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Avian liver organochlorine and PCB from South coast of the Caspian Sea, Iran

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Abstract Liver samples ($n = 43$) of 9 avian species representing the families Phalacrocoracidae, Podicipedidae, Laridae, and Anatidae, were collected from the Iranian coast of the Caspian Sea. Samples were analyzed for organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethane (DDT) and its metabolites, hexachlorobenzene (HCB), hexachlorocyclohexane isomers (HCHs), and seven PCB congeners. p,p'-DDE was predominantly found in all species, at concentrations ranging from the limit of quantification (LOQ) to 340 ng/g ww. Most frequently encountered PCB congeners, in all samples, were 118, 153 and 138; and birds in Phalacrocoracidae had the highest liver PCB (mean 90 ± 32; ranging from <LOQ to 106 ng/g ww) whereas Podicipedidae had the highest OCP (mean 147 ± 49; ranging from <LOQ to 340 ng/g ww) ($P < 0.05$). Differences in the diet, and migratory routes, were important species-specific factors that affected hepatic concentration of OCP and PCB in the species we studied. Range of OCP and PCB concentrations in the present study was lower than those reported for birds in other regions of the world. Hepatic PCB concentration found in our avian species was below toxic effect levels that have been previously reported in birds. To our knowledge this is the first report of persistent organochlorine pollutants in liver of birds from Iran.

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Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) constitute some of the most challenging environmental issues because of their bioaccumulative nature and their serious chronic adverse effects on human health and wildlife. These persistent chlorinated organics are lipophilic and ubiquitous in the environmental; they accumulate in the fatty tissue and biomagnify in the food web (Newton 1988; Choi et al. 2001) such that the species that occupy higher trophic levels tend to accumulate more of these compounds in their bodies than species that are in lower trophic levels. These pollutants are also known to exert toxic effects on wildlife and humans. Reproductive failure due to eggshell thinning, high embryo mortality and chick malformation, abnormal reproductive behavior, immunotoxicity and teratogenesis has been reported in birds (Yamashita et al. 1993; Van den Berg et al. 1994). Population decline or collapse of several aquatic organisms and birds from around the world has been attributed to toxic effects of OCP and PCBs (Elliot and Norstrom 1998; Harris et al. 2003; Murata et al. 2003). In particular, eggshell thinning is attributed to exposure to p,p'-DDE, that leads to breaking of eggs during incubation in a variety of avian species (Blus et al. 1971; Faber and Hickey 1973).

Birds are desirable organisms for bioaccumulation studies on OCP and PCBs because they are highly sensitive to pollution, have a large geographic distribution range, and many birds often occupy positions that are relatively high in the food chain, (Furness 1993). Several factors including habitat and species-specific differences seem to influence bioaccumulation in birds (Jaspers et al. 2007). Diet and the corresponding trophic level also play a significant role in OCP and PCB bioaccumulation in birds (Jaspers et al. 2007). Furthermore, evidence indicates that aquatic predators accumulate higher levels of these toxicants than terrestrial predators (Provini and Galassi 1999).

Despite the fact that production and use of organochlorines, including DDTs and PCBs, were banned in the West during 1970s, these compounds are still sold to the Eastern countries where they are used to maintain public health standards and to deal with problems associated with rapid population increase (Kunisue et al. 2003). Caspian Sea is an invaluable land-locked aquatic ecosystem which receives persistent organochlorines that originate from agricultural and industrial activities in the region. High concentrations of PCBs and OCPs have been found in liver and blubber of the Caspian Seal and fish from this area (Watanabe et al. 1999; Hosseini et al. 2008). Even though compositions of organochlorine pesticides in seals suggested that the contamination status in the Caspian Sea is improving, concerns over the general health of the Caspian Sea ecosystems and birds of this region remains. To protect and preserve the Caspian Sea ecosystems from further degradation, its eco-toxicological status must be investigated and the extent of OCP and PCB contamination must be elucidated. We set out to determine the extent of PCB and OCP pollution in birds of this region in an effort to help environmental assessment projects and eventual clean up of this area. Clarification of the extent of pollution in the Caspian birds would constitute an important step towards protection of these ecosystems and will guide us in promoting sustainable development in this area.

Our goal was to describe persistent organochlorine concentrations in liver of different species of birds from the Iranian coast of the Caspian Sea. We tested the following hypotheses: (1) birds at higher trophic levels would have higher concentrations of persistent organochlorine in their livers than those at lower trophic levels; and (2) persistent organochlorine levels in liver of birds will be similar to levels associated with behavioral deficits and reduced reproductive success.

Materials and methods

Sample collection and preparation

In the winter of 2008, we obtained nine species of aquatic birds ($n = 43$) from the Southern coast of the Caspian Sea in the Iranian province of Mazandaran (Fig. 1). Freshly injured or killed bird carcasses had been confiscated from poachers by the Environmental Protection Agency guards in charge of bird conservation in the area. Samples were brought to the laboratory right away, birds were dissected immediately, and livers were removed, and then homogenized using a mixer. We used a net to trap 10 additional birds; after killing them, we took fresh livers and similarly homogenized them. Homogenized tissue was wrapped in aluminum foil, put in clean plastic bags, and stored at −20°C until analysis. Birds were identified and placed in four families: *Phalacrocoracidae*, *Podicipedidae*, *Laridae*, and *Anatidae* (Table 1).

Chemical analysis

Organochlorine pesticides including HCHs (α-HCH, β-HCH, γ-HCH), hexachlorobenzene (HCB), *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDE, *p,p′*-DDE, *p,p′*-DDD, and target congeners of PCB (IUPAC Nos. PCB 28, 52, 101, 118, 138, 153 and 180) were analyzed. Standards were obtained from Ehrenstorfer Inc. (Augsburg, Germany) and chemicals were purchased from Merck Inc. (Darmastadt, Germany). Sample treatment and analysis followed Jaspers et al. (2006) with minor modifications. Briefly, approximately 2–4 g of liver was homogenized then truly desiccated by blending it with anhydrous sodium sulfate. Samples were spiked with internal standard (PCB 143 and ε-HCH) for analysis.

