## Seasonal Variation of Polychlorinated Biphenyls and Organochlorine Pesticide Levels of Sea and Cultured Farm Fish in the Samsun Region of Turkey

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**Abstract** The concentrations of selected Organochlorine (OC) pesticides ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, HCB, aldrin, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT) and Polychlorinated Biphenyls (PCBs) (28, 70, 74, 81, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187) were measured in two species of cultured freshwater fish (rainbow trout, Oncornhychus mykiss and catfish, Silurus glanis) and two kinds of sea fish (mullet, Mugil cephalus and salmon, Salmo salar) between March 2008 and June 2009 in order to evaluate the status, seasonal changes and potential sources of pollution in the Samsun region of Turkey. Concentrations of total PCBs ranged from 17.6 to 335 ng/g in rainbow trout, 1,063 to 3,234 ng/g in mullet, 21 to 1,887 ng/g in salmon and 108 to 1,172 ng/g lipid in catfish and total OC pesticide concentrations ranged from 303 to 473, 319 to 6,158, 101 to 249 and 34 to 6,069 ng/g lipid in rainbow trout, mullet, salmon and catfish, respectively. It is concluded that the levels of persistent organic pollutants should be monitored regularly and rigorously by the appropriate government agency, with mandatory public reporting.

This study was presented as a poster presentation at the 12th International Congress of Toxicology from 19 to 23 July, 2010 in Barcelona, Spain.

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Organochlorine compounds (OCs), due to their chemical persistence and lipophilicity, have a tendency to accumulate up the food chain. Therefore, human exposure to these pollutants occurs mainly from eating food (Hosseini et al. 2008). Several methods have been proposed for the assessment of the potential human health risks from exposure to these chemicals. Current non-cancer risk assessment methods are typically based on the use of the target hazard quotient (THQ), a ratio between the estimated dose of a contaminant and the reference dose below which there would not be any appreciable risk. If such ratio exceeds unity, there may be a concern for potential health effects. Another approach for estimating exposure and risks through the dietary intake of toxic substances is the use of the toxic equivalency factors (TEFs) and toxic equivalency quotient (TEQ) methodology. This approach assigns relative toxicity values to structurally related chemicals in comparison to a reference chemical (Storelli 2008). To ascertain the potential risk to the health of consumers, the aim of the present study was to determine the seasonal variations of PCBs and OC pesticide concentrations in sea and cultured freshwater fish in the Samsun Region of Turkey.

## **Materials and Methods**

Fish samples were collected from markets and fish farms in the Samsun region from March 2008 to June 2009. In all seasons, 10 samples were collected for each of four fish species which were mullet (*Mugil cephalus*), salmon (Salmo salar), rainbow trout (Oncornhychus mykiss) and catfish (Silurus glanis). The total number of samples was 160.

The method of Bordet et al. (2002) was used for analysis of OC pesticides ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, HCB, aldrin, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT) and PCBs (28, 70, 74, 81, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187) (Dr.Ehrenstorfer, Germany). Firstly, 25 g fish flesh was homogenized. Twenty five millilitres of n-hexane (Merck, Germany) was added to the sample. After mixing, the sample was centrifuged (Nuve, Turkey) and the supernatant was collected. The same procedures were repeated for the sample. The solvent was reduced to 1 mL in a rotary evaporator (Buchi, Switzerland) and then totally evaporated under a nitrogen stream. Cryogenic extraction was used to obtain the OC pesticides and PCBs from fat. Half a gram of fat extract was then placed into a centrifuge tube. Three millilitres of acetonitrile (ACN) and dichloromethane (DCM) (Merck, Germany) (75 + 25, v/v) mixture were added to the fat extract. They were mixed with a vortex (Velp Scientifica, Spain), centrifuged, and the supernatant was collected. For the lower phase, the procedure was repeated using the same solvent mixture. The sample extract was then concentrated to 2 mL under a nitrogen stream (solution A). A C<sub>18</sub> SPE cartridge (Phenomenex, USA) was used for clean-up. The cartridge was twice conditioned with 5 mL each of petroleum ether, acetone, and methanol (Merck, Germany). After conditioning, solution A was poured into the cartridge. The analyte was eluted from cartridge with 10 mL of ACN. One hundred microliters of dodecane (Merck, Germany) was added to the final analyte. The mixture was evaporated under a nitrogen stream. The analyte was dissolved with n-hexane (solution B). The second clean-up was carried out with a florisil cartridge (Phenomenex, USA) which was conditioned with 10 mL of n-hexane. After that, solution B was poured on to the cartridge. The sample was eluted with 10 mL of petroleum ether and diethyl ether (Merck, Germany) (98 + 2, v/v) and following that with 12 mL of petroleum ether-diethyl ether (85 + 15, v/v). The two extracts were mixed and dried under a nitrogen stream. The precipitate was dissolved with 2 mL of n-hexane to produce Solution C.

