



# Concentration of polychlorinated biphenyls and organochlorine pesticides in some edible fish species from the Shadegan Marshes (Iran)

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## ABSTRACT

Concentrations of polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethane (DDT) and analogs, hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB), were determined in 8 fish species collected during October and November 2007 from the largest Iranian wetland, the Shadegan Marshes. Fishes were selected on the basis of their importance in the local diet and feeding behavior. In all samples, OCPs were found in higher concentrations than PCBs. Common carp (*Cyprinus carpio*) had the highest OCs (1680 ng/g lipid wt.), with DDTs being most prevalent and p,p'-DDE contributing by 53–88% to the total DDTs. In all samples, OCs were found in order of DDTs > HCHs > PCBs > HCB. The highest concentration of HCHs was found in common carp ( $410 \pm 180$  ng/g lipid wt.) and  $\alpha$ -HCH was the predominant compound among HCH isomers (range 70–90%, mean 82%) in all species. All samples contained PCBs and CB 28 (37%) and CB 52 (26%) were the most frequently occurring congeners. common barbel (*Barbus barbus*) ( $70 \pm 17$  ng/g lipid wt.) exhibited the highest concentrations of HCB. OC levels in fish were relatively low, but the levels of several OCs in some of our specimens exceed the guidelines for food safety issued by the European Union (EU) and US Food and Drug Administration (FDA).

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## 1. Introduction

Persistent, bioaccumulating organochlorine compounds (OCs), such as polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT), have been recklessly produced and released into the natural environments including aquatic ecosystems. Aquatic ecosystems, which are highly sensitive to the effects of pollution, have evolved to perform vital functions in maintaining and supporting life on earth.

Wetlands, for instance, may have local and international significance as regulators of the hydrological cycle, as nurseries and habitat for freshwater and marine fish and shellfish, as producers of natural raw materials such as timber and fur, and as refuges for endangered species of plants and animals. These critical functions have been seriously compromised, and have led to destruction and degradation of many components of various environments. It has been shown that the removal rate for toxicants in semi-closed systems, such as the Persian Gulf, is very slow and this phenomenon puts inhabitants of such areas at higher risk for secondary chemical poisoning (Wu et al., 1999),

even though the use of OCPs has been banned in Iran since 1983 (Çok et al., 1999; Hosseini et al., 2008).

People can be exposed to OCs by ingesting contaminated food, inhaling polluted air or via absorption through their skin (Safe, 1998). Exposure to OCs is primarily by ingesting contaminated food from animal sources. More than 90% of daily accumulation is derived from the diet and about 90% of dietary accumulation is from animal origin (Furst et al., 1990). Though fish and derived products constitute only about 10% of the average human diet, consumption of fish and fish products are the main routes of exposure to these toxicants in humans (Alcock et al., 1998).

Fish is a valuable bioindicator because its detoxification enzymes (e.g. mono-oxygenases) have lower activity than in mammals and thus allows a higher toxicant bioaccumulation. Moreover, fish can concentrate pollutants through their gills directly from water, as well as through ingestion of food, thus enabling us to assess pollutants transfer through their environment (water) and the food web (Fisk et al., 2001; Boon et al., 2002; Erdogru et al., 2005; Zhou et al., 2008). Data on the presence and distribution of OCs in consumable fish are therefore important not only from a public health perspective, but from an ecological standpoint (Furst, 1993; Erdogru et al., 2005).

The objective of this study was to document the levels of PCBs and OCPs in edible fish from Shadegan Marshes (largest and most

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important Iranian wetland) located in southwest of Iran at the northern part of the Persian Gulf, an area with freshwater, waste agricultural and industrial water inputs.

## 2. Materials and methods

### 2.1. Study area

The Shadegan wetlands are located in southwestern Iran at the head of the Persian Gulf on the lower Jarrahi River in Khuzestan Province near the city of Abadan, Mahshahr, Shadegan (Fig. 1). They cover 400,000 ha and are recognized as Wetlands of International importance under the Ramsar Convention. In 1972, about 296,000 ha were established as a wildlife refuge that surrounds the main wetland area. A variety of habitats, including saltwater, brackish water, freshwater and mud-flats, make up these large wetlands. Large areas of agricultural lands, local fisheries, oil export facilities, a sugar cane plant and a petrochemical plant are found in the general area. Major sources of contamination in this area include the use of fertilizers, herbicides and pesticides in agriculture and the presence of hazardous substance particles from refineries and Mahshahr, Bandar Imam and Abadan chemical and petrochemical factories. Also about 10% of Shadegan marshes have been destroyed in the Iran/Iraq war (1980–1987) via bombardment with chemical weapons. The Marshes may also have suffered some damage as a result of “acid rainfall” during the Gulf War in 1991 (Scott, 1995).

### 2.2. Collection of samples

A total of 95 individual fish, belonging to 8 species were purchased dead from the local fishermen during October and November 2007 from the Shadegan marshes in the Iranian province of Khuzestan (Fig. 1). We examined *Barbus sharpeyi* (Benni,  $n=14$ ), *B. gerypus* (Shirbot,  $n=14$ ), *Cyprinus carpio* (Common carp,  $n=14$ ), *B. barbulus* (Common barbel,  $n=14$ ), *Aspius vorax* (Shelej,  $n=14$ ), *Ctenopharyngodon idella* (Grass carp,  $n=4$ ), *Liza abu* (Abu mullet,  $n=12$ ) and *B. luteus* (Golden barb,  $n=7$ ). The total length, weight and age of each specimen were measured (Table 1). Samples were immediately brought to the laboratory, fishes were dissected, and pieces of dorsal muscles were removed, and then wrapped in aluminum foil, put in clean plastic bags and stored at  $-20^{\circ}\text{C}$  until analysis.

