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Organochlorine Pesticide Residues in Basic Food Products and Diets in the Republic of Belarus

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Inexpensive and efficacious organochlorine pesticides (OC's) are still being used by a number of countries in Latin America, Africa, Asia ignoring its unhealthy consequences. In this connection the problem of the content of OC's in environment objects is given consideration in scientific literature. The content of OC's in human blood and in breast milk as well as their accumulation in adipose tissue was studied in some works (Minelli et al 1996; Burgaz et al 1995). However, in the greater part of studies the pesticide residues in food-stuffs were investigated (Osibanjo et al 1995; Dua et al 1996; Zabik et al 1995; Sofjina et al 1991).

Breast milk of women in Belarus is polluted with OC's, as reported earlier (Barkatina et al 1998). The investigation of OC's in basic food products used by the inhabitants of Belarus as well as the estimation of daily OC's intake based on the amount consumed per day in a usual diet was of great interest.

The purpose of the present study was to test the content of OC's (α–, β–, γ–hexachlorcyclohexane (HCH), heptachlor, aldrin, p,p'-DDE, p,p'-DDD, p,p'-DDT) in food-stuffs of local industry and some imported products. Daily OC's intake based on the amount consumed per day in a usual diet has been estimated.

MATERIALS AND METHODS

Samples of meat (beef pork, chicken), eggs, dairy produce (milk, butter, cottage cheese, sour cream), vegetables (potatoes, carrot, beetroot, cabbage), rye and wheat bread were investigated as basic food-stuffs. The products studied were of local industry and taken from the regions which differ in ecological conditions. Logoysk and Soligorsk towns, Komsomolskaya village of Kopyl district (all Minsk region), Bobruisk town (Mogilyev region), Novopolotsk town (Vitebsk region), Maleshevo village of Slonim district (Brest region) were selected. Komsomolskaya village and Logoysk were chosen as a control zone free from chemical and industrial factories and which are not exposed to radionuclides influence. Potash fertilizers are mined in Soligorsk. Woodworking and tire industries can be found in Bobruisk. Oil-refining industry is concentrated in Novopolotsk. Maleshevo village is known as an area with high sickness rate both

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of grown-ups and children.
Diets of pregnant women and nursing mothers were obtained from the 7th hospital of Vitebsk (Belarus). Freshwater fish samples were taken from Naroch fishing factory. Chilled sea fish and canned fish samples (all imported) were also studied, Besides, OC's in bilberries and cowberries taken from different regions were investigated, as forest-berries are widely consumed by the local inhabitants.

J.T. Baker standards (Ultra Scientific type) were used

Samples collected for analysis were prepared in the following way.

Water samples (50 ml) were placed in a separating funnel. Pesticides were extracted by shaking with 20 ml portions of hexane for 2-3 minutes two times. The extracts were cleaned up with concentrated sulphuric acid and washed then by distilled water and 1% solution of sodium bicarbonate till neutral reaction. The cleaned extract was dried by anhydrous sodium sulfate, filtered into a round-bottom flask, the solvents were evaporated and the residue was dissolved in 1 ml of hexane.

Milk samples were prepared in similar way with breast milk samples preparation (Barkatina et al. 1998).

Sour cream samples were prepared in the following way. 10 ml of saturated solution of sodium chloride was added to sour cream sample (5 g), and the resulted emulsion was placed in a separating funnel with 40 ml acetone and was extracted by chloroform (70 ml). After the phases had been separated the low layer was moved to a round-bottom flask and the solvents were evaporated. The residue was dissolved in 30 ml of hexane and cleaned up with concentrated sulphuric acid. The subsequent analysis was carried out like in water sample case (stated above).

Cottage cheese sample preparation was slightly different from that of sour cream **(stated** above). Sample of cottage cheese was ground in saturated solution of sodium chloride, placed then in an extraction flask and extraction was carried out.

Crumbled bread samples (10 g) were extracted with 30 ml portions of hexane two times. Cleaning and subsequent analysis were carried out like in water sample case (stated above).

