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EFFECT OF HEAT TREATMENT ON ORGANOCHLORINE PESTICIDE RESIDUES IN SELECTED FISH SPECIES

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Key words: organochlorine pesticides, fish, heat treatment, frying

Among persistent organic pollutants that occur in the environment and in food, a significant group is represented by the residues of highly toxic chlorinated pesticides, used for decades mainly in plant protection. As some of the compounds have half-lives measured in years, or even decades, they can accumulate in water and bottom sediments. In consequence, they can penetrate into aquatic organisms and pose health risk to consumers of seafood products.

The research aimed at estimating the effect of frying on concentrations of selected organochlorine pesticides (α-HCH, β-HCH, γ-HCH, heptachlor, aldrin, heptachlor epoxide isomer B, pp'-DDE, endrin, pp'-DDT) in the meat of fish species most commonly consumed in Poland.

Analyses were conducted by gas chromatography method with GC/MS HP 6890 (5973) apparatus.

The study revealed that the dominant compound in the raw fish meat was pp'-DDE, with an average concentration of 3.55 μg/kg wet weight; the highest levels being found in flounder (7.33 μg/kg w.w.), and the lowest in cod (0.58 μg/kg w.w.). The less abundant compound was heptachlor epoxide isomer B.

Frying caused significant ($p<0.05$) losses in concentrations of most organochlorine pesticides examined. The biggest loss was observed for βHCH in carp – 74.05%. Mean losses of the examined compounds ranged from 9.6% for heptachlor epoxide isomer B to 32.3% for β-HCH.

The levels of pesticides detected in the raw fish were low, and did not exceed the maximum permitted levels. Frying still reduced the content of persistent organochlorine pesticides in fish meat, improving the quality of the food product.

INTRODUCTION

Among persistent organic pollutants that occur in the environment and in food, a significant group is represented by the residues of highly toxic chlorinated pesticides, used for decades mainly in plant protection. As some of the compounds have half-lives measured in years, or even decades, they can accumulate in water and bottom sediments. In consequence, they can penetrate into aquatic organisms and pose health risk to consumers of seafood products. Despite the several dozen year ban on the use of organochlorine pesticides, the compounds are still detected in fish bodies [Falandysz, 1999, Falandysz *et al*., 1999, Niewiadomska & Żmudzki, 1996, Ciereszko & Witczak, 2002, Marcotrigiano & Storelli, 2003]. Fish are consumed mainly in a processed form, therefore the assessment of culinary treatment effects on toxic residues in fish products seems to be an important issue, considering consumers safety.

The research was aimed at estimating the effect of frying on levels of selected organochlorine pesticides (α-HCH, β-HCH, γ-HCH, heptachlor, aldrin, heptachlor epoxide isomer B, pp'-DDE, endrin, pp'-DDT) in the meat of fish species most commonly consumed in Poland.

MATERIAL AND METHODS

The study involved muscle tissue collected from edible portions of herring (*Clupea harengus* L.), salmon (*Salmo salar* L.), common carp (*Cyprinus carpio* L.), brown trout (*Salmo trutta m. fario L.)*, flounder (*Platichthys flesus* L.) and cod (*Gadus morhua* L.*)*. The fish were bought as skinned fillets at retail in Szczecin.

Muscle tissue of each fish species was sampled as two combined samples of 5 individuals each. One of the combined samples was examined as raw material, while the other one was pan-fried in plant oil for ten minutes. From each combined sample, three subsamples (10-15 g each) were taken and freeze-dried for 36 h in a LyoLab 3000 apparatus. For quantitative analysis, the Chlorinated Pesticides Mix (SUPELCO, USA 49151) was used, while recoveries were examined by addition of a known amount of the Pesticides Surrogate Spike Mix (SUPELCO, USA, 4-8460), which was an acetone solution of decachlorobiphenyl and 2,4,5,6tetrachloromxylene. The compounds examined were extracted in lipids (Soxhlet extractor, 8 h) with 150 mL of an acetone/hexane mixture (v/v, 3:1). The extracts obtained were concentrated with a rotary vacuum evaporator to *ca.* 2 mL, and fat content was determined gravimetrically. Then the lipids were dissolved in 2 mL of nhexane and purified with 7 mL of oleum (7% in concentrated). Next, the extracts were washed with deionized water, dried over anhydrous sodium sulphate and concentrated to 1 mL using nitrogen evaporation. Analysis was conducted with a GC/MS HP 6890/5973 gas chromatograph ((in Selected Ion Monitoring mode), and operating conditions of the chromatographic analysis were, as follows:

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carrier gas – helium; pressure: 26 psi (1.77 atm); flow rate: 1.2 mL/min, column: CPSIL8 CB LOW BLEED (60 m x 250 μm x 0.25 μm; Chrompaq); column temperature program: 140°C (hold 0.5 min) → increase rate 10°C/min → 200°C (hold 5 min) → increase rate 5°C/min → 280°C (hold 10 min) → increase rate 30°C/min → 300°C (hold 5 min); single sample analysis time: 43.17 min.

Recoveries of the analysed pesticides, determined on the basis of the internal standard recoveries (Pesticides Surrogate Spike Mix), were within the range of 75-91%.

Statistically significant ($p<0.05$) differences in lipids and pesticides content in the raw and fried fish meat were determined using the Student's t-test for independent samples (Table 3).

Figure 1 shows a model chromatogram of an analysed sample.

RESULTS AND DISCUSSION

Lipid content in the raw muscle tissue of the examined fish ranged from 0.55% for cod to 13.71% for herring (Table 1). Average levels of organochlorine pesticides determined in raw and fried fish meat are presented in Tables 1 and 2.

The study revealed that the dominant compound in the raw fish meat was pp'DDE, with an average concentration of 3.55 μg/kg wet weight; the highest level (7.33 μg/kg w.w.) being found in flounder, and the lowest (0.58 μg/kg w.w.) in cod (Table 1). The less abundant compound was heptachlor epoxide isomer B, not detected in trout tissue.

In the fried fish muscles, levels of the pesticides analysed ranged from 0.096 μg/kg w.w. for heptachlor epoxide isomer B to 5.698 μg/kg w.w. for p,p'-DDE, both the values being detected in the flounder tissue (Table 2).

The statistical analysis revealed that frying caused significant ($p<0.05$) changes in lipid content of the muscles of all the examined fish species. However, significant losses in concentrations of all the organochlorine pesticides examined were found only in salmon meat, while no significant changes were observed in herring and carp. In the other fish species,

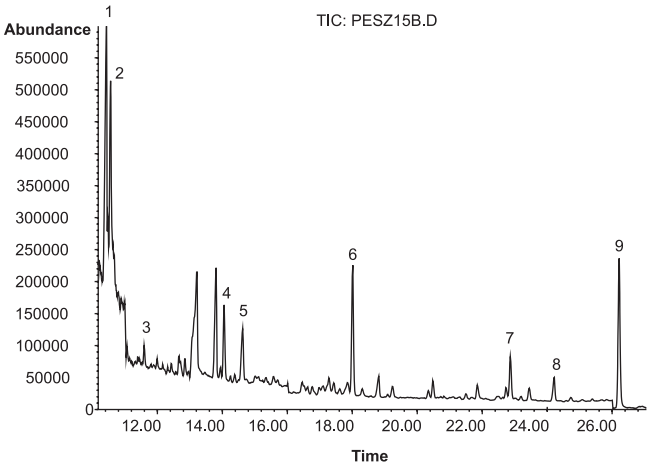

FIGURE 1. A model chromatogram of an analysed sample (flounder muscle tissue) 1 – α-HCH; 2 – β-HCH; 3 – γ-HCH; 4 – Heptachlor; 5 – Aldrin; 6 – Heptachlor epoxide isomer B; 7- pp'- DDE; 8 – Endrin; 9 – pp'-DDT.

TABLE 1. Organochlorine pesticides residues (mean ± standard deviation) in raw fish meat.

