Pak. J. Sci. Ind. Res. 2005 **48**(4) 247-251

Determination of the Level of PCBs in Small Fishes from Three Different Coastal Areas of Karachi, Pakistan

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(received March 31, 2004; revised December 2, 2005; accepted January 5, 2005)

Abstract. The level of congener polychlorinated biphenyls (PCBs) was determined in small fishes. These fishes were collected from the beaches of Korangi Creek, Hawksbay and Clifton, all located in Karachi, Pakistan. The contamination status of PCBs was followed by their concentration in tissues. Higher PCBs were found to be the most persistent organopllutants, present in all the fishes studied.The samples were spiked with 5µl surrogate internal standard solution containing IUPAC numbers 194 and 198. A total of 14 PCBs were screened in each sample. The concentrations of PCBs found were 1.25 ± 0.02 ng/g dry weight of fishes collected from Clifton, 1.01 ± 0.52 ng/g of fishes collected from Hawksbay, and 1.00 ± 0.43 ng/g of fishes collected from Korangi Creek. The congener PCBs 138,153, and in some small fishes 118, were found to be predominant among all the PCBs tested in this study.

Keywords: organic pollutants, PCBs, small fishes, Karachi coast, polychlorinated biphenyls

Introduction

The coastline of Karachi, Pakistan, stretches along the shores for about 135 kilometers. Its growing pollution level is not only due to the increasing volume of trade via the shipping routes through the Karachi port, but is also due to its intake of toxic effluents from a number of industries. This is severely contaminating the mangrove forests and the marine life in the area. The use of polychlorinated biphenyls (PCBs) in Pakistan is mainly for industrial purposes. PCBs are the mixture of upto 209 individual chlorinated compounds and are classified as persistent organic pollutants (Langanathan and Kannan, 1991). They are used in the manufacturing of electrical equipment, heat exchangers, hydraulic systems, and several other specialized applications. PCBs do not readily breakdown in the environment and thus remain there for a very long period of time. PCBs may enter the air, water and soil. In water, a small amount of PCBs may remain dissolved, but most of it sticks to the organic particles, bottom sediments, and binds strongly to the soil. PCBs are taken-up by small organisms and fishes through the contaminated water and may thus get into the food chain of other animals. Through the food chain, therefore, PCBs accumulate in fishes and marine mammals, reaching a level that may be immensly higher than that in the surrounding water. The consumption of PCBs is hazardous as these are suspected to be human carcinogens (CEPA, 2003; ATSDR, 2000).

There are no known natural sources of PCBs, but these have been ragularly found in fishes, wildlife, and humans (Erickson, 1997). Earlier studies on fish have indicated that PCBs are unlikely to affect the growth of cultured fish at concentrations typically found in the environment (Kan-Atireklap *et al*., 1997; Duinker *et al.,* 1980). Commercially produced fish feeds often contain low concentrations of PCBs. However, cultured fish biomagnify PCBs from feeds, resulting in their concentration in the fish tissue to exceed that of fish feed itself (Carline *et al*., 2004). The U.S. Food and Drug Administration (US-FDA) has set the tolerance level of 0.2 ppm (200 ng/g) of PCBs in the finished fish feeds and 2.0 ppm in the fish sold for human consumption.

The objective of the present study was to provide baseline data on organochlorine concentrations in the fishes commonly counsumed as food in Karachi. Samples for the present study were collected from three different locations along the Karachi coast.

Materials and Methods

Sampling locations. The sampling locations included Korangi Creek, Hawksbay and Clifton (Fig. 1). Korangi Creek is situated in the South of Karachi, encircled by muddy creeks. This creek receives effluents from industries and oil refineries. The creek accommodates a few channels used by fishermen (Beg *et al.,* 1984). A long stony wall lies on the East of Hawksbay, receiving intake of effluents, particularly oil, released during loading and unloading of the oil from tankers. Slicks and tarry deposits were observed during the collection of samples from this area. Clifton is one of the sandy shores where fauna is extremely rich and seems to be rather free of pollution. Water currents may, however,

