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Environmental Contamination and Toxicology

Organochlorine Pesticide Residues in Water, Sediment, and Muscle of River Shad, *Hilsa ilisha* (Hamilton 1822) from the South Patches of the Bay of Bengal

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Growing demand for food as a result of increasing population has lead to a substantial increase in the production of agro-chemicals like pesticides and fertilizers, resulting in continued contamination of our environment (Agarwal 1976). Almost every year one third of Bangladesh is submerged under water and that's why pesticides find their way into ponds, streams, and rivers and ultimately to the Bay of Bengal. ESCAP (1988) reported that at least 25% of all pesticides made their way into the Bay of Bengal. Thus, these pesticides contaminate the coastal water, sediment and inhabitants, and ultimately are accumulated in adipose tissues of humans through the food chain. The present investigated area, South Patches is an important fishing ground of the Bay of Bengal (Hussain 1979). It is productive through providing enormous scope for the growth and propagation of numerous marine and brackish water fish species (West 1973). So, it is of utmost importance to know the contaminant levels in the fish as well as the environment.

Monitoring of aquatic pollution can be carried out by means of bio-indicator organisms because hydrophobic compounds show a high affinity for lipid. The pollutant levels in aquatic biota should correlate with concentrations in their environment. Bivalves have been used extensively for these purposes (Goldberg et al. 1978). But fish have also been selected for monitoring because (a) they concentrate pollutants in their tissues directly from water, and also through the diet, thus enabling the assessment and transfer of pollutants through the tropic web (Bruggeman 1982); (b) they generally exhibit a low metabolism for organochlorines and consequently should reflect the levels of pollution in the aquatic environment (Muir et al. 1990); (c) they occupy different habitats in the same ecosystem and have different feeding behaviours, thus offering the potential to study the influence of environmental and biological factors on the bio-accumulation of pollutants (Porte and Albaiges 1993); and (d) data on chlorinated compounds in the edible fishes are also important from the human health view point (Pastor et al. 1996). In the present study River Shad, locally called "Ilish", was selected as a bio-indicator, as it is a carnivorous species that tends to concentrate contaminants to a higher degree than other species. Besides this, it has high commercial value and a higher human consumption rate, and it is feasible to assess the concentration level of persistent organochlorine pesticides in the fish.

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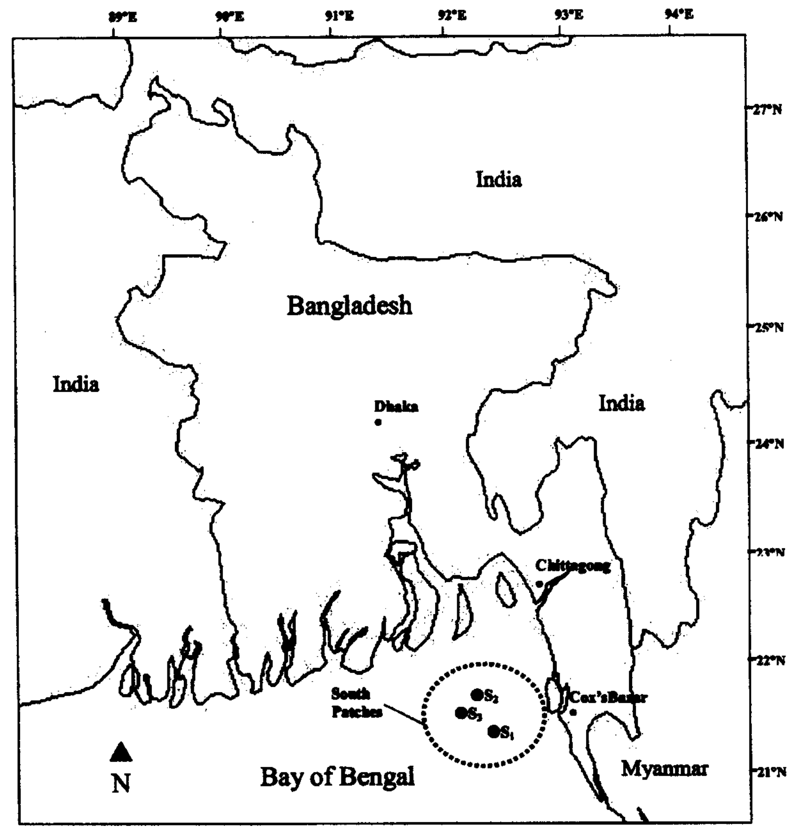

Figure 1. Location map of the three sampling stations (S_1, S_2, and S_3) in the South Patches of the Bay of Bengal.

For this purpose, sea bass was selected in Europe and the USA for monitoring programs (Porte and Albaiges 1993, McDowell et al. 1989). At the same time water and sediment samples were collected for the analysis of OCs that would focus the overall picture of the fishing ground of South Patches.