A Schimadzu GC 17 A (Japan) gas chromatography unit equipped with electron capture detector (GC-ECD) was used in the present study. A capillary column (60 m  $\times$  0.32 mm i.d. with a 25  $\mu m$  thick film of phenyl-methyl silicon) (Teknokroma, Spain) was used in the instrument. The flow rate of the carrier gas nitrogen was 1.5 mL/min. Column oven conditions were as follows: initial temperature 100°C, held for 3 min; a 10°C/min ramp to 200°C, held for 3 min; a 3°C/min ramp to 225°C, held for 3 min; a 2°C/min ramp to 270°C, held for 3 min; and a 1°C/min ramp to 275°C, held for 10 min. One micro liter splitless

injection of solution C was carried out at 260°C and the detector temperature was 280°C.

## **Results and Discussion**

The retention times of PCBs and OC pesticides were between 23.80 and 47.46 min, and 19.53 and 38.97 min, respectively. Recovery percentages of PCBs and OC pesticides were between 68% and 97%, and 69% and 117%, respectively. Recovery percentages were as follows: PCB 28 (86% ± 14%), PCB 70 (84%  $\pm$  7%), PCB 74 (83%  $\pm$  6%), PCB 81  $(68\% \pm 10\%)$ , PCB 99  $(92\% \pm 7\%)$ , PCB 101  $(89\% \pm$ 7%), PCB 105 (86%  $\pm$  5%), PCB 118 (88%  $\pm$  6%), PCB 128 (83%  $\pm$  4%), PCB 138 (88%  $\pm$  7%), PCB 153 (86%  $\pm$ 10%), PCB 156 (76%  $\pm$  5%), PCB 170 (97%  $\pm$  15%), PCB 180 (80%  $\pm$  5%), PCB 183 (83%  $\pm$  2%), PCB 187  $(84\% \pm 2\%)$ ,  $\alpha$ -HCH  $(69\% \pm 3\%)$ ,  $\beta$ -HCH  $(77\% \pm 6\%)$ ,  $\gamma$ - $HCH (76\% \pm 2\%), HCB (69\% \pm 6\%), aldrin (69\% \pm 5\%),$ 2,4'-DDE (72%  $\pm$  9%), 4,4'-DDE (87%  $\pm$  15%), 2,4'-DDT  $(106\% \pm 11\%)$  and 4,4'-DDT  $(117\% \pm 15\%)$ . Limits of detection (LODs) for PCBs and OC pesticides were between 0.31 and 1.88 ng/g, and 0.01 and 0.59 ng/g, respectively. Limits of detection were as follows: PCB 28, 0.72 ng/g; PCB 70, 0.53 ng/g; PCB 74, 0.91 ng/g; PCB 81, 0.69 ng/g; PCB 99, 0.87 ng/g; PCB 101, 0.43 ng/g; PCB 105, 1.88 ng/g; PCB 118, 0.78 ng/g; PCB 128, 0.58 ng/g; PCB 138, 0.45 ng/ g; PCB 153, 1.13 ng/g; PCB 156, 0.70 ng/g; PCB 170, 0.59 ng/g; PCB 180, 0.31 ng/g; PCB 183, 0.34 ng/g; PCB 187, 0.38 ng/g;  $\alpha$ -HCH, 0.02 ng/g;  $\beta$ -HCH, 0.03 ng/g;  $\gamma$ -HCH, 0.02 ng/g; HCB, 0.02 ng/g; aldrin, 0.01 ng/g; 2,4'-DDE, 0.04 ng/g; 4,4'-DDE, 0.02 ng/g; 2,4'-DDT, 0.59 ng/g and 4,4'-DDT, 0.40 ng/g.

