Open Access

Pesticides (OCPs) and Polychlorinated Biphenyls (PCBs) Concentration in Various Fish Species Along the Chesapeake Bay Near Virginia Beach on the Atlantic Coastline

A.B. Munshi[1,*], Gregory D. Boardman[2], George J. Flick[3], Jean Cobb[4] and Robert M. Lane[5]

[1]Pakistan Council of Scientific and Industrial Research, Center of Environmental Studies, Karachi Lab.; [2]Department of Civil and Environmental Engr., 417 Durham Hall (0246), Virginia Tech, Blacksburg, VA 24061; [3]Department of Food Science and Technology, Virginia Tech, Blacksburg, VA 24061; [4]Pesticide Residue Lab., Department of Biochemistry, 352 Litton Reaves Hall (0309), Blacksburg, VA 24061 and [5]Virginia Seafood Agriculture Research and Extension Center, 102 So. King Street, Hampton, VA 23669

Abstract: The accumulation of polychlorinated biphenyls (PCBs), ΣDDTs, Σchlordanes, ΣBHCs, dieldrin, heptachlor epoxide and other organochlorinated pesticides (OCPs) was measured in the tissues of different edible fishes collected along the Virginia Coast by employing the methods: MSPD (Matrix Solid Phase Dispersion) and GC-ECD (Gas Chromatography with Electron Capture Detector). BHC4s were the most predominant contaminants, followed by PCBs, chlordanes, dieldrin and the other OCPs. This study revealed that over the last decade, the concentrations of OCPs have declined in these regions. Even with this decline, the measured concentrations of PCBs and OCPs in edible fish are still worth reporting. It was observed, that concentrations of organochlorines were significantly in same range (low-high) with one another and were in the range of a few to several ngg^{-1} on a wet weight basis.

In the tissue samples, ΣOCPs ranged from 4.30-196 ngg^{-1} w.w with ΣBHC (266.101 ngg^{-1} w.w) and Heptachlor epoxide (196 ngg^{-1} w.w) collectively in all fish. Similarly ΣPCBs had an overall range 7.17-276.16 ngg^{-1} w.w where Aroclor 1221 and Aroclor 1242 were the dominant components.

The redox conditions and the decay processes which affect the organic matter, control the concentrations of PCBs and OCPs in edible fish. These preliminary results suggest that the variations in PCBs and OCPs content in edible fish result largely from digenetic processes rather than changes in pesticide input resulting from local human activities.

Key Words: Endocrine disrupting chemicals (EDCs), organochlorine pesticides residues, Polychlorinated biphenyls (PCB), fish, James River, Chesapeake Bay, Virginia Beach.

1. INTRODUCTION

OCPs and PCBs are ubiquitous environmental contaminants even though most countries have banned their production and use. However, considerable amounts continue to cycle in the ecosphere [1]. Since the ban in the 1970s, concentrations of OCPs have declined in various ecosystems, but the rate of this decline is relatively slow [2].

Measuring chlorinated pesticides in biological samples is important because many of these compounds are lipophilic and environmentally persistent pollutants that tend to accumulate in fish due to their lipophilicity [3]. OCPs can generate harmful effects on human as well as on aquatic life [4]. Additionally, OCPs and PCBs are among those compounds categorized as Endocrine Disrupting Chemicals (EDCs) [5].

The overall objective of this study was to investigate the current status for the occurrence, distribution and fate of all Organochlorine compounds, OCPs and PCBs, in the different fishes sampled from the shores of eastern Virginia, through the use of the matrix solid-phase extraction (MSPD) technique. MSPD technique was employed so as to conserve the marine fauna; only 0.5 gm tissue was used for each sample. A 100% recovery was obtained for each compound.

