



## Levels of DDTs and indicator polychlorinated biphenyls in Whiting (*Merlangius merlangus euxinus* N. 1840) and Horse mackerel (*Trachurus mediterraneus* S. 1868) from the İzmit Bay, Turkey

Gul Celik Cakirogullari<sup>1,\*</sup>, Selcuk Secer<sup>2</sup>

<sup>1</sup> Ministry of Agriculture and Rural Affairs, Ankara Provincial Control Laboratory, Department of Dioxin and PCBs, 06170, Yenimahalle, Ankara, Turkey

<sup>2</sup> Ankara University, Faculty of Agriculture, Department of Fisheries and Aquaculture Engineering, 06110, Dışkapı, Ankara, Turkey.

\* Corresponding Author: Tel.: +90.312 3150089-143; Fax: +90.312 3157934;  
E-mail: gcakirogullari@yahoo.com

Received 18 May 2009  
Accepted 05 March 2010

### Abstract

The concentrations of indicator polychlorinated biphenyls (PCBs) and 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT) and its metabolites were determined in whiting (*Merlangius merlangus euxinus* N. 1840) and horse mackerel (*Trachurus mediterraneus* S. 1868) from the İzmit Bay, Turkey. The results showed that the levels of the total PCBs ranged from 1.49 to 39.69 ng/g fresh weight in whiting, and from 5.61 to 58.61 ng/g fresh weight in horse mackerel. Total DDTs concentrations were found from 1.08 to 66.73 ng/g fresh weight in whiting, and 4.69 to 116.25 ng/g fresh weight in horse mackerel. Concentrations of PCBs and DDTs in horse mackerel were found higher than those in whiting. Congeners IUPAC Nos. 52, 101, 153 were found frequently in whiting and horse mackerel samples. Analysis of DDT and its metabolites showed that *p,p'*-DDE was dominant in both of the fish species. Total PCB and DDT concentrations in fish samples were found lower than the maximum residue limits fixed by legislations.

**Keywords:** Fish, organochlorine contaminants, Marmara Sea.

### Türkiye’de İzmit Körfezi’nden Yakalanan Mezgit (*Merlangius merlangus euxinus* N. 1840) ve İstavrit (*Trachurus mediterraneus* S. 1868) Balıklarında DDT’lerin ve Poliklorlu Bifenillerin Seviyeleri

#### Özet

Türkiye’de İzmit Körfezi’nden yakalanan mezgit (*Merlangius merlangus euxinus* N. 1840) ve istavrit (*Trachurus mediterraneus* S. 1868) balıklarında indikatör poliklorlu bifeniller (PCBs) ile 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT) ve metabolitleri tespit edilmiştir. Total PCB’lerin konsantrasyonları mezgit balıklarında 1,49-39,69 ng/g yaş ağırlık olarak bulunurken, istavrit balıklarında ise 5,61-58,61 ng/g yaş ağırlık olarak tespit edilmiştir. Total DDT konsantrasyonları ise mezgit balığında 1,08-66,73 ng/g yaş ağırlık olarak bulunurken, istavrit balıklarında 4,69-116,25 ng/g yaş ağırlık olarak bulunmuştur. PCB ve DDT konsantrasyonları istavrit balığında mezgit balığına kıyasla daha yüksek bulunurken, her iki balık türünde de tespit edilen en baskın bileşenler PCB52, PCB101, PCB153 ve *p,p'*-DDE’dir. Sonuç olarak total PCB ve DDT konsantrasyonları tebliğlerde belirtilen maksimum kalıntı limitlerinin altında bulunmuştur.

**Anahtar Kelimeler:** Balık, organik klorlu bileşikler, Marmara Denizi.

#### Introduction

Organochlorine compounds such as polychlorinated biphenyls (PCBs) and 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT) and its metabolites are ubiquitous toxic contaminants, due to their bioaccumulative capacity and persistence and specific physico-chemical properties (Everaarts *et al.*, 1998). Polychlorinated biphenyls belong to Persistent Organic Pollutants (POPs) group of chemicals primarily used in transformers, capacitors, paints and printing inks, and also in many other industrial

applications. They are amongst the industrial chemicals banned and included in the list of priority contaminants to be monitored regularly in the western countries (Babu-Rajendran *et al.*, 2005). They have been reported to cause variety of effects including immunologic, teratogenic, carcinogenic, reproductive and neurological problems in organisms (Kodavanti *et al.*, 1998). In addition, some congeners have shown some effects on the endocrine system such as reducing serum concentrations of the thyroid hormones (Koopman-Esseboom *et al.*, 1994). Chlorinated pesticides such as DDT are effective pest

control chemicals, used in agriculture and public health activities (malaria eradication, etc.) worldwide for the past several decades and are still in use in many developing countries. Similar to PCBs, DDTs also cause endocrine disruption and are hazardous to human and/or environmental health (Babu-Rajendran *et al.*, 2005). Organochlorines accumulate in fats of species throughout the food chain (Barrie *et al.*, 1992). Animal diet is generally one of the major routes of contaminants into the human body. In particular, an important significance in this context has been attributed to fish and seafood (Alcock *et al.*, 1998).

