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Distribution of Persistent Organic Pollutants in Farm Fish, Sediments and Water from Punjab (India)

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Abstract

Persistent organic pollutants (POPs) are toxic chemicals that are adversely affecting animal and human health and the environment around the world. They persist for long periods of time in the environment and can accumulate and pass from one species to the next through the food chain. The present study aimed for determination of POPs residues in farm fish and its environment. Total 195 farm fish, 39 sediments and 39 water samples were collected from Punjab and then analyzed by gas chromatography (GC) and confirmed by GC-mass spectrometry. Residues of lindane, p,p'-DDE, p,p'-DDD, endosulfan sulfate, polychlorinated biphenyls (PCB)-28, PCB-138, and PCB-180 were detected with mean levels of 22.6, 15.3, 22.7, 23.7, 26.9, 27.3, and 25.7 ng/g in farm fish samples, respectively. In the fishpond sediment samples presence of lindane and p,p'-DDE residues were noticed with mean levels of 17.7 and 9.4 ng/g, respectively. Residues of p,p'-DDE and endosulfan sulfate were detected with a mean level of 14.9 and 64.4 ng/g in fish pond water samples. The comparison of overall mean residues of POPs observed in fish samples throughout Punjab revealed that the levels were below the maximum residue limits (MRLs) described by EU-MRLs, Italian-MRLs, FDA-2001, and FAO-1983. The presence of POPs residues in the aquatic environment requires continuous monitoring for the safeguard of human health.

Keywords: Farm Fish, Maximum Residue Limits, Persistent Organic Pollutants, Sediments, Water

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1. Introduction

Persistent Organic Pollutants (POPs) are toxic chemicals that are adversely affecting animal and human health and the environment around the world. They persist for long periods of time in the environment and can accumulate and pass from one species to the next through the food chain. Under the United Nations treaty, known as the Stockholm Convention, 90 countries agreed to reduce or eliminate the production, use and/or release of POPs. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are ubiquitous POPs in the environment worldwide.[1] India has produced, imported, and used large amounts of OCPs and PCBs in agricultural and industrial sectors. During the past years, POPs pollution problem in India has exacerbated, especially in rapidly developing regions of the country.[2] The nonjudicious use of chemicals in agricultural and uncontrolled industrial waste discharge has created significant environmental concern. Through surface runoff, river inputs and atmospheric deposition, POPs have spread to every aquatic environment and have entered the aquatic food chain.[3] Aquatic organisms such as fish and shellfish are able to accumulate persistent residues several times higher than the surrounding water.[4] Due to shorter residence times in upper water layers, POPs tend to become part of the sediments and continuously recycle into the water column. POPs in the water system can find way into fish through direct contact

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or feeding, accumulate in the fatty tissues and become available for human consumption.[5]

Food of animal origin is one of the main exposure routes for POPs in human beings; the lipophilic and bioaccumulative properties of POPs are posing threats to human health. Many studies have demonstrated high and increasing levels of POPs in humans.[6] Moreover, food safety problem caused by POPs has become one of the most important serious concerns of the world. Therefore, in view of the importance of POPs in food articles, their biomagnifications potential in fish, increasing concerns and toxicity to human beings, the present study was designed to investigate residual levels of POPs in farm fish from Punjab and identification of potential sources of POPs in fish by examining fish farm water and sediments.

2. Materials and Methods

Punjab is a North-Western state of India and has an area of 50,362 km^2. It extends from the latitudes 29.30° North to 32.32° North and longitudes 73.55° East to 76.50° East. In Punjab, we collected 195 farm fish samples from 39 fish farms and also obtained the farm sediments and pond water. Samples from different organized fish farms were brought to the laboratory under chilled conditions, and representative sample of 5 g was taken for further processing. About 1 L of pond water was collected in glass bottles from the same organized farms. Water from the spot of the collection was used to rinse the bottles 3 times before sampling was done. About 100 g of pond sediments samples were collected from the same organized farms.

The extraction and clean-up of fish samples were carried out by the method as described by Tanabe *et al.*[7] using soxhlet apparatus and florisil clean up. Water samples were extracted as per the methodology described by Hernández *et al.*[8] with slight modifications. The extraction and clean-up of sediment samples were carried out by the method as described by Tanabe *et al.*[7] Estimation of POPs residues was done using Gas Chromatograph (GC) equipped with electron capture detector (Shimadzu 2010). The GC oven temperature for electron capture detector was initially programmed at a temperature of 170°C for 13 min followed by temperature increased to 270°C at the rate of 3°C min^{-1} with hold time for 20 min. The temperature of injection port was set at 280°C whereas the temperature of the detector was adjusted at 310°C. Nitrogen was used as carrier gas. Analytical, technical grade standards with 93–99 % purity for POPs were procured from Sigma-Aldrich (USA). The confirmation of pesticidal POPs residues detected by gas chromatography (GC) was done on GC-mass spectrometry (Shimadzu GCMS QP2010 plus). The mass spectrometer was operated in electron ionization mode. The interface, manifold and ion source temperatures were 290°C, 50°C and 200°C, respectively. The emission current for the ionization filament was set at 80 μA generating electrons with energy of 70 eV. Helium (99.99%) at a flow rate of 0.94 ml min^{-1} was used as carrier and collision gas. In this study, selective ion monitoring method was designed for pesticidal POPs including retention time windows and base peak ions.

