientific Company) were extracted with *n*-hexane for a minimum of 36 hr in a soxhlet apparatus. Following clean-up, florisil was activated and stored according to the procedure described by the (U.S. EPA, 1980). The amount of florisil used was determined by lauric acid titration (Mills, 1968). All non-volumetric glassware used were acetone rinsed then oven-baked at 300 °C for about 24 hr prior to use. Volumetric glassware was sequentially rinsed with acetone and *n*-hexane, followed by air drying.

2.2. Collection of fish

Composite samples of 13 fish species were collected from the NW Arabian Gulf during July 1985 to establish the 'background' residue levels of organochlorine pesticides. Samples of 5 fish species were collected from Hor al-Hammar Lake (Figure 1) to determine the influence of pesticide inputs. Generally, each composite consisted of at least 10 uniform size of adult fish of the same species.

2.3. Preparation of samples

Fish samples (edible tissues only) were pooled and macerated in a food chooper from which at least 5 replicates of 60 g were freeze-dried, ground and sieved through 1 mm metal sieve. 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 and is outlined below.

Exactly 10 g of the dried fish muscles were placed in a pre-extracted cellulose thimble and soxhlet extracted with *n*-hexane for about 24 hr. 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 in a rotary evaporator. The extraction procedure removed volatile constituents of the samples. Further clean-up was achieved by transfering 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 florisil column, and eluted with 6 and 15% diethyl ether in *n*-hexane. The combined elutants were evaporated to about 10 mL in a rotary evaporator, then to exactly 1 mL by a stream of purified N_2.

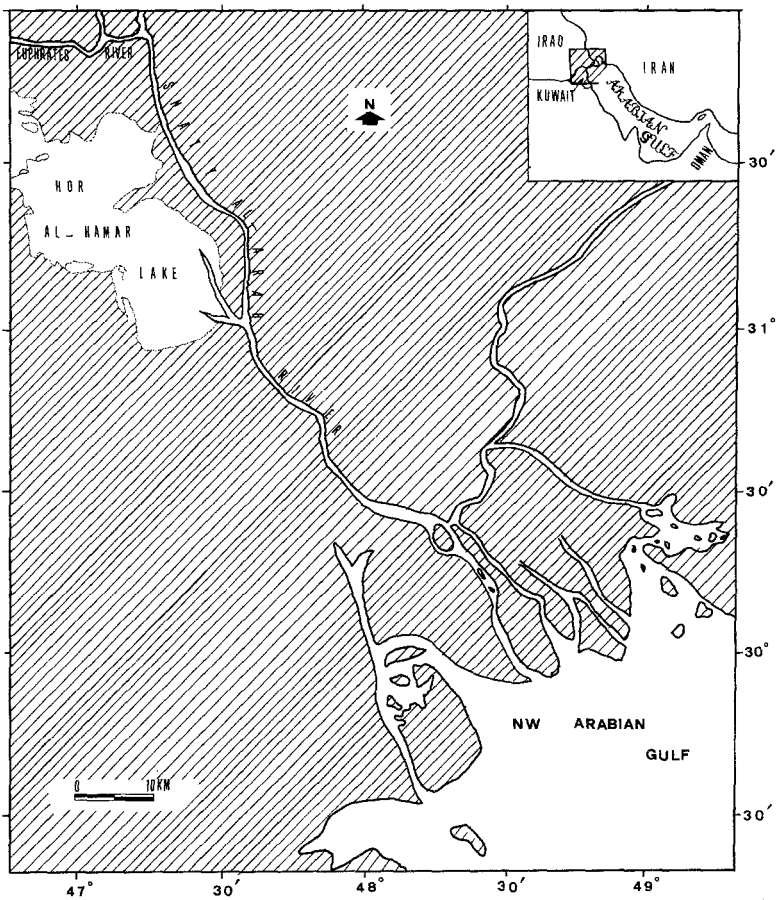

Fig. 1. Map of the NW Arabian Gulf.