Bay of İzmit, located south of İstanbul on the southeast of the Marmara Sea, is the most important semi-enclosed body of water on the sea of Marmara. Sea of Marmara is an inland basin located between the Black Sea and Aegean Sea, and has a two-layer stratification (Algan *et al.*, 1999). İzmit Bay is one of the most polluted areas in Turkey. It is about 50 kms in length, 2-10 kms in width and has a surface area of 310 km<sup>2</sup>. It consists of three district parts which behave semi-independently. The Eastern sector (inner part) is very shallow (30 m) and consists of the most polluted part of the Bay. While the industries of petroleum are based in the Central part, the entrance to the Marmara Sea through a wide and deep channel is located in the Western part (outer part) which is less polluted because of better water exchange (Okay *et al.*, 2003). The Central part is highly affected by the heavy industries discharging their wastewaters through Dil River into the Bay (Morkoç *et al.*, 2007). There are more than 140 large industrial plants scattered around the Bay and commissioning of these and, particularly, the consequent urbanisation of the coastal landscape have completely destroyed Bay of İzmit (Telli-Karakoç *et al.*, 2002). The largest wastewater contribution comes to the Bay from İzmit. Direct estimates of industrial inputs vary from 0.1 kg/day to over 10 t/day for the industry around the İzmit city (Legovic *et al.*, 1995).

On August 17, 1999, a powerful earthquake struck the Marmara region and the Bay ecosystem was strongly affected by the quake and subsequent refinery fire as well as the settlements and industrial regions (Okay *et al.*, 2003). The most widely publicised and spectacular damage to any industrial facility occurred at the massive refinery near the town Körfez operated by the state-owned oil company, Tüpraş. Following the earthquake the tank farm of the refinery burned out of control for several days (Tolun *et al.*, 2006) and following the refinery fire caused by the earthquake, the surface waters of the Bay were partly covered by thick petroleum layers and by a film (Morkoç *et al.*, 2007). After the earthquake, most of the industrial treatment plants had been damaged and the refinery fire caused an increase in the levels of pollutant discharge through Petkim Channel. The results of the long term monitoring studies have shown that the waste inputs via the Dil River and

other sources to the bay drastically affected the inner bay ecosystem. Consequences of the 1999 earthquake in the bay have shown a temporary occurrence of a two-layer ecosystem with a very low oxygen content in the lower layer. Such a system has been shown to have a limited self purification capacity for organic and nutrient inputs (Morkoç *et al.*, 2007).

In this research, whiting and horse mackerel samples collected from İzmit Bay were analyzed monthly between December-2003 and November-2004 to determine the contamination level of indicator polychlorinated biphenyls and DDT compounds threatening environment and human health in İzmit Bay. İzmit Bay is the most important industrial area of Turkey and is heavily urbanized. Most of the toxicology studies in the İzmit Bay have focused on the polycyclic aromatic hydrocarbons and heavy metals (Tolun *et al.*, 2001; Okay *et al.*, 2003), however very little is known on the PCB and DDT contamination in the biota of the İzmit Bay. PCB levels in mussels from the İstanbul strait and the most industrialized bay of the Marmara Sea were published and also found to be high (Telli-Karakoç *et al.*, 2002; Tolun *et al.*, 2007, Okay *et al.*, 2009). Indicator PCBs and total DDTs were determined in different fish species caught from Marmara Sea, Turkey. The results were 209.36 and 455.09 ng/g fat weight for horse mackerel, 363.85 and 577.43 ng/g fat weight for whiting respectively (Coelhan *et al.*, 2006). In another study PCBs and DDTs were determined in different fish species in Black Sea. Total PCB and DDT concentrations were found as 140 and 280 ng/g wet weight for whiting, 210 and 490 ng/g wet weight for horse mackerel respectively (Tanabe *et al.*, 1997a). High concentrations of toxic coplanar PCBs and other isomers were detected in the fishes that were used as porpoises' feed. The results were 50 ng/g wet weight and 140 ng/g wet weight for European anchovy and whiting respectively. It is concluded that the elevated levels of PCB concentrations of samples were because of the contamination of the countries around the Black Sea (Tanabe *et al.*, 1997b). Fish are an excellent indicator organism for pollution in aquatic ecosystems, where trace contaminants are difficult to analyze directly. They also generally possess a low metabolism for organochlorines and should reflect the levels of pollution in the aquatic environment (Muir *et al.*, 1990). However, studies of persistent pollutants in species from the İzmit Bay are very scarce. Because of the reasons mentioned above, present study aims to evaluate the occurrence of the most important organohalogenated pollutants, such as DDTs and PCBs, in whiting and horse mackerel fish samples from the İzmit Bay.

