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Determination of Organochlorine Pesticide Residues in Freshwater Fish Species in Punjab, India

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Abstract The levels of organochlorine pesticides residues were determined in five freshwater fish species in Punjab State, India. These species were selected in view of their importance to local human fish consumer. DDTs were the predominant organochlorine contaminants in all species with pp DDT and pp DDE as the main pollutants. Other organochlorines, such as HCH isomers and dieldrin were also found at lower levels in fish species. The α-HCH was the dominant isomer of HCH in all fish species followed by γ-, β- and δ-HCH. The residues of aldrin, chlordane, heptachlor and endosulphan were not detected in any fish sample. The levels of organochlorines detected in present study were below the tolerance limits recommended at National and International standards.

Keywords Fish · India · Organochlorine · Residues

The usage of Organochlorine pesticides (OCPs) is indispensable in the agricultural production technology and control of vector borne diseases in the developing countries. The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of OCPs have led to their widespread accumulation in food chain (John et al. 2001; Bedi et al. 2005; Aulakh et al. 2006) and subsequent magnification of concentrations in human, a final link in the food chain (Surendernath et al. 2000). The pesticides applied on land eventually find their way to the aquatic environment, thus contaminating it and the OCPs could persist in soil and water for several years and subsequently get accumulated in aquatic organisms (Abdallah et al. 1990). In India, the indiscriminate and injudicious use of OCPs have led to the contamination of water bodies near to lands, rivers and estuarine bodies (Sarkar and Gupta 1988; Singh et al. 2005) resulting in high concentration in aquatic life especially fish, prawns, otters, shrimps etc. (Murray and Beck 1990; Sreenivasa and Rao 2000; Sarkar and Gupta 1998). The consumption of biota from contaminated aquatic body is considered to be an important route of exposure to OCPs (Johansen et al. 1996) in humans resulting in variety of health hazards particularly endocrine dysfunction, births defects, breast cancer, lower sperm count, testicular cancer (Brody and Rudel 2003; Ahmed et al. 1996; Garry et al. 2004; Soto et al. 1998).

Fish are valuable source of high-grade protein and occupy an important position in the socio-economic conditions of South Asian countries. India is the third largest producer of fish and second in inland fish production (Feroz and Panikkar 2006) with annual production of 7.75 million tones. Keeping in view of public health significance of pesticide residues, safety of consumers and legal restrictions on export the present study was proposed to monitor the OCPs levels in edible fish species in Punjab.

Materials and Methods

Punjab is northwestern state of India which has great potential for integration of inland fish farming with agriculture. Randomly nine sampling sites were chosen in state and five species of fish were selected and depending upon their availability three samples of each species were collected (weighing 400–500 g) which constitute a total sampling of 90 fish samples. The samples were transported

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to laboratory under chilled conditions and were stored at −20°C till processing.

Anhydrous sodium sulphate and silica gel extra pure (60–120 mesh) for column chromatography were obtained from Merck. The adsorbents were washed thrice with hexane and activated at 160°C overnight. The solvents (Merck) were glass distilled before use and they did not yield any interfering gas chromatographic peak when concentrated from 10 mL to 100 µL. All individual standards of pesticides α-, β-, γ-, δ-HCH, aldrin, dieldrin, chlordane, α-endosulphan, β-endosulphan, endosulphan sulphate, heptachlor, op DDT, op DDE, pp DDT, pp DDE and pp DDD were obtained from Dr. Ehrenstofer Laboratories (Augsburg, Germany).

The extraction and clean up of fish samples were carried out by the method as described by Abdallah et al. (1990) with slight modifications. Briefly, for extraction high-speed blending was done by using petroleum ether. The clean up of the samples was performed by silica gel chromatography and the final elution was carried out by using 6% diethyl ether in petroleum ether. The eluate was concentrated under vacuum to suitable volume and stored in labelled glass stoppered vials. The quantitative analysis of organochlorines was done by gas liquid chromatography equipped with electron capture detector and a 2 m (length) × 3 mm id. Glass column packed with 1.5% OV-17 + 1.95% OV-210 on chromosorb WHP 80–100 mesh. Temperature of injection port, column and detector were 250, 230 and 260°C, respectively, with N_2 gas flow at rate of 3.0 kg/cm^2 Psig. The limit of detectability was 0.0005 mg/kg for γ-HCH and 0.001 mg/kg for DDT metabolites. Confirmation of results were done on an alternate glass column (1.1 m × 3 mm) packed with OV-210 coated on 100–120 mesh chromosorb WHP.

Results and Discussion

Recoveries of HCH isomers, DDT metabolites, dieldrin, endosulphan and heptachlor spiked at levels of 0.5 and 1.0 mg/kg were ranged from 84% to 94%. The average levels of organochlorine residues and their frequency of detection in different fish species are presented in Table 1. The maximum levels of total HCH (0.007 mg/kg) and DDT (0.014 mg/kg) were detected in common carp. The present study indicates that 100% contamination of fish species by one or metabolites of HCH or DDT. Dieldrin residues were detected in rohu, grass carp and catla only. The residues of aldrin, chlordane, endosulphan and heptachlor were not detected in any fish sample. As far as the total pesticide residue burden is considered in different species, common carp had maximum levels of OCPs as 0.021 mg/kg followed by rohu (0.019), grass carp (0.019),

Table 1 Average residue levels (mg/kg) of OCPs in different edible freshwater fish species in Punjab