Further, extraction was carried out with 100 ml hexane/acetone (3:1, v/v) in Soxtec 2050 (Foss) for 2 h. 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 desiccated sodium sulfate. The column was eluted with 15 ml hexane and 10 ml dichloromethane, respectively. The eluate was concentrated to 100 μl under a gentle nitrogen stream. One micro liter of extract was injected into a gas chromatographic (GC) system. GC analysis was performed using a Dani 1000 gas chromatograph (Monza, Italy) equipped with ^{63}Ni electron capture detector and a DB-5 capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness, Macherey-Nagel). Helium was used as the carrier gas at a flow rate of 2 ml/min. The operating conditions were split (1:1) injection mode. Temperature program was as follows: 100°C (1 min), 10°C/min to 240°C (1 min), 3°C/min to 260°C (1 min), 20°C/min to 300°C (10 min). The injection port temperature and detector temperature were 250 and 300°C, respectively. Multiple-level calibration curves were created for the quantification. Good linearity ($r^2 > 0.99$) was achieved for tested intervals that included the whole concentration range found in the samples. Each analyte was identified by a comparison of its relative retention time to the peaks from the calibration standards. Quantification was based on a comparison with calibration curves in the concentration range of 0.01, 0.05, 0.1, 0.3, 0.5 ppm. Spiking was done at two levels 0.2 and 0.4 ppm. Recoveries of spiked PCBs and OCPs into samples which passed

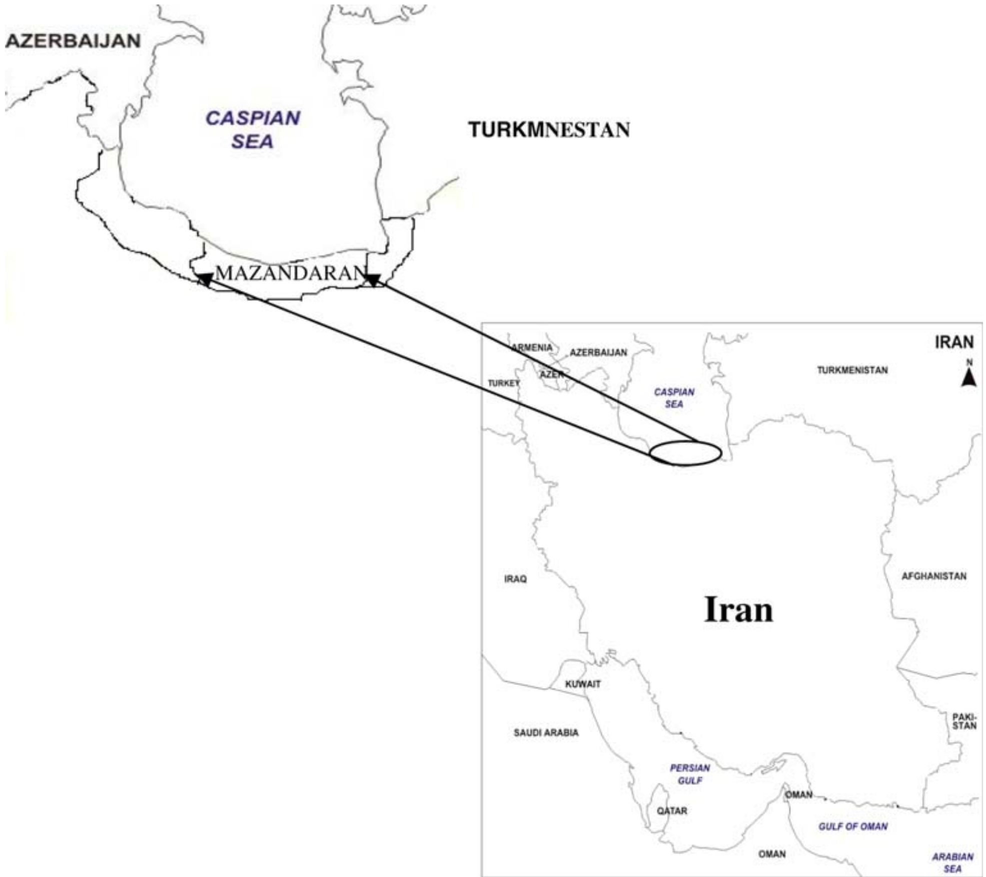

Fig. 1 Sampling sites along the South coast of the Caspian Sea

Table 1 Body weight (g) and feeding habits of birds collected from the South coast of the Caspian Sea arranged from highest to lowest trophic level

Family	Common/scientific name	Weight (g) mean ± SEM and range	N	Feeding habit
Phalacrocoracidae	Great Cormorant (*Phalacrocorax carbo*)	1800 ± 112 (1500–2300)	8	Mainly piscivorous, especially flatfish and eels, insects and frogs
Podicipedidae	Great Crested Grebe (*Podiceps cristatus*)	1060 ± 34 (985–1145)	6	Fish, mollusks and crustaceans
	Black-necked Grebe (*Podiceps nigricollis*)	260 ± 14 (225–325)	3	Chiefly insects and larvae, mollusks, crustaceans, amphibian larvae, and small fish
Laridae	Black-headed Gull (*Larus ridibundus*)	250 ± 16 (185–305)	8	Omnivorous: fish, crustaceans, annelids, mollusks, insect, larva, rats, seed, algae
	Little Gull (*Larus minutus*)	100 ± 30 (90–115)	5	Mainly insects in summer; marine invertebrates and fish in winter and occasionally seaweed and grains
	Common Gull (*Larus canus*)	440 ± 30 (405–500)	3	Omnivorous: fish, egg, crustaceans, annelids, mollusks, insects, small birds, carrion, algae, seeds and fruit
Anatidae	Pintail (*Anas acuta*)	770 ± 30 (745–840)	3	Variety of plants and animals
	Common Teal (*Anas creaca*)	255 ± 15 (230–300)	4	Plant material and some invertebrates
	Mallard (*Anas platyhynchos*)	920 ± 11 (900–940)	3	Mainly weed seeds, and insects, mollusk and worms

through the analytical procedure were between 91 and 105%. Limit of quantification (LOQ) for OCPs ranged between 0.1 and 0.6 ng/g ww; and LOQ for PCBs ranged between 0.1 and 0.8 ng/g ww (RSD $\leq$ 13).