Seasonal changes in concentrations of PCBs and OC pesticides in fish samples are shown in Tables 1 and 2, respectively. Statistical differences between the total PCB concentrations of fish species were determined with the Kruskal-Wallis Test, followed by the Mann-Whitney U Test. Statistical differences between the total OC pesticide concentrations of fish species were determined with the Kruskal-Wallis Test, followed by the Mann-Whitney U Test or one-way ANOVA, followed by Tukey's Test. All data were expressed as mean  $\pm$  standard error of mean (SEM). Differences were considered significant when p values were <0.05. Statistical analysis of seasonal variation of PCBs and OC pesticide concentrations in fish species are shown in Tables 3 and 4, respectively.

Seasonal variability of persistent OC pesticide residues in marine fish along the Indian Ocean coast of Kenya was investigated by Barasa et al. (2008). Higher residue levels were recorded in the rainy season in May than in the dry season in January. That seasonal variation was particularly pronounced in 4,4'-DDT residues which were only detected



Table 1 Seasonal variations in concentrations of PCBs in fish samples<sup>a</sup>

	Rainbow trout	v trout			Mullet				Salmon				Catfish			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Lipid (%)	2,33	1,77	4,3	3,5	0,48	0,16	1,1	1,5	1,10	5,14	3,62	2,05	11,9	0,65	3,25	1,29
Detected	n = 0	n = 2	n = 4	n = 1	n = 6	n = 3	n = 4	n = 7	n = 0	n = 5	0 = 0	n = 1	n = 2	n = 6	n = 4	0 = 0
samples PCB 28	1	18.22-45.17 17.2-162.4 17.68 77.4-1,239	17.2–162.4	17.68	77.4–1,239	347.7–1,011.7	26.56	93–214.6	ı	31–491.5	33.4–134.4	ı	I	29.7–858	26.14-151.3	ı
PCB 74	I	1	ı	ı	ı	ı	ı	53.46	ı	ı	ı	ı	ı	ı	ı	ı
PCB 70	ı	1	I	1	ı	ı	19.92	81.34	I	ı	ı	I	ı	I	I	1
PCB 101	ı	ı	1	1	1	ı	21.38-78.3	24.2-45.88	ı	ı	ı	ı	ı	1	ı	1
PCB 99	ı	I	ı	ı	ı	ı	ı	28.54	ı	ı	ı	ı	ı	ı	ı	ı
PCB 81	ı	1	I	ı	ı	ı	ı	ı	ı	ı	ı	ı	ı	I	I	ı
PCB 118	ı	1	1	1	1	ı	33.4-94.8	32.8-60.52	ı	33.96	ı	ı	1	ı	22.7–33.96	1
PCB 105	ı	ı	ı	ı	ı	ı	22.6	25.6	I	ı	ı	I	ı	ı	20.24	ı
PCB 153	1	ı	ı	ı	47	ı	69.24-184.6	43.1–311.6	ı	ı	ı	ı	38.86-44.82	ı	39.72-44.7	ı
PCB 138	ı	1	1	ı	1	1	33.76–99.6	28.8-60.44	ı	ı	1	ı	24.6	ı	1	1
PCB 183	ı	ı	93.8	ı	1	1,318.7	28.72	28.32	ı	9.706	73.2	21.6	ı	ı	ı	ı
PCB 187	ı	ı	1	ı	1	ı	28.04	1	1	ı	ı	1	ı	ı	1	ı
PCB 128	1	ı	ı	1	1	ı	33.16	28.84	ı	1	1	ı	ı	1	1	ı
PCB 156	1	ı	ı	ı	27.4	ı	15	ı	ı	ı	ı	ı	ı	ı	1	ı
PCB 180	ı	ı	1	ı	1	ı	ı	44.44	1	ı	ı	1	ı	ı	1	ı
PCB 170	1	ı	ı	1	1	ı	ı	1	ı	1	1	ı	ı	1	1	ı
$\sum_{\mathbf{PCB}}$	ı	63.39	335	17.68	2,476.3	3,234.6	1,063.32	1,835.96	ı	1,887.9	643.48	21.6	108.28	1,172.97	338.76	ı
$\sum_{ ext{PCB}^{b}}$	1	63.39	241.2	17.68	2,448.9	1,915.9	915.94	1,784.26	I	980.3	570.28	I	108.28	1,172.97	318.52	ı