2. MATERIALS AND METHODS

2.1. Sample Collection

All fish were supplied by fishermen after being collected along the Chesapeake Bay near Virginia Beach. The most populous area within Virginia is located in the southeast part of the state on the Atlantic coastline. Virginia is bounded by Maryland (northeast), North Carolina and Tennessee (south), Kentucky (west) and West Virginia (northwest). To the east is the Atlantic Ocean. Lying in the Blue Ridge area in the west, Mount Rogers is the highest point of Virginia with a height of 5,729 ft (1,746 mtrs) and the mouth of James River (a navigable river, 1,143 km long). These fishes were collected during the winter season (November-March). All samples were collected during different fishing visits. Biometrical data of fish were recorded immediately after the fish were received. After dissection, samples of tissues and organs were removed, wrapped in aluminum foil and stored in a deep freezer (−20 °C) until analysis. Samples of muscle, liver and gonads were taken out and analyzed individually.

*Address correspondence to this author at the Pakistan Council of Scientific and Industrial Research, Center of Environmental Studies, Karachi Lab; E-mail: aliamunshi@gmail.com

2.2. Sample Analyses

Samples storage, preparation for extraction, concentration and chromatographic separation were conducted in the Pesticides Residues Laboratory and Laboratories of Civil and Environmental Eng Department (CEE) and Food Science and Technology (FST).

2.2.1. Extraction of Samples by MSPD

Fish samples were thawed and cut into small pieces with a stainless steel knife. Finely chopped fish tissue (0.5 g) was weighed in a small plastic weigh boat. The weighed tissue was transferred to a glass mortar and pestle along with 2g Bondesil® C-18 sorbent (Varian Inc. CA). Using the pestle, the tissue and C-18 sorbent were thoroughly ground in the mortar to a homogenous consistency with the appearance of small grains [6]. A 20 ml bond Elute® Florisil solid phase extraction cartridge (Varian Inc. CA) was affixed to a vacuum manifold (Supelco, PA) and the sample/C-18 mixture was transferred to the cartridge using a metal spatula. A polyethylene frit (Varian Inc. CA) was firmly tamped in to the place above the sample /C-18 mixture using a disposable syringe plunger. The sample was eluted from the cartridge under vacuum with successive washes (3 x 5 ml) of dichloromethane. The elute was collected in a glass, 25ml test tube, evaporated to about 1 ml using a nitrogen evaporator [6], and quantitatively transferred to a centrifuge tube using about 10 ml Hexane. Thus evaporated a second time diluted to final volume, and transferred to an auto sampler vial to gas chromatographic analysis.

2.2.2. Gas Chromatographic Separation

All sample extracts were analyzed by Agilent model 6890 gas chromatograph equipped with a micro electron capture (μECD). Each sample was injected in split less mode with the EPC injector temperature at 200°C and the μECD temperature at 350°C. Two capillary columns were used for sample separation, RTX-5 capillary column (30 meters x 0.25 mm ID x 0.25 μM) and RTX35 (30 meters x 0.25 mm ID x 0.25 μM). The oven temperature program for both capillary columns was 60°C for 0 min, 20°C/min to 160°C, hold for 1.00 min. the detector make up gas was nitrogen and the combined carrier and makeup flow rate was 60 mL/min, Hewlett Packard Chemstation software (G 2070AA Rev.A.10.02) was used for data acquisition and analysis.

2.2.3. Pesticide Standards

An organochlorine standard containing 20 components and polychlorinated biphenyl standards such as Arochlors (1016, 1221, 1242, 1248, 1254, and 1260) were purchased from Restek (Bellefonte, PA). Further dilutions were made using pesticides grade solvent for calibration. Identified compounds were quantified using the external standard technique.

2.3. Performance and Quality Control

Properly washed and dried glassware were used by avoiding any rubber or plastic items during the whole study and periodically "Blanks" were analyzed to ascertain contamination free analysis. Internal spiking and reagent blanks were used to determine recovery values. Recovery was calculated by spiked amount of surrogate standard calculated on spreadsheet by the difference of samples results minus blank value. That was found in the range 95–120% and 90–114% for OC and PCBs pesticides, respectively. Precision was estimated 1-10 from the multiple analyses of spiked samples for the different compounds. Limit of detection (LOD) for PCB single congener and organochlorine compounds was 0.01 ngg^{-1} and 1.00 ngg^{-1} respectively.