## Materials and Methods

### Fish Samples

Whiting (*Merlangius merlangus euxinus*)

N.1840) and horse mackerel (*Trachurus mediterraneus* S.1868) fish samples were taken in the Central Fish Market of the İzmit city between December 2003-November 2004 in five replicates (ten individuals for each replicate of fish). Fishes were caught from the İzmit Bay. The fish samples were wrapped in aluminum foil and maintained at <math>4^{\circ}\text{C}</math> in dark until they were returned to the laboratory and stored at <math>-10^{\circ}\text{C}</math> in dark until analyzed (USEPA, 1999).

### Standards

Reference PCBs (7 congeners and mix, each at 10 ng/μl) and DDTs (7 metabolites and mix, each at 10 ng/μl) were obtained from Dr. Ehrenstorfer. Working solutions were prepared by diluting the stock solutions with hexane to prepare solvent and matrix matched calibration solutions for GC analyses in the range of 10-500 ng/ml.

### Sample Extraction

Edible parts (muscle and skin) of fish samples were minced and 10 g of homogenized fish samples were mixed with anhydrous sodium sulphate and then extracted in 250 ml petroleum ether for 8 hours in a Soxhlet extractor. Following Soxhlet extraction, the extracts were evaporated to dryness, and the lipid contents were determined. All results for fish samples were reported on a fresh weight basis. The lipid extracts were redissolved in petroleum ether and residues were partitioned into acetonitrile, and then concentrated extracts were purified by passing through florisil packed column using 200 ml mixture of petroleum/diethyl ether (94:6) as elution solvent with the flow rate of 5 ml/min. All the extracts were concentrated by rotary evaporator and gentle nitrogen blow, and then dissolved in 1 ml n-hexane (CEN, 1996).

### Analyses

PCB and DDT determination was carried out on Hewlett Packard (HP) 6890 gas chromatograph with a micro electron capture detector (μECD). An Agilent 19091S-433, HP-5MS, 30 m 5% phenylmethylpolysiloxane capillary column, 0.25 mm i.d. and 0.25 μm film thickness was used with helium as the carrier gas at a pressure of about  $1.5 \times 10^5$  Pascal and nitrogen as the purge gas at a velocity of about 40 ml/min. Injection port was maintained at 250°C, and the sample was injected in splitless mode. Detector temperature was 350°C. Column temperature was held at 90°C for initial 4 min, and then programmed at 35°C/min to 160°C, held for 1 min, ramped at 3°C/min to 244°C and held for 10 min (CEN, 1996). The peaks were identified by matching the retention times of the peaks in the sample with those of authentic standards in the calibration solution.

PCB/DDTs in samples were confirmed by GC/MS using primarily a HP 6890 gas chromatograph fitted with an HP 5973 quadropole mass spectrometer and a Agilent 19091S-433, HP-5MS, 30 m 5% phenylmethylpolysiloxane capillary column, 0.25 mm i.d. and 0.25 μm film thickness was used with helium as the carrier gas at a flow rate of about 1.9 ml/min. Injection port was maintained at 250°C, and the sample was injected in splitless mode. Column temperature was held at 70°C for initial 2 min, and then programmed at 25°C/min to 150°C, held for 0 min, ramped at 3°C/min to 200°C and held for 0 min, ramped at 8°C/min to 280°C and held for 10 min (Meng and Szelewski, 2000). And secondly Varian CP3800 gas chromatograph with an electron capture detector was also used for confirmation.

### Quality Assurance

Before analysis, relevant standards were run to check column performance, peak area, height and resolution, and limits of detection (LoD). For each set of samples to be analysed, a field blank, a procedural blank and a standard mixture were run in sequence to check for contamination, peak identification and quantification.

Compounds were identified mainly by their retention times. To assure quality control, spiked samples were analysed for each set of samples (Von Holst *et al.*, 2000; Von Holst and Müller, 2001; EC. SANCO., 2004). Recoveries of spiked whiting and horse mackerel samples were 72-107% and 70-111% respectively. The detection limits for whiting and horse mackerel samples were determined as 1 ng/g and 1 ng/g (fresh weight) respectively for both PCB congeners and DDT metabolites. In addition, the errors involved in sampling were assessed by carrying out five replicate sampling of fish samples.