Fish and meat samples (5 g) were rubbed in a mortar with anhydrous sodium sulfate and placed in an extraction flask. Pesticides were extracted with 30 ml portions of 1:1 hexane-acetone mixture for 1,5 hours two times. The united extracts were filtered into a round-bottom flask and the solvents were evaporated. The dry residue was dissolved in 30 ml of hexane, cleaned up with sulphuric acid. The subsequent analysis was carried out like in water sample case (stated above).

50 ml of acetone was added to egg (only yolks had been taken and the calculation of the results for the whole egg were made then) and butter samples (5 g). The mixture was heated in hot water bath till the solvent's boiling. After it had been cooled, 10 ml of 2% solution of sodium sulfate was added to the flask and the mixture was frozen for 45 min. The acetone layer was filtered through cotton wool into a round-bottom flask. Acetone extraction and the following freezing of fat were repeated two more times. Acetone was evaporated out of the united extracts and pesticides were extracted out from the water phase with 20 ml portions of hexane. The extracts were cleaned up then with sulphuric acid and the subsequent analysis was carried out like in water sample case (stated above).

Vegetables samples as well as forest-berries (10 g) were ground and placed in a flask. Pesticides were extracted with 30 ml portions of 4:1 hexane:acetone mixture two times. The extracts were filtered. The solvent was evaporated, the dry residue was dissolved in 30 ml of hexane, cleaned up with sulphuric acid and the subsequent analysis was carried out like in water sample case (stated above).

Gomogenized diets samples (10 g) were placed in a flask. Pesticides were extracted with 30 ml portions of 1:2 hexane:acetone mixture three times. The subsequent analysis was carried out like in vegetables samples.

A Perkin Elmer Model 8700 gas chromatograph equipped with electron capture detector and a fused silica capillary column (30 m length, 0.25 mm id) with methyl-silicon liquid phase DB-1 were used. The range of programmed temperature was from 170 to 230°C speed 3°/min. The injector and detector temperature were 210° and 300°C. Argon was used as a carrier gas. Quantitative analysis was carried out by an absolute calibration method on peak squares, Each product was analyzed three times. The recovery of OC's was ranged within 75-90%. The mean relative square deviation of OC's determination did not exceed 15%. Sensitivity of the method made up 0,01-0,05 μg/kg of product.

RESULTS AND DISCUSSION

The content of OC's in main food-stuffs of local industry is given in Table 1. Heptachlor, aldrin, DDT and its metabolite DDD were not detected in all the tests, More toxic than DDT itself its metabolite DDE was found most often (in 43 from 58 tests) in trace or small quantities (from 0.1 μg/L in water to 7 μg/kg in sour cream). Small quantities of HCH-isomers (from 0.5 μg/kg in potatoes and beetroot to 11 μg/kg in sour cream) were detected in 17 from 58 tests. Moreover a-HCH was found in 3 tests only (in beef, butter and eggs), γ-HCH - in 5 tests (in cottage cheese, pork eggs, potatoes and beetroot). HCH was in the p-form in the rest of the tests. Only in eggs from Logoysk town of Minsk region HCH-isomers were tested simultaneously in the α–, β– and γ-forms. The content of OC's in basic food products of local industry was much less than FAO/WHO standards (FAO/WHO 1993). In forest berries from various regions of Belarus trace or small quantities of OC's were found: from <0.1 to 0.2 μg/kg of DDE in 5 tests of cowberries, from 0.1 to 1.6 μg/kg of DDE and from 0.2 to 1.5 μg/kg of

Table 1. Organochlorine pesticide residues content in main food-stuffs in some regions of the Republic of Belarus (μg/kg)