MATERIALS AND METHODS

Surface water samples were collected by glass container from three stations (S_1, S_2 and S_3) during dry and wet seasons. Surface sediment samples were collected from the bed of the South Patches of the Bay of Bengal using an Ekman Grab Sampler. The location of the sampling stations are shown in Fig.1.

Each season (dry and wet) total 25 water samples and 25 sediment samples were collected from each station. The samples were then transported and stored at the Pesticide Research Laboratory, Bangladesh under refrigeration of – 20^0 C to preclude hydrolysis or bio-degradation. 25 mature River Shad fish were collected from each station by trawl twine net, mesh size 55 mm and code end 45 mm, during the dry season (Winter 1999) and during the wet season (Rainy season 2000). The samples were collected from $21^0 30'$ N - $21^0 19'$ N Latitude to $91^0 25'$ E - $91^0 48'$ E Longitude and about 20 to 25 km west of Cox's Bazar and encompassing an area of 3,108 km^2. The fishes were dressed and the muscles separated out. Then the muscles were weighed, coded, labeled and wrapped in aluminum foil and quickly preserved in cold storage at $-20^0C \pm 2$. Details of the extraction procedure were given elsewhere (Das et al. 2002). One μl of final volume was injected and the analysis was carried out using a Gas Chromatograph (GC) model, PU 4500 equipped with Electron Capture Detector (ECD). Twenty grams of homogenate was taken and mixed with 20g anhydrous sodium sulphate and ground to powder in a mortar. The powder was taken in a paper thimble and set up in a Sohxlet apparatus using 250 ml of solvent [1:1 of double distilled hexane + dichloromethane] for 6 hours at 200^0C. The collected extract was evaporated to dryness to calculate the fat content. Then, 0.3 g of fat was cleaned up through glass column chromatography with deactivated Florisil (Sigma, USA, Mesh- 60-100) and the extract was eluted through a glass column with 100 ml eluting mixture (1:1double distilled hexane and dichloromethane). The extract was evaporated to dryness and taken to final volume (5ml) with double distilled hexane for GC analysis. Identification of pesticide residues was based on comparison of the measured retention times to those of known standards and also by co-injecting the samples with standards. Pesticides were quantified by comparing the areas of each peak with the area of the standard peak. An output device (computer integrator, Unicom-4815) was used for determination of the level of organochlorine pesticide residues as data graphics along with dialogues and reports i.e., peak, area%, time retention and area below the curve (BC). The conditions for the GC were- capillary column; column temperature; 200^0C; Injector Temperature-210^0C; Detector Temperature-225^0C; Carrier Gas - Nitrogen (purity-99.997%); Gas Flow Rate - 25 ml min^{-1}. Standards 100 ppm for each pesticide residue in hexane were prepared according to the catalogue of ASTM International, Pennsylvania, USA. The GC result was verified by Thin Layer Chromatography (TLC). The recovery performances were 89 to 90%. Three replicates of each sample were analyzed.

RESULTS AND DISCUSSION

The mean length and weight of River Shad, *Hilsa ilisha* (Hamilton 1822) were 35 cm and 700 g respectively during dry season. The average weight of River Shad was recorded as 610 g during wet season. Levels of pesticide concentrations in the surface water, sediment and muscle samples are in Table 1 and Table 2. Pesticide residues were found to be higher in the muscles of larger fish (size 36-37cm) as they contained more fat than the smaller ones (Georgakopoulos-Gregoriades et al. 1991; Stout 1980). All the samples contained the DDT group, lindane and heptachlor. The residues were found in decreasing order of ΣDDT > heptachlor >lindane > aldrin. In the present investigation the OC concentrations in water and sediment samples were found to be higher than the values detected by Silvana et al. (1993), Tanguan et al. (1990), Sarker and Gupta (1988), and Bevenus et al. (1981), whereas the concentrations were found to be lower than the findings of Mittal et al. (1980) and the permissible limit recommended by FAO/WHO (1993). The concentration of OCs in water as well as sediment were found to be higher at S_2 and lower at S_3. It was observed that the OC concentrations in sediments was positively correlated with concentrations in waters. The reasons are that the sampling area is far away from the coast with lower land drainage than estuarine areas and the surface current is much reduced resulting in stagnant water.