### Results and Discussion

The concentrations from the analyses of the whiting and horse mackerel fish samples for the indicator PCBs and DDT metabolites are listed in Tables 1 and 2 on a fresh weight basis together with summaries of collection time, length and lipid content data. The percentage lipid was determined according to CEN (1996). Among the PCB congeners 52, 153, 101 and 138 congeners were found dominant in both fish species. Chlorination of organic chemicals often increases both their persistence and their lipid solubility. Therefore PCBs bioaccumulate especially well. Increasing number of chlorines increases both lipid solubility and bioaccumulation. However, the optimal bioaccumulation capacity is at about 6 chlorines, probably because higher chlorinated congeners (esp. octa-) are so poorly water soluble that their bioavailability is low (Tuomisto *et al.*, 1999). Our results are also in accordance with this finding. In particular, the ranges of total PCB ( $\Sigma\text{ICEST}$ )

**Table 1.** The concentrations of PCBs and DDTs in whiting fish samples (ng/g fresh weight) from İzmit Bay in Turkey (2003-2004)

Whiting (Mean±SE)	Collection times											
	December 2003	January 2004	February 2004	March 2004	April 2004	May 2004	June 2004	July 2004	August 2004	September 2004	October 2004	November 2004
<b>PCB congeners</b>												
PCB28	2.86±0.75	n.d.*	n.d.	n.d.	2.48	n.d.	2.53±0.69	4.46±1.64	1.42±0.19	n.d.	2.28	n.d.
PCB52	6.95±1.84	2.75±0.24	2.02±0.63	2.29	5.34±4.23	4.53±0.37	12.01±4.97	21.78±7.91	9.56±1.43	n.d.	11.18±8.07	14.26±11.42
PCB101	12.56±2.69	2.66±0.69	n.d.	n.d.	4.94±2.52	n.d.	2.01±0.76	1.88±0.18	3.19±1.43	1.49±0.16	n.d.	1.03
PCB118	3.52±0.31	n.d.	n.d.	n.d.	n.d.	n.d.	1.48±0.06	1.25±0.03	n.d.	n.d.	3.85	n.d.
PCB138	4.21±1.16	1.24	n.d.	n.d.	4.37±0.64	n.d.	3.35±0.56	2.13±0.35	1.28±0.08	n.d.	1.60±0.07	n.d.
PCB153	6.41±1.45	1.35±0.31	n.d.	1.06	5.16±0.79	1.37±0.09	4.30±0.48	3.94±0.80	2.79±0.34	n.d.	1.44±0.10	n.d.
PCB180	3.19±0.38	n.d.	n.d.	n.d.	2.92±0.01	n.d.	1.39±0.20	1.15	n.d.	n.d.	n.d.	1.87
ΣICES7PCB	39.69	8.00	2.02	3.35	25.19	5.90	27.06	36.59	18.24	1.49	20.34	17.15
<b>DDT metabolites</b>												
<i>o,o'</i> -DDE	10.83±3.19	n.d.	n.d.	n.d.	1.50±0.21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<i>o,p'</i> -DDE	8.46±2.31	n.d.	1.40	n.d.	3.68±2.16	n.d.	3.43±1.20	n.d.	n.d.	1.48±0.22	n.d.	1.08
<i>p,p'</i> -DDE	25.56±4.98	9.03±1.32	5.06±1.38	5.15±1.10	14.80±2.17	n.d.	13.61±3.23	7.86±1.83	2.93±0.47	n.d.	13.27±0.77	n.d.
<i>o,p'</i> -DDD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<i>p,p'</i> -DDD	14.66±3.87	3.52±0.75	3.35±0.32	2.06±0.28	5.49±1.83	2.60±0.09	8.37±1.33	3.32±0.35	n.d.	5.80	4.68	n.d.
<i>o,p'</i> -DDT	1.89±0.44	n.d.	n.d.	n.d.	1.51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<i>p,p'</i> -DDT	5.33±1.44	1.30±0.28	1.47±0.20	1.61±0.05	2.70±0.07	n.d.	4.99±2.09	n.d.	n.d.	n.d.	3.50	n.d.
ΣDDTs	66.73	13.85	11.27	8.82	29.67	2.60	30.40	11.18	2.93	7.28	21.45	1.08
<i>p,p'</i> -DDE / Σ <i>p,p'</i> -DDTs	0.56	0.65	0.51	0.58	0.64	-	0.50	0.70	-	-	0.62	-
Lipid content (%)	2.61±0.0	1.78±0.01	1.69±0.01	1.23±0.0	1.16±0.0	1.05±0.0	0.95±0.0	1.11±0.01	1.22±0.0	1.57±0.05	1.95±0.01	2.30±0.0
Length (cm)	30.0±0.1	31.6±0.2	30.5±0.2	31.1±0.2	32.2±0.2	32.0±0.2	31.8±0.2	33.0±0.3	32.4±0.2	32.5±0.2	31.1±0.1	30.4±0.1

\*not detected

**Table 2.** The concentrations of PCBs and DDTs in horse mackerel fish samples (ng/g fresh weight) from İzmit Bay in Turkey (2003-2004)

