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Residues of Organochlorine Pesticides in Fish from the Gomti River, India

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Abstract This study reports the levels and distribution patterns of some organochlorine pesticides (OCPs) in fish samples of the Gomti river, India, collected from three sites. In the fish muscles $\sum$OCPs ranged between 2.58–22.56 ng g^{-1} (mean value: 9.66 ± 5.60 ng g^{-1}). Neither spatial nor temporal trends could be observed in distribution of the OCPs. Aldrin was the predominant OCP, whereas, HCB and methoxychlor could not be detected. α-HCH and β-HCH among the isomers of HCH and pp-DDE among the metabolites of DDT were the most frequently detected OCPs. The results revealed that the fish of the Gomti river are contaminated with various OCPs.

Keywords Fish muscles · *Channa punctatus* · GC-ECD · Pesticides

Organochlorine pesticides (OCPs) are among the most serious global environmental contaminants of concern. Due to their resistance to environmental degradation, OCPs have remained major pollutants with numerous investigations reporting the continued and ubiquitous presence of OCPs in the global atmosphere (Hung et al. 2002). OCPs are mainly used to control the soil and crop pests in agricultural fields, and find their way into aquatic systems through discharges of domestic sewage and industrial wastewater, runoff from agricultural fields and direct dumping of wastes into river systems. Subsequently, pesticides may distribute among the river ecosystem components, such as water and sediment and accumulate in the aquatic biota. Since the pesticides are lipophilic in nature, their cumulative accumulation at low concentrations in the body fat of mammals might pose potential hazards in the long run (Metcaff 1997). OCPs have also been linked to human breast and liver cancers, testicular tumors and lower sperm counts in humans (Davies and Barlow 1995). In India, the residues of chlorinated pesticides have been detected in almost all the segments of environment due to their extensive use in past, which have shown potential to biomagnify/accumulate in animal tissue, human blood, adipose tissue and breast milk (Beg et al. 1989). The water and bed sediments of the Gomti River, one of the major tributaries of the river Ganga in northern India are contaminated with polycyclic aromatic hydrocarbons (PAHs) and OCPs (Malik et al. 2004; Singh et al. 2005a). However, there is no published information available on levels of these hazardous contaminants in the biota of the river. The river water is abstracted for domestic and drinking purpose, irrigation, recreation and fishing during its course. The presence of contaminants, which are usually carcinogenic in nature, in fish of the river may pose serious health hazards to the local population. Therefore, this study was undertaken to examine the levels and distribution patterns of some persistent OCPs in the fish samples of the Gomti river system, India.

Materials and Methods

The fish (*Channa punctatus*) samples were collected from the Gomti River (India). The Gomti River, flowing through eight districts in Uttar Pradesh drains a catchments area of about 25,000 km^2 and traverses a total distance of about 730 km before it merges with the Ganga River. Throughout its stretch, there are a few small tributaries (Kathna,

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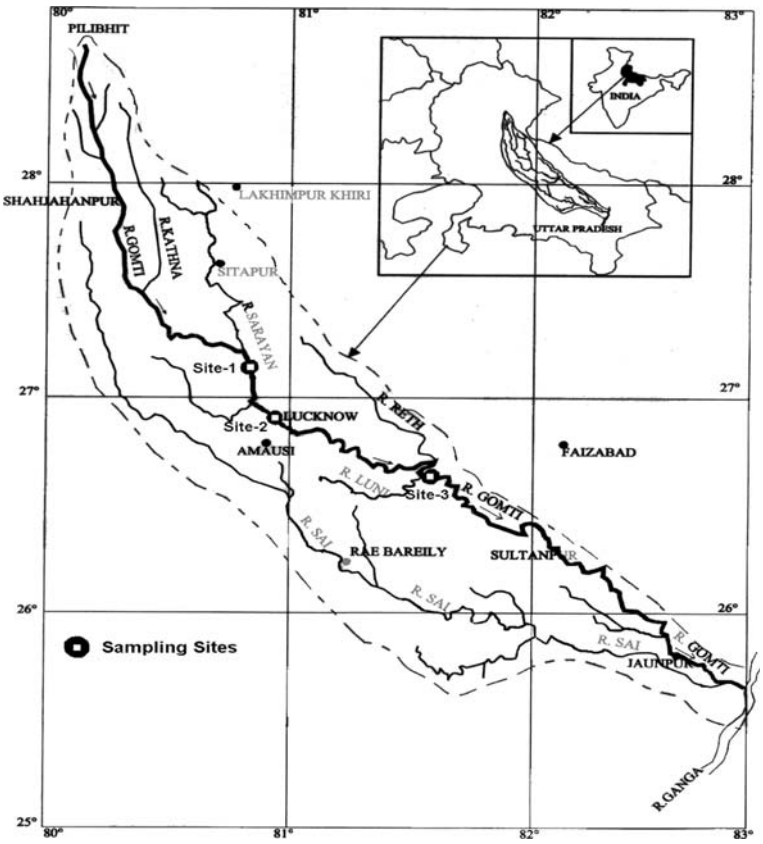

