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Organochlorine Pesticides and Polychlorinated Biphenyls in Fish and Fish Products Consumed by the Population of the Republic of Belarus

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Polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and dioxins are on the list of persistent organic environmental pollutants (POPs). In 2001 in Stockholm Convention on POPs was passed which was signed by Belarus among others. According to the Convention the states-members undertake not to produce, sell, buy, use, carry through their territories, to destroy available supplies and to control POPs in the environmental objects. All these compounds have persistence, chemical stability, toxity, lipophilicity and tend to bioaccumulate in the adipose tissue of humans and animals.

Earlier we studied the levels of OCPs in human milk, foodstuffs and human adipose tissue in Belarus (Barkatina et al. 1998; 1999; 2002). It has been shown that among foodstuffs fish and fish products have the highest POP concentrations (Renterghem et al. 2002). Therefore it was of great interest to study the levels of residual quantities (RQ) of PCBs and OCPs in fish and fish products consumed by the Belarusian population.

In Belarus the sum of RQs of PCBs and the following OCPs are considered to be normal: the sum of isomers of hexachlorocyclohexane (HCH) (α-, β-, γ-isomers), heptachlor, aldrin, p, p'-DDT and its metabolites p, p'-DDD and p, p'-DDE (total).

Seven PCB congeners called prevalent are found mostly in the environment (Renterghem et al. 2002). They are PCB 28 (2,4,4' - trichlorobiphenyl), PCB 52 (2,2',5,5'-tetrachlorobiphenyl), PCB 101 (2,2',4,5,6'-pentachlorobiphenyl), PCB 118 (2,3',4,4',5'-pentachlorobiphenyl), PCB 138 (2,2',3, 4,4',5,5'-hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'- hexachlorobiphenyl), PCB 180 (2,2',3, 4,4',5,5'-heptachlorobiphenyl). In the present paper RQs of 15 contaminants in samples of fish and fish products were determined (eight OCPs and seven PCBs).

MATERIALS AND METHODS

The fresh-frozen fish and fish products samples were taken in the shops of Minsk in 2004.

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J.T. Baker standards (P.O. Box 1, Deventer 7400 AA, Holland) were used for the determination of OCPs. Restek Corporation standards, which are the solutions of individual PCBs at a concentration of 10 μg/ml in isooctane, were used for determination of PCBs.

The fish and fish products samples (5g) were ground with anhydrous sodium sulfate and placed then into an extraction flask. Pesticides and polychlorinated biphenyls were extracted with two 50 ml portions of mixture of hexane and acetone 1: 1 each for 1.5 hours. The combined extracts were filtered into a round-bottom flask, the solvent was evaporated using a rotary evaporator for 20 min at 35°C until 1 ml. The residue was dissolved in 30 ml of hexane and cleaned up with concentrated sulfuric acid, washed with distilled water and with 1% sodium bicarbonate solution and again with water until a neutral reaction. The cleaned extract was dried by anhydrous sodium sulfate, filtered into a round-bottom flask, the solvent was evaporated using a rotary evaporator for 7-8 min at 35°C until 1-2 ml. The residue was evaporated with nitrogen to dryness and further dissolved in 1 ml of hexane.

A Perkin Elmer Model 8700 gas chromatograph with electron capture detector and a silica capillary column DB-1701 (30m length, 0,25 mm id, 0,25 μm film thickness) were used. To verify the results a silica capillary column RTX-1 (60 m length, 0,32 mm id, 0,25 μm film thickness) was used. The temperature programme was the following: from 100°C to 200°C, speed 30° /min, then to 260°C, speed 3°/min and to 280°C, speed 30°/min (3 min hold). The injector temperature was 250°C, detector temperature - 300°C. Hydrogen was used as a carrier gas.

Quantitative analysis was carried out by an absolute calibration method on peak squares. Each sample was analysed three times. The recovery of OCPs and PCBs ranged within 80-90%. The mean relative square deviation did not exceed 15%. Sensitivity of the method was 0.1 ng/g of the natural product. The method used allows the analyzing of RQs of the seven prevalent PCBs and eight OCPs in one sample as the components being determined separate under the indicated conditions.