### 2.3. Chemical analysis

Organochlorine pesticides including p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT (the sum expressed as DDTs), hexachlorobenzene (HCB),  $\alpha$ -,  $\beta$ - and  $\gamma$ -hexachlorocyclohexane (HCH) isomers (the sum expressed as HCHs) and 7 PCB congeners (IUPAC nos. 28, 52, 101, 118, 138, 153, 180) were analyzed. All standards were obtained from Ehrenstorfer Inc. (Augsburg, Germany) and chemicals were purchased from Merck Inc. (Darmstadt, Germany). Sample treatment and analysis followed the method described by Covaci et al. (2006) with minor modifications. Approximately 10 g fish muscle were ground in commercial grinder (SAYA, model: Promeat W-1800, Tehran) and homogenized with

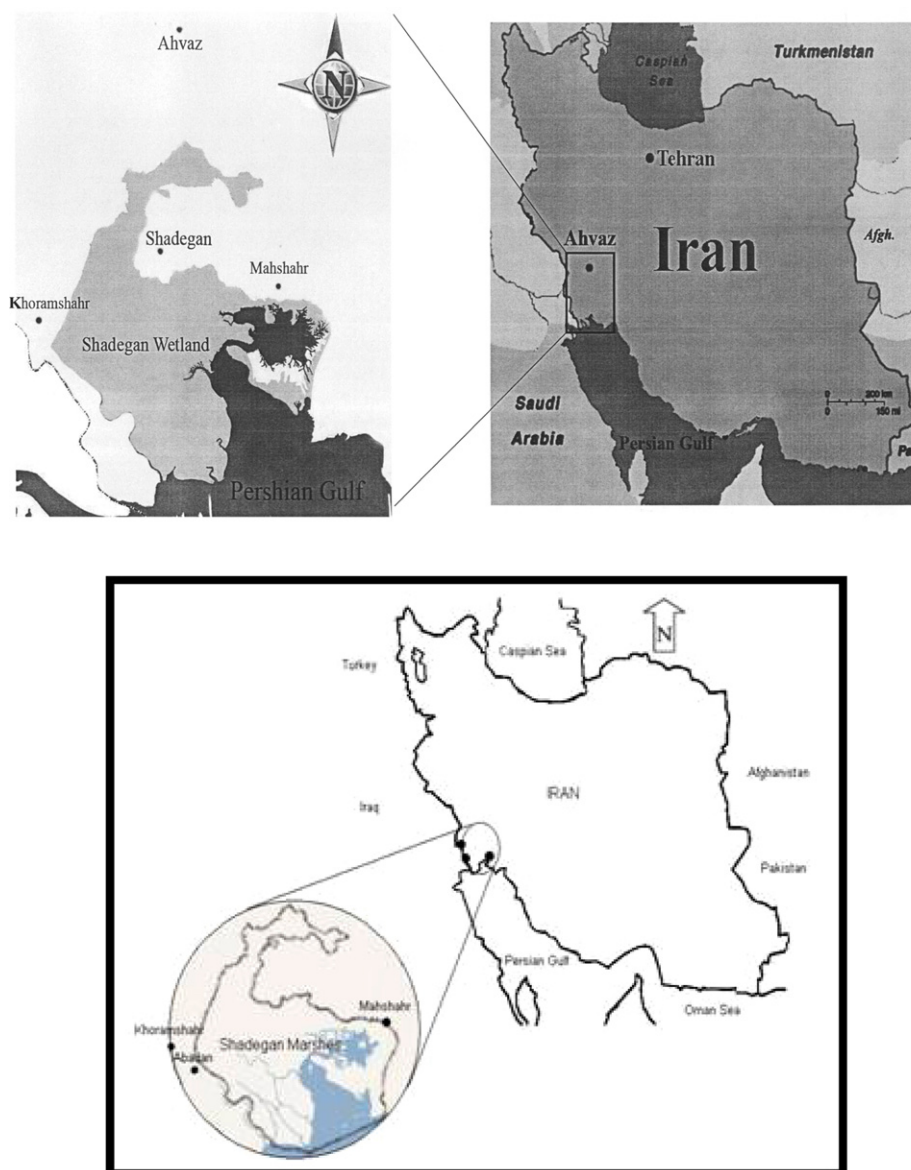


Fig. 1. Geographical location of Shadegan Marshes (sampling area), Khuzestan, southwest Iran.

**Table 1**  
Biometry and lipid content (median and range) of the analyzed specimens.

Common/scientific name	n		Weight (gr)	Total length (cm)	Age (year)	Lipid (%)	Diet of species
Golden barb ( <i>Barbus luteus</i> )	7	Range	108–230	19–25	2–4	2–4	Herbivorous
		Median	150	21	3	3	
Abu mullet ( <i>Liza abu</i> )	12	Range	34–48	13–16	2–3	2–3	Herbivorous
		Median	41	15	3	3	
Grass carp ( <i>Ctenopharyngodon idella</i> )	4	Range	345–445	29–32	3–4	3–4	Herbivorous
		Median	435	31	4	4	
Shelej ( <i>Aspius vorax</i> )	14	Range	100–650	23–43	2–4	2–4	Carnivorous
		Median	275	31	3	3	
Common barbel ( <i>Barbus barbulus</i> )	14	Range	175–700	27–49	3–6	3–6	Carnivorous
		Median	332	33	4	4	
Common carp ( <i>Cyprinus carpio</i> )	14	Range	140–700	21–35	2–4	2–4	Omnivorous
		Median	373	29	3	3	
Shirbot ( <i>Barbus gerypus</i> )	14	Range	34–48	13–16	2–3	2–3	Herbivorous
		Median	41	15	3	3	
Benni ( <i>Barbus sharpeyi</i> )	14	Range	108–230	19–25	2–4	2–4	Herbivorous
		Median	150	21	3	3	