Horse mackerel (Mean±SE)	Collection times											
	December 2003	January 2004	February 2004	March 2004	April 2004	May 2004	June 2004	July 2004	August 2004	September 2004	October 2004	November 2004
<b>PCB congeners</b>												
PCB28	n.d.*	n.d.	n.d.	n.d.	1.57±0.39	3.99	4.06±1.28	4.19±0.53	3.28±0.69	1.49±0.32	n.d.	n.d.
PCB52	2.58±0.78	2.75±0.45	13.66±3.89	6.48±1.35	5.96±1.53	n.d.	8.58±0.72	25.82±6.90	10.37±0.69	n.d.	13.75±10.21	1.82±0.09
PCB101	1.65±0.28	2.44±0.68	1.30	n.d.	2.39±0.35	n.d.	8.59±1.56	9.92±2.67	3.17±1.05	4.26±0.98	3.34±0.23	n.d.
PCB118	1.39±0.17	2.32	n.d.	n.d.	n.d.	n.d.	2.98±0.38	2.82±0.38	n.d.	n.d.	n.d.	1.79
PCB138	2.71±0.57	2.16±0.74	n.d.	n.d.	n.d.	n.d.	5.52±0.46	3.89±0.57	2.15±0.36	1.66±0.34	n.d.	2.31±0.07
PCB153	3.14±0.47	2.16±0.54	1.10	n.d.	1.29±0.02	1.63±0.05	8.02±0.88	10.56±4.76	4.28±0.59	2.34±0.21	20.57	3.21±0.47
PCB180	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.90±0.27	1.41±0.12	1.88±0.44	n.d.	n.d.	n.d.
ΣICES7PCB	11.48	11.83	16.05	6.48	11.19	5.61	39.64	58.61	25.14	9.75	37.66	9.13
<b>DDT metabolites</b>												
<i>o,o'</i> -DDE	n.d.	1.19±0.12	2.01±0.62	n.d.	n.d.	1.54	2.53	2.23	n.d.	3.43±1.92	1.13±0.05	4.83±1.61
<i>o,p'</i> -DDE	n.d.	2.12±0.99	n.d.	n.d.	2.20±0.64	n.d.	13.52±3.19	14.31±2.40	8.53±2.03	5.53	2.23±1.09	n.d.
<i>p,p'</i> -DDE	43.27±6.46	26.00±11.03	7.41±1.43	4.47±0.84	6.29±0.83	15.59±0.37	36.92±3.47	25.84±3.55	10.58±1.36	31.43±12.31	n.d.	7.43±0.71
<i>o,p'</i> -DDD	3.28±0.50	5.47±0.69	1.58±0.30	1.33±0.07	n.d.	n.d.	14.39±8.61	33.99±10.14	n.d.	14.94±1.43	1.34±0.12	n.d.
<i>p,p'</i> -DDD	17.44±3.33	15.30±4.94	5.19±1.18	3.80±0.45	3.96±0.95	14.21±0.71	45.99±6.00	31.83±6.42	13.85±2.56	n.d.	n.d.	3.36±0.08
<i>o,p'</i> -DDT	2.20±0.39	21.54±5.44	n.d.	n.d.	1.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<i>p,p'</i> -DDT	9.80±2.09	4.36±0.05	2.59±0.53	n.d.	n.d.	n.d.	2.91±0.48	2.93±0.78	n.d.	5.05±2.02	n.d.	n.d.
ΣDDTs	75.99	75.97	18.79	9.60	13.48	31.33	116.25	111.12	32.96	60.36	4.69	15.62
<i>p,p'</i> -DDE / Σ <i>p,p'</i> -DDTs	0.61	0.57	0.49	0.54	0.61	0.52	0.43	0.43	0.43	0.86	-	0.69
Lipid content (%)	14.14±0.14	11.04±0.06	9.44±0.09	8.01±0.05	7.71±0.03	6.25±0.02	6.06±0.01	5.37±0.03	4.57±0.01	6.66±0.06	10.95±0.10	13.14±0.04
Length (cm)	15.2±0.2	16.1±0.1	15.8±0.1	15.7±0.1	16.0±0.1	15.1±0.1	15.0±0.1	15.3±0.2	14.9±0.1	14.8±0.1	14.7±0.2	15.3±0.2

\*not detected

concentrations in fish samples were 1.49 (September 2004) - 39.69 (December 2003) ng/g fresh weight in whiting and 5.61 (May 2004) - 58.61 (July 2004) ng/g fresh weight in horse mackerel respectively. Among the DDT metabolites *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT metabolites were found dominant in both fish species. In particular, the ranges of total DDT (sum of the seven metabolites) concentrations in fish samples were 1.08 (November 2004) - 66.73 (December 2003) ng/g fresh weight in whiting and 4.69 (October 2004) - 116.25 (June 2004) ng/g fresh weight in horse mackerel respectively. In marine mammals, a ratio of  $p,p'$ -DDE/ $\sum p,p'$ -DDTs ( $\sum p,p'$ -DDTs= $p,p'$ -DDT+ $p,p'$ -DDE+ $p,p'$ -DDD) below 0.6 has been considered as fresh DDT exposure (Aguilar, 1984; Coelhan *et al.*, 2006). In the present study, the ranges of this value in fish samples was 0.50-0.70 in whiting and 0.43-0.86 in horse mackerel respectively. The values are listed in Tables 1 and 2. In general total DDT concentrations were found higher than total PCB concentrations in both of the fish species. Moreover, the concentrations of PCBs and DDT metabolites showed that the residual levels in fish samples were always below the MRLs fixed by legislations of various countries (Hietaniemi and Kumpulainen, 1995; USEPA., 2000; EC. ELICC., 2004; Julshamn *et al.*, 2004).