2.4. Statistical Analysis

All calculations were carried out by using MS Excel for Windows on the basis of linear equation.

3. RESULTS AND DISCUSSION

Biometric data for the various fish analyzed in this study is shown in Table **1**. Results of spiking fish tissue with pesticides to determine the recovery, lower detection limit (LOD)

Table 1. Biometry of Fish Analyzed

Fish	Sex	Weight (gm)	Total Length (cm)
Rock (*Morone saxatilis*)	M	5000	35
Stripped Bass (*Centropristis striate*)	F	62.82	19.46
Stripped Bass (*Centropristis striate*))	M	104.76	22.24
Summer Flounder (*Paralichthys dentatus*)	M	1455	50
Blue fish (*Pomatomus saltatrix)*	F	120	11
Blue fish (*Pomatomus saltatrix)*	M	137	12
Croaker (*Micropogon undulatus*)	M	580.65	36
Croaker (*Micropogon undulatus*	F	423.37	31
Spotted Seatrout (*Cynoscion nebulosus*)	M	338.04	39
Spotted Sea trout (*Cynoscion nebulosus*)	F	410.65	40
White Perch (*Morone americana*)	M	127.64	27.80
White Perch *(Morone americana*)	F	141.64	25.02

and (LOR) lower reportable limit of the method are presented in Table **2**.

Overall recoveries ranged from 93-210% in the spiked surrogate standard with the concentration of 4 ngg^{-1}. The LOD for chlorinated pesticides ranged from 0.1 to 1.00 ngg^{-1}. MSPD sample were found to be a reliable method for the confirmation and quantification of chlorinated pesticides [7].

Results for the OCPs and PCBs are shown in Tables **3** and **4**, respectively. ΣBHC and heptachlor epoxies were among the most dominant OCPs in this study. Other chlorinated pesticides like DDTs, Dieldrin, Endrin and chlordane, were present at low concentrations in all samples as compared to the results for mean concentrations of OC pesticides determined in the fish from different parts of world are shown in (Table **5**). The highest concentration of ∑BHCs was present in Perch with a mean concentration of 56 ngg^{-1} w.w, but the level was only slightly lower that of Bluefish (54 ngg^{-1} w.w.). The level in Trout was much lower (19 ngg^{-1} w.w.). Alpha BHC was found in Bluefish and Rockfish, whereas beta BHC was found only in Bluefish, Flounder, and Perch. Delta BHC was found in all but Perch. Gamma BHC was only determined in Bluefish and Perch (Table **3**).

Table 2. List of the 20 Organochlorine Pesticides (OCPs) and 7 Polychlorinated Biphenyl (PCBs) with their Statistics

Organochlorine	Reproducibility	Recoveries	R.S.D (%)	LOD ngg^{-1}	LOR ngg^{-1}
Aldrin	03	93%	4.6	0.10	1.00
Alpha BHC	05	115%	5.1	0.099	0.99
Alpha chlordane	03	119%	5.0	0.015	1.05
Beta BHC	03	115%	4.1	0.098	0.98
Delta BHC	04	169%	5.2	0.099	0.99
Dieldrin	03	145%	4.5	0.100	1.00
Endosulfan I	05	138%	5.2	0.099	0.99
Endosulfan II	03	140%	6.0	0.089	0.89
Endosulfan sulfate	03	210%	4.3	0.105	1.05
Endrin	04	113%	5.4	0.105	1.05
Endrin aldehyde	03	181%	4.7	0.089	0.89
Endrin ketone	05	192%	5.2	0.100	1.00
Gamma BHC	03	149%	6.0	0.089	0.89
Gamma-chlordane	05	117%	4.3	0.099	0.99
Heptachlor	03	118%	4.7	0.100	1.00
Heptachlor epoxide	03	114%	5.2	0.100	1.00
Methoxychlor	04	NR*	6.0	0.098	0.98
p,p DDD	03	149%	4.3	0.099	0.99
p,p DDE	05	121%	5.4	0.100	1.00
p,p DDT	03	NR	4.7	0.099	0.99
Polychlorobiphenyl	03				
Aroclor1016	03	122%	4.7	0.01	0.10
Aroclor1221	05	145%	5.2	0.009	0.09
Aroclor1232	03	98%	6.0	0.01	0.10
Aroclor1242	03	172%	4.3	0.008	0.08
Aroclor1248	04	108%	5.4	0.011	0.11
Aroclor1254	03	134%	4.7	0.01	0.10
Aroclor1260	03	209%	5.2	0.01	0.10