Statistical analysis

Data were tested for normality using a Kolmogorov–Smirnov test. Differences in concentration of OCPs and total PCBs among different species and families were evaluated by one-way analysis of variance (ANOVA). When significant differences were observed among the different species and families, the Tukey–Kramer multiple-comparison test was applied to determine which means were significantly different. Samples that had frequencies of lower than three were removed from statistical analysis. Compounds in which over 50% of the measurements were below the LOQ were excluded from our statistical analysis to ensure accuracy. SPSS software (Version 11.5) was utilized for Statistical analysis and $P < 0.05$ was set to indicate significance.

Results and discussion

Toxicant patterns and contamination levels

Organochlorines: Table one describes information about the species we studied. Concentrations of OCPs, as well as PCBs, in the liver samples are shown in Tables 2 and 3. OCPs concentration varied widely in our samples since our birds belonged to different families and occupied varying trophic levels. In all species the following pattern: DDTs > HCHs > HCB emerged. Ninety percent of the livers we tested contained *p,p′*-DDE with a mean of 43 ± 10 ng/g ww it was highest of all other OCPs. Furthermore, *p,p′*-DDE contributed over 60% of the total DDTs in most of the samples (Fig. 2). These finding are similar to studies in Caspian Sturgeon and feathers of birds from South-West Iran that were found to have *p-p′* DDE (Hosseini et al. 2008; Dahmardeh Behrooz et al. 2009a, b). The similarity between our observations is probably due to high chemical stability in living tissue and persistence of *p,p′*-DDE in the environment (Naso et al. 2003; Sakellarides et al. 2006). Mean concentration of *p,p′*-DDD and *p,p′*-DDT were 9.5 ± 3 and 9 ± 2 ng/g ww and they were detected in 78 and 87% of the analyzed samples, respectively.

In this study, mean levels of *p,p′* DDE ranged from 92 to 7.5 ng/g wet weight; while levels of much less common *o,p′* DDE varied from 2 to 0.5 ng/g wet weight (Table 2).

In marine mammals, *p,p′*-DDE/*p,p′*-DDTs (*p,p′*-DDTs = *p,p′*-DDE + -DDT + -DDD) ratios lower than 0.6

Table 2 Concentration of OCPs (mean and range, ng/g wet weight) in liver of birds from South coast of the Caspian Sea, Iran

Family	Scientific name	HCB	α-HCH	β-HCH	γ-HCH	*p,p′* DDE	*o,p′* DDE	DDT[a]	DDD
Phalacrocoracidae	*Phalacrocorax* carbo	3.5 (1.5–105)	2.5 (0.7–5.0)	2.5 (0.5–8.0)	6.5 0 (6–15.5)	16.0 (2.5–49.5)	2 (<LOQ–7)	8.0 (0.5–20.00)	2.5 (<LOQ–5.00)
Podicipedidae	*Podiceps cristatus*	15.0 (4.0–61.5)	1.0 (<LOQ–2.5)	20.0 (0.5–55.0)	12.0 (<LOQ–49.5)	92.0 (11.0–339.5)	5 (<LOQ–13)	11.5 (<LOQ–26.0)	24.5 (<LOQ–116.5)
	Podiceps nigricollis	5.6 (3.4–8.5)	0.8 (<LOQ[b]–1.5)	4.5 (3.5–6.5)	15.0 (7.5–23.5)	42.0 (8.0–108.5)	2 (1–4)	5.5 (<LOQ–16.0)	34.5 (0.5–99.0)
Laridae	*Larus ridibundus*	13.0 (1.0–52.0)	3.5 (<LOQ–2.0)	11.0 (1.5–36.5)	8.0 (<LOQ–36.0)	20.0 (<LOQ–56.0)	2 (<LOQ–5)	6.0 (<LOQ–15.0)	1.5 (<LOQ–3.0)
	Larus minutus	4.5 (1.5–7.5)	1.0 (0.5–1.5)	24.5 (<LOQ–58.5)	1.0 (<LOQ–2.5)	88.0 (11.5–232.0)	1 (<LOQ–3)	26.0 (2.00–70.0)	13.5 (3.0–40.0)
	Larus canus	1.5 (0.5–3.5)	0.5 (<LOQ–1.0)	27.5 (1.5–77.5)	8.5 (<LOQ–24.5)	63.0 (5.5–170.5)	(<LOQ)	5.5 (2.0–10.0)	4.0 (1.0–10.0)
Anatidae	*Anas acuta*	0.5 (<LOQ–0.8)	(<LOQ)	0.5 (<LOQ–0.7)	(<LOQ)	39.0 (2.5–89.0)	(<LOQ)	10.0 (0.5–25.0)	16.0 (3.0–30.0)
	Anas creaca	0.1 (<LOQ–0.5)	0.5 (<LOQ–2.5)	8.5 (<LOQ–23.5)	1.0 (<LOQ–3.5)	7.5 (<LOQ–29.0)	(<LOQ)	2.5 (<LOQ–10.0)	0.5 (<LOQ–2.5)
	Anas platyhynchos	2.5 (1.5–3.5)	0.5 (<LOQ–1.0)	12.5 (2.5–31.5)	8.0 (1.5–12.5)	11.0 (<LOQ–17.0)	0.5 (<LOQ–0.5)	4.5 (<LOQ–9.0)	1.0 (<LOQ–2.0)

