ORGANOCHLORINE PESTICIDE RESIDUES IN FISH FROM QATARI COASTAL WATERS.

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Abstract

Very little is known about the level of organochlorine contamination in the Arabian Gulf around Qatar. Six species of common fish in Qatar were chosen in 1987 and were analyzed for oraganochlorine pesticide residues. The results obtained by gas chromatography and confirmed by thin layer chromatographic techniques revealed low levels of organochlorine in fish samples. Pesticide contaminants found most frequently were Lindane (Y- HCH), p,p - DDE, and p,p-DDT.

INTRODUCTION

Organochlorine pesticides were reported to persist for several years and to accumulate in aquatic organisms (Crosby, 1973). Fish like some other aquatic organisms could be used as an indicator organism for monitoring pollution with pesticide residues (Hill and Wright, 1978). Although there were relatively few sources of organochlorine compounds within Qatar, coastal waters and organisms could be exposed to organochlorine compounds derived from agricultural land drainage of the surrounding countries.

The aim of the work reported here is to establish the background residue levels of organochlorine pesticides in six commercially important fish species from the

Qatari coastal waters.

MATERIALS AND METHODS

Apparatus and Reagents

a) Gas chromatograph. - PYE Unicam model 304 with ^{63}Ni electron capture detector. A 25 m x 0.53 mm id wide bore column of BP-1 bonded phase (Aluminium clad) was used for separation. Operating temperatures were 270 and 300°C for injector and detector, oven was held for 2 minutes at 160°C then increased gradually at the rate of 3°C /minute to 260°C, then kept for 40 minutes at 260°C. Helium was used as a carrier gas at a flow rate of 4 ml/minute and detector make-up gas (10% methane-argon) at 10 ml/minute. The CP-Sil-5CB, WCOT Fused Silica wide bore column 50 m x 0.53 mm id (Operating conditions previously adopted were used) and thin-layer chromatographic detection (Sec. 411-PAMI, 1971) were used as confirmatory tests.

b) Thin-layer chromatography. - Al_2O_3 thin - layer precoated plates (20 x 20 cm) were used for confirmatory tests. Plates were developed in n-heptane and residues were detected by $AgNo_3$ and 2-phenoxy ethanol spray followed by UV exposure (Sec. 411.3 (1-5)-PAMI, 1971),

c) Florisil-PR grade, 60-100 mesh, handled and tested according to the procedure described in the (PAMI, 1971).

d) All solvents were redistilled in all-glass prior to use and tested by EC.GLC.

e) Pesticides reference standards: DDT comples (p,p DDT, p,p DDD, p,p DDE, op DDD and op DDT), hexachlorocyclohexane (HCH) isomers (alpha, beta and gamma (Lindane); heptachlor, heptachlor expoxide, aldrin and dieldrin were provided by USEPA. Pesticides & Industrial Chemicals Repository. Research Triangle Park, NC 27711, U.S.A. Standard solutions of reference materials. All standard solutions were prepared in hexane.

Sample Preparation

Eighteen samples from six species of common fish in Qatar (three samples from each species) were collected from local market during October 1987 (Table 1). Samples were prepared for analysis in accordance with the edible protein guide (PAMI, 1971). Before extraction, the edible portion of each sample was thoroughly mixed and ground in a meal grinder as described in sec. 142.4 (PAMI, 1971). Fat

Extraction and Clean-up

Because fat content never exceeded 2% by weight in all fish samples, residues were extracted from 100 g homogenized fish samples with acetonitril as described in sec. 212.13a (PAMI, 1971) for high moisture nonfatty foods and for fish containing less than about 10% fat (Sec. 211.13f - PAMI, 1971). Residues were then transferred from acetonitril to petroleum ether (Sec. 211.14a - PAMI, 1971).

Samples were cleaned up using florisil column chromatography (Sec. 211. 14d - PAMI, 1971).

Recovery studies with fortified samples have indicated that recovery efficiency exceeded 80% for all compounds measured. Residue levels of pesticides were adjusted acording to their recoveries.

Table 1. Common and texonomic names of fish collected in the survey (Sivasubramaniam and Ibrahim, 1982).

Common name	Taxonomic name
Black banded trevally	*Seriolina nigrofasciata* (Ruppell)
Mojarra	*Gerres oyena* (Forsskal)
Grouper	*Epinephellus tauvina* (Forsskal)
Mackerel	*Scomberomorus commerson* (Lacepede)
Orange spotted emperor	*Lethrinus kallopterus* (Bleeker)
Porgy	*Mylio bifasciatus* (Forsskal)

RESULTS AND DISCUSSION

Fish samples were analyzed for residues of all chemicals listed as pesticide reference standards.

Table 2 and 3 indicate the detected residues in fish samples. Four compounds were identified and quantified in fish namely, Y-HCH (Lindane), p,p DDE, pp DDD and p,p DDT. Y-HCH was detected in 16.6% of all fish examined with the mean concentration 0.43 ng/g (Wet weight). p,p DDE was found in 66.6% of all fish species and its concentration ranged between 0.01 to 0.36 ng/g (wet weight). p,p-DDD was detected in 33.3 % of all fish examined and its concentration ranged between 0.08 to 0.11ng/g (wet weight). The frequent detection of p,'p-DDE and p,'p-DDD in fish sam-

ples indicated the degradation of DDT to its metabolites.