* = not calculated.

Table 3. Results for Organochlorine Measured in Virginia Fish (ngg^{-1} wet weight)

Organochlorine	Bluefish (*Pomatomus saltatrix*)	Spotted Sea Trout (*Cynoscion nebulosus*)	Rock (*Morone saxatilis*)	Summer Flounder (*Paralichthys dentate)*	Croaker (*Micropogon undulates)*	White Perch (*Morone americana*)	Striped Bass (*Centropristis striate*)
Aldrin	<LOD*	11.11	8.4	8.10	8.91	6.00	8.430
alpha-BHC	6.24	<LOD	13.32	<LOD	<LOD	<LOD	<LOD
beta-BHC	8.98	<LOD	<LOD	12.30	0.000	12.10	<LOD
delta-BHC	17.30	19.15	24.08	20.31	21.53	<LOD	24.20
gamma-BHC	21.43	ND	<LOD	<LOD	<LOD	43.70	<LOD
alpha-chlordane	<LOD	10.98	16.00	19.36	6.71	0.000	6.20
gamma-chlordane	7.46	13.95	<LOD	2.54	<LOD	5.12	<LOD
p,p-DDD	NA	0.000	0.000	ND	<LOD	<LOD	<LOD
p,p-DDE	5.25	17.75	5.33	3.30	3.70	3.72	6.87
p,p DDT	22.17	<LOD	49.00	<LOD	<LOD	<LOD	<LOD
dieldrin	<LOD	8.47	9.900	5.00	4.70	4.82	4.21
endosulfan I	6.46	6.62	5.50	6.12	3.86	3.15	3.62
endosulfan II	<LOD	1.80	7.64	2.00	2.00	7.47	<LOD
endosulfan sulfate	4.28	ND	<LOD	<LOD	<LOD	<LOD	<LOD
endrin	1.87	7.83	2.30	<LOD	<LOD	<LOD	5.27
endrin aldehyde	5.81	<LOD	5.30	<LOD	<LOD	<LOD	<LOD
endrin ketone	4.74	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heptachlor	3.92	5.83	3.83	10.74	1.67	4.11	4.80
heptachlor epoxide	8.20	27.63	45.64	12.80	15.30	28.00	42.52
methoxychlor	12.23	23.37	26.00	<LOD	<LOD	<LOD	61.60

* Lower detection limit.

Table 4. Results for Concentrations (w.w ngg^{-1}) of Polychlorinated Biphenyl (PCBs) Determined in Fish Tissue from Virginia Coast

PCBs	Bluefish (*Pomatomus saltatrix*)	Spotted Seatrout *(Cynoscion nebulosus)*	Rock (Morone saxatilis)	Summer Flounder *(Paralichthys dentatus)*	Croaker *(Micropogon undulatus)*	White Perch *(Morone americana)*	Striped Bass *(Centropristis striate)*	Bluefish (*Pomatomus saltatrix*)
ACR –1016	<LOD*	1.34	1.32	2.14	0.002	N.D	1.02	1.20
ACR –1221	<LOD	0.00	4.13	0.00	0.00	3.05	0.00	0.00
ACR –1232	236.90	<LOD	<LOD	5.96	0.01	N D	27.94	5.40
ACR –1242	0.147	0.00	0.00	7.12	0.01	0.00	6.55	7.40
ACR- 1248	40.00	11.30	11.30	127.67	0.00	4.30	45.17	0.00
ACR –1254	0.00	5.32	5.32	0.00	0.01	4.13	<LOD	6.27
ACR –1260	8.45	5.37	5.37	8.68	0.01	<LOD	<LOD	0.00

* Lower detection limit.