2.4. ANALYSES

Accurately 1 μL of the concentrated extract was injected into a Pye–Unicam model 304 gas chromatograph equipped with a constant current Ni^{63} electron capture detector and a grob split/splitless injection port. A wall coated open tubular (WCOT) fused silica capillary column (30 m × 0.25 mm i.d.) with 0.22 μm film thickness coated with SE-30 (methysilicon) was used. Operating temperatures were 220, 270, and 300 °C for column, injector, and detector, respectively. A mixture of 95 + 5% Ar/CH_4 was used as the carrier gas with a linear velocity of 75 cm s^{-1} and split ratio of 10 : 1. An Ar/CH_4 mixture was also used as a make-up gas to boost the flow in the detector to 60 mL min^{-1}. Quantification of peaks and identification of pesticides in chromatograms was achieved by Spectra-Physics computing integrator (model SP-4100). Abate (*O*, *O*, *O'*, *O'*-tetramethyl-*O* ,*O'*-thiodi-*p*-phenylene phosphorathioate) was used as an internal standard. The detection limit for each individual compound was determined to be 1 μg kg^{-1} wet weight. Results of capillary gas chromatography were compared in

about 10% of the amples by injection into a glass column (1.5 m × 4 mm i.d.) packed with 1.5% OV-17 + 1.95% OV-210 on chromosorb W HP. Operating temperatures were 200, 220, and 300 °C for column, injector and detector, respectively. A mixture of 90 + 10% Ar/CH_4 was used as a carrier gas at a flow of 30 mL min^{-1}. Results of gas chromatographic analyses were confirmed by TLC according to AOAC procedure (AOAC, 1975).

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 blanks of fish muscle tissue. Therefore, apart from that, the sample values were not corrected for procedural blanks.

Recovery studies with fortified samples have indicated that recovery efficiency exdeeded 85% for all compounds measured, except BHC (65%), HCB (45%), and heptachlor (70%). Results were not adjusted for percent recovery.

2.5. Fat content

Fat content was determined by soxhlet extracting 5 g of the freeze-dried tissues with 2 : 1 mixture of *n*-hexane and acetone for about 24 hr. The extracts were reduced in volume in a rotary evaporator, and subsequently reduced to exactly 1 mL by a stream of purified N_2. Sub-samples (10 μL) of the concentrated extracts were taken by a Hamilton syringe and weighed after evaporation of the solvent on a CAHN 29 Automatic Electrobalance.

3. Results and Discussion

The multiresidue extraction procedure utilized in the present survey followed by electron capture-gas chromatographic determinations should screen most of the common organochlorine pesticides. Our data have confirmed residues of DDT, endrin and dieldrin in the Arabian Gulf, which is consistent with the fact that these compounds have been used in Iraq. On the other hand, αBHC, HCB, βBHC, heptachlor, aldrin, heptachlor epoxide, α-endosulfane, α-chlordane, γ-chlordane and β-endosulfane were below the detection limit of 1 μg kg^{-1} wet weight. The mean values of ΣDDT, endrin and dieldrin in fish tissues are given in Table I, the range is also shown for each species and is bracketed.

In all of the 13 fish species examined, ΣDDT was the most prevalent organochlorine pesticide, with average concentrations ranging from 2 μg kg^{-1} wet weight in sea catfish to 11 μg kg^{-1} in silverbanded croacker. The ΣDDT in fish obtained from he NW Arabian Gulf was mainly comprised of *p, p'*-DDT and *p, p'*-DDE (average concentrations were 3 and 2 μg kg^{-1} wet weight, respectively). The latter was detected in all of the samples analyzed, while the average percentage occurrence of *p, p'*-DDT was approximately 85%. In most cases, conversion of DDT into DDE is initiated by soil micro-organisms immediately after it enters the environment. Other factors such as alkaline pH, light, or heat may also produce chemical changes in the original DDT molecule. Thus, the above observation may be due to metabolic conversion (Bridges

TABLE I

Mean concentrations (ppb weight wet, edible tissue) and ranges of organochlorine pesticides in fishes from the NW Arabian Gulf