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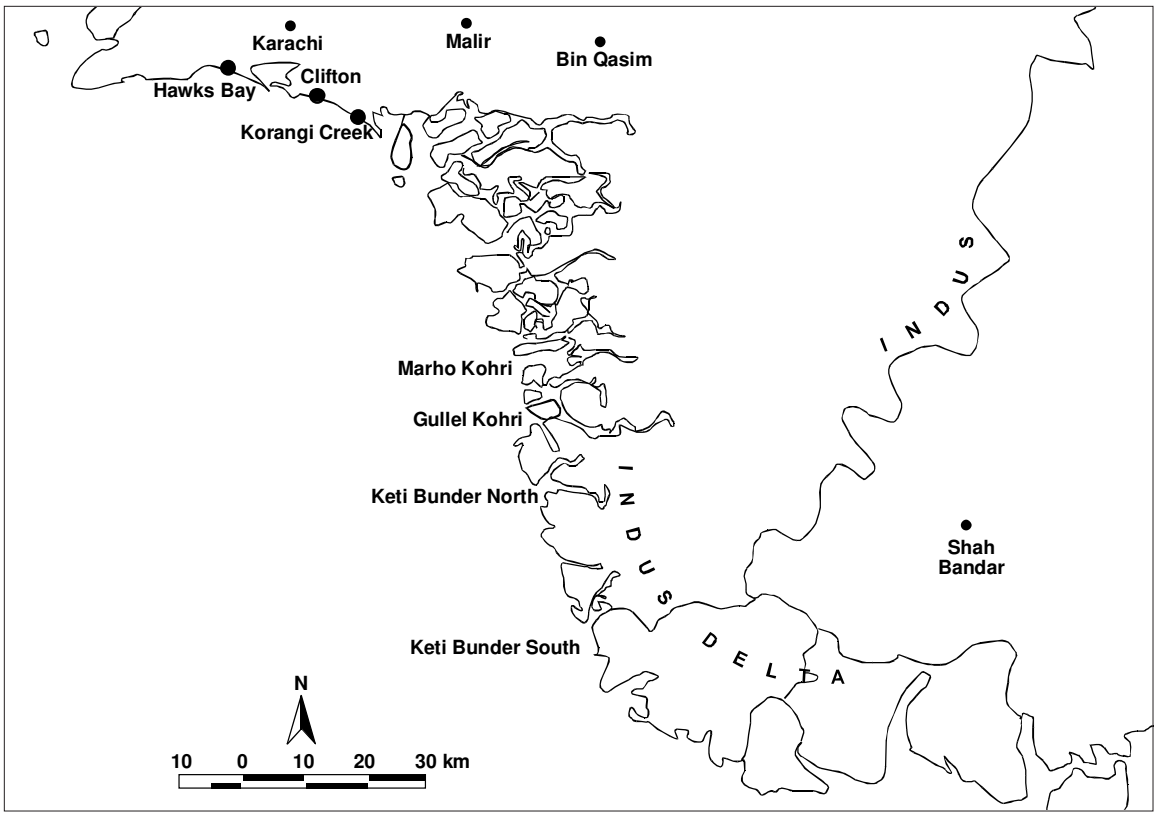

Fig. 1. Sampling locations of fish for their PCBs load along the coastline of Karachi, Pakistan.

transport a part of the industrial and domestic wastes to this beach.

Sample preparation and analysis. Different species of fishes were collected using catching nets with the help of fishermen on small trawlers. These samples were washed with sea water and then placed in glass bottles, brought to the laboratory, and were deep-frozen to −20 °C. The fishes were identified, measured and their wet weight was determined. Individuals of the same species were packed in aluminium foil and stored at −20 °C until their analysis. The biometric data related with fish length and body weight, with the number of specimens collected from different locations, is given in Tables 1-3. The most dominant fish species found in these areas were mullet and *Otolithes rubber,* locally known as mushka. Both are commonly consumed in Karachi. The congener PCBs were analysed according to the procedures given below.

Extraction of lipids. Two samples of each group of fishes were selected for their trace chemical analysis. About 20 g (wet weight) of the edible portion of fish was dried and ground to a homogeneous powder with about 120 g AR grade anhydrous sodium sulphate. The homogenized sample was then extracted in a Soxhlet apparatus for 16 h by using *n*-hexane. The sample extracts were reduced in volume using a Kuderna-Danish (K-D) apparatus and lipid contents were calculated.