The salty water of the Arabian Gulf therefore contains very low residues near the coasts as a result of human activity.

Residues of alpha HCH, beta HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, o'p-DDD and o'p-DDT were not detected in any of the analyzed samples.

The data indicate gamma HCH presence and not alpha or beta, and p,'p-DDT with the highest concentrations, which both lead to the conclusion of a recent use of HCH and DDT pesticides since the residues are not aged, i.e. in the form of DDE and B-HCH.

The highest residue of DDT isomers (p-'p-DDT, p,'p-DDD and p,'p- DDE) was reported in black banded trevally and amounted to 1.24 ng/g wet weight, while the lowest value 0.03 ng/g wet weight was found in porgy.

Comparison of organochlorine pesticide residue levels detected in fish from the Qatari coastal waters have indicated that they were below the range of values reported on fish from the coastal waters of Oman, Iraq and Kuwait (Burns *et al.,* 1982; Dou Abul *et al.,* 1987 and Villeneuve *et al.,* 1987, respectively).

The Codex Committee for Pesticide Residue (CCPR) does not establish MRLs for pesticide residues in fish. The amounts of DDT complex and gamma-HCH (Lindane) residues detected in fish samples, on fat weight or whole sample basis were compared to the legal limit established by the different countries and published by the Food and Agriculture Organization of the United Nations (1983), (Table 4). The concentrations of DDT isomers and Y-HCH detected in this investigation were below the MRL'S.

In light of the above reasoning, we may thus conclude that there was no direct input of organochlorine pesticides to the Qatari coastal waters. Transportation via natural processes appeared to be the sole source for these contaminants.

The present work was only a start. The current limited monitoring program should be implemented on al larger scale including several other species of fish.

Table 2. Organochlorine residues in fish samples from Qater (ug/kg wet weight).

Fish species	- HCH	p,'p - DDE	p,'p - DDD	p,'p - DDD	p,'p - DDD
	X**	X-	X-	X-	X-
Black banded trevally	ND***	0.53	0.08	0.72	1.15
	ND ND	0.35 0.35	0.10 0.10	0.75 0.75	1.20 1.20
	ND	0.36	0.11	0.77	1.24
	0.42	0.02	ND	0.85	0.87
Mojarra	0.43 0.43	0.06 0.06	ND ND	0.86 0.86	0.92 0.92
	0.45	0.09	ND	0.88	0.97
Grouper	ND	ND	0.09	0.01	0.10
	ND ND	ND ND	0.09 0.09	0.03 0.03	0.12 0.12
	ND	ND	0.10	0.06	0.16
	ND	ND	ND	0.96	0.96
Mackerel	ND ND	ND ND	ND ND	0.97 0.97	0.97 0.97
	ND	ND	ND	0.97	0.97
Orange spotted emperor	ND	0.03	ND	0.05	0.08
	ND ND	0.04 0.04	ND ND	0.07 0.07	0.11 0.11
Porgy	ND	0.05	ND	0.08	0.13
	ND	0.01	ND	ND	0.01
	ND	0.03 0.03	ND ND	ND ND	0.03 0.03
		0.04	ND	ND	0.04

* Sum of p,'p-DDE, p,'p-DDD and p,'p-DDT

** X = Mean concentration of the three samples from every species.

*** ND = not detectable.

Table 3 . Organochlorine residues in fish samples from Qater (ug/kg wet weight).

Fish species	% Fat	- HCH	p,'p - DDE	p,'p - DDD	p,'p - DDT*
Black banded trevally	1.42	ND**	0.025	0.007	0.085
Mojarra	1.71	0.025	0.004	ND	0.054
Grouper	0.66	ND	ND	0.013	0.017
Mackerel	1.40	ND	ND	ND	0.069
Orange spotted emperor	0.18	ND	0.024	ND	0.061
Porgy	0.17	ND	0.018	ND	0.018

* Sum of p,'p-DDE, p,'p-DDD and p,'p-DDT

** ND = not detectable.

Table 4 . Range of legal limits* in different countries for organochlorine pesticides in fish.

Pesticide	Range (ppm)
HCH isomers	0.2-0.5
Lindane	0.5
DDT complex	0.2-0.5
Heptachlor	0.01-0.3
Aldrin + dieldrin	0.1-0.5
Hexa chlorobenzene	0.2-0.5
Oxychlordane	0.01-0.3
PCBs	2.0-5.0

* Limits issued from Canada FRC, Denmark, Sweden, United States and Thailand (FAO, 1983).

content from fish species did not exceed 2% (Table 3). Each subsample consisted of 100 g tissue.

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متبقيات مبيدات الكلور العضوية فى أسماك المياه الساحلية القطرية

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المعلومات المتوافرة عن مستوى التلوث بالمبيدات الكلورينية فى الخليج العربى حول قطر قليلة ، ولذلك أخذت ستة أنواع من الاسماك الشائعة فى قطر عام ١٩٨٧ وحللت لتقدير المبيدات الكلورينية بها . والنتائج المتحصل عليها التى قدرت بواسطة كروماتوجرافيا الغاز G.C. وعززت بالطبقة الرقيقة TLC أظهرت كميات قليلة من المبيدات الكلورنية فى عينات السمك وكان اغلب التلوث الحادث كان بمبيدات اللندين ، بارابارا د.د. إى ، بارابارا د.د.د. ، بارابارا د.د.ت.