[a] Sum *p,p′*-DDT, *o,p′*-DDT

[b] *LOQ* limit of quantification

Table 3 Concentration of PCBs (mean and range, ng/g wet weight) in liver of birds from South coast of the Caspian Sea, Iran

Family	Scientific name	PCB28	PCB52	PCB 101	PCB118	PCB153	PCB138	PCB180
Phalacrocoracidae	*Phalacrocorax* carbo	11.0 (<LOQ[a]–3.5)	0.5 (<LOQ–2.5)	2.5 (0.5–7.5)	26.0 (3.5–106.5)	26.5 (7.0–91.0)	28.0 (5.0–83.0)	3.0 (<LOQ–12.0)
Podicipedidae	*Podiceps cristatus*	3.5 (<LOQ–7.0)	0.8 (<LOQ–2.0)	3.5 (<LOQ–16.0)	15.0 (2.5–24.5)	10.8 (2.5–16.55)	15.5 (2.5–32.5)	7.5 (1.0–18.0)
	Podiceps nigricollis	6.5 (6.0–7.0)	(<LOQ)	2.0 (1.0–3.5)	8.0 (2.0–19.5)	23.0 (2.0–65.0)	15.5 (0.5–45.5)	2.5 (<LOQ–6.5)
Laridae	*Larus ridibundus*	1.5 (<LOQ–4.0)	1.0 (<LOQ–7.0)	1.5 (<LOQ–2.0)	12.5 (<LOQ–53.5)	16.5 (<LOQ–60.0)	20.5 (<LOQ–60.0)	5.0 (<LOQ–15.5)
	Larus minutus	4.5 (3.0–6.0)	1.5 (<LOQ–4.5)	1.5 (<LOQ–4.5)	19.5 (3.5–33.5)	20.5 (3.0–36.5)	32.5 (<LOQ–57.5)	10.5 (<LOQ–34.0)
	Larus canus	4.5 (0.5–7.0)	(<LOQ)	0.5 (0.5–1.0)	9.0 (2.0–12.5)	11.5 (9.0–14.0)	13.0 (2.5–20.5)	5.0 (2.0–11.0)
Anatidae	*Anas acuta*	3.5 (1.0–8.5)	(<LOQ)	(<LOQ)	10.5 (8.0–12.0)	8.5 (1.0–14.0)	13.5 (0.5–22.0)	4.0 (<LOQ–9.5)
	Anas creaca	3.0 (<LOQ–4.5)	(<LOQ)	0.5 (<LOQ–1.5)	1.5 (<LOQ–4.5)	1.5 (<LOQ–4.5)	1.0 (<LOQ–2.0)	5.5 (4.5–8.5)
	Anas platyhynchos	5.5 (4.5–8.0)	2.0 (<LOQ–5.5)	0.8 (<LOQ–2.5)	12.0 (0.5–29.0)	12.0 (0.5–32.0)	1.0 (<LOQ–2.5)	8.5 (<LOQ–18.5)

[a] Limit of quantification

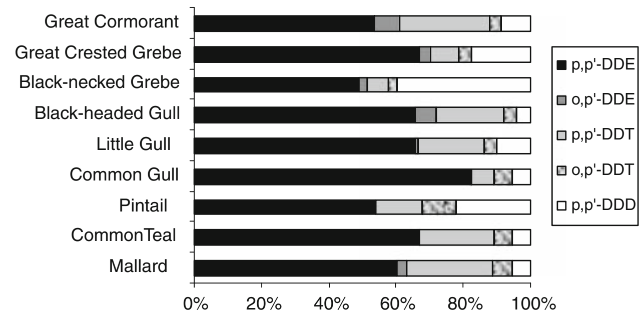

Fig. 2 Comparison of DDT compounds in liver of birds from the South coast of the Caspian Sea

constitute fresh DDT exposure (Aguilar 1984). In our samples DDE/DDT was between 0.5 and 0.8, indicating that despite severe restrictions on the use of these compounds in Iran, they are still in use. A study of organochlorines content of women's milk and fish from the area indicates similar recent exposure to these toxicants (Hosseini et al. 2008; Dahmardeh Behrooz et al. 2009c). In HCH family, the β-HCH isomer occurred at a high frequency (89% of samples) and with an average concentration of 12 $\pm$ 9 ng/g ww, while γ-HCH isomer (70% of samples) and α-HCH (75%) average concentration was 6.5 $\pm$ 1.5 and 1 $\pm$ 0.2 ng/g ww, respectively. It is known that HCH isomers are created by photochemical chlorination of benzene and produce a substance called technical-HCH. Technical-HCH contains mainly five isomers: α-HCH (53–70%), β-HCH (3–14%), γ-HCH (11–18%), delta-HCH (6–10%) and ε-HCH (3-5%). Despite the fact that β-HCH is resistant to enzymatic action and should therefore bioaccumulate at a faster rate, in this study, β-HCH contributed less than γ- and α-HCH to technical HCH. Currently in Iran, technical HCH is produced, mostly as lindane (γ-HCH), and is available in the market. It is conceivable that this technical HCH has contributed to the residues we report in our birds. In agreement with our data, current literature indicates that sea birds readily metabolize γ-HCH and α-HCH isomers, but β-HCH, which is more recalcitrant, biomagnifies in the food web (Braune et al. 2007; Willett et al. 1998). Nevertheless, in our study, over 50% of HCH in Great Cormorant, Black-necked Grebe was γ-HCH; and in Great Crested Grebe, Black-headed Gull and Mallards, γ-HCH was as high as 40% (Fig. 3) of all HCH we studied. Nazari et al. (2001) studied 18 rivers in the costal provinces neighboring the Caspian Sea and found significant lindane contamination in the area. The high lindane (γ-HCH) concentrations we report here corroborate with Nazari's findings and indicate a recent use of this organochlorine pesticide. HCB was detected in almost all samples up to 105 ng/g ww. The high concentration of HCB in this study may be due to the fact that it is a by-product in the manufacturing of various chlorine-containing chemicals and an impurity in several pesticides (Naso et al. 2003).