Purification and separation. Lipids in the extracts were removed using the alumina (Al_2O_3) dry column chromatographic technique (Duinker and Hillebrand, 1997). The sample extract was then concentrated and subjected to silica gel column chromatography for clean-up and the separation of PCB congeners (Duinker *et al.*, 1980).

Quantification of polychlorinated biphenyls. The PCBs were analysed using a Fisons (Carlo-Erba) 8000 series gas chromatograph (GC) with an on-column auto-sampler/injector. The GC was equipped with a DB-5 and DB-35 capillary column (30 m length; 0.32 mm internal dia; 0.25 mm film thickness) and a ^{63}Ni electron capture detector. The column oven temperature programme was 40 °C, holding for 1 min, increasing at 4 °C/min to 140 °C, followed by increasing at 4 °C/min to 290 °C, then maintained at that temperature for 10 min. The detector temperature was set at 310 °C. Hydrogen gas at 2 ml/min and nitrogen gas at 30 ml/min were used as the carrier and make-up gases, respectively. The PCB Mix 7 and Mix 19 (obtained from Ehrenstorfer Reference Materials, Dr. Ehrenstorfer GmbH, bgm-Schlosser- Str. 6, A-86199, Augsburg, Germany) was used in a dilution series as the external cali-

bration standard for the quantification of polychlorinated biphenyl congeners.

Quality assurance and quality control measures included the use of reagent blanks, and surrogate and matrix spike recovery. Calibration and calibration verifications were routinely checked at the beginning and the end of each batch of 6 samples. All laboratory batches of samples contained one procedural blank, one laboratory control sample, and a duplicate sample. The procedural blank was spiked with the solvent and surrogate internal standard PCB congeners 198 and 194. All samples were spiked with the surrogate compound to determine efficiency. Results were calculated on the basis of the mean value of specimens.

Results and Discussion

The concentration of polychlorinated biphenyls (PCBs) in the analysed fish samples are shown in Tables 1-3. Fourteen dominant PCB congeners were studied. The level of different PCBs in the various fish species studied ranged from 0.001-8.86 ng/g of tissue, which was a relatively uncontaminated value, when compared to the data on fishes from the USA (Langanathan and Kannan, 1991). The composition of PCB congeners in each type of fish, for every location, was found to be different from any commercial PCB preparation, implying their alteration by various factors (for example, metabolism, biological transport, hydrodynamic transport, adsorption, and deposition rates).

A review of Tables 1-3 shows that the fishes from Hawksbay and Korangi Creek were found to be less contaminated by PCBs. The most contaminated species by ΣPCBs (the sum of significant values of PCBs concentrations) were *Sardinella sindensis* and *Pristiopoma hasta* for Hawksbay and Korangi Creek, respectively, probably due to the higher lipid contents (5.37- 7.23%) of these species. At Hawksbay, Lyari river is the main source for draining PCBs at the northern side. However, at Korangi Creek the main source of PCBs is industrial effluents generated by oil refineries situated in this region. The Clifton beach was found to be highly contaminated by PCBs, as compared with the other two locations. *Cynoglossus sindensis* was the most contaminated species at this location. Main source for PCBs at this area is the effluents discharge from the nearby located plastics, paints and polymer industries.

On an overall basis, the concentration of lower-chlorinated congeners was found to be higher than that of the higher-chlorinated ones. This may be probably due to the indiscriminate discharge of effluents from a variety of PCB

Table 1. Biometric data of the fish species caught from Clifton beach, Karachi, Pakistan and the various polychlorinated biphenyls (PCBs) detected from their bodies (ng/g tissue)