Fig. 1 Map of the Gomti River showing sampling sites

Sarayan, Reth, Luni, Kalyani, Sai) originating within short distances and carrying the wastewater and industrial effluents from different towns and industrial units in the basin. On the banks of the river, Lucknow, Sultanpur and Jaunpur are the three major urban settlements. The river serves as one of the major source of drinking water for the Lucknow City, the State capital of Uttar Pradesh with a population of about 3.5 million. The river, subsequently, receives the untreated wastewater and effluents from Lucknow, Jagdishpur, Sultanpur and Jaunpur directly in its course through more than 40 wastewater drains. The fish samples were collected during 2004–2005, in the pre- and post-monsoon seasons, from three selected sites (Fig. 1). The sampling sites on the river are located at upstream (Site-1), mid of town (Site-2) and downstream (Site-3) of the Lucknow City representing low (Site-1) and high (Site-2 and Site-3) pollution stretches, respectively. As much as it was possible, similar sized fish samples were selected. Each fish was measured (cm), tagged, and placed on ice and later frozen until they were processed and analyzed. In the laboratory, each fish was weighed (g) and the skin was removed with steel knife and steel tweezers from muscle in the middle of the fish. Then a sub-sample (~10 g) was cut from the muscle. This sub sample was ground with activated sodium sulfate until a homogeneous mixture was obtained. The mixture was transferred to a paper thimble and extracted in a soxhlet apparatus using 100 mL of solvent (*n*-hexane:dichloromethane, 1:1, v/v) for 6 h. The extract was concentrated on a rotary evaporator to about 1–2 mL in a water bath, and then purified on a glass column packed as follows: glass wool, 6 g of activated florisil and 2 g of sodium sulfate. The packed column was pre-rinsed with 70 mL of *n*-hexane:dichloromethane (1:1, v/v). The elution was carried out using 50 mL of *n*-hexane containing 25% (v/v) dichloromethane. The effluent was concentrated to 2–3 mL and then was reduced finally to a volume of 1 mL.

The OCPs in the extracts were analyzed with Gas Chromatograph (Varion CP-3800) equipped with an Ni^{63} ECD (electron capture detector) and capillary column (Fused Silica CP-Sil 19 CB capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness). The instrumental analyses were made employing nitrogen as carrier gas (2 mL min^{-1}) and operating temperatures were: 300°C for the injector port and detector and 210°C for column. Injected volume for, both sample and standard (mixture) were 1 μL. The split ratio of 1:2 was used. The selected OCPs were identified by retention time comparison by reference to the corresponding standard. The limit of detection for all OCPs was 0.1 ng g^{-1} wet weight.

The quality assurance measures included rigorous contamination control (strict washing/cleaning procedures), monitoring of blank levels of solvents, equipment and other materials, analysis of procedural blanks, recovery of spiked standards, monitoring of detector response and linearity. The pesticides standards (99.9% purity) were supplied by Sigma-Aldrich, USA. All analysis was carried out in duplicate and the recoveries of individual pesticides were determined through the spiked sample method, which were found between 79 and 108%. Recovery correction factors were applied to the final results. Results are presented as minimum, maximum and mean values with standard deviation. Means were computed by treating the concentrations of the non-detected analytes as zero. Values below the detection limits are reported as BDL.