anhydrous  $\text{Na}_2\text{SO}_4$  (1/3, w/w) and left for 4 h in dark. Sample was spiked with internal standards ( $\epsilon$ -HCH and PCB 143) and extracted for 8 h by Soxhlet apparatus with 100 ml hexane/acetone (3/1, v/v). Then the solvent was evaporated using a rotary evaporator (Heidolph WB 2000, Kelheim, Germany). The lipid content of samples was gravimetrically determined. The extract was treated with concentrated sulfuric acid for lipid purification and further cleanup was accomplished on a column filled with 8 g acidified silica gel and anhydrous sodium sulfate. The column was eluted with 15 ml hexane and 10 ml dichloromethane. The eluate was concentrated to 100  $\mu\text{l}$  under a gentle nitrogen stream. One  $\mu\text{l}$  of extract was injected into a gas chromatographic (GC) system. GC analysis was performed using a Dani 1000 gas chromatography (Monze, Italy) with electron-capture detector ( $^{63}\text{Ni}$  ECD). GC system was equipped with a DB5 capillary column (60 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness, Macherey-Nagel). Helium (99.999% purity) was used as the carrier gas at the flow rate 2 ml/min. The operating conditions were split (1:1) injection mode, temperature program: 100  $^\circ\text{C}$  (1 min), 10  $^\circ\text{C}/\text{min}$  to 240  $^\circ\text{C}$  (1 min), 3  $^\circ\text{C}/\text{min}$  to 260  $^\circ\text{C}$  (1 min), 20  $^\circ\text{C}/\text{min}$  to 300  $^\circ\text{C}$  (10 min). The injection port temperature and detector temperature were 250 and 300  $^\circ\text{C}$ , respectively. Multi-level calibration curves were created for the quantification and good linearity ( $r^2 > 0.998$ ) was achieved for tested intervals that included the whole concentration range found in samples. Each analyte was identified by a comparison of its relative retention time to the peaks from the calibration standards.

#### 2.4. Quality assurance and recovery

Quantification was based on a comparison with calibration curves in the concentration range of 0.01, 0.05, 0.1, 0.3 and 0.5 mg/l. Spiking was done at three level 0.05, 0.1 and 0.5 mg/l. The method limits of quantification (LOQ) for individual PCBs and OCPs were between 0.1–0.3 and 0.1–0.2 ng/g lipid wt., respectively. Recovery rate for OCPs compounds were between 93% and 110% and for PCBs congeners it was between 90% and 108% and RSD for the recoveries of OCPs and PCBs were below 10% (OCPs 3–9.8% and PCBs 3.5–10.1%). The analyses of OCs were performed at the department of Environment of Tarbiat Modares University, Noor, Iran.

#### 2.5. Statistical analysis

The statistical analyses were carried out using SPSS software version 11.5. Our data were not normally distributed. In the first step we tried to log-transform the data, but even then most of them were still not normally distributed. Therefore we further used non-parametric tests for these data. For general comparisons, we used  $k$ -independent sample and if difference was significant ( $p < 0.05$ ), subsequent multiple comparisons between groups were tested using Mann-Whitney  $U$ -test. Individual PCB congeners and DDT and HCH derivatives in samples, which over 50% of the measurements were  $< \text{LOQ}$  were excluded from our statistical analysis to ensure accuracy. We presumed a  $P$  value  $< 0.05$  to be statistically significant.

### 3. Results and discussion

Organochlorine contaminants were detected in all fish samples. The concentrations of OCs in fish samples are shown

in Table 2. Mean value of organochlorines were  $790 \pm 760$  ng/g lipid wt. that generally followed this pattern: DDTs  $>$  HCHs  $>$  PCBs  $>$  HCB. Furthermore, the highest concentrations of OCs were found in Common carp (Kruskal Wallis and  $U$ -test,  $P < 0.05$ ) (1680 ng/g lipid wt.), which is a bottom feeder with a high percentage of benthos in its diet. The sediment is a continuing and important source of contamination by such persistent chemicals (Moon et al., 2006).

Although less important as objective, we have not observed any clear patterns of contaminants (DDTs, HCHs, HCB and PCBs) according to the various diets (Kruskal Wallis,  $P > 0.05$ ) and trophic positions of the studied fishes.

#### 3.1. Concentration of DDT in samples

DDT and related compounds were found at moderate to high levels by large variations in concentration among species. Mean concentration of  $\Sigma\text{DDT}$  was  $330 \pm 335$  ng/g lipid wt. Golden barb with  $520 \pm 640$  ng/g lipid wt. and Benni (Kruskal Wallis and  $U$ -test,  $P < 0.05$ ) with  $100 \pm 30$  ng/g lipid wt. had highest and lowest mean concentrations across species, respectively (Fig. 2). DDT has a higher persistency and hydrophobic properties than other OCPs. The higher concentrations of DDT and metabolites might be due to their higher bioaccumulative properties and to large past usage or continuous release into aquatic environment (Sudaryanto et al., 2007). For the measured DDT components,  $p,p'$ -DDE was found in the highest level in all fish muscle with values ranging from  $70 \pm 36$  in Shelej to  $490 \pm 445$  ng/g lipid wt. in Golden barb (mean:  $230 \pm 270$  ng/g lipid wt.).