Species		Fat	Dieldrin	Endrin	*p, p*-DDE	*o, p'*-DDD	*o, p'*-DDT	*p, p'*-DDT	ΣDDT	Total residue
Scientific name	Common name	%								
NW Arabian Gulf:										
Arius thalassinus	Sea catfish	5.8 (5.6–5.9)	nd	2 (1–3)	1 (nd–2)	nd	nd	1 (nd–2)	2	4
Eleutheronema tetradactnum	Fourfingered threadfin	2.9 (2.8–3.1)	nd	2 (nd–3)	2 (nd–3)	nd	1 (nd–2)	nd	3	5
Johnieops sina	Croaker	2.1 (2.0–2.1)	nd	1 (nd–2)	1 (nd–3)	nd	nd	3 (nd–4)	4	5
Cynoglosus arel	Large-scale tongue sole	4.6 (4.5–4.6)	nd	1 (nd–3)	1 (nd–2)	nd	nd	3 (2–3)		5
Platycephalus indicus	Indian flathead	2.1 (2.1–2.2)	nd	nd	1 (nd–3)	nd	3 (1–5)	1 (nd–3)	5	5
Pomadasys argenteus	Silvery grunt	2.5 (2.4–2.5)	1 (nd–3)	2 (1–3)	1 (nd–3)	nd	nd	4 (2–5)	5	7
Ilisha elongata	Elongate ilisha	4.1 (4.0–4.3)	nd	1 (nd–2)	2 (nd–3)	nd	nd	5 (nd–7)	7	8
Tylosurus strongylurus	Forktail needlefish	2.6 (2.4–2.6)	nd	4 (2–5)	2 (nd–3)	nd	nd	2 (nd–3	4	8
Nematalosa nasus	Threadfin shad	6.0 (5.9–6.0)	2 (nd–5)	4 (2–7)	5 (3–6)	3 (1–4)	nd	nd	8	12
Thryssa hamiltonii	Hamiltons thryssa	5.7 (5.6–5.7)	nd	8 (5–10)	2 (nd–4)	nd	nd	3 (nd–5)	5	13
Acanthopagrus latus	Yellowfin seabream	5.9 (5.8–5.9)	4 (1–5)	14 (7–19)	2 (nd–3)	2 (nd–3)	2 (nd–3)	2 (nd–3)	8	22
Liza dussumeiri	Mullet	5.9 (5.7–6.0)	2 (nd–3)	19 (14–24)	3 (nd–5)	1 (nd–3)	nd	5 (2–7)	9	28
Otoliths argenteus	Silverbanded croaker	6.1 (6.0–6.1)	nd	28 (12–45)	2 (nd–3)	nd	3 (nd–5)	6 (2–13)	11	39

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

et al., 1963) and/or dehydrochlorination (Hannon *et al.*, 1970) in the warm, rather alkaline waters of the Arabian Gulf. Moreover, because the volatility of DDE is several times greater than that of DDT (Spencer, 1975), it is logical to presume that DDE is more readily transferred via the atmosphere to the coastal Arabian Gulf. Since the presence of the original compound, *p, p'*-DDT, suggests recent inputs of DDT to aquatic ecosystem (Aguilar, 1984) we may thus conclude that there was continuing contribution of DDT to the Arabian Gulf. However, DDT has been officially banned in Iraq, hence its residues must be originated from a more remote source or more likely, from continuing illegal use. Technical DDT generally contains $<25\%$ *o, p'*-DDT, an impurity, however, *o, p*-isomers are less persistent than their *p, p'*-analogs (Fry and Toone, 1981). This phenomenon may be accounted for the relatively low percentage occurrence of both *o, p'*-DDT and *o, p'*-DDD which were 30 and 20%, respectively. A strong correlation ($r = 0.9$) was evident between lipid content and ΣDDT in the fishes from the Arabian Gulf which agrees with the well established fact that maximum occurrence of ΣDDT coincides with the high fat content (Rickard and Dulley, 1983). Comparison of ΣDDT residues in fish tissue from the NW Arabian Gulf with those from Hor al-Hammar Lake revealed that the latter retained significantly higher concentrations (residue levels ranged from 5 $\mu g\ kg^{-1}$ wet weight in the carp to 72 $\mu g\ kg^{-1}$ in the minnow) (Table II). The rather elevated values may be due to the fact that Hor al-Hammar Lake used to be sprayed with technical DDT until recently. Similar results of direct applications have been observed in numerous water bodies (Johnson, 1968). Furthermore, ΣDDT in fishes from the NW Arabian Gulf were an order of magnitude lower than the range of values reported for *Epinephelus tauvina* and *Lethrinus nebuluosus* captured from the coastal waters of Oman (Burns *et al.*, 1982). Since the Omani territorial waters are much further down from the Shatt al-Arab Delta than the NW Arabian Gulf, our previous contention that there is an additional source of DDT to the Arabian Gulf apart from the Shatt al-Arab Delta and the Tigris-Euphrates River Basin is further supported.