Assortment	Content (μg/kg w.w.)							
	α-HCH	β-HCH	γ-HCH	Heptachlor	Aldrin	Heptachlor epoxide isomer B	pp'-DDE	Endrin	pp'-DDT
Herring	0.889±0.148	0.200±0.084	0.072±0.007	0.134±0.008	0.546±0.026	0.043±0.014	4.314±1.098	3.270±0.941	2.195±0.754
Salmon	4.760±1.690	0.099±0.014	0.111±0.008	0.141±0.096	0.059±0.010	0.047±0.010	4.771±1.645	1.308±0.843	2.017±0.094
Carp	0.838±0.155	1.179±0.861	0.732±0.127	0.114±0.009	0.135±0.074	0.020±0.009	1.777±0.870	0.775±0.068	0.474±0.170
Trout	3.375±0.967	0.188±0.976	0.379±0.134	0.221±0.101	0.641±0.127	nd	2.509±0.957	nd	0.847±0.127
Flounder	2.212±0.970	0.712±0.124	0.333±0.152	0.660±0.265	0.350±0.102	0.097±0.023	7.329±2.697	1.247±0.075	2.004±0.096
Cod	0.250±0.087	0.518±0.114	0.501±0.973	0.206±0.059	0.368±0.110	0.077±0.021	0.579±0.168	nd	0.465±0.120
Assortment	Lipid content (%)	Content (μg/kg lipids)							
		α-HCH	β-HCH	γ-HCH	Heptachlor	Aldrin	Heptachlor epoxide isomer B	pp'-DDE	Endrin	pp'-DDT
Herring	13.71	6.48±1.09	1.46±0.85	0.53±0.11	0.98±0.27	3.98±1.09	0.31±0.009	31.47±4.59	23.85±3.99	16.01±2.06
Salmon	9.40	50.64±7.03	1.05±0.72	1.18±0.07	1.50±0.91	0.63±0.18	0.50±0.18	50.76±6.47	13.92±1.81	21.46±3.67
Carp	5.79	14.47±3.80	20.36±3.61	12.64±2.19	1.97±0.88	2.33±1.07	0.35±0.16	30.69±4.97	13.39±2.33	8.19±2.48
Trout	4.78	70.61±5.71	3.93±1.097	7.93±1.64	4.62±1.15	13.41±3.98	nd	52.49±7.91	nd	17.72±2.90
Flounder	5.75	38.47±8.24	12.38±3.45	5.79±1.13	11.48±3.19	6.09±2.47	1.69±0.09	127.46±10.8	21.69±3.15	34.85±4.98
Cod	0.55	45.45±6.19	94.18±5.74	91.09±7.19	37.45±4.87	66.91±6.97	14.00±2.48	105.27±9.74	nd	84.55±7.15

nd = not detected

TABLE 2. Organochlorine pesticides residues (mean ± standard deviation) in fried fish meat.