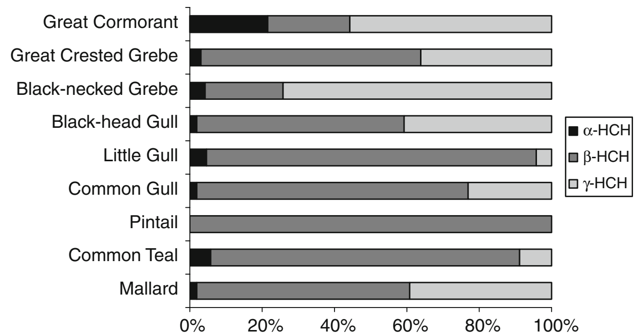

Fig. 3 Composition of HCH isomers in liver of birds from the South coast of the Caspian Sea

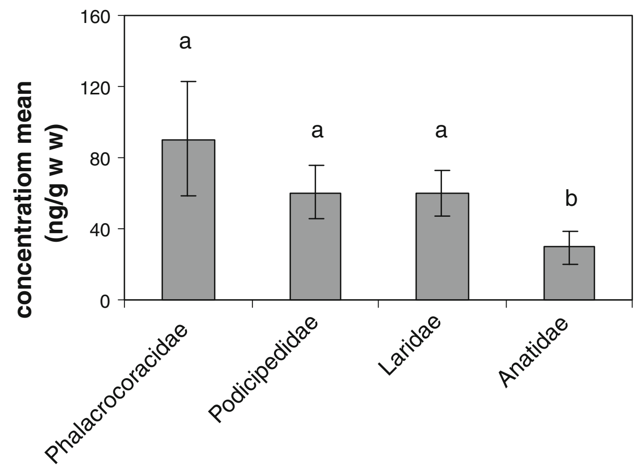

Fig. 5 Comparison of the concentration of PCBs in bird's liver of different family from the South coastal of Caspian Sea. Different letters indicate significant differences $P < 0.05$

Polychlorinated biphenyls: PCBs were found in all bird species, and their concentrations ranged from <LOQ to 106.0 ng/g ww. Congeners with highest concentrations in all species were 138, 153 and 118 but PCB 52 and 101 were below the detection limit in most our samples as have been reported elsewhere (Malcolm et al. 2003; Bouwman et al. 2008). This may be due to lack of un-substituted adjacent meta and para positions on the biphenyl rings, hexa-, and penta- chlorinated congeners 138, 153 and 118 are refractory to metabolic attack mediated by cytochrome P450 (Walker 2001). But PCB 52 and 101 are more rapidly metabolized and excreted, especially by species at the higher trophic levels (Oliver and Niimi 1988).

The ratio of ΣOCPs/ΣPCBs was >1 in all species, except *Phalacrocorax carbo*, indicating dominance of agro-chemical sources of persistent organic compounds in the region in comparison to industrial sources (Fig. 4). This can simply be attributed to the intensive agricultural activities and increasing use of pesticides in provinces that border the Caspian Sea in Iran. From the year 2000 to 2001, over 27,000 tonnes of pesticides were used nationally; 60% of which was applied to the land under cultivation in the three Northern provinces neighboring the Caspian Sea (Heidari 2003).

Effects of diet and migration route

Significant differences in PCB and OCPs levels were detected between families we examined in this study. PCBs, from highest to lowest, were found in *Phalacrocoracidae* > *Podicipedidae* > *Laridae* > *Anatidae* (Fig. 5). OCPs, from highest to lowest, were found in Podicipedidae > Laridae > Phalacrocoracidae > Anatidae (Fig. 6). Significant differences in mean concentrations of OCPs were detected among species. For example, concentrations of OCPs were significantly greater in Black-headed Gull than in Common Teal. The highest concentration of PCBs

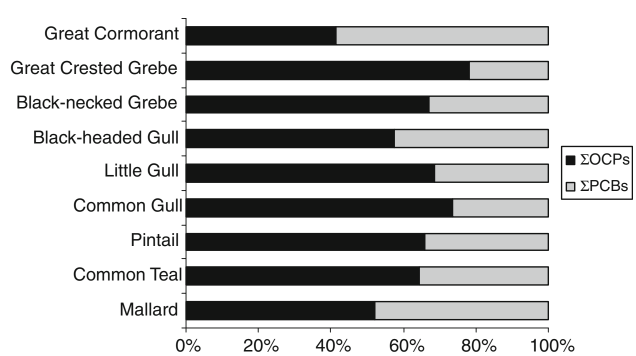

Fig. 4 Comparison of concentrations of ΣOCPs and ΣPCBs in bird's liver from the South coast of the Caspian Sea