Endrin is considered to be the most toxic of all commercial insecticides to fish (Johnson and Finley, 1980) and this was the second most dominant compound in fishes from the NW Arabian Gulf. Endrin residues were detected in approximately 90% of these fishes, with a mean values ranging from 1 $\mu g\ kg^{-1}$ in large scalesole, croaker, and elongate ilisha, to 28 $\mu g\ kg^{-1}$ wet weight in silverbanded croaker. Slightly higher concentrations of endrin have been detected in fishes from the Hor al-Hammar Lake, with residue levels ranging from 3 $\mu g\ kg^{-1}$ in carp to 67 $\mu g\ kg^{-1}$ wet weight in minnows. Endrin has not been detected in the Arabian Gulf before, which may be due to the fact that this insecticide is relatively short-lived and has been used in few ocassions in this region.

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 fishes from the NW Arabian Gulf were at or near the detection threshold of 1 $\mu g\ kg^{-1}$ wet weight. More frequent residues of dieldrin were observed in the Hor al-Hammar Lake (approximate percentage occurrence was

TABLE II

Mean concentrations (ppb weight wet, edible tissue) and ranges of organochlorine pesticides in fishes from the Hor al-Hammar Lake

Species		Fat	Dieldrin	Endrin	*p, p*-DDE	*o, p'*-DDD	*o, p'*-DDT	*p, p'*-DDT	ΣDDT	Total residue
Scientific name	Common name	%								
Hor al-Hammar Lake:										
Cyprinus carpio	Carp	2.5 (2.4–2.6)	nd	3 (1–4)	1 (nd–2)	nd	nd	4 (nd–6)	5	8
Aspius vorax	Minnow	2.2 (2.1–2.2)	2 (nd–3)	15 (14–20)	4 (1–8)	3 (1–4)	nd	9 (6–10)	16	33
Barbus scheich	The cyprinid	3.3 (3.2–3.3)	2 (nd–3)	13 (10–17)	18 (16–22)	4 (nd–5)	nd	11 (7–16)	33	48
Barbus grypus	Minnow	3.4 (3.2–3.5)	2 (nd–4)	9 (5–13)	53 (40–61)	10 (3–14)	nd	9 (3–11)	72	83
Mesopotamichthys sharpeyi	Minnow	5.1 (4.9–5.2)	3 (nd–4)	67 (57–83)	13 (8–15)	3 (nd–5)	nd	29 (9–44)	45	115

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

80%) with an average concentration of 2 μg kg^{-1} wet weight (Table II). Thus, dieldrin might have been adsorbed to the suspended particulate matter carried by the Euphrates River and deposited in considerable amounts in the Hor al-Hammar Lake. It has been shown (Dawson and Riley, 1977) that elevated dieldrin levels in the water are associated with the high levels of suspended particulates. Dieldrin is a metabolite of aldrin, and the residue of the latter was below the detection limit of 1 μg kg^{-1} wet weight, which may be due to active conversion of aldrin to dieldrin (Ludke *et al.*, 1972).

On the basis of total organochlorine pesticide residues, the 13 fish species examined could be arranged sea catfish < fourfingered threadfin < croaker < largescale tongue sole < indian flathead < silvery grunt < elongate ilisha < forktail needlefish < threadfin shad < hamiltons thryssa < yellowfin seabream < mullet < silverbanded croaker. The linear correlation between total organochlorine pesticide residues and lipid content in fishes from the NW Arabian Gulf was $y = 4.034x - 5.088$ ($r = 0.622$).

The major conclusions that can be drawn from the present study are that DDT and endrin occurred in almost all fish samples examined. However, ΣDDT concentrations were relatively lower than those reported previously in the Arabian Gulf. Dieldrin residues were present in fewer fish species. Other organochlorine pesticides were at or below the detection limit of 1 μg kg^{-1} wet weight.

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