<sup>a</sup> These values are the lowest and highest concentrations. Single values were determined in only one sample

<sup>b</sup> This value is the sum of indicator PCB 28, 101, 118, 138, 153 and 180



 Fable 2
 Seasonal variations in concentrations of OC pesticides in fish samples

	Rainbow trout	, trout			Mullet				Salmon				Catfish			
	Spring	Spring Summer Autumn Winter	Autumn	Winter	Spring	Summer Autumn	Autumn	Winter	Spring	Summer	Summer Autumn Winter	Winter	Spring	Summer	Summer Autumn	Winter
Lipid (%) 2,33	2,33	1,77	4,3	3,5	0,48	0,16	1,1	1,5	1,10	5,14	3,62	2,05	11,9	0,65	3,25	1,29
Detected samples	n = 10	n = 0	n = 0	n = 7	n = 5	n = 1	n = 10	0 = 0	n = 2	n = 0	n = 0	n = 5	n = 2	n = 0	n = 2	n = 8
д- НСН	ı	ı	ı	ı	54.7-137.2	ı	ı	26.2	ı	ı	ı	I	1	ı	1	ı
$\beta$ - HCH	ı	ı	1	1	ı	1	35.9–55.7	19.06-30.4	I	I	1	ı	1	1	1	1
$\gamma$ -HCH	ı	ı	ı	16.8-20.9	I	ı	22.22–30.2	21.8	I	į	1	I	ı	ı	16.84-17.88	ı
HCB	ı	ı	ı	6.99	I	ı	ı	36.1	I	ı	ı	I	1	ı	ı	ı
Aldrin	ı	ı	1	ı	69.4	319	1	ı	ı	ı	1	1	1	1	1	ı
2,4'-DDE	ı	1	ı	1	ı	1	1	ı	ı	1	1	ı	ı	ı	1	1
4,4′-DDE	33.1- 79.8	I	I	26.3-39.8	I	I	94–308.2	56.6–398.7 41.7–59.4	41.7–59.4	I	I	37.2–77.5	37.2–77.5 1,424.94–2,520.3	I	1	302.4–2,238
2,4'-DDT	ı	ı	ı	I	I	ı	ı	1	I	ı	ı	I	1	ı	ı	ı
4,4'-DDT	ı	ı	1	ı	1	ı	4,187.58	728.3	I	I	ı	ı	1,240.94	1	ı	ı
$\Sigma$ oc	473.21	I	ı	303.86	501.2	319	6,158.57	2,385.36	101.1	I	ı	249.6	5,186.18	ı	34.72	6,069.7
a These va	lues are th	ie lowest ar	rd highest c	concentration	s. Single valu	ies were det	<sup>a</sup> These values are the lowest and highest concentrations. Single values were determined in only one sample	ly one sample	47							

