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Organochlorine levels in edible fish from the Marmara Sea, Turkey

Mehmet Coelhan [a,*], Johanna Strohmeier [b], Hulusi Barlas [c]

[a] Research Center for Brewing and Food Quality, Technical University of Munich, Alte Akademie 3, 85350 Freising-Weihenstephan, Germany
[b] Department of Chemical–Technical Analysis and Chemical Food Technology, Technical University of Munich, Weihenstephaner Steig 23, 85350 Freising-Weihenstephan, Germany
[c] Department of Environmental Engineering, University of Istanbul, Avcilar Campus, 34850 Avcilar-Istanbul, Turkey

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Abstract

Samples of 12 edible fish species from the Marmara Sea were analyzed for organochlorines (PCBs, DDTs, HCB, HCHs, toxaphene, etc.). The results showed that the total concentrations ranged from 329.41 ng/g fat to 1453.87 ng/g fat. DDT group components made up almost half or more of organochlorine contamination. Levels in red mullet were compared with those from neighbor seas. The sum of DDTs as well as HCHs concentrations were markedly lower than in the Black Sea but higher in the Aegean Sea and Mediterranean. Thus, inflow from the Black Sea might be considered as a contamination source for DDT and HCH contamination. On the other hand, total PCB concentration (sum of congeners 28, 52, 101, 118, 138, 153 and 180) detected in this study was comparable or lower than those from the Aegean Sea and Mediterranean. Toxaphene was a minor contaminant. Measured values were below maximum residue levels for human consumption.

Keywords: Fish; PCBs; DDTs; HCHs; HCB; Toxaphene; Marmara Sea; Turkey

1. Introduction

Organochlorines have been produced in large quantities in the past 60–70 years for several industrial purposes. In animal studies, chronic exposure to organochlorines results in a broad range of undesired effects including carcinogenity, teratogenicity, neurotoxicity, reduction of fertility and endocrine disruption (Ecobichon, 1991; Reijnders, 1986). 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).

The Marmara Sea is a semi-enclosed inland sea with an area of 11,350 km^2, which is connected through the straits of Bosphorus and Dardanelles to the Black Sea and the Aegean Sea, respectively. Because of the salinity difference in these seas, there is an upper flow in the straits from north to south and an under flow in the opposite direction. This phenomenon forms an upper layer and a lower layer in the Marmara Sea (Ünlüata et al., 1990). The volume of inflow as well as outflow has been estimated as 1668 km^3/year (UNEP, 2002). The northeast coast of the Marmara Sea is the most important industrial area of Turkey and is heavily urbanized. However, studies of persistent pollutants in species from the Marmara Sea are very scarce. 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). Despite this, very little information has been published on the presence of organochlorines in the Marmara Sea and in its inhabitants. We have previously reported concentrations of some organochlorines in five fish species from the Marmara Sea and off the south coast of Turkey in the Mediterranean (Coelhan and Barlas, 1998). We have found that the total pollution of the fish samples from the Marmara Sea was significantly higher, than levels from the Mediterranean. Recently, PCB levels in mussels from the most industrialized bay of the Marmara Sea were published and also found to be high (Telli-Karakoc et al., 2002). In the present study, concentrations of PCBs, DDTs, toxaphene, chlordane

* Corresponding author. Tel.: +49 8161 71 4280; fax: +49 8161 71 4418.
E-mail address: coelhan@wzw.tum.de (M. Coelhan).

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components, hexachlorocyclohexanes and hexachlorobenzene were measured in 12 edible fish species from the Marmara Sea. Results were compared for red mullet with those from the Black Sea, the Aegean Sea and the Mediterranean since this fish species has been investigated usually before.

2. Materials and methods

Acetone, *n*-hexane, of quality for residue analysis, and sulphuric acid (95–97%) were purchased from Merck. Dichloromethane was distilled over a 1-m glass column. Silica gel 60 (63–230 mesh, Merck) was activated at 200 °C for 24 h and deactivated by addition of 3% H_2O. Anhydrous sodium sulfate p.a. (Fluka) was used as obtained. All organochlorine standards were obtained from Ehrenstorfer GmbH, Germany.

Fish samples were taken in the Central Fish Market of the city of Istanbul in December 2003 (Table 1). Fishes were caught from the Marmara Sea. After freezing at −24 °C, samples were transported in Styropor boxes to Germany. Three whole fish or filet samples of a species were minced in a commercial grinder. 20 g of homogenized fish was mixed with 100 g of anhydrous sodium sulfate and filled in a glass column (50 cm × 2.4 cm i.d.) and left for 4 h. The extraction was performed with 200 ml of pentane–acetone mixture (2:1, v/v). The lipid contents were determined gravimetrically. A maximum of 2 g of the lipid was dissolved in 10 ml of *n*-hexane and placed into a centrifuge tube with a Teflon lined screw cap. The sample was then treated carefully with 10 ml of conc. sulfuric acid and mixed several times. Next, the sample was placed into an oven at 60 °C to complete the decomposition of lipids for 2 h and, subsequently, centrifuged at 3000 rpm for 5 min. The hexane phase was reduced to 0.3 ml and passed through a Pasteur pipet packed with 1 g of silica gel. Before adding the sample to the silica gel, the column was washed with 5-ml *n*-hexane. PCBs and organochlorine pesticides were fractionated with 8-ml hexane (fraction 1) and 7-ml *n*-hexane/dichloromethane (1:1, fraction 2). Fraction 2 contained HCHs, o,p′-DDD, p,p′-DDD, p,p′-DDT, *cis*- and *trans*-nonachlor, *cis*-chlordane completely, o,p′-DDE and o,p′-DDT, and some of toxaphene components partly. PCBs, HCB, o,p′-DDE, p,p′-DDE, heptachlor and chlorden were found completely in the fraction 1.