Table 5. Mean Concentrations Mean of PCBs and DDTs in Fish from Different Parts of World

Area	Species	∑PCBs (ng g^{-1})	∑DDTs (ng g^{-1})	References
Rio Grande Basin (RGD)	Sea trout	46-63	10-23	[4]
Thames River UK	*Anguilla anguilla*	0.77-3.32	0.08-4.94	[7]
Hudson river estuary, NY, USA	Mumichogs	652-5796	--	[8]
NW Mediterranean Sea	*Mora moro*	60-104	32-55	[9]
Douro estuary (NW Portugal)	Flounder and mullet	52-345	8-69	[18]
Lake Ganzirri and Straits of Messina (Sicily, Italy)	Mullet *Liza aurata*	317-800	44-141	[19]
Australia, Sydney harbor	Sea mullet	4330-16,443	630-5039	[20]
Antarctic Ocean	*Chaenocephalus aceratus*	0.4-2.35	15-20	[21]
Indian Ocean	*Mullet*	2.23-4.27	72-125	[22]
Ebro Delta, NW Mediterranean Sea	Sea bass	19-27	11-17	[23]
	Red mullet	38-88	19-73	

A significant correlation was noted among the concentrations of the various OCPs in all fish. Correlation factors (r2) are provided in Table **6**.

Heptachlor was found in all fish with a mean value of 4.61 ngg^{-1} with the maximum concentration of 10.74 ngg^{-1} w.w seen in Flounder (Table **3**). The relative order of ∑OCPs was Heptachlor epoxide > ∑BHC > ∑endosulfan > ∑ chloradan.

As DDT is metabolized to DDE, the ratio of DDE to total DDT can be used as an indicator for the source of the DDT. The total value of 120.30 ngg^{-1} has been reported as a critical limit in previous studies (Tsydenova *et al.*, 2004). A ratio of 0.9 (∑DDT: individual compound of same group) is indicative of a lack of recent inputs of DDT. In samples of Rock fish, Blue fish and other fish this ratio equals to 0.99, 0.24 and zero respectively. Therefore, Virginia is not receiving significant new inputs of DDT. This situation is more evident if the DDE / DDT ratio is considered. Chlordanes group was also detected in all the fish. The highest ∑chloradan concentrations were found in Trout (25 ngg^{-1} w.w.) followed by PCBs congeners, was determined in fish tissue from Virginia Coast Table **4**.

Summed concentrations of 7chlorobiphenyl congeners (∑PCBs) ranged from 7.17 ngg^{-1} w.w. to 276.20 ngg^{-1} w.w with the lowest concentrations occurring in the Croaker and Trout as well as Perch were at quite the same level, and the highest value in Bluefish followed by Flounder. The levels of PCBs congeners 1232 and 1248 in the Bluefish were markedly higher than those found in the other fish due to different point of collection, as well as the significantly higher lipid content.

The relative distribution of the mean concentrations of PCB congeners are reported in the analyzed fish. Aroclor 1232, Aroclor 1260 and Aroclor 1254 predominate, up to 42.93%, 4.33% and 3.29% of ∑PCBs respectively followed by Aroclor 1242 and Aroclor 1016 (3.27% and 1.12% as lowest ratio of ΣPCB). Concentrations of ∑PCBs was found to be in the same range in Trout, Perch, (Striped Bass, Black

Table 6. Correlation (r2 Value) Matrix of Organochlorine Concentrations in All Fish