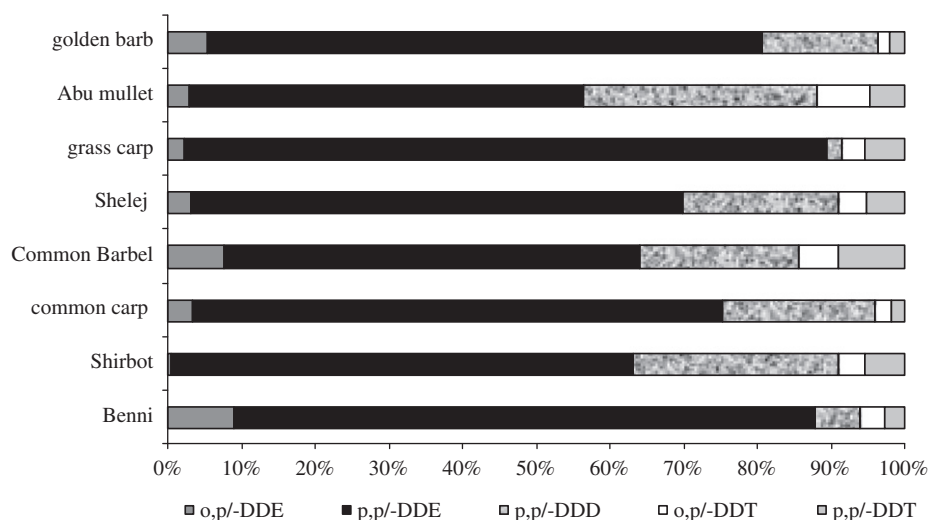
DDT and its derivatives followed this general order in this study: DDE  $>$  DDD  $>$  DDT (Fig. 2). Our results are in accordance with reported order of metabolites of DDT in fish from Iran or other countries (Perugini et al., 2004; Naso et al., 2005; Covaci et al., 2006; Sudaryanto et al., 2007; Hosseini et al., 2008). These results are not surprising considering the high chemical stability and hydrophobicity of  $p,p'$ -DDE (log Kow value of 6.36) and its long half-life and, hence, persistence in both abiotic and biotic components of the aquatic ecosystems (Naso et al., 2005).  $p,p'$ -DDT levels were very low in all fishes, most probably because of its shorter half-life ( $\sim 8$  months) than  $p,p'$ -DDD and  $p,p'$ -DDE ( $\sim 7$  years) (Binelli and Provini, 2003; Covaci et al., 2006).

The DDE/DDT ratio is commonly used to assess the chronology of DDT input into the ecosystems (Bordajandi et al., 2003). This ratio ranged between 4.43 in Common Barbel and 22.53 in Golden barb. It was remarkably higher than the ratio found

**Table 2**

Concentrations of organochlorines in muscle tissue of fish (ng/g lipid wt.) from Shadegan Marshes.

Scientific name		PCBs <sup>a</sup>	DDTs <sup>b</sup>	HCHs <sup>c</sup>	HCB
<i>Barbus luteus</i> N=7	Mean ± SE	245 ± 78	645 ± 195	320 ± 90	39 ± 12
	Min–Max	89–700	190–1590	71–660	6.5–89
	Median	185	345	220	28
<i>Liza abua</i> N=12	Mean ± SE	130 ± 45	155 ± 20	145 ± 21	2.6 ± 0.4
	Min–Max	74–220	130–193	105–174	2–3.4
	Median	101	140	150	2.4
<i>Ctenopharyndro idela</i> N=4	Mean ± SE	230 ± 102	304 ± 26	282 ± 22	34 ± 15
	Min–Max	71–422	257–347	260–305	6.3–60
	Median	200	310	280	35
<i>Aspius vorax</i> N=14	Mean ± SE	115 ± 18	120 ± 11	32 ± 11	9 ± 1.4
	Min–Max	41–230	74–175	2.8–135	1.2–16
	Median	95	108	14	8
<i>Barbus barbulus</i> N=14	Mean ± SE	220 ± 37	340 ± 47	49 ± 17	70 ± 17
	Min–Max	51–515	105–655	Nd <sup>d</sup> –220	25–197
	Median	215	340	34	57
<i>Cyprinus carpio</i> N=14	Mean ± SE	230 ± 79	555 ± 150	410 ± 51	44 ± 17
	Min–Max	60–1060	95–1540	170–870	1.9–130
	Median	135	360	420	23
<i>Barbus gerypus</i> N=14	Mean ± SE	56 ± 12	390 ± 66	175 ± 66	10.8 ± 3.2
	Min–Max	Nd–167	105–800	12–950	1.6–33
	Median	50	410	105	5.5
<i>Barbus sharpeyi</i> N=14	Mean ± SE	78 ± 15	105 ± 9.4	79 ± 9.4	50 ± 12
	Min–Max	24–211	43–165	31–130	13–135
	Median	62	105	76	30

<sup>a</sup> ∑PCBs=sum of seven target congener of PCB (28, 52, 101, 118, 138, 153, 180).<sup>b</sup> ∑DDT=p,p'-DDE+o,p'-DDE+p,p'-DDD+o,p'-DDT+p,p'-DDT.<sup>c</sup> ∑HCH=α-HCH+β-HCH+γ-HCH.<sup>d</sup> Non-detected.**Fig. 2.** Composition of DDT isomers in muscle fish from Shadegan Marshes, Khuzestan, Iran.

in fish studied in Hosseini et al. (2008), Szlinder-Richert et al. (2008), Li et al. (2008) in the northern of Iran, the southern Baltic Sea and the Gaobeidian Lake in China (ranged 2.5–3.3, 0.2–0.7 and 0.5–0.9, respectively). High concentrations of DDE and low DDT and levels in fish suggest that DDTs have not been recently used in agriculture after their ban (Perugini et al., 2004). The usage of DDT in agriculture has been banned in Iran since 1983 (Çok et al., 1999). Another metabolite of DDT, p,p'-DDD, was also found, but in lower amounts than p,p'-DDE. Higher proportions of p,p'-DDE to p,p'-DDD suggested that DDT endured aerobic transform in organisms (Zhou et al., 2008).

