Levels and distribution of organohalogenated contaminants in 5 fish species from Sır Dam Lake, Kahramanmaraş, Turkey

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Introduction

In Turkey, OCPs have been used since 1945, with large quantities of these chemicals being used during the 1960s and 1970s. Since 1983, the usage of OCPs has been severely restricted or banned[1]. Only few studies have investigated the presence of OCPs in Turkish aquatic environment, where they have been evidenced in relatively high concentrations[2-4]. The aim of this study was to investigate the levels and distribution of organohalogenated contaminants in several fish species from Sır Dam Lake (Kahramanmaraş, Turkey), an artificial lake with great economical importance for the region.

Materials and methods

Sampling

The Sır Dam Lake is the 2nd important artificial lake in the Ceyhan river basin (Eastern Turkey). Several potential sources of pollution are present around the lake and they include paper, textile, oil and milk industries, but also waste from slaughterhouses or household.

A total of 83 individual fishes, representing 5 species *Acanthobrama marmid*, *Cyprinus carpio* (carp), *Chondrostoma regium* (nose-carp), *Barbus rajanorum* (barbel), *Siluris glanis* (wels), were obtained from fishermen along the Sır Dam Lake. The first 4 species belong to the *Cyprinidae* family and are benthopelagic fishes with an omnivorous feeding mode (insect larvae, crustaceans, annelids, plants and molluscs), except for the nose-carp with a more herbivorous diet (phytoplankton and zooplankton). Wels belongs to the *Siluridae* family and is mainly carnivore with its main diet composed of fish, amphibians, and small aquatic animals. Fishes were caught between January and June 2003. Only the excised muscle and liver samples were collected and they were stored at -20°C until analysis.

Materials

The organochlorine pesticides under investigation were hexachlorobenzene (HCB), *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT (expressed as DDTs), α-, β-, γ- isomers of hexachlorocyclohexane (expressed as HCHs), oxychlordane (OxC), *trans*-nonachlor (TN), *trans*-(TC) and *cis*-chlordane (CC) (expressed as CHLs). The following polychlorinated biphenyl (PCB) congeners (IUPAC numbers) were targeted: 28, 74, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187, 194 and 199. Brominate flame retardants included polybrominated diphenyl ethers (PBDEs) congeners 28, 47, 99, 100, 153, 154 and 183 and brominated biphenyl (BB) 153.

The methods used for sample preparation and analysis were described in detail by Covaci et al.[5]. *After Soxhlet extraction and clean-up on acidified silica, PCBs were measured by GC-ECD, while PBDEs and OCPs were measured by GC/ECNI-MS. Method limits of detection (LOD) for individual OCPs, PCB and PBDEs congeners ranged between 0.02 and 0.1 ng* g^{-1} *wet weight (ww).*

Results and discussion

Lipid percentages in muscle are similar for *Acanthobrama marmid*, nose-carp, and wels, but are higher ($p<0.01$) than lipid percentages in carp and barbel.

DDTs were the prevalent organohalogenated contaminants found in the 5 fish species from Sır Dam Lake. The dominant metabolite was *p,p'*-DDE, which constituted 93 - 95% of the sum DDTs in each fish species, followed by *p,p'*-DDD (5 - 7%) and *p,p'*-DDT (< 0.5%). The concentrations of DDTs in carp samples were similar with those reported by Ayas *et al.*[2] for carp from the Göksu Delta, but were lower than those reported by Barlas *et al.*[3] for the Upper Sakarya basin. The mean *p,p'*-DDE/ *p,p'*-DDT ratio in the muscle of the five investigated species ranged from 100 to 650 and can be correlated with past exposure to DDT (high *p,p'*-DDE content) and with low present exposure to DDT (low *p,p'*-DDT levels).

Table 1. Lipid percentages and concentrations of organohalogenated pollutants (expressed in ng/g wet weight) in muscle of selected fish species from Sır Dam Lake Turkey.