in samples in the rainy season at all sampling sites. The high DDT/DDE and aldrin/dieldrin concentration ratios also indicated that the sources of those residues were recent. The presence of OC pesticides and PCBs was investigated in wild and farmed gilthead seabream (Sparus aurata) in the western Mediterranean Sea in Spain by Serrano et al. (2008). DDTs, PCBs and HCB were detected in both wild and farmed fish. The highest concentrations of contaminants were in the liver, and an increase in contamination levels was observed in autumn, before spawning. Wild gilthead seabream had significantly higher concentrations of DDTs and PCBs than farmed fish from the same area. Organochlorine residues were determined in the hepatic and muscular tissues of European eel, crucian carp and catfish from the Vaccares Lagoon in the National Nature Reserve of Camargue in France in order to compare their geographical and seasonal distribution (Roche et al. 2000). Total levels appeared to be higher in fatty eels than in crucian carp and catfish. The highest OC concentrations were detected in liver (total PCB) and in muscle (γ-HCH) in spring in fish from a site located near the mouth of a canal draining irrigation water from rice fields. Organochlorine pesticide residues in aquatic systems and organisms in the Upper Sakarya Basin in Turkey were analysed by Barlas (1999). In fish samples, DDT and its metabolites were detected at high levels in October. Heptachlor epoxide, which is a degradation product, was found at higher levels in adipose tissue. Those levels were significantly higher than in fish collected there in February, May and August. In February, dieldrin, heptachlor epoxide and 2,4'-DDT residue levels in adipose tissue were higher than in May and August. Seasonal trends and tissue distribution of OC pesticides and PCBs were investigated in gilthead seabream from the Western Mediterranean by Blanes et al. (2009). DDTs and PCBs were present in different tissues, with the highest concentrations in tissues with high lipid content. Concentrations of OCs in seabream tissues strongly correlated with seasons and the biological cycle of the species. In general, cultured fish had lower concentrations and seasonal variability of contaminants than wild fish. Trace levels of contaminants were found in fish muscle throughout the year, but always below the maximum level recommended for human consumption.

The concentrations of PCBs, PCDDs and PCDFs in sea fish and seafood on the Spanish Atlantic southwest Coast were investigated by Bordajandi et al. (2006). The total PCB concentrations ranged between 861 and 23,787 pg/g wet weight (ww). Sardine and white seabream showed the highest concentrations (14,642–23,787 pg/g ww), while prawns and both shellfish species showed the lowest levels (861-3,445 pg/g ww). The concentrations of 2,3,7,8-PCDD/Fs ranged from 0.2 to 1.18 pg/g www and WHO-TEQ concentrations ranged from 0.038 to 0.186 pg WHO-



**Table 3** Statistical analysis of PCB concentrations in fish species (mean  $\pm$  SEM)

	Spring	Summer	Autumn	Winter
Rainbow trout	<lod< td=""><td><math>31.7 \pm 13.48^{a}</math></td><td><math>67 \pm 27.32</math></td><td><math>17.68 \pm 0^{a}</math></td></lod<>	$31.7 \pm 13.48^{a}$	$67 \pm 27.32$	$17.68 \pm 0^{a}$
		(18.22–45.17)	(17.2–162.4)	PS:1
		PS: 2	PS: 5	
Mullet	$309.54 \pm 145.25^{x}$	$808.65 \pm 219.36^{\mathrm{b,y}}$	$59.08 \pm 10.9^{z}$	$83.45 \pm 15.97^{b,z}$
	(27.4–1,239)	(347.7–1,318.7)	(15–184.6)	(24.2–311.6)
	PS: 8	PS: 4	PS: 18	PS:22
Salmon	<lod< td=""><td><math>314.65 \pm 137.04^{a}</math></td><td><math>64.35 \pm 10.91</math></td><td><math>21.6 \pm 0^{a}</math></td></lod<>	$314.65 \pm 137.04^{a}$	$64.35 \pm 10.91$	$21.6 \pm 0^{a}$
		(31–907.6)	(33.4–134.4)	PS:1
		PS: 6	PS: 10	
Catfish	$36.09 \pm 6$	$195.5 \pm 132.89^{a}$	$48.39 \pm 17.48$	<lod< td=""></lod<>
	(24.6–44.82)	(29.7–858)	(20.24–151.3)	
	PS: 3	PS: 6	PS: 7	