3. Results

The trueness of the method used for extraction and estimation was validated by the processing of spiked fish, sediments, and water samples with standard POPs at concentrations of 50 and 100 μg/kg. The mean recovery values of spiked samples were ranged from 78.3 for PCBs and 89.4% for aldrin, which was in accordance with the acceptable recovery range of 70–120 %.[9] Repeatability of the method aligned with association of analytical chemists[9] estimations by relative standard deviation of the recoveries values which were below 10%. The calculated concentrations of residues in samples were not corrected for recovery. The detection limits of the method were ranged from 7.0 ng/g for p,p'-DDE and dieldrin to 20.0 ng/g for PCBs.

Among different POPs analyzed in the present study, detectable residues of hexachlorocyclohexane (HCH), DDT and endosulfan were observed in farm fish samples [Table 1]. However, residues of aldrin, dieldrin, chlordane, methoxychlor, heptachlor, mirex, and endrin were not observed in any fish sample. Out of six congeners of PCBs analyzed, residues of PCB-28, PCB-138, and PCB-180 were observed in farm fish samples. The occurrence of p,p'-DDE and p,p'-DDD was reported highest with mean levels of 6.4 and 3.3 ng/g followed by lindane and endosulfan sulfate. Residues of γ-HCH, p,p'-DDE, p,p'-DDD, endosulfan sulfate, PCB-28, PCB-138, and PCB-180 were detected in 2.5, 42.0, 14.8, 0.5, 1.5, 1.5, and 1.5% of fish samples, respectively. A total 39 fishpond sediment samples collected from fish farms revealed the presence of γ-HCH (10.2%) and p,p'-DDE (56.4%) residues with

mean levels of 1.8 and 5.3 ng/g and fluctuation of 14.3–23.4 and 7.1–13.4 ng/g, respectively. The analysis of fish pond water samples reflected the occurrence of p,p'-DDE and endosulfan sulfate with mean levels of 3.0 and 28.0 ng/g, respectively in 20.5 and 43.5% of water samples.

4. Discussion

In this study, residues of γ-HCH were detected in fish, pond sediment and water. γ-HCH (lindane) continues to be manufactured in India and used for crop protection. The substantial change in the isomeric composition of HCH in fish samples was found in the present study as compared to earlier reports. In the earlier reports, Battu *et al.*[10] reported α-HCH residues at maximum, while Kannan *et al.*[11] reported highest levels of β-HCH isomer followed by α-HCH, δ-HCH and γ-HCH. In the present study, the occurrence of lindane in fish samples can be justified with its ongoing use. However, the absence of other isomers (α, β, δ) indicated the effectiveness of a ban on the use of technical HCH mixture in Punjab.

DDT continues to have limited use in India for the control of malaria. Regarding the occurrence of DDT metabolites in the present study, p,p'-DDE was leading imitated its long-term bioaccumulation in living beings. Based on DDT/DDE ratio, to differentiate the current and historical exposure to DDT a low DDT/DDE ratio indicates high persistence in the environment and ongoing biomagnifications, whereas a high DDT/DDE ratio implies both unceasing and also ongoing exposure to DDT.[12] In this study, it can be presumed that it was due to past exposure to DDT. However, the presence of traces of p,p'-DDD (reduced metabolite of DDT in living beings) can be interpreted as an evidence of low fresh exposure to DDT. Dogheim *et al.*[13] reported high levels of DDT in fish collected from two Egyptian governorates and found o,p' DDT as the main contaminant, while in the earlier reports of Battu *et al.*,[10] Kannan *et al.*[11] p,p'-DDE was the main contaminant followed by p,p'-DDD and p,p'-DDT.

Endosulfan comprises two isomers, endosulfan I and II, with I/II ratio of about 2.3 in the technical mixture. Both isomers break down in the environment to produce endosulfan sulfate. In this study, residues of endosulfan sulfate were detected in fish and water samples, however, in some earlier studies higher endosulfan residues were detected and contributed 11.8% to a total of POPs residues in farm fish samples.[14] In addition, endosulfan is commonly used by fish cultivators to harvest their produce, probably for minimizing the cost of harvesting. Thus, there is the likelihood of accumulation of endosulfan residues in the fish tissues after harvesting.[15] However, in the present study, we did not detect any endosulfan I and II residues in fish may be because we collect live samples of fish directly from the ponds before harvesting.