	Σ Aroclor	ΣBHC	Σ Chlordane	Dieldrin	Σ Endrin	Σ Heptachlor	ΣDDT	Aldrin
Σ Aroclor	1	0.99	0.98	0.96	0.95	0.89	0.75	0.74
ΣBHC		1	0.99	0.98	0.92	0.87	0.73	0.71
Σ Chlordan			1	0.95	0.92	0.96	0.86	0.82
Dieldrin				1	0.88	0.88	0.76	0.74
Σ Endrin					1	0.95	0.86	0.78
Σ Heptachlor						1	0.84	0.75
ΣDDT							1	0.67
Aldrin								1

Striped fish) and Rock. It was minimum in croaker and maximum in bluefish. Aroclor 1016 was found in lowest amount (7.2 ngg^{-1}), and not found in Bluefish. It was not within the detection limit in Trout, Flounder, Croaker, Tilapia and Striped Bass fish. For Aroclor 1221, the levels varied between 5.96-24 ngg^{-1} in Flounder and Bluefish. Minimum concentration of ΣPCB was found in Croaker and maximum in Bluefish as 312.54 ngg^{-1}.

PCB congener patterns were same in Perch, (Black striped fish and Striped Bass). Other studies have also demonstrated that unlike congener profiles, total PCB content does differ dramatically amongst fish and that PCB differences among fish can vary with site [8]. A clear trend of the greater metabolic activity for the lower chlorinated congeners [9] was difficult to recognize in fish samples because of the very low concentrations of PCBs. Lipid content was not measured during processing of MSPD however bioaccumulation in fish depends upon their fat content [10]. In fact, for ∑PCBs and ∑OCPs the mean level on w.w. basis of contamination in the examined tissues always have a linear relationship with their mean lipid content [11]. Generally, lipid content of fish tissue in net mass is about 15%, mainly being composed of phospholipids, triacylglycerolipids, and cholesterol and sterol esters [12].

Indeed, these congeners (Aroclor 1016 -1260) are present in higher proportions in industrial PCB formulations [13] and seem to be responsible of the persistence and bioaccumulative properties. It means the Aroclor 1221, 1248, and 1260 congeners were found in higher concentration in Bluefish and Perch species but these are not more than 1.12% of total PCBs. Moreover, there was little difference in the pattern of relative percentages of each congener to the total PCBs found in different fish. PCBs with higher chlorine content are usually more difficult to metabolize and so their persistence and bioaccumulation are greater [14]. ∑PCBs and ∑OCPs varied in male and female fish but the difference between male and female are not determined (Fig. **1**).

ΣOCPs in trout was found markedly higher (155 ngg^{-1}). A significantly similar pattern of ΣOCPs was found in Bluefish, Perch, Rock, (Black Striped fish and Striped Bass). This variability can be the result of different feeding habits and/or dissimilar ability of the different species to accumulate pollutants.

Much progress in the development of analytical methodologies for accurate determination of chlorinated pesticides in the environment and in biological tissues has been made during last decade. Most scientists are using solid phase extraction technique in place of the soxhlet extraction method, along with application advance software analysis, especially in USA. Results of present study, however, showed that OCPs are still among the most prevalent environmental pollutants, and they can be found in various environmental compartments at any time. Their widespread presence is due to their extremely persistent and lipophilic nature. These properties cause these persistent organic pollutants (POPs) to bioaccumulate in the adipose tissues of fish resulting in the enrichment throughout the food chain [15] because the prolonged exposure to these pollutants can interfere with normal physiology and biochemistry [16]. The composition of lipids can also influence the bioaccumulation of organochlorine compounds [17]. It is postulated that an organism's burden of contaminants depends upon a number of factors, such as feeding habit, metabolic ability, and reproductive cycles.

4. CONCLUSION

The levels of ∑PCBs and ∑OCPs detected in the tissues of different fish from the lower James River and Chesapeake Bay along the Virginia coast, was found that organochlorine contaminants concentrations in fish decreased in the order of Rock>Trout>Bluefish>Perch>Black Striped Bass >Flounder>Croaker. And with respect of PCBs, the profile was Bluefish > Flounder > Rock > Striped Bass > Perch > Trout > Croaker.