PS positive samples

TEQPCDD/Fs/g ww. When the WHO-TEQPCBs values were added, the species exhibiting the highest total WHO-TEQ concentration (the sum of WHO-TEQPCDD/Fs and WHO-TEQPCBs) were sardine and white seabream with a range of 0.562-0.990 pg WHOTEQ/g ww. The presence of OCs, including PCBs, DDTs, HCB, HCHs and toxaphene, was investigated in 12 edible fish species in the Marmara Sea, Turkey by Coelhan et al. (2006). The total concentrations of OCs ranged from 329.41 ng/g fat to 1,453.87 ng/g fat. DDT group compounds made up half or more of the OC contamination. The total concentrations of DDTs and HCHs were markedly lower than in the Black Sea but higher than in Aegean and Mediterranean Sea red mullet. The total concentration of PCBs (the sum of congeners 28, 52, 101, 118, 138, 153 and 180) detected in the study was comparable or lower than from the Aegean Sea and Mediterranean Sea. Toxaphene values were lower than the maximum residue levels approved for human consumption. Concentrations of persistent OC residues were determined in fish from many locations in eastern and southern Asia and Oceania by Kannan et al. (1995). DDT and its derivatives were the predominant compounds in most locations. In general, the concentrations of OCs in tropical fish were lower than those in fish from temperate regions. DDT concentrations were highest in fish from all the South East Asian countries (Thailand, Vietnam, and Indonesia), while both HCH and DDT constituted the dominant OCs in Indian fish. The contamination pattern in Australian fish was different from those observed in Asian countries, with PCBs in the highest concentrations, followed by chlordanes. The concentrations of HCB were uniformly low in fish from all the countries studied. In an Indian study, seasonal differences in OC pesticide

concentrations of zooplankton and fish in the Arabian Sea were studied by Shailaja and Nair (1997). In the monsoon season, the total concentrations of DDT and aldrin in zooplankton were 4 and 5 times higher, respectively, than the pre-monsoon concentrations, while the corresponding increases in fish were 10-30 times and 3-40 times, respectively. The presence of considerable amounts of primary DDT in samples obtained during the monsoon season, coinciding with peak agricultural activity on land, indicated that the pesticide residue levels in those organisms were determined by the pattern of land use and that the pesticide compounds entering that environment rapidly entered the food chain. Also, pesticide accumulation by fish was apparently dictated by their feeding habits. As observed in lipid-normalised values, pelagic varieties accumulated more residues than demersal ones during the pre-monsoon season, while the opposite was true for the monsoon season. DDT was the major DDT metabolite present in all the samples. The concentrations of indicator PCBs, DDT and its metabolites were determined in whiting and horse mackerel from the Izmit Bay in Turkey by Celik Cakirogullari and Secer (2010). The total concentrations of PCBs ranged from 1.49 to 39.69 ng/g ww in whiting and from 5.61 to 58.61 ng/g ww in horse mackerel. Total DDT concentrations were from 1.08 to 66.73 ng/g ww in whiting and from 4.69 to 116.25 ng/g ww in horse mackerel. Concentrations of PCBs and DDTs in horse mackerel were higher than those in whiting. Analysis for DDT and its metabolites revealed that 4,4'-DDE was at the highest levels in both species. However, total PCB and DDT concentrations in those fish were lower than the legislated maximum residue limits. Bioaccumulation of PCBs was investigated by Fu and Wu (2005) in mullet in two



a,b Means in the same column with different superscript differ significantly (p < 0.05)