Products	Komsomolskaya village				Soligorsk				Logoysk				Bobruisk				Novopolotsk				Maleshevo village			
	DDE	HCH			DDE	HCH			DDE	HCH			DDE	HCH			DDE	HCH			DDE	HCH		
		α	β	γ		α	β	γ		α	β	γ		α	β	γ		α	β	γ		α	β	γ
Water	*	*	*	*	0,1	*	*	*	0,1	-			*	*	*	*	0,1	*	*	*	-	-		
Milk	*	*	*	*	1,0	*	*	*	1,0	-			*	*	3,0	*	-	-			2,6	*	0,7	*
Cottage cheese	*	*	*	*	2,0	*	*	*	2,0	-			0,2	*	*	2,5	*	*	*	*	-	-		
Sour cream	-	-			-	-			1,5	-			*	*	5,0	*	1,0	*	2,0	*	7,0	*	11,0	*
Wheat bread	-	-			-	-			1,0	-			*	*	0,8	*	0,2	*	*	*	-	-		
Rye bread	-	-			-	-			*	*	*	*	1,0	*	*	*	*	*	*	*	-	-		
Beef	-	-			-	-			2,0	*	*	*	*	*	*	*	1,5	0,5	*	*	3,0	*	*	*
Pork	0,6	*	*	*	1,0	*	*	*	-	-			0,5	*	*	*	1,0	*	1,0	1,5	3,0	*	*	*
Force-meat	-	-			1,0	*	*	*	-	-			-	-			-	-			-	-		
Chicken	-	-			-	-			6,0	*	*	*	*	*	4,0	*	*	*	1,0	*	-	-		
Eggs	-	-			-	-			2,0	0,3	1,3	0,1	0,3	*	0,7	*	0,3	*	1,4	*	1,0	*	*	*
Butter	-	-			-	-			-	-			-	-			1,5	2,5	6,0	*	-	-		
Potatoes	*	*	*	*	*	*	*	*	0,4	*	*	*	*	*	*	*	*	*	*	*	0,6	*	*	0,5
Beetroot	1,0	*	*	*	1,0	*	*	*	0,2	*	*	*	0,1	*	*	*	*	*	*	*	0,8	*	*	0,5
Carrot	0,2	*	*	*	*	*	*	*	-	-			-	-			0,2	*	*	*	1,0	*	*	*
Cabbage	-	-			1,0	*	*	*	0,7	*	*	*	-	-			0,2	*	*	*	-	-		

Foot-note: FAO/WHO (FAO/WHO 1993) standards. The sum of DDT-metabolites: cereal grains 0,1 mg/kg; eggs 0,5 mg/kg; meat 5,0mg/kg; milk – 0,05 mg/kg. Lindane: cereal grains 0,5 mg/kg; eggs – 0,1 mg/kg, meat 2 mg/kg; milk 2 mg/kg. * - not found.

β -HCH in 24 tests of bilberries. DDE and β -HCH were found in each test of bilberries.

The results of OC's studying in 19 samples of freshwater fish, chilled sea fish and canned fish consumed in Belarus are given in Table 2. Heptachlor and aldrin were not found in all the tests. There were α–, β–, γ-isomers of HCH as well as DDT and its metabolites DDE and DDD in fish products. α–, β–, γ-HCH, DDE, DDD, DDT were detected in 4 from 19 samples. The residues of 5 OC's were found in 6 of 19 samples investigated: in 3 cases - α–, β–, γ-HCH and DDE, DDD, DDT, in other cases - α–, β–, γ-HCH and DDE, DDD. The maximum quantity of OC's was present in eel from Swir lake (Belarus) and in cod liver (Ust-Louzhskiy fishing factory, Russia). In the first case the total quantity of HCH-isomers made up 15.5 μg/kg, and that of DDT-isomers did 76.5 μg/kg, in the second case the sum of HCH-isomers made up 0.8 μg/kg, and that of DDT-isomers did 65 μg/kg. Chromatogram turned out of the investigation of OC's in fresh bream from Myastro lake (Belarus) is given in Fig. 1.

For the rest of fish samples analysed the OC's-values changed within the limits from 0.1 to 11.0 μg/kg of the sum of HCH-isomers and from 0.1 to 26.0 μg/kg of the sum of DDT-isomers.