With regard to DDT and its metabolites, a maximum residue limit (MRL) for fish has not yet been established, while in some food products of animal origin (meat, milk and eggs), the

European Union (EU) has recommended a tolerance limit of 1000 ng/g of lipid wt. for the sum of p,p'-DDE, p,p'-DDD, p,p'-DDT and o,p'-DDD (Decreto Ministeriale 19 maggio, 2000). According to this standard, all samples in the present study were below this proposed value for human consumption.

### 3.2. Concentration of HCHs in samples

In comparison to DDTs, HCHs had lower concentrations. This is expected because HCHs are much less bioaccumulative than other OCs, are relatively less lipophilic, and have a shorter half-life in biological systems. Chemical properties of HCHs also indicate that these compounds are easily evaporated into the air. After



becoming airborne, HCHs are transported by air for long distances (Sudaryanto et al., 2007). Total HCH in our samples was  $170 \pm 200$  ng/g lipid wt. Highest and lowest HCHs were in Common carp and Shelej (Kruskal Wallis and *U*-test,  $P < 0.05$ ), respectively ( $410 \pm 180$  and  $32 \pm 11$  ng/g lipid wt., respectively). Regarding HCH isomers, high proportions of  $\alpha$ -HCH (range 70–90%, mean 82%) were observed in all fish samples followed by  $\gamma$ -HCH (5–17%, mean 11%) and  $\beta$ -HCH (4–13%, mean 17%) (Fig. 3).

$\alpha$ -HCH was the dominant HCH isomer in our samples and coincided with results from Cambodia, India, and the west coast of Sri Lanka (Monirith et al., 1999; Pandit et al., 2001; Guruge and Tanabe, 2001). This may suggest the preferential usage of the technical mixture of HCHs ( $\alpha$ -HCH: 65–70%,  $\beta$ -HCH: 5–6%,  $\gamma$ -HCH: 12–14% and  $\delta$ -HCH: 6%) than lindane ( $\gamma$ -HCH > 99%) in agriculture. Other studies have shown  $\beta$ -HCH to be the predominant HCHs isomer in fish (Yim et al., 2005; Hosseini et al., 2008; Zhou et al., 2008).  $\beta$ -HCH has a higher bioconcentration factor in aquatic organisms and is more persistent than  $\alpha$ - and  $\gamma$ -HCH (Willett et al., 1998). The interspecies variation in  $\beta$ -HCH levels may be attributed to feeding habits of the fish and their biotransformation capabilities (Yim et al., 2005). Low concentration of  $\gamma$ -HCH in fish of this area indicates that lindane ( $\gamma$ -HCH > 99%) has not been used in this region. Our results suggest recent usage of HCH, particularly technical HCH, in this area.

### 3.3. Levels of HCB in specimen

Although the usage of HCB has been banned, all analyzed fish samples contained HCB residues. Mean HCB was  $34 \pm 40$  ng/g lipid wt. HCB ranged from 2.6 to 70 ng/g lipid wt. in Abu mullet and Common Barbel (Kruskal Wallis and *U*-test,  $P < 0.05$ ) (Table 2). HCB levels were higher in this study than what has been reported for other regions. Range values reported by Monirith et al. (1999), Sudaryanto et al. (2007) and Hosseini et al. (2008) are as follows: 0.2–4.6, 0.22–28 and 7.4–12.7 ng/g lipid wt., respectively. The specific sources of HCB contamination in this region are unknown, but HCB can be released from high temperature industrial processes. It may also be present as impurity in other OCPs (Erdogrul et al., 2005). Incineration may also contribute to HCB pollution (Sudaryanto et al., 2007). We suspect that HCB is still used in this area.

### 3.4. Concentration of PCBs and seven target congeners

Total PCB concentration (the sum of seven congeners 28, 52, 101, 118, 138, 153, 180) varied in range between 22 and 1059 ng/g

lipid wt., with an average value of  $151 \pm 106$  ng/g lipid wt. The lowest and the highest concentrations of PCBs were observed in Shirbot (56 ng/g lipid wt.) and Golden barb (Kruskal Wallis and *U*-test,  $P < 0.05$ ) (245 ng/g lipid wt.) respectively (Table 2). Mean concentration of PCB in the present study is lower than Hosseini et al. (2008) (429 ng/g lipid wt.) in north of Iran (four sturgeon species of coastal water of the Caspian Sea). Of course, industrial activity, including petrochemical facilities, refineries, oil wells, alloy steel factories and discharges of industrial wastewater are more concentrated in the south of Iran than in the north, and we anticipated that PCB's concentration in fish samples in our sampling area would be higher than that collected in northern Iran by Hosseini et al. (2008). However, in fact, PCB concentrations were lower in the samples we analyzed. This difference could be related to the age, size and to the fish species sampled by Hosseini et al. (2008); in that study, sturgeons were sampled, which were much older and larger than any of our sampled fishes. The PCB levels reported here were lower than those reported for other species living in extensive industrialization areas. For example, fishes from the coastal waters of Latvia were found to contain 410–3600 ng/g lipid wt. PCBs (Olsson et al., 1999), while fishes from Poland (Falandysh et al., 2002) contained 9000 ng/g lipid wt. PCBs and fishes sampled from the Danube Delta, Romania (Covaci et al., 2006), contained 46–1416 ng/g lipid wt. PCBs.