The relatively smaller concentrations reflect the distance from anthropogenic source of contamination, atmospheric sources of pollution, and large dilution factor.

ACKNOWLEDGMENTS

This study was conducted at the Virginia Polytechnic Institute and State University in Virginia and funded by the Council for International Exchange of Scholars (CIES) under the Fulbright Scholar Program on behalf of the United States Department of State.

Alia Bano Munshi would also like to thank all staff members of USEF/P and CIES for providing the opportunity by awarding the Fulbright scholarship.

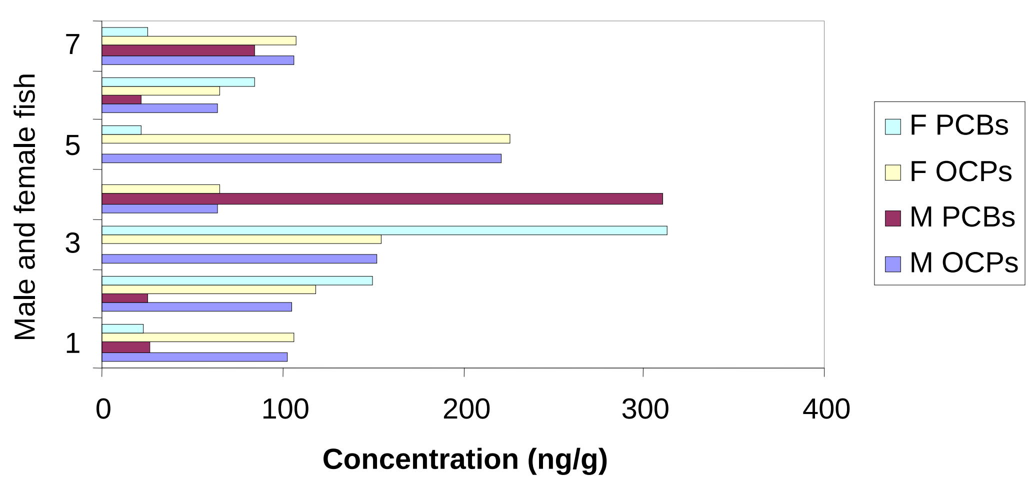

Fig. (1). OCPs and PCBs in male and female fishes.

Dave Kuhn and Amy Cheatham are also appreciated for their sincere efforts for this study.

REFERENCES

[1] OckendenWA, Breivik K, Meijer SN, Steinnes E, Sweetman AJ, Jones KC. The global re-cycling of persistent organic pollutants is strongly retarded by soils. Environ Pollut 2003; 121: 75-80.

[2] Meijer SN, Ockenden WA, Sweetman A, Breivik K, Grimalt JO, Jones KC. Global distribution and budget of PCBs and HCB in background surface soils: implications or sources and environmental processes. Environ Sci Technol 2003; 37: 667-72.

[3] Smith AG Gangolli SD. Organochlorine chemicals in seafood: occurrence and health concerns. Food Chem Toxicol 2002; 40: 767-79.

[4] Schmitt CJ, Hinck JE, Blazer VS, *et al.* Environmental contaminants and biomarker responses in fish from the Rio Grande and its U.S. tributaries: Spatial and temporal trends. Sci Total Environ 2006; 366: 549-78.

[5] Portelli M, deSolla SR, Brooks RJ, Bishop CA. Effect of dichlorodiphenyl trichloroethane on sex determination of the common snapping turtle (*Chelydra serpentina serpentina*). Ecotox Environ Safety 1999; 43: 284-91.

[6] Barker SA, Hung NN. MSPD: New Methods for the Rapid Extraction and Analysis of Pesticides in Food. Varian Sample Preparation Products, Harbor City, California. MSPD Method 1999.

[7] Tsydenova TB, Minh N, Kajiwara V, Batoev A, Tanabe S. Recent contamination by persistent organochlorines in Baikal seal (*Phoca sibirina*) from Lake Baikal, Russia. Mar Pollut Bull 2004; 48: 749-58.