 $<sup>^{</sup>x,y,z}$  Means in the same row with different superscript differ significantly (p < 0.05)

**Table 4** Statistical analysis of OC pesticide concentrations in fish species (mean  $\pm$  SEM)

	Spring	Summer	Autumn	Winter
Rainbow trout	$47.32 \pm 4.23^{a,x}$	<lod< td=""><td><lod< td=""><td><math>22.94 \pm 2.71^{a,y}</math></td></lod<></td></lod<>	<lod< td=""><td><math>22.94 \pm 2.71^{a,y}</math></td></lod<>	$22.94 \pm 2.71^{a,y}$
	(33.1–79.8)			(13.9–39.8)
	PS: 10			PS: 10
Mullet	$83.53 \pm 11.52^{a}$	$319 \pm 0$	$359.27\pm226.37^a$	$149.09 \pm 47.7^{b}$
	(54.7–137.2)	PS: 1	(22.22–4,187.58)	(19.06–728.3)
	PS: 6		PS: 18	PS: 16
Salmon	$50.55 \pm 8.85^{a}$	<lod< td=""><td><lod< td=""><td><math>49.91 \pm 7.32^{b}</math></td></lod<></td></lod<>	<lod< td=""><td><math>49.91 \pm 7.32^{b}</math></td></lod<>	$49.91 \pm 7.32^{b}$
	(41.7–59.4)			(37.2–77.5)
	PS: 2			PS: 5
Catfish	$1,728.73 \pm 399.33^{\mathrm{b}}$	$16.84 \pm 0$	$17.88 \pm 0$	$758.71 \pm 225.76^{\circ}$
	(1,240.94–2,520.3)	PS: 1	PS: 1	(302.4–2,238)
	PS: 3			PS: 8

 $<sup>^{</sup>a,b,c}$  Means in the same column with different superscript differ significantly (p < 0.05)

formerly PCB contaminated areas in Taiwan, the Ann-Ping harbour and the Er-Jen estuary, and in fish farms located near those areas. The PCB burdens in fish samples were proportional to the contamination levels of their location. Concentrations of PCBs in the estuarine mullet had decreased to approximately 50% of the peak concentration of the 1990s. Although the concentration of PCBs in farmed fish near the two contaminated areas was greater than the average for those fish from local fish markets in Taiwan, particularly high levels were not detected. Fish collected in the formerly heavily contaminated Er-Jen estuary had the highest total PCB levels in autumn  $(0.72 \mu g/g)$  and spring  $(0.34 \mu g/g)$  samples, followed by those in the harbour in autumn  $(0.22 \mu g/g)$  and in spring  $(0.069 \mu g/g)$  and in the fish farm in autumn  $(0.022 \mu g/g)$ .