Fish species	No. of samples	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	opDDT	ppDDT	ppDDD	ppDDE	ΣDDT	Dieldrin
Rohu *Labeo rohita*	27	0.002 (77.8)	BDL	0.002 (100)	0.001 (22.2)	0.005 (100)	0.001 (33.3)	0.004 (77.8)	0.003 (88.9)	0.005 (100)	0.013 (100)	0.001 (33.3)
			–									
Common carp *Cyprinus carpio*	24	0.003 (75.0)	0.001 (25)	0.003 (87.5)	BDL	0.007 (100)	0.003 (75.0)	0.004 (62.5)	0.003 (87.5)	0.004 (100)	0.014 (100)	BDL
					–							–
Grass carp *Ctenopharyngodon idella*	21	0.003 (100)	BDL	0.003 (100)	BDL	0.006 (100)	0.004 (85.7)	0.003 (57.2)	0.002 (71.4)	0.003 (100)	0.012 (100)	0.001 (14.2)
			–		–							
Catla *Catla catla*	12	0.003 (100)	BDL	0.002 (100)	BDL	0.005 (100)	0.004 (100)	0.003 (75)	0.001 (25)	0.003 (100)	0.011 (100)	BDL
			–		–							–
Silver carp *Hypophthalmichthys molitrix*	06	0.002 (100)	BDL	0.002 (50)	0.002 (100)	0.006 (100)	0.002 (50)	0.005 (100)	0.001 (50)	0.003 (100)	0.011 (100)	0.001 (25)
			–									
Total	90	0.013	0.001	0.012	0.003	0.029	0.014	0.019	0.010	0.018	0.061	0.003

Figure in parentheses indicates frequency of detection
BDL-below detectable limits

catla (0.017) and silver carp (0.017). Among the organochlorines, DDT contributed more as compared to HCH and dieldrin. The proportion of DDT in rohu, common carp, grass carp, catla and silver carp were 68.4%, 66.6%, 63.1%, 68.7% and 61.1%, respectively.

In some earlier studies in India, Battu et al. (1984) detected OCPs in fresh water fish in Ludhiana, residues of both DDT and HCH were present in all the samples and maximum levels of DDT were found to be 3.02 mg/kg, while Kannan et al. (1992) reported mean levels of HCH and DDT as 0.002 and 0.015 mg/kg, respectively, in fish. Amaraneni and Pillala (2001) analysed fish samples in Andra Pardesh, India and the maximum concentration of α-, γ-HCH and pp DDT were found to be 123.8, 98.70 and 157.4 mg/kg, respectively. Anupma et al. (2001) detected residue levels of DDT in fish samples from Ganga River, India with range of 0.0726–1.666 mg/kg.

In present study, among various isomers of HCH, α-HCH was predominant followed by γ-HCH, while β-HCH was detected only in common carp. Amaraneni and Pillala (2001) reported α-HCH as the predominant isomer of HCH with maximum concentration of 123.8 μg/g followed by γ-HCH (98.7 μg/g). Pandit et al. (2001) also reported the α-HCH to be more dominant isomer of HCH in fish. Among DDT metabolites pp DDT and pp DDE were at highest levels followed by op DDT and pp DDD. Kannan et al. (1992) reported pp DDE as main contaminant metabolite of DDT followed by pp DDD and pp DDT; similarly Jiang et al. (2005) detected pp DDE as predominant metabolite while Amaraneni and Pillala (2001) reported higher levels of pp DDT among DDT metabolites.

India banned DDT for agricultural purposes in 1989, but continues to use between 5,000–10,000 kg/year for malaria control. Technical HCH, once the most heavily used pesticide in India with annual consumption exceeding 6×10^7 kg was banned in 1997, but lindane (γ-HCH) has been used as a replacement since that time (Santilo et al. 1997). In present study α-HCH was detected in all fish species despite the ban which indicates the current or recent use of HCH technical mixture. The presence of op DDT and pp DDT in fish species also indicates its recent exposure and pp DDE and pp DDD indicates the outcome of metabolic process in body of fish (Kannan et al. 1997). Moreover the α-HCH and pp DDE have the highest biomagnifications potential as compared to other isomers/metabolites of HCH and DDT (Manirakiza et al. 2002). In China, DDT was banned 20 years ago, inspite of this organochlorine pesticides were detected in soil, water, fish and sediment samples. DDT residues in fish ranged from 3.7 to 23.5 μg/kg and HCH ranged from 3.7 to 132 μg/kg. These results demonstrate an accumulation through food chain, from soil–water–sediment–microbes–crop–fish etc. (Feng et al. 2003). Some other South-Asian countries also reported the contamination of fish species with pesticide residues. In Pakistan, Saqqib et al. (2005) detected DDE, aldrin and dieldrin residues in fish tissues while Jabber et al. (2001) in Bangladesh reported the levels of DDT, aldrin, dieldrin, lindane and heptachlor in different organs of fish.

Table 2 Comparison of total OCPs residue levels in fish of present study with national and international standards

Pesticide	Present study (mg/kg)	National* (mg/kg)	International* (mg/kg)
Aldrin/dieldrin	0.003	0.02	0.11 ± 0.09
DDT (either DDE, DDT, DDD or combination)	0.061	1.0	7.0
α-HCH	0.013	0.25	–
β-HCH	0.001	0.25	–
γ-HCH	0.012	0.25	0.2 ± 0.1
δ-HCH	0.003	0.25	–

*Mohindru (2005)

The results obtained in this study were compared with the recommended tolerance limits of the Ministry of Health, Government of India and FAO/WHO for the organochlorine residues which showed that concentrations were below the limits (Table 2). More importantly, in comparison to earlier reports in India the present levels of the contaminants are substantially lower which indicate the gradual phase out of these compounds, but keeping in mind the long term health hazards of pesticide residues it is advisable to regularize the monitoring of pesticide contaminants in fish as these are highly lipophilic and persist in nature and moreover fish has tremendous capacity to concentrate them.

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