Assortment	Content (μg/kg w.w.)							
	α-HCH	β-HCH	γ-HCH	Heptachlor	Aldrin	Heptachlor epoxide isomer B	pp'-DDE	Endrin	pp'-DDT
Herring	0.639±0.260	0.140±0.097	0.061±0.028	0.041±0.023	0.180±0.076	0.041±0.011	3.866±1.363	2.852±0.997	1.924±1.113
Salmon	3.078±1.34	0.091±0.054	0.107±0.086	0.127±0.231	0.043±0.011	0.034±0.017	2.903±1.369	0.508±0.235	1.291±0.968
Carp	0.619±0.246	0.306±0.147	0.311±0.123	0.104±0.067	0.119±0.046	0.019±0.009	1.671±0.966	0.453±0.133	0.462±0.123
Trout	3.021±1.350	0.138±0.094	0.354±0.192	0.203±0.099	0.599±0.047	0.018±0.007	1.247±0.890	nd	0.557±0.265
Flounder	1.506±0.354	0.323±0.145	0.139±0.097	0.386±0.137	0.327±0.088	0.096±0.018	5.698±1.369	1.123±0.801	1.937±1.057
Cod	0.217±0.046	0.515±0.259	0.429±0.134	0.191±0.037	0.354±0.035	nd	0.555±0.117	nd	0.336±0.087
Assortment	Lipid content (%)	Content (μg/kg lipids)							
	α-HCH	β-HCH	γ-HCH	Heptachlor	Aldrin	Heptachlor epoxide isomer B	pp'-DDE	Endrin	pp'-DDT
Herring	19.64	3.25±1.40	0.71±0.42	0.31±0..19	0.21±0.13	0.92±0.51	0.21±0.14	19.68±4.09	14.52±5.14	9.80±3.10
Salmon	9.71	31.70±3.16	0.94±0.11	1.10±0.06	1.31±0.06	0.44±0.23	0.35±0.17	29.90±6.76	5.23±1.19	13.30±2.16
Carp	14.32	4.32±1.60	2.14±1.9	2.17±0.29	0.73±0.60	0.83±0.54	0.13±0.09	11.67±3.07	3.16±0.53	3.23±1.30
Trout	10.28	29.39±7.54	1.34±0.85	3.44±1.04	1.98±0.90	5.83±2.13	0.18±0.09	12.13±3.34	nd	5.42±2.66
Flounder	16.75	8.99±2.11	1.93±0.15	0.83±0.69	2.30±0.23	1.95±0.55	0.57±0.27	34.02±13.70	6.70±2.96	11.56±3.94
Cod	3.48	6.24±1.60	14.80±2.17	12.33±1.06	5.49±1.13	10.17±3.50	nd	15.95±1.32	nd	9.66±4.07

nd = not detected

significant ($p<0.05$) changes in muscle tissue pesticide content were observed in the case of single compounds only (Table 3).

Of all the pesticides examined, the highest losses on the wet weight basis were observed for β-HCH (32.3%) and endrin (31.4%) residues. Of all the fish species examined, the highest losses of the pesticides analysed occurred in salmon and herring meat (28%), and the lowest were found in cod meat (10%).

According to Sikorski [2004], meat of lean marine fish usually contained *ca.* 0.1 μg of DDT and its metabolites per 1 g tissue, comparing to 1-2.5 μg/g in fatty fish meat and *ca.* 10 μg/g in their liver. As all organochlorides dissolve well in lipids, the other chlorinated pesticides are also more abundant in fatty fish.

In fish harvested from ocean fisheries significantly lower pesticide levels were detected than in the fish from the Baltic catches. This might result from previous higher (by 40%) use of DDT in some Baltic countries. In Germany, for example, lindane was extensively used for forest pest control, and significant amounts of the compound were discharged with water to the sea [Bignert *et al.,* 1998; Barceló & Kettrup, 2004; Bonenberg, 1996].

High amounts of most organochlorine pesticides were also reported in fish oil. Research conducted in the early 1980s revealed, that fish oil concentrations of DDT and PCBs exceeded the maximum permitted levels in foodstuffs up to 200-fold [Biziuk *et al*., 2001; Biziuk, 2001].

Pesticide levels obtained in this study were significantly lower. However, as the fish were bought at retail and their origin is unknown, it is hard to directly compare the results with data reported in the literature.

Zabik *et al*. [1995a] reported that heat treatment of chinook salmon (*Oncorhynchus tshawytscha*) and common carp (*Cyprinus carpio*) resulted in a reduction of HCB, dieldrin and total DDT (sum of DDT isomers and metabolites) residues by 30-41%. Roasting, deep-frying or grilling reduced dieldrin content in meat of walleye (*Sander vitreus vitreus*) by 23.1% [Zabik *et al*., 1995b]. Pan-frying of white bass (*Morone chrysops*) was reported to reduce average levels of total DDT by 35.8%, chlordane complex by 37.5% and dieldrin by 34.8% [Zabik *et al.*, 1995b]. In the muscle tissue of lake trout (*Salvelinus namaycush namaycush*) subjected to different heat treatment techniques, the highest (over 50%) losses of HCB, total DDT and chlordane complex resulted from hot smoking. In contrast, boiling or grilling were less effective and reduced pesticide content by 12-38% on average [Zabik *et al*., 1996]. Puffer & Gossett [1983], in their study on white croaker (*Genyonemus lineatus*), observed that pan-frying resulted in 39-74% losses in the total DDT level.