Recent studies from India have shown that the open municipal dumping sites common around the outskirts of many metropolitan cities are a potential emission source of PCBs.[16] In India, PCBs have been banned in transformers and capacitors since 1997. A 1996 World Bank study estimated approximately 2000–4000 tons of PCBs existed in India.[17] In this study, the presence of PCBs congeners (PCBs 28, 138, and 180) in fish samples has been detected in Punjab. Some earlier reports from India and other countries have reported the occurrence

Table 1. POPs residue levels (ng/g) in farm fish, fish pond sediments and fish pond water in Punjab

POPs	Fish (n=195)		Sediments (n=39)		Water (n=39)	
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
Lindane	0.6±3.97 (2.5)	16.7–31.2	1.8±5.5 (10.2)	14.3–23.4	ND	-
p,p'-DDE	6.4±9.0 (42.0)	7.1–65.1	5.3±4.9 (56.4)	7.1–13.4	3.0±6.4 (20.5)	8.9–23.7
p,p'-DDD	3.3±8.4 (14.8)	15.7–44.6	ND	-	ND	-
Endosulfan sulfate	0.1±1.6 (0.5)	ND–23.7	ND	-	28.0±36.6 (43.5)	21.4-94.5
PCB-28	0.4±3.3 (1.5)	24.5–31.4	ND	-	ND	-
PCB-138	0.4±3.4 (1.53)	22.7–34.1	ND	-	ND	-
PCB-180	0.3±3.1 (1.5)	24.5–26.4	ND	-	ND	-

ND=Not detected, Figures in parentheses indicate the percentage positive, SD=Standard deviation, POPs=Persistent organic pollutants, PCB=Polychlorinated biphenyl

Compound	EU-MRL (ng/g)[a]	Italian MRL (ng/g)[a]	FDA, 2001 (ng/g)[b]	FAO, 1983 (ng/g)[b]	Present study	
					Mean (ng/g)[c]	Absolute mean (ng/g)[d]
Chlordane	50	50			-	-
DDT	1000	1000	5000	300	17.3	4.9
Dieldrin	200	200	300	300	-	-
Heptachlor	200	200	300	300	-	-
HCB	200	200			-	-
α-HCH	200	200			-	-
β-HCH	100	100	300	300	-	-
γ-HCH	1000	1000	300	300	22.6	0.6
Endrin	50	50	0.3	300	-	-
ΣPCBs	200				26.9	0.3

[a]Stefanelli et al. 2004,[22] [b]Sankar et al. 2006,[21] [c]Mean=Negative samples were excluded in calculation for mean, [d]Absolute=Negative samples were included for calculation of mean. OCPs=Organochlorine pesticides, PCB=Polychlorinated biphenyl, MRLs=Maximum residue limits, FDA=Food and Drug Administration, FAO=Food and Agriculture Organization, EU-MRL=European Union maximum residue limit, HCH=Hexachlorocyclohexane, HCB=Hexachlorobenzene

of PCBs residues in the aquatic environment.[18] Newsome and Andrews[19] reported the PCBs contamination in Eel and trout species of fish at the levels of 633 ng/g. Similarly, Yamaguchi *et al.*[20] observed levels of PCBs in Thames catchment area, UK with a range between <0.77 and 3.32 ng/g.

4.1 Contaminant Presence of Persistent Organic Pollutants Residues in Farm Fish, Pond Sediments and Pond Water

In this study, the results indicated the contamination of fish pond sediments and water with residues of lindane, p,p'-DDE and endosulfan which can be a source for occurrence of residues in fish. However, residues of p,p'-DDD and PCBs were also encountered in fish tissues which were not seen in sediments and water. In addition, endosulfan residues were detected in water samples and not recorded in fish pond sediment samples. POPs residues in sediments or water could have been suffered environmental degradation, may be being below the detection limit or the contaminated sediment or water components were not sampled even though we took composite samples. Other reason may be the bioaccumulation potential of POPs which is being observed in different fish species, even though the POPs residue level in sediment and water were not detected. Another plausible reason may be that many fish species take their feed as surface sediment which may be the source of contamination also. The POPs residues transference is influenced by the quantity ingested, absorption, metabolism, and excretion by fishes. Therefore, the best risk management tool is the prevention of exposure either through feed or from the environment of the fish to these contaminants.

4.2 Comparison of Current Persistent Organic Pollutants Residue Levels in Fish with Maximum Residue Limits

The health effects of POPs cannot be underestimated, and thus Maximum Residue Limit (MRL) has been recommended by various agencies to regulate human consumption of these chemicals.[21] In this study, the comparison of overall mean residues of POPs observed in fish samples throughout Punjab revealed that the levels were below the MRLs described by EU-MRLs, Italian-MRLs, FDA-2001, and FAO-1983 [Table 2]. It could be concluded that exposure of humans through fish consumption from the farm fish of Punjab do not appear to be harmful presently although chronic exposures could lead to serious health problems.

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