	Acanthobrama marmid (n=24)	*Barbus rajanorum* (n=3)	*Cyprinus carpio* (n=17)	*Chondrostoma regium* (n=17)	*Siluris glanis* (n=22)
	Median / Max	Median / Max	Median / Max	Median / Max	Median / Max
Lipids	0.60 / 4.04	0.43 / 1.05	0.34 / 2.63	1.63 / 3.56	0.95 / 11.53
Sum BDEs	0.67 / 1.6	0.34 / 1.2	0.15 / 1.3	0.08 / 1.5	0.50 / 6.7
Sum PCBs	3.0 / 12.4	0.59 / 1.3	0.94 / 4.8	0.39 / 10.0	3.4 / 42.3
HCB	0.16 / 0.45	0.05 / 0.09	0.07 / 0.41	0.11 / 0.34	0.19 / 1.5
Sum HCHs	0.22 / 0.65	0.09 / 0.10	0.21 / 0.75	0.08 / 0.33	0.43 / 2.2
Sum CHLs	0.35 / 1.7	0.05 / 0.05	0.05 / 1.4	0.08 / 0.72	0.17 / 3.6
p,p'-DDE	73.5 / 272.5	21.8 / 49.8	13.3 / 156.1	32.3 / 232.8	50.2 / 901
p,p'-DDD	5.3 / 16.6	0.66 / 2.6	0.82 / 13.0	2.3 / 12.1	3.2 / 54.3
p,p'-DDT	0.13 / 0.55	0.09 / 0.12	0.08 / 1.23	0.09 / 0.74	0.62 / 4.5
Sum DDTs	77.4 / 289.7	22.5 / 52.6	14.4 / 170.3	34.8 / 245.6	53.8 / 960

The three HCH isomers were present in different proportions in the fish species, with a higher contribution of α-HCH to the sum HCHs in wels and a higher contribution of γ-HCH in *Acanthobrama marmid* and carp. The levels and distribution of α-, β- and γ-HCH isomers in the fish species from Sir Dam Lake are similar to values found by Barlas *et al.*[2] in the Sakarya basin suggesting that similar pollutant factors as present in the two aquatic systems.

For all species, the PCB profile was dominated by the tri- to penta-CB isomers, which constituted between 53 and 90% of the total PCBs. The most persistent PCB congeners (no. 138, 153 and 180) were present in higher percentage in *Acanthobrama marmid* and barbel, but in general they had a much lower contribution to sum PCBs than reported for similar species from other worldwide locations[6,7]. The contamination degree with PCBs of the fish samples from the Sır Dam Lake is lower or similar to PCB levels found in other countries. The PCB levels in the fish species from Sır Dam Lake are also below the tolerance limits set for freshwater fish from European countries (1.4 μg/g ww in Germany).

PBDEs were detected in all muscle and liver samples from the 5 fish species, except few samples of carp liver and nose-carp muscle. The PBDE levels

were lower than the PCB levels, but they were at the same level or higher than HCB, HCHs and CHLs. PBB 153 was not found in any samples, indicating the very limited usage of Firemaster technical mixtures of PBBs in Turkey. The PBDE levels, which were measured for the first time in fish species from Turkish aquatic systems, had a maximum value of 6.7 ng/g ww found in a wels sample and were low compared to values found in freshwater fish from industrialised countries (8). BDE 47 was the predominant BDE congener in the fish samples, in accordance with its previously reported selective bioaccumulation[9]. Despite the present low concentrations of PBDE in fish, the vicinity of textile industry in particular close to the Sır Dam Lake can constitute a potential source of PBDEs and therefore, concentrations of PBDEs in fish may increase in time.

Table 2. Distribution of organohalogenated contaminants between liver and muscle of carp, nose-carp and wels, expressed as $c_{liver}/(c_{muscle} + c_{liver})$. Values lower than 0.50 indicate a preferential accumulation in the muscle.

	Cyprinus carpio (carp) (n=8)	*Chondrostoma regium* (nose-carp) (n=3)	*Siluris glanis* (wels) (n=8)
α-HCH	0.34 ± 0.13	0.55 ± 0.14	0.39 ± 0.06
β-HCH	0.33 ± 0.12	0.46 ± 0.16	0.36 ± 0.09
HCB	0.38 ± 0.11	0.49 ± 0.07	0.41 ± 0.07
p,p´-DDE	0.46 ± 0.10	0.48 ± 0.13	0.36 ± 0.06
p,p´-DDD	0.48 ± 0.09	0.50 ± 0.09	0.40 ± 0.08
p,p´-DDT	0.45 ± 0.29	0.62 ± 0.26	0.33 ± 0.12
PCBs	0.25 ± 0.11	0.57 ± 0.11	0.24 ± 0.08
PBDEs	0.38 ± 0.22	0.58 ± 0.22	0.33 ± 0.14

A preferential accumulation in muscle compared to liver was observed for all OCPs, PBDEs and PCBs for wels and carp, while for nose-carp, no preference was observed for β-HCH, HCB, *p,p'*-DDE and *p,p'*-DDD and a preferential accumulation in liver was observed for PBDEs, *p,p'*-DDT and PCBs (Table 2).