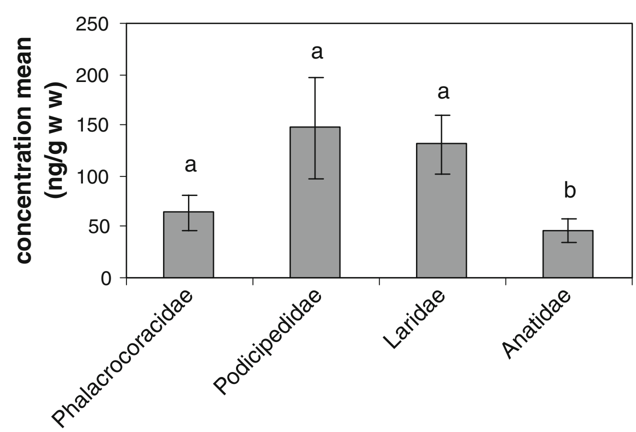

Fig. 6 Comparison of the concentration of ΣOCPs in bird's liver of different family from the South coast of the Caspian Sea. Different letters indicate significant differences $P < 0.05$

was found in the Great Cormorant while OCPs highest levels were found in Great Crested Grebe and Black-headed Gull, it is now well established that feeding habits could explain most of the variation found in pollutant levels in birds (Fang et al. 2007; Bouwman et al. 2008; Drooge et al. 2008). Black-headed Gull which forages on agricultural lands and near drainage channels exhibit high concentration of OCPs (Naso et al. 2003). A recent publication by Jaspers et al. (2007) describes how the opportunistic Gulls can alter their nutrient source. In Iran a similar phenomenon was reported on; where Black-headed Gulls were found feeding on human garbage in landfills and near drainage pipes consuming a variety of items (Mansoori 1999). Scavenging habit of Black-headed Gulls may have contributed significantly to their exposure to various xenobiotics via ingestion of contaminated food items. Other feeding habits, as in the Great Crested Grebe and Great Cormorant, that primarily consume fish facilitate an extraordinary tendency to concentrate and bioaccumulate OCs (Cid et al. 2007).

Fish accumulate highly lipophilic compounds from their environment both by direct absorption from water through the gills, and by ingestion of food items. In general, piscivorous birds are excellent bioaccumulators of lipophilic pollutant (Naso et al. 2003). We found that even though Great Cormorant and Great Crested Grebe are both fish-eating birds, the order of OC concentration was reverse in the two birds. Great Cormorant had PCBs > DDTs while Great Crested Grebe had DDT > PCBs. Their differing migratory routs may explain this discrepancy in the two birds. Great Crested Grebe winters exclusively in the Caspian while Great Cormorant winters partly in the Caspian and travels down to the Persian Gulf area for some of the winter. Dahmardeh Behrooz et al. (2009b) report similar levels in birds wintering in Khuzestan province in south western Iran, where PCB > DDT. In migratory birds, accumulation of organochlorines depends not only on the degree of pollution in the area of collection, but pollution in stopover sites and breeding grounds. We know that many birds that winter in Iran have their breeding ground in Russia, where high levels of DDTs have been reported in Ringed Seal from the Russian Arctic; suggesting that DDTs are widely distributed in this region (Nakata et al. 1998). It should be noted that wintering areas can vary from year to year, making comparisons between birds more difficult. Different diet composition in different areas can offer another source of variability in OC pollution levels in bird species. *Anatidae* family, which feed on lower trophic levels, had lowest OCPs and PCBs; these birds consume variable proportions of animal and plant material (Fang et al. 2007) hence the lowest intake of organic pollutants and little accumulation of these toxins compared to other birds in this study.

Metabolism and biotransformation

Ability of organisms to biotransform environmental toxicants varies and plays an important role in tissue accumulation and distribution of compounds (Furness 1993; Fossi et al. 1995). In general, omnivorous birds with high Mixed Function Oxidase (MFO) activities are better adapted and/or more adaptable to life in polluted environments. Omnivorous and opportunistic species of birds like Gulls are known to have a high adaptive capacity under varying environmental conditions. They seem to be able to modulate enzyme activities in response to the quantity and nature of the chemical insult they receive (Fossi et al. 1991); and their success, in living with pollution, is thought to have risen from their ability to respond according to the level of environmental need for biotransformation of toxicants. Then again, Naso et al. (2003) has shown that small number of cytochrome P450-associated enzyme and resulting low capacity for OC biotransformation of his gulls contributed to large accumulation of OCs (Table 2). Specialized predators like the Cormorants with low MFO activity, bioaccumulate lipophilic organochlorine compound readily (Fossi et al. 1995). Birds in our study, in general, had lower OCP and PCB levels than similar birds in other parts of the world. For example, Great Cormorants in our study had lower OCP and PCB in their liver than those reported from Japan (Guruge et al. 2000); and similar levels to those from Greece (Sakellarides et al. 2006). Gulls in the present study had less OCPs and PCBs in their liver than those reported from Denmark (Cleemann et al. 2000a, b), and Italy (Naso et al. 2003). Knowledge and understanding of the different ‘species-specific’ detoxification abilities is a useful tool for determining which species are at higher risk in polluted areas, and can help in prioritizing conservation efforts that are needed to protect birds of this region.

Reproductive impairments

Organochlorines have been linked to severe and serious reproductive impairments in birds including: decreased fertility, abnormal reproductive behavior, skewed sex ratios, differential sex related mortalities and de-feminization of male embryos (Wiemeyer et al. 1989; Peakall et al. 1990; Colborn et al. 1993). In birds of prey, >100 μg/g p,p'-DDE in liver can cause acute poisoning (Cook et al. 1982). Moreover, 16 μg/g of ΣPCBs ww has been associated with disruption of growth, reproduction, metabolism, and behavior (Eisler 1986). No observed effect (NOE) concentrations of ΣPCB for mallard were found to be at 29.5 μg/g ww (Barron et al. 1995). The lowest observed effect concentration (LOEC) of liver ΣPCBs which resulted in mortality of Common Cormorant (*Phalacrocoracidae carbo*) was found to be 319 μg/g ww (Koeman et al. 1973). Moreover, it has been reported that concentrations higher than 15–29 μg/g ww of ΣPCBs can elicit immunosuppressive effects and possibly an increased susceptibility to parasites in Glaucous Gull (Naso et al. 2003). Maximum concentration of *p,p′*-DDE and PCBs, for all birds in the present study, were 340 ng/g ww and 106.5 ng/g ww, respectively. Levels of PCBs and OCPs in the present study are lower than what has been associated with adverse effects, however; scarcity of studies that accurately investigate effects of exposure to mixture of toxicants warrants more serious protection of coastal birds. We know for example, that PCBs increase effects of *p,p′*-DDE (Provini and Galassi 1999). It has also been suggested that OCs and food stress may have a synergistic relationship; effects of which, on susceptibility to toxicants, is not yet know (Walker 2001; Cid et al. 2007).