In the current study, the total PCB concentrations in mullet were significantly higher than in the other fish species in spring, summer and winter (p < 0.05). For autumn, the highest total PCB concentration was in rainbow trout (p < 0.05). With respect to seasonal variation between fish species, there was a difference only mullet samples (p < 0.05). The total PCB concentrations were higher in spring than in autumn and winter (p < 0.05). However, there was no difference in mullet samples between autumn and winter (p > 0.05). Mullet samples collected in summer had higher levels of contaminants than samples collected in other seasons (p < 0.05). Organochlorine pesticide concentrations were higher for catfish than for the other species in spring (p < 0.05). There was only one positive sample in summer. For that reason, comparisons could not be made. However, in autumn, OC pesticide concentrations in mullet were significantly higher than in catfish (p < 0.05). In winter, there was no difference between mullet and salmon (p > 0.05) and OC pesticide concentrations in rainbow trout were significantly lower than in the other species (p < 0.05). Organochlorine pesticide levels of catfish samples were higher than in the other three species (p < 0.05) in winter. In terms of seasonal variation, there was a difference only in rainbow trout samples (p < 0.05) in which there was a great variation between spring and winter seasons (p < 0.05). In summer and winter, total PCBs were higher in mullet samples than in the other species. The higher residue levels in mullet samples may be related to the ecology and feeding behaviour of the fish. Mullet live in coastal areas of the sea. The main food items of mullet are insect larvae, worms, small crustaceans and fish fry. These organisms are contaminated via nutrition and respiration and are exposed to higher pesticide levels because they live in in-shore waters. In contrast, it has been suggested that fish that live in deep water has lower OC levels (Uluocak and Egemen 2005). In spring, inflows of water, soil particles and residues to rivers and dams are due to run-off and erosion due to snow-melt and rainfall. The reason for high OC pesticide levels in the catfish may be due to its bottom feeding behaviour during which it is exposed to disturbed sediments. Rainbow trout samples were collected from the Derbent Dam Lake on the Kizilirmak River which is the longest river in Turkey. Its catchment area includes a very large area of central Anatolia, including major agricultural, industrial and urban areas. Currently, there are no legislated protection measures for the impoundment and its environment (Taş 2005). The seasonal differences in OC pesticide residues in rainbow trout observed between spring and autumn may be related to soil erosion because of the rainfall regime.



x,y Means in the same row with different superscript differ significantly (p < 0.05)

PS positive samples

In the present study, 3 mono-ortho PCBs (PCB-105, -118 and -156) and one non-ortho PCB (PCB-81) which are dioxinlike PCBs were investigated. According to a re-evaluation by the World Health Organisation in 2005, the TEF values for PCB-105, -118 and -156 is 0.00003. For PCB-81, the TEF value is 0.0003 and the maximum TEQ value for dioxin and dioxin-like PCBs is 8 pg/g ww of fish (Van den Berg et al. 2006). In the Turkish Food Codex and European Commission Directive, the maximum residue limits for OC pesticides have not been determined for fish and the other seafood yet (Aksoy et al. 2011). Therefore, except for the dl-PCBs, the residue levels of OC compounds could not be evaluated in terms of food safety and public health. There were no residues of PCB-81 in fish samples. Mono-ortho PCB residues were detected in one salmon, two catfish and five mullet. In one autumn catfish sample, PCB-118 residue was detected and the TEQ value for this compound was 1.02 pg/g ww. In the other autumn catfish sample, PCB-105 and -118 were detected and the TEQ value for these compounds was 1.29 pg/g ww. In one autumn mullet sample, PCB-105, -118 and -156 residues were found and the TEQ value was 2.13 pg/g ww. In another autumn mullet sample, PCB-118 was detected and the TEQ value was 2.84 pg/g ww. One spring mullet sample was positive for PCB-156 residue and the TEQ value was 0.82 pg/g ww. In one winter mullet sample, PCB-105 and -118 were detected and the TEQ value was 2.59 pg/g ww. In another winter mullet sample, PCB-118 was found and the TEQ value was 0.98 pg/g ww. In one salmon sample, PCB-118 was detected and the TEQ value was 1.02 pg/g ww. However, there were no samples above the maximum TEQ value of 8 pg/g ww. According to those values, the levels of the dl-PCBs in the investigated samples were not hazardous to people.

The results from this study are important as a snapshot for current food safety and environmental health assessment and for baseline data for subsequent studies. It is also concluded that the levels of persistent organic pollutants should be monitored regularly and rigorously by the appropriate government agency and that there be mandatory public reporting. At the same time, it is imperative that resource managers, producers and consumers be educated about the hazards of these compounds and how to manage fisheries, fish and fish products to minimise contamination.

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