Svobodova *et al.*[7] has also observed lower concentrations of DDT and its metabolites in liver of wels compared to muscle (both expressed per lw or ww). Contrarily, nose-carp had preferential accumulation of pollutants in its liver. Burreau *et al.*[10] have observed that BDE 47 accumulated in lipid rich tissues in pike (lean fish) and this includes liver (<10%) and perivisceral adipose tissue. With exception of sole, Voorspoels et al.[11] have also observed a preferential

accumulation of PBDE congeners in liver (containing up to 50% lipids) of marine fish, such as plaice, bib and whiting.

For all compounds, lipid-based concentrations were higher in wels than in other species, in accordance with its feeding mode. Contrarily, concentrations of pollutants in nose-carp were the lowest, which agrees with its more herbivorous feeding mode.

Concentrations of POPs were significantly related to percent lipid (Figure 1) and the best correlations were obtained for *p,p'*-DDE and *p,p'*-DDD, which are the major organohalogenated contaminants in the Sir Dam Lake. (R^2=0.793 and 0.780, respectively). Being significantly correlated, the lipid percentage is a good predictor for the concentrations of POPs expressed per wet weight. Interestingly, similar slopes for the equation lg (conc. ng/g ww) = f (lg lipid%) were obtained for *p,p'*-DDE and *p,p'*-DDD (1.142 and 1.121, respectively), suggesting a similar rate of bioaccumulation. PCBs and PBDEs were showing the smallest correlation coefficients (R^2=0.355 and 0.331, respectively) suggesting that the high variation in concentrations is due to non-uniformly distributed sources.

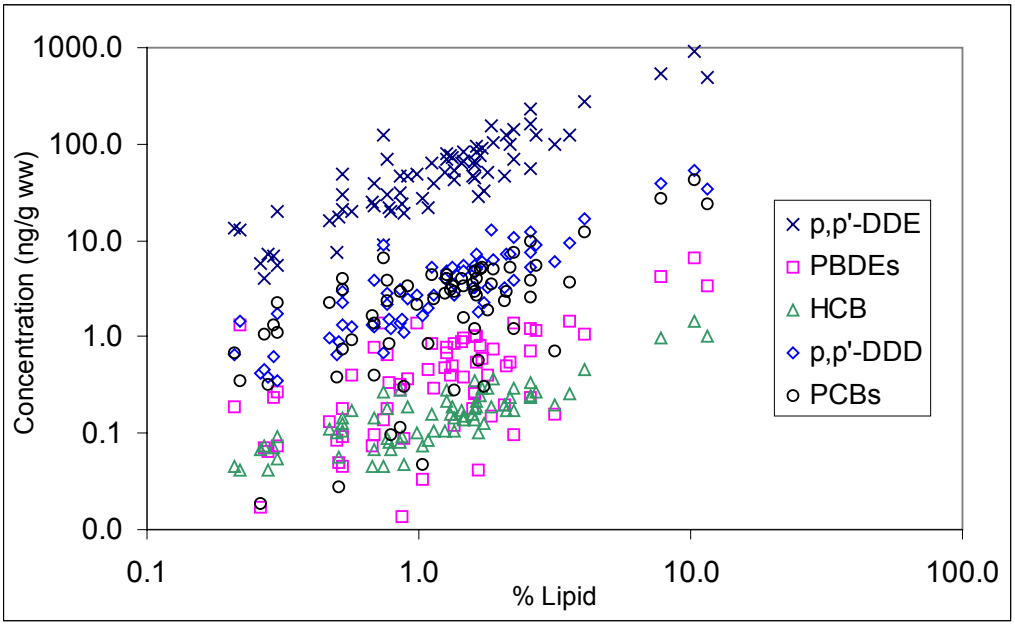

Figure 1. Relationships between concentrations of pollutants (ng/g ww) and lipid percentage.

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