Chlorobiphenyl species (PCB congener)	IUPAC number	*Cynoglssus sindensis*	*Equula splendens*	*Arius serratus*	*Pristiopoma hasta*	*Otolithes rubber*
		n = 8 l = 15 (10-20) w = 80 (70-89)	n = 12 l = 8 (5-15) w = 100 (80-120)	n = 5 l = 25 (20-35) w = 21 (15-25)	n = 2 l = 22 (18-25) w = 365 (319-410)	n = 10 l = 122 (80-150) w = 20 (18-25)
2,2,5-Trichlorobiphenyl	18	4.45	2.90	0.25	0.01	0.19
2,4,4- Trichlorobiphenyl	28	6.18	nd	0.69	0.02	0.03
2,4,5- Trichlorobiphenyl	31	5.06	nd	nd	0.03	0.04
2,2,3,5- Tetrachlorobiphenyl	44	1.09	0.24	0.37	0.01	nd
2,2,5,5- Tetrachlorobiphenyl	52	8.26	nd	0.56	0.03	nd
2,2,4,5,5- Pentachlorobiphenyl	101	7.89	nd	0.71	0.10	0.07
2,3,3,4,4- Pentachlorobiphenyl	105	0.93	0.37	0.12	0.01	0.02
2,3,4,4,5- Pentachlorobiphenyl	118	5.33	0.20	0.50	0.02	0.05
2,2,3,4,5,6- Hexachlorobiphenyl	138	6.28	0.18	0.61	0.02	0.05
2,2,3,4,5,6- Hexachlorobiphenyl	149	5.001	0.20	0.4	0.01	0.04
2,2,4,4,5,5- Hexachlorobiphenyl	153	8.86	0.03	0.76	0.02	0.08
2,2,3,3,4,4,5- Heptachlorobiphenyl	170	1.52	nd	0.12	0.003	0.01
2,2,3,,4,4,5,5- Heptachlorobiphenyl	180	2.46	nd	0.20	0.01	0.002
2,2,3,3,4,4,5,5- Octachlorobiphenyl	194	0.02	nd	0.02	0.001	nd

n = number of fish catch; l = mean length (cm), within paranthesis is the range; w = mean weight (g), within paranthesis is the range; nd = not detected

Table 2. Biometric data of the fish species caught from Hawksbay, Karachi, Pakistan and the various polychlorinated biphenyls (PCBs) detected from their bodies (ng/g tissue)

Chlorobiphenyl species (PCB congener)	IUPAC number	*Stromateus sinenbis*	*Scomberoides commersannianus*	*Gerres filamentosus*	*Engraulis purava*	*Sardinella sindensis*
		n = 5 l = 10 (9-12) w = 60 (54-70)	n = 6 l = 30 (25-35) w = 120 (110-155)	n = 4 l = 22 (15-25) w = 130 (110-155)	n = 3 l = 20 (18-25) w = 45 (40-55)	n = 6 l = 18 (15-20) w = 85 (80-100)
2,2,5-Trichlorobiphenyl	18	0.002	0.59	0.44	0.48	1.73
2,4,4-Trichlorobiphenyl	28	0.01	1.65	0.68	0.30	4.53
2,4,5-Trichlorobiphenyl	31	0.002	0.86	0.21	0.78	2.42
2,2,3,5-Tetrachlorobiphenyl	44	0.003	0.67	0.01	0.27	0.40
2,2,5,5-Tetrachlorobiphenyl	52	0.002	n.d	0.02	0.43	3.22
2,2,4,5,5-Pentachlorobiphenyl	101	0.01	0.46	0.16	0.44	2.90
2,3,3,4,4-Pentachlorobiphenyl	105	0.002	0.11	0.03	0.44	0.70
2,3,4,4,5-Pentachlorobiphenyl	118	0.01	0.28	0.07	0.37	2.10
2,2,3,4,5,6-Hexachlorobiphenyl	138	0.01	0.37	0.44	0.17	2.73
2,2,3,4,5,6-Hexachlorobiphenyl	149	0.003	0.27	0.12	0.18	2.11
2,2,4,4,5,5-Hexachlorobiphenyl	153	0.01	0.35	0.74	0.83	3.41
2,2,3,3,4,4,5-eptachlorobiphenyl	170	0.002	0.09	0.18	0.20	0.30
2,2,3,,4,4,5,5-eptachlorobiphenyl	180	0.002	0.09	0.33	0.16	1.09
2,2,3,3,4,4,5,5-tachlorobiphenyl	194	0.001	0.01	0.30	0.03	0.09

n = number of fish catch; l = mean length (cm), within paranthesis is the range; w = mean weight (g), within paranthesis is the range