The fish samples were examined for the following compounds: α-, β-, γ- and δ-hexachlorocylohexanes (HCHs), hexachlorobenzene (HCB), heptachlor, *cis*-chlordane, α-chlordene, *cis*- and *trans*-nonachlor, o,p′- and p,p′-isomers of DDT, DDD and DDE, seven indicator PCB congeners (PCB 28, 52, 101, 118, 138, 153 and 180). For toxaphene analysis, a standard containing 22 single congeners was used (Kimmel et al., 1998).

2.1. Quantification

HRGC/ECD measurements were performed using a Model 86.10 instrument from Dani, equipped with a 60-m DB-5 column (Phenomenex, i.d. 0.32, film thickness 0.25 μm), flow rate (N2) 1.5 ml/min. The chromatographic conditions were as follows: splitless/split injection (split open after 30 s), temperature program: 100 °C (3 min), 10 °C/min to 200 °C (3 min), 3 °C/min to 225 °C (3 min), 20 °C/min to 270 °C (15 min). Injection port temperature: 260 °C, detector temperature: 280 °C, injection volume: 2 μl. For confirmation, a second HRGC-ECD system from Dani, equipped with a 30-m OV 1701 column (Phenomenex, i.d. 0.25 mm, film thickness 0.25 μm) was used.

Table 1
List of fish and their % fat contents

Fish no.	Fish	Scientific name	% Fat
1	Anchovy	*Engraulis encrasicolus*	19.7
2	Horse Mackerel	*Trachurus mediterraneus*	11.0
3	Blue Whiting	*Micromesistius poutassou*	3.9
4	Sardine	*Sardina pilchardus*	11.3
5	Pickerel	*Smaris alceda*	14.3
6	Black Goby	*Gobius niger*	4.3
7	Allis Shad	*Alosa alosa*	11.4
8	Gurnard	*Trigla lucerna*	5.1
9	Striped Red Mullet	*Mullus surmuletus*	4.8
10	Young Bluefish	*Pomatomus saltator*	19.1
11	Bluefish	*Pomatomus saltator*	7.0
12	Mullet	*Mugil cephalus*	3.1
13	Sea Bass	*Dicentrarchus labrax*	6.2

3. Results and discussion

Concentrations of the compounds found in the fish studied are listed in Tables 2 and 3. 15 of 22 toxaphene components were not detected in any of the samples (Table 3). In comparison with the other organochlorine residues, either p,p′-DDE or p,p′-DDD was the major organochlorine contaminant in all fish samples. Levels of contaminants followed mainly the order of DDTs > PCBs > HCHs ≈ cyclodiene insecticides ≈ toxaphene > HCB. A mean value of 847.33 ng/g fat for organochlorines was measured.

3.1. DDTs

Total concentrations of DDT compounds as a group varied between 211.58 ng/g fat and 810 ng/g fat, and made up about half or more of the total organochlorine contamination (Table 2). p,p′-DDE was the major organochlorine contaminant in 7 of the 12 samples and p,p′-DDD was detected as the predominant contaminant in the remaining five samples. In marine mammals, a ratio of p,p′-DDE/Σp,p′-DDTs (Σp,p′-DDTs = p,p′-DDT + p,p′-DDE + p,p′-DDD) below 0.6 has been considered as fresh DDT exposure (Aguilar, 1984). In the present study, this value were in 11 of 12 samples between 0.24 and 0.54, while only sample 8 (gurnard) showed with 0.70 a ratio above 0.6 (Table 2). In our previous work, the mean concentration of DDT compounds but not the p,p′-DDE/Σp,p′-DDTs ratio was higher in samples from the Marmara Sea than those from the south coast of Turkey at the Mediterranean. Results were presented for organochlorine contamination in several harbor porpoises and seven fish species from the Black Sea coast of Turkey (Tanabe et al., 1997a). In that study, p,p′-DDE/Σp,p′-DDTs ratios were given as lower than 0.6.

Since the benthic red mullet has been largely used as an indication of level of contamination, results will be discussed for this fish (Table 4). A total burden of 1700 ng/g fat of DDTs was reported in striped red mullet from the Black Sea (Tanabe et al., 1997a). In the present study, total DDT contamination was measured as 731.42 ng/g fat in striped red mullet (sample 9) from the Marmara Sea, which is connected from the north side by Bosphorus to the Black Sea. In red mullet from the Marmara Sea, the total DDT was previously reported as 1262 ng/g fat (Coelhan and Barlas, 1998). In two studies (Kucuksezgin et al., 2001; Giouranovits-Psyllidou et al., 1994), total DDT concentrations were given as 454 and 552 ng/g fat, respectively, for red mullet samples from Aegan Sea, which is connected to south side of the Marmara Sea by Dardanelles. Adriatic Sea samples showed with 190 ng/g fat (only p,p′-DDE, Bayarri et al., 2001) or 233.8 ng/g fat (Di Muccio et al., 2002) much lower total DDT levels than Aegean or Marmara or Black Sea samples. For Gulf of Naples, reported values were at the range of 220.6 ng/g fat (Naso et al., 2005). Total DDT level in samples from western Mediterranean with 320 ng/g fat (Pastor et al., 1996) was slightly higher than Adriatic Sea but still noticeable lower than the other seas mentioned above. As a consequence, it can be concluded that there is a recognizable tendency for DDT concentrations in fish to decrease from the Black Sea to the Marmara Sea, to the Aegean Sea and to the Adriatic Sea. A north–south decline for organochlorines in red mullet has already been reported for the Aegean Sea (Giouranovits-Psyllidou et al., 1994). The results lead to the supposition that DDT