Results and Discussion

In the muscles of the fish $\sum$OCPs (sum of all OCPs) ranged between 2.58 and 22.56 ng g^{-1} with a mean value of 9.66 ± 5.60 ng g^{-1}. The residues of OCPs detected in the fish muscles are summarized in Table 1. The samples collected from the Site-1 and Site-3 showed the lowest and highest concentrations of $\sum$OCPs, respectively. The Fig. 2 presents the spatial variation of seasonal means of $\sum$OCPs residues. Although, no clear spatial or temporal trend could be found, however, in general relatively higher concentrations were observed at Site-3 during the study period except in pre-monsoon season of 2005, and relatively lower concentrations were found at Site-1. The higher residues at Sites- 2 and 3 as compared to Site-1 may be attributed to the input of waste water from drains and tributaries of the river. The Site-2 is located at mid of the Lucknow City, and before the site, there are some six drains carrying partially treated/untreated sewage and industrial wastewater from different parts of the city, discharging directly into the river. Two tributaries viz. Reth and Luni carrying urban waste water as well as mixed industrial effluents from Barabanki town and Gosaiganj township, respectively, join the river just before Site-3.

The detection frequencies (DF) of individual OCPs in the fish muscles are presented in the Fig. 3a. Aldrin (DF = 100%) was the predominant compound followed by dieldrin (DF = 75%), whereas, HCB and Methoxychlor could not be detected in any of the sample. Among the HCH isomers, α- and β-HCH dominated, followed by γ- and δ-isomers. In the DDT metabolites, it was the pp-DDE which was detected in most of the fish samples.

Figure 3b represents the overall average residue concentration of individual OCPs. In the fish muscles, aldrin, dieldrin and endrin ranged from 0.30 to 7.84 ng g^{-1}, BDL-3.75 and BDL-0.75 ng g^{-1}, respectively. The aldrin residues are lower than that reported by Bakre et al. (1990) for the same collected from a reservoir in Jaipur (India). The aldrin and dieldrin dominated over the endrin, both in terms

Table 1 OCPs residues (ng g^{-1} wet wt) in fish muscles of the Gomti River

Pesticides	Site-1 Range (mean ± SD)	Site-2 Range (mean ± SD)	Site-3 Range (mean ± SD)
Aldrin	0.30–3.27	0.70–4.34	0.46–7.84
	1.48 ± 1.36	2.55 ± 1.49	2.53 ± 3.56
α-HCH	BDL-0.57	BDL-1.33	BDL-0.35
	0.21 ± 0.27	0.65 ± 0.54	0.18 ± 0.15
β-HCH	BDL-0.31	BDL-0.57	BDL-0.68
	0.13 ± 0.16	0.30 ± 0.26	0.32 ± 0.28
γ-HCH	BDL-0.65	BDL-1.05	BDL-1.93
	0.28 ± 0.33	0.46 ± 0.54	0.84 ± 0.93
δ-HCH	BDL-2.13	BDL-1.43	BDL-0.90
	0.53 ± 1.07	0.36 ± 0.72	0.23 ± 0.45
α-Endosulfan	BDL-1.41	BDL-3.58	BDL-6.00
	0.35 ± 0.71	1.51 ± 1.80	2.76 ± 2.95
β-Endosulfan	BDL-0.23	BDL-0.14	BDL-0.41
	0.06 ± 0.12	0.04 ± 0.07	0.16 ± 0.20
Endosulfan sulfate	BDL-0.42	BDL-0.63	BDL-0.40
	0.16 ± 0.20	0.33 ± 0.32	0.15 ± 0.18
op-DDT	BDL-0.35	BDL-0.38	BDL-0.25
	0.12 ± 0.17	0.12 ± 0.18	0.08 ± 0.12
pp-DDT	BDL-0.52	BDL-0.45	BDL-0.27
	0.20 ± 0.25	0.21 ± 0.24	0.10 ± 0.13
pp-DDE	BDL-0.45	BDL-0.83	BDL-7.61
	0.16 ± 0.21	0.44 ± 0.40	2.54 ± 3.56
pp-DDD	BDL-0.47	BDL-0.52	BDL-0.47
	0.20 ± 0.23	0.25 ± 0.29	0.17 ± 0.22
HCB	BDL	BDL	BDL
Heptachlor	BDL-0.52	BDL-0.47	BDL-0.41
	0.18 ± 0.25	0.20 ± 0.24	0.22 ± 0.19
Heptachlor epoxide A	BDL-0.21	BDL-0.51	BDL-0.14
	0.08 ± 0.10	0.19 ± 0.24	0.06 ± 0.07
Heptachlor epoxide B	BDL-3.50	BDL-0.31	BDL-0.85
	1.02 ± 1.66	0.12 ± 0.15	0.34 ± 0.42
α-Chlordane	BDL-1.31	BDL-0.24	BDL-0.65
	0.55 ± 0.55	0.06 ± 0.12	0.29 ± 0.34
γ-Chlordane	BDL-0.49	BDL-0.89	BDL-1.05
	0.12 ± 0.25	0.30 ± 0.42	0.34 ± 0.50
Dieldrin	BDL-1.98	BDL-1.20	0.60–3.75
	0.79 ± 0.97	0.74 ± 0.58	1.85 ± 1.48
Endrin	BDL-0.56	BDL-0.46	BDL-0.75
	0.14 ± 0.28	0.11 ± 0.23	0.19 ± 0.38
Methoxychlor	BDL	BDL	BDL
ΣOCPs	2.58–11.38	2.59–14.18	6.33–22.56
	6.75 ± 4.09	8.92 ± 3.79	13.33 ± 7.34