[8] Monosson E, Ashley JTF, McElroy AE, Woltering D, Elskus AA. PCB congener distributions in muscle, liver and gonad of *Fundulus heteroclitus* from the lower Hudson River Estuary and Newark Bay. Chemosphere 2003; 52: 777-87.

[9] Sole M, Porte C, Albaiges J. Hydrocarbons PCBs and DDT in the NW Mediterranean deep-sea fish Mora moro, Deep Sea ReseAroclorh Part I: Oceanographic Res Aroclorh Papers 2001; 48: 495-513.

[10] Almansa E, Perez MJ, Cejas JR, Badia P, Villamandos JE, Lorenzo A. Lipid and fatty acid composition of ovaries from wild fish and ovaries and eggs from captive fish of White Sea bream (*Diplodus sargus*). Aquaculture 2003; 216: 299-313.

[11] Antunes P , Gil. OPCB and DDT contamination in cultivated and wild sea bass from Ria de Aveiro, Portugal. Chemosphere 2004; 54:1503-7.

[12] Cejas JR, Almansa E, Villamandos JE, Badia P, Bolanos A, Lorenzo A. Lipid and fatty acid composition of ovaries from wild fish and ovaries and eggs from captive fish of white sea bream (*Diplodus sargus*). Aquaculture 2003; 170: 323.

[13] Schulz DE, Petrick G, Diunker JC. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography--electron capture detection. Environ Sci Tech 1989; 23: 852-9.

[14] Safe SH. Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. Crit Rev Toxicol 1994; 24: 87-149.

[15] de Voogt P, Wells DE, Reutergardh L, Brinkman UA. The Biological activity, determination and occurrence of planar, mono- and di-ortho PCBs. Int J Environ Anal Chem 1990; 40: 1-46.

[16] Picard A, Palavan G, Robert S, Pesando D, Ciapa B. Effects of organochlorine pesticides on maturation of starfish and mouse oocytes. Toxicol Sci 2003; 73,141-8.

[17] Kawai M, Fukushima N, Miyazaki, Tatsukawa R. Relationship between lipid composition and organochlorine levels in the tissues of striped dolphin. Mar Pollut Bull 1988; 19(3): 129-33.

[18] Ferreira M, Moradas-Ferreira P, Reis-Henriques MA. Oxidative stress biomarkers in two resident species, mullet (*Mugil cephalus*) and flounder (*Platichthys flesus*), from a polluted site in River Douro Estuary. Portugal Aqua Toxicol 2004; 1(71): 39-48.

[19] Licata P, Di Bella G, Dugo G, Naccari F. Organochlorine pesticides, PCBs and heavy metals in tissue of the mullet *Liza aurata* in lake Ganzirri and Straits of Messina (Sicily, Italy). Chemosphere 2003; 52: 231-8.

[20] Roach AC, Runcie J. Levels of selected chlorinated hydrocarbons in edible fish tissues from polluted areas in the Georges/Cooks Rivers and Sydney Harbour: New South Wales, Australia. Mar Pollut Bull 1998; 36(5): 323-244.

[21] Weber K, Goerke H. Persistent organic pollutants (POPs) in antarctic fish: levels, patterns, changes. Chemosphere 2003; 53: 667-78.

[22] Munshi AB, Detlef SB, Schneider R, Zuberi R. Organochlorine concentrations in various fish from different locations at Karachi Coast. Mar Pollut Bull 2004; 49(7-8): 597-601.

[23] Pastor J, D Mladenoff Y, Haila J, Bryant S. Payette. Biodiversity and ecosystem processes in boreal regions. In: Mooney HA, Cushman JH, Medina E, Sala OE, Schulze E-D, Eds. Functional roles of biodiversity: a global perspective. Wiley Press: New York, USA 1996; 33-70.

Received: September 2, 2008 Revised: December 18, 2008 Accepted: January 9, 2009