A high variability in the concentrations and proportions of specific PCB congeners was observed within the species. PCB 28 (37%) was the predominant congener in all samples followed by PCB 52 (26%) and PCB 101 (3%) was the lowest congener among PCBs congeners. Profiles of PCBs were similar among most species with the exception of Shirbot (69%) and Grass carp (57%) for which PCB 28 was predominant. This is probably due to differences in the species' ability to metabolize, bioaccumulate or eliminate PCB congeners. According to the result, in Benni (57%) and Common carp (55%), PCB 52 had the highest percentage (Fig. 4). The highest and lowest concentrations of PCB 28 were in Grass carp (455.91 ng/g lipid wt.) and Shelej (4.59 ng/g lipid wt.), respectively.

The distribution of PCB congeners in the fish species from Shadegan Marshes (Fig. 4) showed a predominance of low chlorinated PCB congeners (mainly composed of tri- and tetra-CB congeners) in most species, which together with the low PCB concentrations measured in fish suggest a diffuse contamination through the water column in which these congeners have a higher solubility (Erdogrul et al., 2005). Although the lower chlorinated biphenyls have an increased mobility from the substrate to

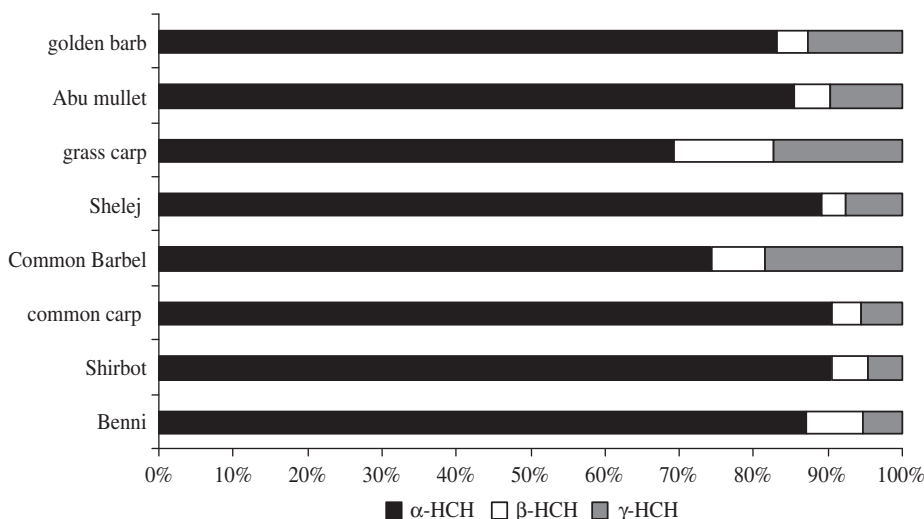


Fig. 3. Percentage composition of HCH isomers in muscle fish from Shadegan Marshes, Khuzestan, Iran.

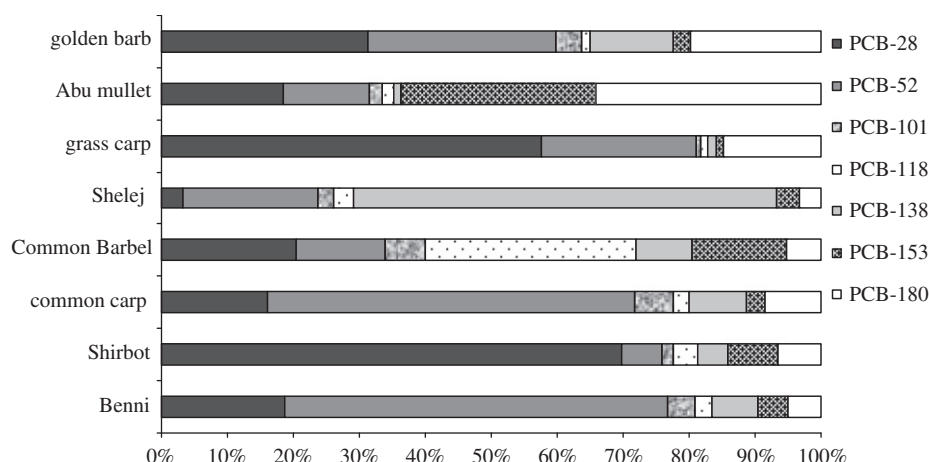


Fig. 4. Percentage composition of PCB congeners in muscle fish from Shadegan Marshes, Khuzestan, Iran.

water and are therefore more available to aquatic organisms (Voorspoels et al., 2004), they are very susceptible to metabolism and are eliminated rapidly in the marine environment.

In Stefanelli et al. (2004), Storelli et al. (2004), Covaci et al. (2006), Coelhan et al. (2006), Yang et al. (2006) and Hosseini et al. (2008), congeners CB 138 and CB 153 had the highest concentration among PCB congeners. In general, higher chlorinated PCB congeners accumulated more than lower chlorinated congeners in most of the samples. This is a consequence of increase in the accumulative properties of PCB congeners with the number of chlorine atoms on the biphenyl rings and of the resulting increase in their lipophilicity (Yang et al., 2006; Masmoudi et al., 2007).

On the one hand, it may be due to their past use in Aroclor mixtures production, on the other hand to their persistence in environment (Perugini et al., 2004). CB 153 and CB 138 have chlorines at 2, 4 and 5 positions in one or both rings. This feature seems to be responsible for the persistency and bioaccumulative properties (Masmoudi et al., 2007). CB 153 is one of the major components of commercial PCB mixtures (e.g. 4.26% in Aroclor 1254 and 10.20% in Aroclor 1260) (Sethajintanin et al., 2004) and it is one of the most frequently reported abundant PCB congeners in environmental samples (Hansen, 1999). In all fish samples tested in the present study, the PCB congeners followed the order  $28 > 52 > 180 > 138 > 153 > 118 > 101$ .