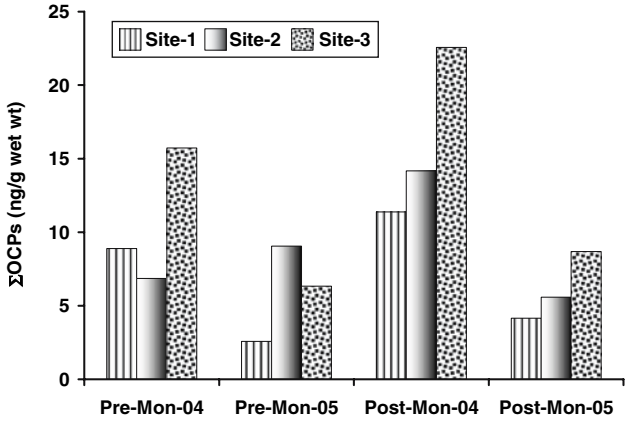

Fig. 2 Spatial variation of seasonal means of ΣOCPs in fish samples

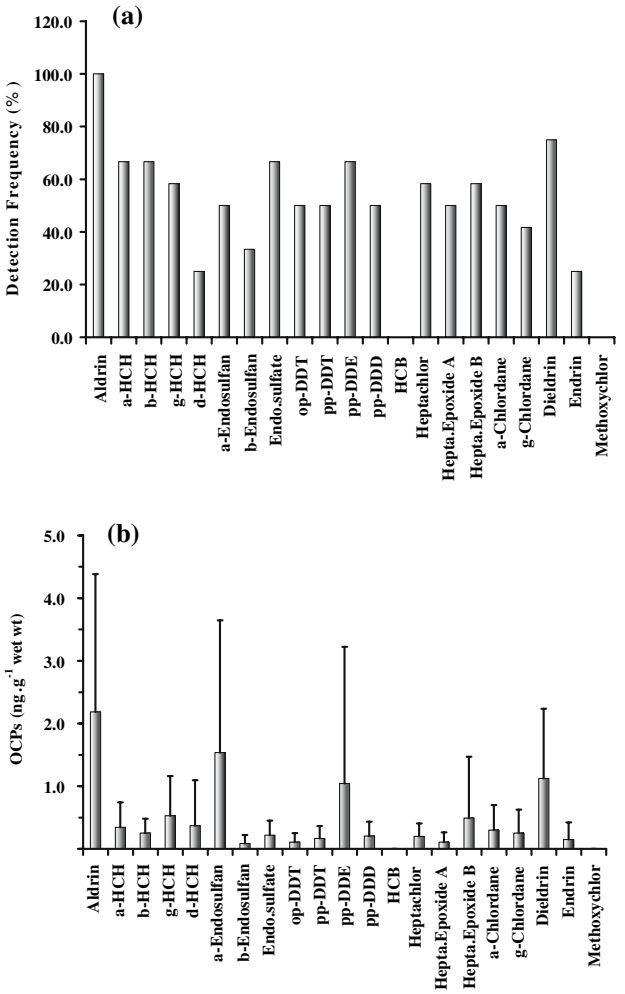

Fig. 3 **a** The detection frequencies, and **b** average residue levels of OCPs in fish samples