Our study demonstrated pesticide residue losses (by average 10-32%) resulting from fish meat frying, however, the losses were slightly lower than those reported by other authors [Puffer & Gossett, 1983; Zabik *et al*., 19955a, b, 1996].

TABLE 3. Differences in lipids and pesticides content in the raw and fried fish meat ($p<0.05$), n=5.

Assortment	Lipids	α-HCH	β-HCH	γ-HCH	Heptachlor	Aldrin	Heptachlor epoxide isomer B	pp'-DDE	Endrin	pp'-DDT
Herring	+									
Salmon	+	+	+	+	+	+	+	+	+	+
Carp	+									
Trout	+		+				+	+		
Flounder	+				+					
Cod	+						+			

TABLE 4. Maximum residue levels of selected organochlorine pesticides in and on foodstuffs [Polish Journal of Laws 2007, No 119, item 817].

Pesticide name	Maximum Residue Levels (mg/kg product)		
	Fat contained in meat products	Milk and milk products	Eggs without eggshells
Aldrin (sum of aldrin and dieldrin, expressed as dieldrin)	0.2	0.006	0.02
DDT (sum of DDT, DDE and DDD) 1,1,1-tetrachloro-2,2-bis(4-chlorophenyl)ethane	1.0	0.04	0.05
Endrin	0.05	0.001	0.005
α-HCH alpha-hexachlorocyclohexane	0.2	0.004	0.02
β-HCH beta-hexachlorocyclohexane	0.1	0.003	0.01
γ-HCH gamma- hexachlorocyclohexane	0.7 poultry 0.02 other products	0.001	0.1
Hexachlorobenzene (HCB)	0.2	0.01	0.02
Heptachlor (sum of heptachlor and heptachlor epoxide expressed as heptachlor) 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	0.2	0.004	0.02
Metoxychlor (DMDT) 1,1,1-trichloro-2,2-bis(4-methoxyphenyl)ethane	0.01	0.01	0.01

Heat treatment was found to decrease the content of persistent organochlorine pesticides not only in fish meat, but also in other foodstuffs. Soliman [2001] reported that in fried potatoes lindane content was reduced by 30.1%, while that of HCB and p,p'-DDT – by 35%.

In the European Union legislation, maximum residue levels (MRL) of chlorinated pesticides in crops and food stuffs have been set regarding division into products of animal and plant origin. In Poland, maximum pesticide residue levels in crops and food stuffs are set by the Regulation of the Minister of Health of 16 May 2007 [Polish Journal of Laws 2007, No 119, item 817]. Classification of foodstuffs of animal origin is presented in Annex 3 to this Regulation [Polish Journal of Laws 2007, No 119, pos. 817, Annex 3, part A]. Levels of organochlorine pesticides analysed in this study were significantly lower than the legally binding MRLs (Table 4).

CONCLUSIONS

In the raw fish meat, the dominant compound was pp'DDE; with its highest level (7.33 μg/kg w.w.) being found in flounder, and the lowest (0.58 μg/kg w.w.) in cod.

In all the examined fish species, the less abundant compound was heptachlor epoxide isomer B.

Frying reduced levels of persistent organochlorine pesticides in fish meat by 10-32% on average. The biggest loss was observed for βHCH in carp – 74.05%. Mean losses of the examined compounds ranged from 9.6% for heptachlor epoxide isomer B to 32.3% for β-HCH.

The levels of pesticides detected in the raw fish were low, and did not exceed the maximum permitted levels. Frying still reduced the content of persistent organochlorine pesticides in fish meat, improving the quality of the food product.

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