Table 3. Biometric data of the fish species caught from Korangi Creak, Karachi, Pakistan and the various polychlorinated biphenyls (PCBs detected from their bodies (ng/g tissue)

Chlorobiphenyl species (PCB congener)	IUPAC number	*Otolithes rubber*	*Pristiopoma hasta*	*Lepturacanthus savala*	*Sphyraena foresteri*	*Mugil cephalus*
		n = 6 l = 20 (1921) w = 72 (64-80)	n = 3 l = 28 (26-30) w =232 (210-255	n = 3 l = 22 (16-25) w = 187 (150-225)	n = 4 l = 10 (8-12) w = 27 (20-35)	n = 8 l = 9 (3-12) w = 45 (40-50)
2,2,5-Trichlorobiphenyl	18	0.008	0.275	0.008	0.014	0.04
2,4,4- Trichlorobiphenyl	28	0.077	0.031	0.011	0.033	0.076
2,4,5- Trichlorobiphenyl	31	0.086	0.023	0.014	0.014	0.077
2,2,3,5- Tetrachlorobiphenyl	44	0.073	0.023	0.019	0.017	0.032
2,2,5,5- Tetrachlorobiphenyl	52	0.108	0.022	0.028	0.031	0.072
2,2,4,5,5- Pentachlorobiphenyl	101	0.133	0.067	0.034	0.03	0.098
2,3,3,4,4- Pentachlorobiphenyl	105	0.018	0.027	0.01	0.013	0.026
2,3,4,4,5- Pentachlorobiphenyl	118	0.063	0.02	0.014	0.024	0.091
2,2,3,4,5,6- Hexachlorobiphenyl	138	0.007	0.039	0.01	0.029	0.104
2,2,3,4,5,6- Hexachlorobiphenyl	149	0.045	0.164	0.014	0.008	0.06
2,2,4,4,5,5- Hexachlorobiphenyl	153	0.067	0.044	0.035	0.011	0.055
2,2,3,3,4,4,5- Heptachlorobiphenyl	170	0.017	0.035	0.005	0.004	0.019
2,2,3,,4,4,5,5- Heptachlorobiphenyl	180	0.03	0.07	0.005	0.008	0.032
2,2,3,3,4,4,5,5- Octachlorobiphenyl	194	0.002	0.005	0.001	0.002	0.002

n = number of fish catch; l = mean length (cm), within paranthesis is the range; w = mean weight (g), within paranthesis is the range

sources. The difference in molecular size of PCBs may play a role in the uptake of chlorinated PCBs (Goutner *et al.,* 2000). However, for a greater understanding of the pattern of accumulation of congeners in the fishes of the region, further detailed research with a broader perspective is suggested.

At Hawksbay, ΣPCBs ranged from 0.069-27.73 ng/g of tissue. PCB congeners 28 and 153 were observed to be in higher concentration generally in all the species. The PCB congener 194 was found at its highest concentration of 0.30 ng/g of tissue in *Gerres filamentosus* than all the other species, and all other locations.

Levels of ΣPCBs in the Korangi Creek area ranged from 0.21-0.84 ng/g of tissue in all fishes. In every species, PCBs 194 and 180 were observed at the lower concentration of 0.001-0.005 and 0.01-0.07 ng/g of tissue, respectively. At the lower congener numbers of 18-52, the average concentration ranged from 0.01-0.11 ng/g of tissue in the various fish species collected from this location.

The most polluted location for PCBs was Clifton, where ΣPCBs level ranged from 0.294-63.98 ng/g of tissue, which values were higher than the concentrations reported from other areas in different species (Bopp *et al.,* 1998). At this location, the PCB congener 194 was found to be at the lower concentrations of 0.001-0.02 ng/g of tissue, than the other PCB congeners. Some fishes from this region contained lower PCBs, even below the levels reported in the fish from USA (US EPA, 1992).

Levels of PCBs in fishes from all the three locations were found to be lower than the United State Food and Drug Administration (US FDA) permissible limits for human consumption (Macauley *et al.,* 1992).

It may be emphasized in conclusion that PCBs emanating from industrial effluents should be controlled at the source, otherwise their increased intake by marine life is likely to pose a serious biological threat.

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