RESULTS AND DISCUSSION

In the samples analysed heptachlor, aldrin, β-HCH and DDT were not found. α-, γ-isomers of HCH were found in 33% and 11% of the samples (0.0010-0.0057 mg/kg natural product (np) and 0.0004-0.0005 mg/kg np respectively). DDE and DDD were found in 61% and 21% of the samples (0.0002-0.0320 and 0.0003 - 0.0152 mg/kg np respectively). Of the seven PCBs in the studied samples the most frequent congeners were PCBs 101 and 118 (50 % of the samples; 0. 0016-0.0130 mg/kg np and 0.0004-0.0118 mg/kg np respectively). PCB 153 was found in 33% of the samples (0.0003-0.0258 mg/kg np). PCBs 128 and 138 were found in 28% of the samples (0.0006 -0.0044 mg/kg np and 0.0010-0.0032 mg/kg np respectively).

The results were compared with the certified standards of the Republic of Belarus (Table 1.). Concentrations of OCPs found in the samples are much lower than the certified standards. The total quantity of PCBs in the analysed fish and fish products samples are also far lower than the standards and range between "not found" and 0.0804 mg/kg.

Table 1. Residual quantities of isomers of HCH, DDT and metabolites, sums of polychlorinated biphenyls in fresh-frozen fish and fish products compared with certified standards of the Republic of Belarus, mg/kg natural product.

Species	HCH isomers		DDT and metabolites		Totals of PCBs	
	Results of the study	Certified standards	Results of the study	Certified standards	Results of the study	Certified standards
Haddock (Iceland)	0.0004	0.2	0.0004	0.2	0.0020	2.0
Navaga (Russia)	0.0010	0.2	*	0.2	0.0007	2.0
Horse-mackerel (N. Zealand)	0.0028	0.2	*	0.2	0.0079	2.0
Hake (USA)	*	0.2	*	0.2	*	2.0
Pike (Belarus)	*	0.2	*	0.2	*	2.0
Cusk (Norway)	0.0020	0.2	0.0013	0.2	0.0022	2.0
Hunchback salmon (Russia)	0.0040	0.2	0.0008	0.2	0.0032	2.0
Mackerel (Norway)	0.0020	0.2	*	0.2	*	2.0
Sprat (Russia)	0.0012	0.2	0.0115	0.2	0.0089	2.0
Saithe (Russia)	*	0.2	0.0010	0.2	0.0032	2.0
Argentine (Norway)	0.0016	0.2	*	0.2	*	2.0
Herring (Norway)	*	0.2	0.0002	0.2	0.0036	2.0
Salmon (Denmark)	0.0057	0.2	0.0078	0.2	0.0052	2.0
Shrimps (Russia)	0.0020	0.2	*	0.2	*	2.0
Canned red caviar (Russia)	0.0044	0.2	0.0002	2.0	0.0036	2.0
Sprats in oil (Russia)	*	0.2	0.0039	0.4	0.0079	2.0
Scomber (cold smoking) (Norway)	0.0036	0.2	0.0021	0.4	0.0136	2.0
Canned cod liver (Russia)	0.0055	1.0	0.0472	3.0	0.0804	5.0

* - not found

The highest level of RQ of OCPs and PCBs are found in cod liver. To compare contamination levels of OCPs and PCBs in fish and fish products with

the results of other authors the moisture in the studied samples was determined and concentration of the contaminants in mg/kg dry mass (dm) was calculated (Tables 2 and 3). The highest level of PCB contamination in fish in the USA, Canada, and France is 2 mg/kg dm (Lazaro et al. 1999). In the studied fish and fish products samples concentrations of RQs of OCPs in the cleanest fish is 540 times as low as the standard and in the most contaminated fish - 15 times as low as the standard. (Table 3).

Table 2. Residual quantities of OCPs in fresh-frozen fish and fish products samples, mg/kg dry mass.

Species	HCH isomers			DDT and metabolites		
	α- HCH	γ- HCH	Sum of isomers	DDE	DDD	Sum of metabolites
Haddock	*	0.0014	0.0014	0.0014	*	0.0014
Navaga	0.0053	*	0.0053	*	*	*
Horse-mackerel	0.0073	0.0020	0.0093	*	*	*
Hake	*	*	*	*	*	*
Pike	*	*	*	*	*	*
Cusk	0.0102	*	0.0102	0.0066	*	0.0066
Hunchback salmon	0.0128	*	0.0128	0.0026	*	0.0026
Mackerel	0.0068	*	0.0068	*	*	*
Sprat	0.0045	*	0.0045	0.0169	0.0263	0.0432
Saithe	*	*	*	0.0042	*	0.0042
Argentine	0.0062	*	0.0062	*	*	*
Herring	*	*	*	0.0008	*	0.0008
Salmon	0.0110	*	0.0110	0.0116	0.0035	0.0151
Shrimps	*	*	0.0020	*	*	*
Canned red caviar	0.0148	*	0.0148	0.0007	*	0.0007
Sprats in oil	*	*	*	0.0052	0.0011	0.0063
Scomber (cold smoking)	0.0071	*	0.0071	0.0035	0.0006	0.0041
Canned cod liver	0.0089	*	0.0089	0.0517	0.0246	0.0763
Mean level	0.0052	0.0002	0.0056	0.0058	0.0031	0.0090

* - not found

FAO/WHO recommends the following highest levels for OCPs in meat and poultry: for the sum of DDT metabolites 5 mg/kg dm and for γ- HCH 2 mg/kg dm (Kannan et al.1997). The samples we have studied have RQs of OCPs

much lower than those recommended by FAO/WHO.