Fish in village ponds of India has OC's for the sum of HCH-isomers of 6300 μg/kg and for the sum of DDT-metabolites of 7077 μg/kg (Dua et al 1996). White perch and walleye from the Great Lakes (the USA) contain the residues of the sum of DDT-metabolites of 110-139 μg/kg and 78-83 μg/kg respectively (Zabik et al 1995). Fish in Venezuela (Urdaneta H et al 1995) contains HCH-isomers (from 79 to 831 μg/kg), heptachlor, aldrin, endosulphan, endrin, metoxychlor and DDT-metabolites (from 37 to 1315 μg/kg). OC's content in sea and freshwater fish from various reservoirs of the Caspian Sea basin was studied too (Zimakov et al 1991). Sea and freshwater fish contain the residues of the sum of HCH-isomers and the one of DDT-metabolites ranged within 12-18 μg/kg and 199-262 μg/kg respectively.

14 hospital diets were studied for the estimation of daily pesticides intake per person. It has been showed that 10 diets contained only the residues of DDE and 4 samples didn’t contain OC's. The daily intake of the sum of DDT-metabolites per person made up 2-5 μg, and the values of the mean daily intake of OC' s per kg of human body mass varied within the limits of 0.03-0.05 μg/kg. The results coincide well with those given in scientific studies. So, according to the data of the Japanese scientists (Nakagawa 1995) the daily intake of the sum of DDT-metabolites per person makes up 1.42 μg in Japan, and the mean daily OC's intake based on the amount consumed per day makes up 0.007-0.7 μg per kg of human mass (Sofina 1991) in Krasnodar territory of Russia. In the study of Spanish investigators (Herrera et al 1996) the mean daily OC's intake of the inhabitants of Spain is estimated as the sum of DDT-metabolites equal to 1.22 μg a day. The permissible daily standards of FAO/WHO make up 1200 μg/day for

Table 2. Organochlorine pesticide residues content in fish and canned fish (μg/kg)

№	Fish	Storing place	α-HCH	β-HCH	γ-HCH	DDE	DDD	DDT
Freshwater fish								
1	Bream	Myastro lake	0,4	*	0,5	4,0	0,3	0,4
2	Perch	Swir lake	0,1	*	0,1	7,5	0,3	0,3
	Roach	Myastro lake	0,1	*	0,1	2,0	*	*
4	Eel	Swir lake	6,0	3,5	6,0	64,0	10,0	2,5
5	Crucian Chilled	Kazakhstan	0,2	0,3	0,3	0,2	*	*
Chilled sea fish								
1	Hake	The Atlantic	0,4	1,0	0,7	1,4	0,2	0,3
2	Pollack	---«---	*	*	0,1	0,5	*	*
3	Cod	---«---	*	0,4	0,1	4,0	*	*
4	Pollack	---«---	*	*	*	0,1	*	*
5	Pollack	---«---	0,1	0,5	0,1	0,8	<0,1	0,3
6	Herring	---«---	0,1	*	0,5	7,0	2,0	5,0
7	Poutasseau	---«---	1,0	2,5	0,7	1,0	0,1	0,1
8	Scomber	---«---	0,1	*	*	0,1	*	*
Canned fish								
1	Maasbanker	Russia	0,2	*	0,1	0,6	*	*
2	Baltic spiced sprats in tomato sauce	Countries of the Baltic Sea	0,4	0,8	0,4	3,0	7,0	*
3	Rigas sprats	---«---	2,0	6,0	3,0	16,0	10,0	*
4	Sprats pate	---«---	1,5	2,0	1,0	10,0	4,0	*
5	Natural herring with oil additives	---«---	2,0	*	2,0	*	0,8	*
6	Cod liver	OAO Ust-Louzhskiy fishing factory, Russia	0,8	*	*	30,0	3,0	32,0