Conclusions

We investigated liver OCPs and PCBs in water birds from the Southern coast of the Caspian Sea. In general, OC levels were higher in birds that ate higher on the trophic level. PCB congeners including 118, 138, and 153 were detected at higher concentrations than other congeners. *p,p′*-DDE dominated pesticides burden in the great majority of the samples, and although strict regulations against use of these compounds have been in effect in Iran, recent exposure of birds to *p,p′*-DDE was detected in this study. Diet and differing migratory route could explain most of the differences we observed in bird contamination with OC. Maximum *p,p′*-DDE and PCBs were not associated with hatching failure or embryonic deformities or mortality at this time, limited information is available about mixture toxicity in birds, or synergistic effects of diet and toxicant; two compelling reasons to air on the side of caution in wildlife protection.

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References

Aguilar A (1984) Relationship of DDE/ΣDDT in marine mammals to the chronology of DDT input into the ecosystem. Can J Fish Aquatic Sci 41:840–844

Barron MG, Galbraith H, Beltman D (1995) Comparative reproduction and developmental toxicology of birds. Comp Biochem Physiol 112:1–14

Blus LJ, Health RG, Gish CD, Belisle AA, Prouty RM (1971) Egg shell thinning in the brown pelican: implication of DDE. Bio sci 21:1213–1215

Bouwman H, Polder A, Venter B, Skaare JU (2008) Organochlorine contaminant in cormorant, darter, egret, and ibis eggs from South Africa. Chemosphere 71:227–241

Braune BM, Mallory ML, Gillchrist HG, Letcher RJ, Drouillard KG (2007) Levels and trends of organochlorines and brominated flame retardants in ivory gull egg from the Canadian Arctic, 1979 to 2004. Sci Total Environ 378:403–417

Choi JW, Matsuda M, Kawano M, Min BY, Wakimoto T (2001) Accumulation profiles of persistent organochlorines in waterbirds from an estuary in Korea. Chemosphere 41:353–363

Cid FD, Anton RI, Caviedes-Vidal E (2007) Organochlorine pesticide contamination in three bird species of the Embalse Lake Florida water reservoir in sediarid Midwest of Argentina. Sci Total Environ 385:86–96

Cleemann M, Riget F, Paulsen GB, Dietz R (2000a) Organochlorines in Greenland glaucous gulls (*Larus hyperboreus*) and Icelandic gulls (*Larus glaucoides*). Sci Total Environ 17(245(1–3)): 117–130

Cleemann M, Riget F, Paulsen GB, Dietz R (2000b) Organochlorines in Greenland glauccous gull (*Larus hyperboreus*) and Icelandic gulls (*Larus glaucoides*). Sci Total Environ 254:117–130

Colborn T, Vom Sall FS, Soto AM (1993) Development effects of endocrine-disrupting chemicals in wild life and humans. Environ Health Perspect 101:378–384

Cook AS, Bell AA, Hass MB (1982) Predatory birds pesticides and pollution. Institute of Terrestrial Ecology, Cambridge

Dahmardeh Behrooz R, Esmaili-Sari A, Ghasempouri M, Bahramifar N, Covaci A (2009a) Organochlorine pesticide and polychlorinated biphenyl residues in feathers of birds from different trophic levels of South-West Iran. Environ Int 35:285–290

Dahmardeh Behrooz R, Esmaili-Sari A, Ghasempouri M, Bahramifar N, Hosseini M (2009b) Organochlorine pesticides and polychlorinated biphenyl in feathers of resident and migratory birds of south-west Iran. Archives Environ Contam Toxicol. doi:10.1007/s00244-008-9211-9

Dahmardeh Behrooz R, Esmaili-Sari A, Bahramifar N, Ghasempouri M (2009c) Organochlorine pesticide and polychlorinated biphenyl residues in human milk from the southern coast of Caspian sea, Iran. Chemosphere 74:931–937

Drooge BV, Mateo R, Vives I, Cardiel I, Guitart R (2008) Organochlorine residue levels in livers of birds of preys from Spain: inter-species comparison in relation with diet and migratory patterns. Environ Pollut 153:84–91

Eisler R (1986) Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Department of Interior, Biological Report 85, Contamination Hazard Review Report No.7

Elliot JE, Norstrom RJ (1998) Chlorinated hydrocarbon contaminants and productivity of bald eagle populations on the pacific coast of Canada. Environ Toxicol Chem 17:1142–1153

Faber RA, Hickey JJ (1973) Eggshell thinning, chlorinated hydrocarbons, and mercury in inland aquatic bird eggs, 1969 and 1970. Pestic Monit J 7:27–36

Fang L, Zheng M, Zhang B, Gao L, Liu W, Zhao X (2007) Polychlorinated dibenzo- p-dioxins and dibenzofurans in eggs of eight avian species from Dongting Lake, China. Chemosphere 69:411–421

Fossi M, Leonzio C, Focardi S, Lari L, Renzoni A (1991) Modulation of mixed-function oxidase activity in black-headed gulls living in anthropic environments: biochemical acclimatization or adaptation? Environ Toxicol Chem 10(1):179–188

Fossi MC, Massi A, Lari L, Marsili L, Focardi S, Leonzio C, Renzoni A (1995) Interspecies differences in mixed function oxidase activity in birds: relationship between feeding habits, detoxication activities and organochlorine accumulation. Environ Pollut 90:15–24

Furness RW (1993) Birds as monitors of pollutant. In: Furness RW Greenwood, JJD (eds) Birds as monitors of environmental changes. Chapman Hall, London, pp 86–143