The results obtained show the presence of low concentrations of DDT metabolites and indicator PCBs in both fish species caught in the İzmit Bay, Turkey. Regarding the content of the DDT metabolites and PCB congeners only *p,p'*-DDE, *p,p'*-DDD, PCB 52 and PCB 153 were found in almost all fish samples. The presence of *p,p'*-DDE could be correlated to a previous use of DDT in agricultural activity, to high environmental persistence because of their chemical and thermal stability, to different climatic environmental conditions, to marine currents, to different migratory habits of aquatic organisms and to different feeding habits as Di Bella *et al.* (2006) mentioned. The bioaccumulation of organochlorine compounds is a complex phenomenon governed by either physico-chemical properties of these compounds or ecological and biological factors such as feeding behaviours, growth rate, habit, age, sex, state of health as well as the lipid composition of an animal's tissue or organs (Barlas, 1999; Robertson and Hansen, 2001; Storelli *et al.*, 2004; Di Bella *et al.*, 2006).

In the present study, there is no correlation between the concentration of contaminant and the amount of lipid in the fish. Stow *et al.* (1997) determined that lipid content is not a variable in PCB body burdens among species. Our results are in accordance with this observation. This situation may reflect relatively rapid changes in lipid content within individual fish as compared to the slow uptake and depuration of persistent organic contaminants within the same fish as Manchester-Neesvig *et al.* (2001) mentioned. Also the lipid content of whiting was low,

1.55±0.53%, and did not change significantly throughout the year.

Contamination levels in horse mackerel samples show values, in terms of total DDT concentration, similar to those found by Coelhan *et al.* (2006) in horse mackerel and lower than those reported by Tanabe *et al.* (1997a), but in whiting higher than those reported from the Marmara Sea in Turkey (Coelhan *et al.*, 2006) and lower than those reported by Tanabe *et al.* (1997a) from the Black Sea. This study about contamination in horse mackerel shows values, in terms of total indicator PCB concentration, lower than those found in horse mackerel from the Marmara Sea in Turkey (Coelhan *et al.*, 2006) but in whiting higher than those reported by Coelhan *et al.* (2006) and lower than those reported by Tanabe *et al.* (1997b). In general, DDTs and indicator PCBs contamination is lower in samples from the İzmit Bay than in samples from the Black Sea. Some studies indicate that DDT is still used illegally in agriculture and has been used intensively in recent years in the countries around the Black Sea (Tanabe *et al.*, 1997a; Tuncer *et al.*, 1998; Barlas, 1999; Fillmann *et al.*, 2002; Coelhan *et al.*, 2006).

In conclusion, generally higher concentrations were determined in horse mackerel samples than whiting samples but the low residual levels of PCB congeners and metabolites of DDT in fish samples at concentrations below legislation limits indicate a situation without toxicological risks for animal and human health.

### Acknowledgements

This study was supported by the Turkish Ministry of Agriculture and Rural Affairs through grant no TAGEM/GY/03/11/01/097. We would like to thank Mr. Özden Çelik, Mr. Mesut Özben and Mr. Serkan Çakıroğulları for their valuable assistance in sampling.

### References

- Aguilar, A. 1984. Relationship of DDE/ $\sum$ DDT in marine mammals to the chronology of DDT input into the ecosystem. Canadian Journal of Fisheries and Aquatic Sciences, 41: 840-844.
- Alcock, R.E., Behnisch, P.A., Jones, K.C. and Hagenmaier, H. 1998. Dioxin-like PCBs in the environment-human exposure and the significance of sources. Chemosphere, 37(8): 1457-1472.
- Algan, O., Altıok, H. and Yüce, H. 1999. Seasonal variation of suspended particulate matter in two-layered İzmit Bay, Turkey. Estuarine Coastal and Shelf Science, 49: 235-250.
- Babu-Rajendran, R., Imagawa, T., Tao, H. and Ramesh, R. 2005. Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. Environment International, 31: 503-512.
- Barlas, M.E. 1999. Determination of organochlorine pesticides residues in aquatic system and organisms in