A positive correlation was observed between total organochlorine residues ($\sum$OCs and $\sum$DDT) and the % fat content in muscle ($r = +0.67$ for both $\sum$OCs and $\sum$DDT). A positive correlation between organochlorine pollutants and lipid content has already been reported for marine and freshwater fishes (Georgakopoulos-Gregoriades et al. 1991, Stout 1980). Between the two seasons, pesticide residues were found to be higher during the dry season (winter) with possible reasons being (a) the water was stagnant and the contaminants settled with organic substances fed on by the fish (Ruiz and Llorente 1991); (b) before spawning, the fish stored fat during the dry season and the contaminants accumulated in the fatty tissues. During the breeding season (wet) the River Shad migrate with the flow of freshwater effluent from the inland rivers, and naturally it occurs with the commencement of the south-west monsoon and consequent flooding of all the major rivers draining down to the Upper Bay of Bengal. When the fish spawns, the lipid concentration and pollutant body burden decreases in fish (Vassilopoulous and Georgakopoulos-Gregoriades 1993). As a result, the contaminants were found to be lower during wet seasons (Rainy). Among water, sediment and muscle samples, organochlorine pesticide residues were found to be higher in the muscle and it was found in decreasing order of muscle > sediment > water. Field, laboratory and modeling studies have investigated the influence of lipid on organochlorine bio-accumulation in fish and the mobilization and loss of organochlorine residues from the body tissues during gamete production (Guiney et al. 1979, Westin et al. 1983, Thomann and Connolly 1984, Black et al. 1988, Niimi 1983). These works provided evidence that somatic lipid concentration and the percentage of fat transferred into the developing eggs significantly influences the transfer of organochlorine pesticide residues in fishes. This is in agreement with the present investigation. In all the samples the p,p′ DDT group was present, which demonstrated that the p,p′ DDT group is still being used in our country in various names, although it is banned (Matin et al. 1993) or might be due to environmental persistence of pesticides.

Table 1. Seasonal variation of organochlorine pesticide (OCs) residues in surface water and sediment samples collected from three stations of the South Patches of the Bay of Bengal.

Specification			Organochlorine pesticide residues (ng l^{-1} of water and ng g^{-1} of sediment)							
Sample type	Sampling Stations	Seasons	p,p′ DDT	p,p′ DDD	p,p′ DDE	Σ DDT	Aldrin	Lindane	Heptachlor	ΣOCs
Water	S_1	Dry	1.85	1.42	1.18	1.72	0.02	0.30	2.29	4.37
		Wet	0.92	0.88	0.35	0.58	0.01	0.03	1.21	0.91
	S_2	Dry	0.85	0.72	0.15	4.45	0.02	0.32	2.31	7.02
		Wet	0.22	0.23	0.13	2.15	0.01	0.02	0.29	3.49
	S_3	Dry	1.21	0.71	0.01	1.93	0.01	0.32	1.18	3.46
		Wet	0.48	0.04	0.004	0.52	0.02	0.02	0.05	0.61
Sediment	S_1	Dry	4.56	1.39	0.94	6.93	1.23	1.32	3.03	12.48
		Wet	2.83	0.53	0.09	3.44	0.12	0.83	2.72	7.13
	S_2	Dry	3.48	2.53	5.03	11.34	1.23	ND	3.07	15.65
		Wet	1.21	1.65	4.21	7.08	1.12	0.93	1.23	10.36
	S_3	Dry	4.12	2.12	1.31	7.56	3.14	1.21	3.61	15.52
		Wet	2.38	1.23	1.10	4.72	0.96	0.62	1.22	7.52

Table 2. Seasonal variation of organochlorine pesticide (OCs) residues in muscle sample of River Shad, *Hilsa ilisha* (Hamilton 1822) collected from the South Patches of the Bay of Bengal.

Size (cm)	Seasons	Fat Obtained		Organochlorine pesticide residues (ng g^{-1}) of wet wt. Sample							
		(g)	%	p,p′ DDT	p,p′ DDD	p,p′ DDE	Σ DDT	Aldrin	Lindane	Heptachlor	ΣOCs
32-33	Dry	3.93	15.72	275.57	1183.49	497.83	1956.91	148.56	79.83	557.82	2743.12
	Wet	1.52	6.08	209.83	1107.78	467.62	1792.83	106.92	62.22	510.65	2472.63
34-35	Dry	3.72	14.80	315.54	1209.32	500.66	2025.53	290.00	83.55	691.15	3090.24
	Wet	1.83	7.32	210.13	1203.97	357.56	1771.67	185.23	60.34	486.37	2503.61
36-37	Dry	3.56	14.24	333.25	1390.93	529.93	2254.12	373.43	102.13	952.04	3681.73
	Wet	1.79	7.16	238.81	1232.57	518.84	1990.23	113.45	56.31	556.33	2716.32

The organochlorine pesticide residues accumulated in lipid might be mobilized into the eggs and transferred to the fingerlings after spawning. It is possible the new fingerlings might not survive with this body burden and day by day the fish population could decline. The year-round monitoring program should be undertaken to acquire adequate information regarding the level of organochlorine pesticide residues in fishes as well as the environment.

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