Guruge KS, Tanabe S, Fukuda M (2000) Toxic assessment of PCBs by 2,3,7,8-tetrachlorodibenzo-dioxin equivalent in common cormorant (*Phalacrocoracidae carbo*) from Japan. Environ Contam Toxicol 38:509–521

Harris ML, Elliot JE, Butler RW, Wilson LK (2003) Reproductive success and chlorinated hydrocarbon contamination of great blue herons (*Ardea herodias*) from coastal British Columbia, Canada, 1977 to 2000. Environ Pollut 121:207–227

Heidari H (2003) Farmer field schools (FFS) slash pesticides use and exposure in Islamic Republic of Iran. Agro-chemicals Report; 1-3

Hosseini SV, Behrooz RD, Esmaili-Sari A, Bahramifar N, Hosseini SM, Tahergorabi R, Hosseini SF, Feas X (2008) Contamination by organochlorine compound in the edible tissue of four sturgeon species from the Caspian Sea (Iran). Chemosphere 73:272–279

Jaspers VLB, Covaci A, Voorspoels S, Dauwe T, Eens M, Schepens P (2006) Brominated flame retardants and organochlorine pollutants in aquatic and terrestrial predatory birds of Belgium: levels, pattern, tissue distribution and condition factors. Environ Pollut 139:340–352

Jaspers VLB, Voorspoels S, Covaci A, Lepoint G, Eens M (2007) Evaluation of the usefulness of bird feathers as a non-destructive biomonitoring tool for organic pollutants: a comparative and meta-analytical approach. Environ Int 33:328–337

Koeman JH, Vanvelzen-Bald HCW, Devries R, Vos JG (1973) Effects of PCB and DDE in cormorant and Evaluation of PCB residues from an experimental study. J Reprod Fertil Suppl 19:353–364

Kunisue T, Watanabe M, Subramanian A, Sethuraman A, Titenko AM, Qui V, Prudente M, Tanabe SH (2003) Accumulation features of persistent organochlorines in resident and migratory birds from Asia. Environ Pollut 125:157–172

Malcolm HM, Osborn D, Wright J, Wienburg CL, Sparks TH (2003) Polychlorinated biphenyl (PCB) congener concentrations in Seabirds found dead in mortality incidents around the British coast. Environ Contam Toxicol 45:136–147

Mansoori J (1999) Field guide to birds of Iran. University of Tehran, Iran

Murata M, Iseki N, Masunaga S, Nakanishi J (2003) Estimation of effects of dioxins and dioxin-like PCBs on wild life population—a case study on common cormorant. Chemosphere 53:337–345

Nakata H, Tanabe S, Tatsukawa R, Koyama Y, Miyazaki N, Belikov S, Boltunov A (1998) Persistent organochlorine contaminants in ringed Seals (*Phoca hispida*) from the Kara sea, Russian Arctic. Environ Toxicol Chem 17:1745–1755

Naso B, Perrone D, Ferrante MC, Zaccaroni A, Lucisano A (2003) Persistent organochlorine pollutants in liver of birds of different trophic levels from from coastal area of Campania, Italy. Environ Contam Toxicol 45:407–414

Nazari Z, Haghghi S, Eimandel K, Hosseini S, Parriz M, Kalantari H (2001) Determination of organochlorine pesticides residue in river to Caspian sea and sea station. In: Second national conference on optimum utilization of chemical fertilizers and pesticides in agriculture. Ministry of agriculture, Karaj, Islamic Republic of Iran

Newton I (1988) Determination of critical pollutants levels in wild population, with examples from organochlorine insecticides in birds of prey. Environ Pollut 55:29–40

Oliver BJ, Niimi AJ (1988) Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environ Sci Technol 22:388–397

Peakall DB, Noble DG, Elliot JE, Somers JD, Erickson G (1990) Environmental contaminants in Canadian peregrine falcons, *Falco peregrinus*: a toxicological assessment. Can Field Nat 104:244–254

Provini A, Glassi S (1999) Polychlorinted biphenyls and chlorinated pesticides in bird eggs from Calabria (Southern Italy). Ecotoxicol Environ Saf 43:91–97

Sakellarides TM, Konstantantinou IK, Hela DG, Lambropoulou D, Dimou A, Albanis TA (2006) Accumulation profiles of persistent organochlorines in liver and fat tissues of various waterbird species from Greece. Chemosphere 63:1392–1409

Van den Berg M, Cranne BLHJ, Sinnige T, Van morik S, Dirksen S, Boudewijn T (1994) Biochemical and toxic effects of polychlorinated (PCBs), dibenzo-p-dioxins (PCDDs), and dibenzofurans (PCDFs) in the cormorant (phalacrocoracidae carbo) after in vivo exposure. Environ Toxicol Chem 13:803–816

Walker CH (2001) Organic pollutants—an ecotoxicological perspective. Taylor Francis, London

Watanabe M, Tanabe S, Tatsukawa R, Amano M, Miyazaki N, Petrov EA, Khuraskin SL (1999) Contamination levels and specific accumulation of persistent organochlorines in Caspian Seal (*Phoca Caspica*) from the Caspian Sea, Russia. Arch Environ Contam Toxicol 37:396–407

Wiemeyer SN, Spann JW, Bunck CM, Krynisky AJ (1989) Effect of kelthane on reproduction of captive eastern screech owls. Environ Toxicol Chem 8:903–913

Willett KL, Ulrich EM, Hites RA (1998) Different toxicity and environmental fates of hexachlorocyclohexane isomers. Environ Sci Technol 32:2197–2207

Yamashita N, Tanabe S, Ludwing JN, Kurita H, Ludwig ME, Tatsukawa R (1993) Embryonic abnormalities, organochlorine contamination in double-crested cormorants (*Phalacrocorax auritus*), caspian terns (*Hydroprogne casppia*) from the upper Great Lakes in 1988. Environ Pollut 79:163–173