- upper Sakarya Basin, Türkiye. Bulletin of Environmental Contamination and Toxicology, 62: 278-285.
- Barrie, L.A., Gregor, D., Hargrave, B., Lake, R., Muir, D., Shearer, R., Tracey, B. and Bidleman, T. 1992. Arctic contaminants: sources, occurrence and pathways. Science of the Total Environment, 122 (1-2): 1-74.
- CEN. 1996. European Standard. European Committee for Standardization. ICS 67.040. CEN 1528 (1-4). November 1996. Brussels.
- Coelhan, M., Strohmeier, J. and Barlas, H. 2006. Organochlorine levels in edible fish from the Marmara Sea, Turkey. Environmental International, 32: 775-780.
- Di Bella, G., Licata, P., Bruzzese, A., Naccari, C., Trombetta, D., Lo Turco, V., Dugo, G., Richetti, A. and Naccari, F. 2006. Levels and congener pattern of polychlorinated biphenyl and organochlorine pesticide residues in bluefin tuna (*Thunnus thynnus*) from the Straits of Messina (Sicily, Italy). Environment International, 32: 705-710.
- EC. ELICC., 2004. European Commission, Dioxins and PCBs: Environmental levels and human exposure in candidate countries. Reference: ENV.C.2./SER/2002/0085. Final report. ELICC. Consortium: Environmental levels in candidate countries under supervision of Gunther Umlauf (JRC). BIPRO (Beratungsgesellschaft für integrierte Problemlösungen). Brussels, 333 pp.
- EC. SANCO. 2004. SANCO/825/00 rev. 7. European Commission. Directorate General Health and Consumer Protection. Brussels, 16 pp.
- Everaarts, J.M., Van Weerlee, E.M., Fischerm, C.V. and Hillebrand, Th.J. 1998. Polychlorinated biphenyls and cyclic pesticides in sediments and macro-invertebrates from the coastal zone and continental slope of Kenya. Marine Pollution Bulletin, 36(6): 492-500.
- Fillmann, G., Readman, J.W., Tolosa, I., Bartocci, J., Villeneuve, J.P., Cattini, C. and Mee, L.D. 2002. Persistent organochlorine residues in sediments from the Black Sea. Marine Pollution Bulletin, 44: 122-133.
- Hietaniemi, V. and Kumpulainen, J.T. 1995. Contents of PCBs, Organochlorine Pesticide Residues and PAH Compounds in Finnish Foodstuffs. In toim. Jorma Kumpulainen. Proceedings of the technical workshop on trace elements, natural antioxidants and contaminants. Helsinki-Espoo August 25-26, August. REU Technical Series: 49: 157-167.
- Julshamn, K., Lundebye, A.K., Heggstad, K., Berntssen, M.H.G. and Boe, B. 2004. Norwegian monitoring programme on the inorganic and organic contaminants in fish caught in the Barents Sea, Norwegian Sea and North Sea, 1994-2001. Food Additives and Contaminants, 21(4): 365-376.
- Kodavanti, P.R.S., Ward, T.R., Derr-Yellin, E.C., Mundy, W.R., Casey, A.C., Bush, B. and Tilson, H.A. 1998. Congener-specific distribution of PCBs in brain regions, blood, liver, and fate of adult rats following repeated exposure to Aroclor 1254. Toxicology and Applied Pharmacology, 153(2): 199-210.
- Koopman-Esseboom, C. Morse, D.C., Weisglas-Kuperus, N., Lutkeschipholt, I.J., Ven der Paauw, C.G., Tuinstra, L.G.M.T., Brouwer, A. and Sauer, P.J.J. 1994. Effects of dioxins and polychlorinated biphenyls on thyroid hormone status of pregnant women and their infants. Pediatric Research, 36: 468-473.
- Legovic, T., Morkoç, E., Okay, O.S., Egesel, L., Tüfekçi, V. and Tüfekçi, H. 1995. Mass balance of total phosphorus in the İzmit Bay. Water Science and Technology, 32(2): 193-198.
- Manchester-Neesvig, J.B., Valters, K. and Sonzogni, W.C. 2001. Comparison of Polybrominated Diphenyl Ethers (PBDEs) and Polychlorinated Biphenyls (PCBs) in Lake Michigan Salmonids. Environmental Science and Technology, 35(6): 1-17.
- Meng, K.C. and Szelewski, M.J. 2000. Fast screening of PCB congeners using the Agilent 6890/5973N GC/MSD system. Agilent application note. Agilent Technologies, Inc. 2850 Centerville Road Wilmington, DE 19808-1610 USA, 4 pp.
- Morkoç, E., Legovic, T., Okay, O., Tüfekçi, H., Tüfekçi, V., Tolun, L. and Karakoç, F. 2007. Changes of oceanographic characteristics and the state of pollution in the İzmit Bay following the earthquake of 1999. Environmental Geology, 53: 103-112.
- Muir, D.C.G., Norstrom, R.J. and Simon, M. 1990. Organochlorine in arctic marine food chains: accumulation of specific polychlorinated biphenyls and chlordane-related compounds. Environmental Science and Technology, 22: 1071-1079.
- Okay, O.S., Tolun, L., Telli-Karakoç, F., Tüfekçi, V., Tüfekçi, H., Olgun, A. and Morkoç, E. 2003. The changes of T-PAH levels and health status of mussels in İzmit bay (Turkey) after Marmara earthquake and subsequent refinery fire. Environment International, 28: 671-675.
- Okay, O.S., Karacık, B., Başak, S., Henkelmann, B., Bernhöft, S. and Schramm, K.W. 2009. PCBs and PCDD/F in sediments and mussels of the İstanbul strait (Turkey). Chemosphere, 76(2): 159-166.
- Robertson, L.W. and Hansen, L.G. 2001. PCBs Recent Advances in Environmental Toxicology and Health Effects. The University Press of Kentucky, 663 South Limestone Street, Lexington, Kentucky 40508-4008, USA, 449 pp.
- Storelli, M.M., Storelli, A., Barone, G. and Marcotrigiano, G.O. 2004. Polychlorinated biphenyl and organochlorine pesticide residues in *Lophius budegassa* from the Mediterranean Sea (Italy). Marine Pollution Bulletin, 48: 743-748.
- Stow, C.A., Jackson, L.J. and Amrhein, J.F. 1997. An examination of the PCB:lipid relationship among individual fish. Canadian Journal of Fisheries and Aquatic Sciences, 54: 1031-1038.
- Tanabe, S., Madhusree, B., Öztürk, A.A., Tatsukawa, R., Miyazaki, N., Özdamar, E., Aral, O., Samsun, O. and Öztürk, B. 1997a. Persistent organochlorine residues in harbour porpoise (*Phocoena phocoena*) from the Black Sea. Marine Pollution Bulletin, 34(5): 338-347.
- Tanabe, S., Madhusree, B., Öztürk, A.A., Tatsukawa, R., Miyazaki, N., Özdamar, E., Aral, O., Samsun, O. and Öztürk, B. 1997b. Isomer-specific analysis of polychlorinated biphenyls in harbour porpoise (*Phocoena phocoena*) from the Black Sea. Marine Pollution Bulletin, 34(9): 712-720.
- Telli-Karakoç, F., Tolun, L., Henkelmann, B., Klimm, C., Okay, O. and Schramm, K.W. 2002. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) distributions in the Bay of Marmara Sea: İzmit Bay. Environmental Pollution, 119: 383-