Toxicological risks related to PCBs can be assessed through comparison of measured concentrations and legal limits, if available. A typical case is represented by PCBs, for which there is only a limit of 2 mg/kg fresh weight, proposed by the FDA (2001) for human consumption of fish products, while there is no corresponding EU limit. The EU Directive 1999/788 establishes a maximum value of 200 ng/g lipid wt. for the sum of seven PCB congeners (IUPAC 28, 52, 101, 118, 138, 153, 180) in meat, eggs, poultry and related products (Commission of the European Communities, 1999), without taking into consideration the consumption of fish. Nevertheless, comparing the concentrations of PCBs measured in all the fish species sampled in Shadegan Marshes (Table 2) to the FDA limit, all the results fell below the range, but according to EU limit in Common carp (230 ng/g lipid wt.), Common barbel (220 ng/g lipid wt.), Grass carp (230 ng/g lipid wt.) and Golden barb (245 ng/g lipid wt.) were above the limit.

Comparison of OCPs (DDTs+HCHs+HCB) and PCBs (sum of PCB congeners) in fish indicated that the mean concentration of OCPs in all fish species was higher than the mean concentration of PCBs. Shelej (OCPs=58%, PCBs=42%) and Shirbot (OCPs=91%,

PCBs=9%) have minimum and maximum of the OCPs/PCBs ratio. Generally, OCPs, such as DDTs and HCHs, were the predominant compounds in fish from suburban and agricultural areas (Shadegan and around marshes) than PCBs. Significantly higher concentrations of DDTs ( $p < 0.05$ ) were noticed in suburban and rural areas, indicating considerable exposure to DDTs in the farming areas in around the marshes. High OCP concentrations in these locations may be due to their intensive usage in agricultural activities such as the cultivation of dates and sugarcane.

#### 4. Conclusions

To our knowledge, the presence of PCBs and OCPs in edible fish from Shadegan Marshes is reported here for the first time. It could be concluded that the Shadegan Marshes are among the Asian environments to have maintained a "Clean Environment" from organochlorine contaminant's standpoint. The contaminant's concentrations were at the lower end of ranges reported from similar sites in Europe. However, concentrations of HCHs and DDTs in fish indicate that OCPs were used inside and around the wetlands in the past and may also be entering the area nowadays. It is also necessary to implement measures to control industrial waste discharge and to avoid dispersion of these persistent and toxic contaminants into this unique environment.

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#### References

- Alcock, R.E., Behnisch, P.A., Jones, K.C., Hagermaier, H., 1998. Dioxin-like PCB in environment human exposure and the significant of source. *Chemosphere* 37, 1457–1472.
- Binelli, A., Provini, A., 2003. POPs in edible clams from different Italian and European markets and possible human health risk. *Mar. Pollut. Bull.* 46, 879–886.
- Boon, J.P., Lewis, W.E., Tjoen-A-Choy, M.R., Allchin, C.R., Law, R.J., de Boer, J., ten Hallers-Tjabbes, C.C., Zegers, B.N., 2002. Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. *Environ. Sci. Technol.* 36, 4025–4032.