of detection and concentrations. These results are in accordance with Ayas et al. (1997) and Barlas (1997) reporting dominance of aldrin over the dieldrin in fish samples. Normally, aldrin is converted to its epoxide analogue by mammals, micro-organisms, plants, and insects (Matsumura 1985). Similar distribution patterns for aldrin and dieldrin have been reported in water and bed-sediments of the Gomti river (Malik 2006) and in the soil, surface water and groundwater of the adjoining areas (Singh et al. 2005b, 2007). These results suggest continued and recent use of aldrin in the study area. Ayas et al. (1997) and Erkmen and Kolankaya (2006) have also attributed dominance of aldrin to its current and continuing use in the study area. On an average, among the chlordane isomers, α-chlordane dominated over the γ-chlordane both in terms of detection frequency and residue levels. The α-chlordane ranged between BDL-1.31 ng g^{-1} and γ-chlordane ranged between BDL-1.05 ng g^{-1} with the mean values 0.30 ± 0.40 and 0.25 ± 1.13 ng g^{-1}, respectively. Among the endosulfan isomers/metabolites, residue levels of α-endosulfan (range: BDL-6.00 ng g^{-1}, mean ± SD: 1.54 ± 2.11 ng g^{-1}) were relatively higher than others viz. β-Endosulfan (range: BDL-0.41 ng g^{-1}, mean ± SD: 0.08 ± 0.14 ng g^{-1}) and endosulfan sulphate (range: BDL-0.63 ng g^{-1}, mean ± SD: 0.22 ± 0.24 ng g^{-1}).

The residue levels as well as detection frequency of heptachlor epoxide-A were relatively lower as compared to heptachlor and heptachlor epoxide-B. The residue levels ranged from BDL-0.52 ng g^{-1} (mean: 0.20 ± 0.20 ng g^{-1}), BDL-0.51 ng g^{-1} (mean: 0.11 ± 0.15 ng g^{-1}) and BDL-3.5 ng g^{-1} (mean: 0.49 ± 0.98 ng g^{-1}) for heptachlor, heptachlor epoxide-A and heptachlor epoxide-B, respectively. In general, as a whole, residue levels of heptachlor epoxides were higher than heptachlor residues. This is a usual situation, because, heptachlor is metabolized to heptachlor epoxides in the soils, plants and animals, which are more stable in biological systems. Barlas (1999) has also reported higher levels of heptachlor epoxides than heptachlor in the fish samples.

Among the isomers of the HCH, α and β-isomers were the most widely distributed, showing detection frequency of 66.67% followed by γ-HCH (DF = 58.33%) and δ-HCH (25.00%). Erkmen and Kolankaya (2006) have also observed the predominance of α and β-isomers of HCH in the fish samples of Meric delta (Turkey). The wide distribution of α-HCH isomer in the fish samples may be explained as the γ-HCH can be easily degraded by microorganisms in soil and bottom sediments (Benezet and Matsumura 1973) and photochemically isomerized to the α-isomer (Malaiyandi and Shah 1984), whereas β-isomer is highly persistent in the environment. In terms of residual concentrations, no specific trend could be observed in the distribution of HCH isomers (Fig. 4a). However, in general it was γ-HCH which showed elevated levels (range: BDL-1.93 ng g^{-1}, mean ± SD: 0.53 ± 0.64 ng g^{-1}). These residues levels are lower than that reported by Bakre et al. (1990) for the same collected