- 397.
- Tolun, L.G., Okay, O.S., Gaines, A.F., Tolay, M., Tüfekçi, H. and Kıratlı, N. 2001. The pollution status and the toxicity of surface sediments in İzmit Bay (Marmara Sea), Turkey. *Environment International*, 26: 163-168.
- Tolun, L., Martens, D., Okay, O.S., Schramm, K.W. 2006. Polycyclic aromatic hydrocarbon contamination in coastal sediments of the İzmit Bay (Marmara Sea): Case studies before and after the İzmit Earthquake. *Environment International*, 32: 758-765.
- Tolun, L., Telli-Karakoc, F., Henkelmann, B., Schramm, K.W. and Okay, O.S. 2007. PCB pollution of İzmit Bay (Marmara Sea) mussels after the earthquake. In: E. Mehmetli and B. Koumanova (Eds.), *NATO Science for Peace and Security Series C: Environmental Security. The Fate of Persistent Organic Pollutants in the Environment*. Springer Netherlands: 127-139.
- Tuncer, G., Karakas, T., Balkas, T.I., Gökçay, C.F., Aygün, S., Yurteri, C. and Tuncel, G. 1998. Land-based sources of pollution along the Black Sea Coast of Turkey: Concentrations and annual loads to the Black Sea. *Marine Pollution Bulletin*, 36(6): 409-423.
- Tuomisto, J., Vartiainen, T. and Tuomisto, J.T. 1999. Synopsis on dioxins and PCBs. KTL (National Public Health Institute, Finland), Division of Environmental Health. Kuopio.
- USEPA. 1999. Method 1668, Revision A: Chlorinated Biphenyl Congeners in water, soil, sediment and tissue by HRGC/HRMS. United States Environmental Protection Agency. Office of water (4303). EPA No. EPA-821-R-00-002, United States of America, 127 pp.
- USEPA. 2000. Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1. Fish sampling and analysis. Third edition. Fish and human health. United States Environmental Protection Agency. Office of Water (4305). EPA 823-B-00-007. Office of Science and Technology. Washington, DC., 470 pp.
- Von Holst, C., Müller, A. and Anklam, E. 2000. Method Description. Determination of PCBs in food and feedingstuffs samples by GC/MS. EUR 19571 EN. European Commission Joint Research Centre. Institute for Health and Consumer Protection Food Products and Consumer Goods Unit. I-21020 Ispra (VA) Italy.
- Von Holst, C. and Müller, A. 2001. Intercomparison study for the determination of Polychlorinated Biphenyls in animal feed. DG Joint Research Centre. Institute for Health and Consumer Protection Food Products Unit. Produced on behalf of European Commission, DG Health and Consumer Protection. Ispra, 39 pp.