* - not found

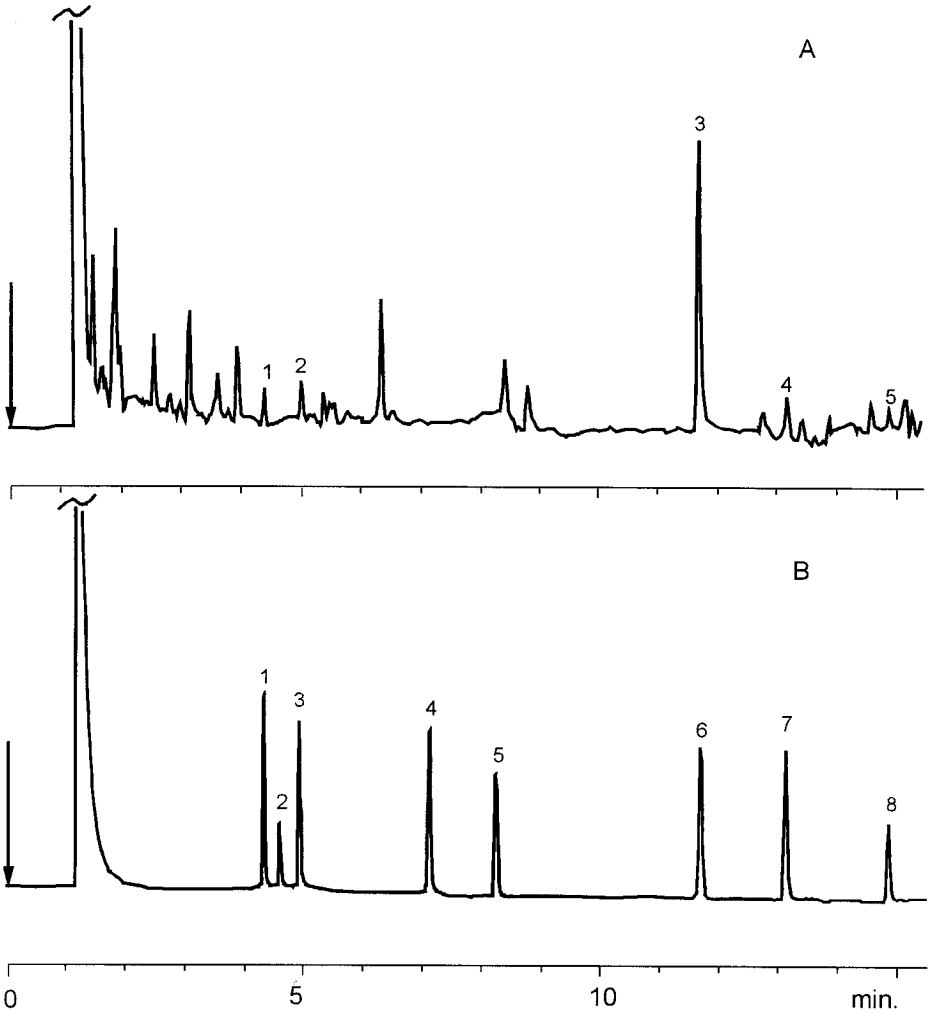

Figure 1. A. A gas chromatogram of organochlorine pesticide residues in fresh bream from Myastro lake (Belarus). 1- α-HCH, 2 - γ-HCH, 3 - DDE, 4 - DDD, 5 - DDT. **B.** A gas chromatogram of organochlorine pesticide standards in hexane (concentration 20 ng/μL). 1,2,3 - α–,β–, γ-HCH, 4 - heptachlor, 5 -aldrin, 6 - DDE, 7 - DDD, 8 - DDT.

the sum of DDT-metabolites and 480 μg/day - for the lindane (Herrera 1996). Thus, the test of basic food-stuffs and hospital diets from various regions of Belarus as well as fish and fish products of local industry and imported has showed the presence of small quantities of HCH-isomers and DDT-metabolites. Samples of food-stuffs which contained OC's above FAO/WHO standards haven't been found. The estimation of hospital diets has showed that the mean daily OC's intake was below FAO/WHO standards too.

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