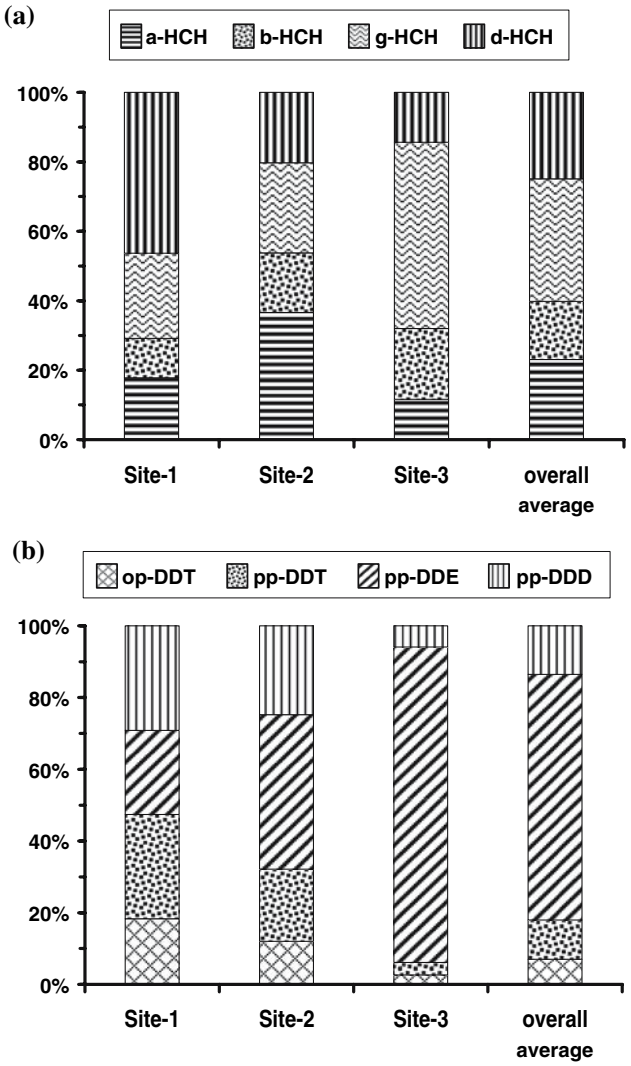

Fig. 4 Contribution of different (**a**) isomers to the ΣHCH, and (**b**) metabolites to the ΣDDT in fish samples

from a reservoir of Jaipur (India). However, Bakre et al. (1990) observed elevated levels of β-HCH followed by α-HCH. Considering the persistence order of HCH isomers ($\alpha < \gamma < \beta$), these results indicate historical input of HCH and a relatively recent use of lindane (γ-HCH) in the catchments (Kauras et al. 1998).

Among the DDT metabolites, pp-DDE was the most detected metabolite of DDT (DF = 66.67%) and with relatively higher concentrations ranging from BDL-7.61 ng g^{-1} with a mean value of 1.04 ± 2.18 ng g^{-1} (Figs. 3, 4b). The other metabolites, i.e. op-DDT, pp-DDT and pp-DDD ranged from BDL-0.38 ng g^{-1} (0.11 ± 0.14 ng g^{-1}), BDL-0.52 ng g^{-1} (0.17 ± 0.20 ng g^{-1}) and BDL-0.52 ng g^{-1} (0.21 ± 0.23 ng g^{-1}), respectively. These results are comparable with those of Bakre et al. (1990). In fish samples, at all the sites pp-DDE dominated over the other metabolites. Dominance of pp-DDE, among the DDT metabolites reflects earlier usage of DDT in the catchments. Sethajintanin et al. (2004) and Yang et al. (2007) have also reported dominance of pp-DDE in the fish samples. pp-DDE is a highly persistent metabolite in the environment and organisms. DDT and its metabolites undergo strong biomagnification along trophic transfer. Metabolism of DDT in fish is generally accomplished through dechlorination to DDE but generally not to DDD (Schmitt et al. 1999). Therefore the presence of pp-DDD in fish tissue can be from direct input of pp-DDD from the environment.

The results of this study show that fish of the Gomti River are contaminated with various persistent OCPs. The low levels of OCPs can cause an increase in mixed function oxidase activity in fish (Fossi et al. 1986). Since very little work has been carried out previously, the present results could serve as baseline data. More detailed investigations, in terms of sampling network and sampling frequencies are required in view of increasing global concern for persistent organic pollutants and their hazardous impact on environmental and human health.

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