- Bordajandi, L.R., Gomez, G., Fernandez, M.A., Abad, E., Rivera, J., Gonzalez, M.J., 2003. Study on PCBs, PCDD/Fs, organochlorine pesticides, heavy metals and arsenic content in freshwater fish species from the river Turia (Spain). *Chemosphere* 53, 163–171.
- Coelhan, M., Strohmeier, J., Barlas, H., 2006. Organochlorine levels in edible fish from the Marmara Sea, Turkey. *Environ. Int.* 32, 775–780.
- Covaci, A., Gheorghe, A., Hulea, O., Schepens, P., 2006. Level and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediment and biota from the Danube Delta, Romania. *Environ. Pollut.* 140, 136–149.
- Çok, I., Karakaya, A.E., Afkham, B.L., Burgaz, S., 1999. Organochlorine pesticide contaminants in human milks samples collected in Tabriz (Iran). *Bull. Environ. Contam. Toxicol.* 63, 444–450.
- Decreto Ministeriale 19 maggio, 2000. Maximum limit of pesticide residue in foods (Recepimento delle Direttive n. 97/41/CE, n. 1999/65/CE e n. 1999/71/CE). G. U. 207 del 05/09/2000 (in Italian).
- Erdogrul, O., Covaci, A., Schepens, P., 2005. Levels of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in fish species from Kahramanmaraş, Turkey. *Environ. Int.* 31, 703–711.
- Falandysz, J., Wyrzykowska, B., Strandberg, L., Puzyn, T., Strandberg, B., Rappe, C., 2002. Multivariate analysis of the bioaccumulation of polychlorinated biphenyls (PCBs) in the marine pelagic food web from the southern part of the Baltic Sea, Poland. *J. Environ. Monit.* 4, 929–941.
- FDA, 2001. Fish and Fisheries Products Hazards and Controls Guidance third ed. Center for Food Safety and Applied Nutrition, US Food and Drug Administration.
- Fisk, A.T., Hobson, K.A., Norstrom, R.J., 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwest Polynya marine food web. *Environ. Sci. Technol.* 35, 732–738.
- Fürst, P., 1993. Contribution of different pathways to human exposure to PCDDs/PCDFs. *Organohalogen Compd.* 13, 1–8.
- Furst, P., Furst, C., Groebel, W., 1990. Levels of PCDDs and PCDFs in foodstuffs from Federal Republic of Germany. *Chemosphere* 20, 787–792.
- Guruge, K.S., Tanabe, S., 2001. Contamination by persistent organochlorines and butyltin compounds in the West Coast of Sri Lanka. *Mar. Pollut. Bull.* 42, 179–186.
- Hansen, L.G., 1999. The *ortho* Side of PCBs: Occurrence and Disposition. Kluwer Academic Publishers, Norwell, MA.
- Hosseini, S.V., Behrooz, R.D., Esmaili-Sari, A., Bahramifar, N., Hosseini, S.M., Tahergorabi, R., Hosseini, S.F., Feas, X., 2008. Contamination by organochlorine compound in the edible tissue of four sturgeon species from the Caspian Sea (Iran). *Chemosphere* 73, 972–979.
- Li, X., Gan, Y., Yang, X., Zhou, J., Dai, J., Xu, M., 2008. Human health risk of organochlorine pesticide (OCPs) and polychlorinated biphenyls (PCBs) in edible fish from Huiyuan Reservoir and Gaobeidian Lake in Beijing, China. *Food Chem.* 109, 348–354.
- Masmoudi, W., Romdhane, M.S., Kheriji, S., El Cafsi, M., 2007. Polychlorinated biphenyl residue in the golden grey mullet (*Liza aurata*) from Tunis Bay, Mediterranean Sea (Tunisia). *Food Chem.* 105, 72–76.
- Monirith, I., Nakata, H., Tanabe, S., Tana, T.S., 1999. Persistent organochlorine residue in marine and freshwater fish in Cambodia. *Mar. Pollut. Bull.* 38, 604–612.
- Moon, J.Y., Kim, Y.B., Lee, S.I., Song, H., Choi, K., Jeong, G.H., 2006. Distribution characteristics of polychlorinated biphenyls in crucian carp (*Carassius auratus*) from major rivers in Korea. *Chemosphere* 62, 430–439.
- Naso, B., Perrone, D., Ferrante, M.C., Bilancion, M., Lucisano, A., 2005. Persistent organic pollutants in edible marine species from the Gulf of Naples, Southern Italy. *Sci. Total Environ.* 343, 83–95.
- Olsson, A., Vitiñish, M., Plikshs, M., Bergman, Å., 1999. Halogenated environmental contaminants in perch (*Perca fluviatilis*) from Latvian coastal areas. *Sci. Total Environ.* 239, 19–30.
- Pandit, G.G., Rao, A.M.M., Jha, S.K., Krishnamoorthy, T.M., Kale, S.P., Raghu, K., Murthy, N.B.K., 2001. Monitoring of organochlorine pesticide residues in the Indian marine environment. *Chemosphere* 44, 301–305.
- Perugini, M., Cavaliere, M., Giammarino, A., Mazzone, P., Olivieri, V., Amorena, M., 2004. Levels of polychlorinated biphenyls and organochlorine pesticides in some edible marine organisms from the Central Adriatic Sea. *Chemosphere* 57, 391–400.
- Safe, S.H., 1998. Development validation and problems with the toxic equivalency factor: approach of risk assessment of dioxins and related compound. *Anim. Sci.* 76, 134–141.
- Scott, D.A., 1995. A Directory of Wetlands in the Middle East. IUCN and IWRB, Slimbridge, pp. 118–177.
- Sethajintanin, D., Johnson, E.R., Loper, B.R., Anderson, K.A., 2004. Bioaccumulation profiles of chemical contamination in fish from the lower Willamette River, Portland Harbour, Oregon. *Environ. Contam. Toxicol.* 46, 114–123.
- Stefanelli, P., Di Muccio, A., Ferrara, F., Barbini, D., Generali, T., Pelosi, P., Amendola, G., Vanni, F., Di Muccio, S., Ausili, A., 2004. Estimation of intake of organochlorine pesticide and chlorobiphenyls through edible fishes from the Italian Adriatic Sea during 1997. *Food Control* 15, 27–38.
- Storelli, M.M., Storelli, A., Addabbo, R.D., Barone, G., Marcotrigiano, G.O., 2004. Polychlorinated biphenyl residues in deep-sea fish from Mediterranean Sea. *Environ. Int.* 30, 343–349.
- Sudaryanto, A., Monirith, I., Kajivara, N., Takahashi, S., Hartono, P., Mouawanah, M., Omori, K., Takeoka, H., Tanabe, S., 2007. Level and distribution of organochlorines in fish from Indonesia. *Environ. Int.* 33, 750–758.
- Szinder-Richert, J., Barska, I., Marzarski, J., Usydus, Z., 2008. Organochlorine pesticides in fish from the southern Baltic Sea: levels, bioaccumulation features and temporal trends during the 1995–2006 period. *Mar. Pollut. Bull.* 56, 927–940.
- Voorspoels, S., Covaci, I., Maervoet, A., Meester, J., Schepens, P., 2004. Levels and profiles of PCBs and OCPs in marine benthic species from the Belgian Sea and the Western Scheldt Estuary. *Mar. Pollut. Bull.* 49, 393–404.
- Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environ. Sci. Technol.* 32, 2197–2207.
- Wu, Y., Zhang, J., Zhou, Q., 1999. Persistent organochlorine residues in sediments from Chinese river/estuary systems. *Environ. Pollut.* 105, 143–150.
- Yang, N., Matsuda, M., Kawano, M., Wakimoto, T., 2006. PCBs and organochlorine pesticides (OCPs) in edible fish and shellfish from China. *Chemosphere* 63, 1342–1352.
- Yim, U.H., Hong, S.H., Shim, W.J., Oh, J.R., 2005. Levels of persistent organochlorine contaminants in fish from Korea and their potential health risk. *Environ. Contam. Toxicol.* 48, 358–366.
- Zhou, R., Zhu, L., Chen, Y., Kong, Q., 2008. Concentrations and characteristics of organochlorine pesticides in aquatic biota from Qiantang River in China. *Environ. Pollut.* 151, 190–199.