Table 3. Polychlorinated biphenyls in fresh-frozen fish and fish products samples, mg/kg dry mass.

Species	PCB 28	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	Sum of PCB congeners
Haddock	*	0.0068	*	*	*	*	0.0068
Navaga	*	*	0.0037	*	*	*	0.0037
Horse-mackerel	*	0.0230	0.0030	*	*	*	0.0260
Hake	*	*	*	*	*	*	*
Pike	*	*	*	*	*	*	*
Cusk	0.0030	0.0081	*	*	*	*	0.0111
Hunchback salmon	*	0.0103	*	*	*	*	0.0103
Mackerel	*	*	*	*	*	*	*
Sprat	*	0.0128	0.0068	0.0038	0.0102	*	0.0336
Saithe	*	0.0134	*	*	*	*	0.0134
Argentine	*	*	*	*	*	*	*
Herring	0.0054	0.0066	0.0017	*	0.0012	*	0.0149
Salmon	*	*	0.0014	0.0043	0.0045	*	0.0102
Shrimps	*	*	*	*	*	*	*
Canned red caviar	0.0088	*	0.0034	*	*	*	0.0122
Sprats in oil	*	*	0.0026	0.0037	0.0042	0.0023	0.0128
Scomber (cold smoking)	0.0014	0.0098	0.0016	0.0063	0.0071	0.0006	0.0268
Canned cod liver	0.0071	0.0210	0.0191	0.0325	0.0417	0.0044	0.1300
Mean level	0,0014	0.0062	0.0024	0.0028	0.0038	0.0004	0.0173

- * - not found
- PCB 52 present only in canned cod liver (0.0042 mg/kg dm); mean level 0.0002 mg/kg dm

In Table 4 the data from the literature on OCP and PCB contamination of fish and fish products are given. If to compare the results we have obtained with the data in the literature it becomes evident that the contamination levels of OCPs and PCBs in fish and fish products in the sample analysed range within those given in the scientific literature.

Table 4. Concentrations of PCB and OCP residual quantities in fish (mg/kg) according to the scientific data.

№	Species	PCB	OCP	Literary source
1	Fish Upper Thames	<0.00077-0.00332 7 congeners PCB: 28, 52, 101, 118, 138, 153, 180	Lindane <0,00008-0,00494	Yamaguchi et al. 2003
2	Fish (np) Lake Baikal, Russia	0.02-0.193		Yufit 1998
3	Fish Mean concentrations of contaminants (dm), Canada	Sum of 102 congeners - 0.0816	Sum of HCH 0.00216; sum of DDT 0.0579	Kidd et al. 1998
4	Sea fish Mean concentrations of contaminants (dm), Canada Canned fish	PCB 28 - 0.00001; PCB 52 - 0.00016; PCB 118 - 0.00039; PCB 153 - 0.00063; PCB 138 - 0.00543; PCB 180 - 0.00022; PCB 28 - 0.00014; PCB 52 - 0.00018; PCB 118 - 0.00020; PCB 153 - 0.00031; PCB 138 - 0.00028; PCB 180 - 0.00008		Newsome, Davies 1998
5	Fish Atlantic	0.114 - 0.748		Salama et al. 1998
6	Fish Mean concentrations of contaminants (dm), Indonesia Vietnam Australia India	0.0038 0.0031-0.0240 0.00022-0.72 <0.01-0.11	HCH 0.0014; DDT 0.0290 HCH 0.00058-0.0040 DDT 0.0039-0.0760 Aldrin and dieldrin <0.0001-0.0011 HCH <0.00001-0.0021 DDT 0.00014-0.230 Heptachlor <0.01 Aldrin and dieldrin <0.01	Kannan et al. 1997

Residual quantities of the seven prevalent PCBs and eight OCPs determined in the tested samples of fish and fish products were much lower than the standards adopted in the USA, Canada, France, the Republic of Belarus and also those recommended by FAO/WHO.

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