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RESIDUES OF CHLORINATED PESTICIDES AND TOXIC ELEMENTS IN SOME MARINE FISH SPECIES

SPIRIĆ AURELIJA, SAIČIĆ SNEŽANA, JANKOVIĆ S. and RADIČEVIĆ TATJANA

Institute of Meat Hygiene and Technology, Kaćanskog 13, P.O. Box 33-49, 11000 Belgrade, Yugoslavia

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The use of many chemicals in agriculture and industry, with the aim of public health protection, requires evaluation of their concentrations in the environment as well as in the food chain. Among these chemicals, chlorinated pesticides and toxic elements (As, Pb, Cd, Hg) are the most extensively studied due to their toxicity and bioaccumulation. In marine fish, residues of these chemicals might have two impacts on public health: by human consumption of fish or through fish meal, which as a component of animal diets might carry residues into the animal body. By consumption of meat, an individual is indirectly exposed to chlorinated pesticides and toxic elements. Therefore, the aim of this work was to examine the content of chlorinated pesticides and toxic elements in some imported marine fish species, as an indication of the degree of exposure.

The content of chlorinated pesticides and toxic elements was determined in eight species of imported marine fish that are most often consumed in this country. Chlorinated pesticides were determined in 192 and toxic elements in 153 fish samples. Of all chlorinated pesticides, lindane residues were detected in the largest number of examined samples (65.62%) and in the highest quantities (mean value 2.62 mg/kg fat). Total DDT was detected in 52.08% of the fish samples, with the highest mean value of 0.58 mg/kg of fat. The residues of other chlorinated pesticides detected in the examined fish samples were negligible. The results obtained indicate that the toxic element content of the examined marine fish samples does not present a potential health risk for consumers because levels were well below allowable limits.

Key words: residues, chlorinated pesticides, toxic elements, marine fish.

INTRODUCTION

Since 1947, when DDT was released for sale as the first pesticide, in order to increase food production, the number of compounds used as pesticides, the number of registered formulated products and the production of pesticides has

gradually increased (Matsumura *et al.*, 1972). The widespread use of these chemicals in the environment and the acquired knowledge concerning their persistence in the treated crops and in the earth, as well as the discovery of their genotoxic effects (mutagenic, teratogenic and carcinogenic) led to an official restriction or ban of the use of many pesticides (Brooks, 1975; Spendler, 1983; Doong and Lee, 1999). However, some chlorinated pesticides still remain the pesticides of choice for control of some insects in Third World countries (Abdulkah and Hassan, 1990; Kaphalia *et al.*, 1990).

Long term use of pesticides in agriculture and for public health protection has certainly led to pollution, not only of the lithosphere and its flora and fauna, but these contaminants also reach the hydrosphere. Pesticide contamination of the hydrosphere results from direct application to water media and wetlands for the control of vector insects or from discharge of industrial and sewage effluents. There are also some indirect sources of water contamination such as transport of residues from contaminated agricultural soils through erosion processes, aerial application of pesticides, and wash-off from atmosphere by precipitation, etc. Rivers subsequently contaminate salt waters by flowing into the sea. However, it is more likely that pesticide residues reach sea water from the atmosphere through rain or dust or even by surface interchange (Biddinger and Gloss, 1984). After the pesticides enter the aquatic environment, they may remain in solution, be precipitated and enter sediments or they might be adsorbed on suspended particles and enter plant and animal tissues, depending on their water solubility, adsorption properties and partition coefficients (Mulla *et al.*, 1981; Strandberg *et al.*, 1998a). The persistent and liposoluble chlorinated pesticides have a rather strong potential of food chain biomagnification and accumulate in fish and other aquatic fauna. This depends on the nature of the pesticide, pH-value, temperature, water salinity, redox potential, etc (Biddinger and Gloss, 1984; Strandberg *et al.*, 1998b; 1998c). The data on marine contamination by pesticides have been based on residue determination in plankton, aquatic invertebrates, fish and mammals (Edwards, 1975; Lehmann and Oetjen, 1998).

The presence of metal ions and metallic compounds in oceanic waters is a consequence of three main influences - natural occurrence, transport through river flows and atmospheric deposition. At present, it is more likely that oceans have been polluted mainly by atmospheric transport of anthropogenic aerosols (Nriagu, 1984; Alloway and Ayres, 1984).

Data in the literature suggest that, the lower marine forms of living organisms show higher accumulation of most of the toxic elements than the higher forms (Biddinger and Gloss, 1984; Nriagu, 1984). It seems that biomagnification of these chemicals, with the exception of mercury and arsenic, at higher trophic levels is not a problem in the marine environment (Bu Olayan and Al Yakoob, 1998; Parsons, 1998). Thus, apart from mercury and arsenic, the other toxic elements probably do not present a danger to human consumers of fish. Residues of chlorinated pesticides, and toxic elements in marine fish might have a direct impact on public health, through consumption of fish. The indirect public health concern arises because residues can enter the animal body and further into the human food supply through fish meal, which is a component of animal feeds.

In this work we present the results of a four-year investigation of chlorinated pesticides and toxic elements in imported marine fish.

MATERIAL AND METHODS

According to the official Instructions on Sampling (Uputstvo o načinu uzimanja uzoraka, 1978), samples were randomly taken by the veterinary inspection at the state border, properly packed and marked. Accompanied by the appropriate documentation, samples in the frozen state were sent to our laboratory for analysis.

The head, tail, back bone and fins were removed from the partially frozen fish. Edible parts were chopped into 2-3 cm thick portions and homogenised with a mixer. Appropriate amounts of each sample were weighed for determination of fat content (in duplicate), chlorinated pesticides and toxic element residues.

Fat content in fish samples was determined by Soxhlet extraction (JUS ISO 1444, 1998). Residues of chlorinated pesticides and toxic elements were detected according to the USDA Analytical Chemistry Laboratory Guidebook (1991). Chlorinated hydrocarbons were extracted and separated from fat by elution in small glass columns filled with partially deactivated alumina. The eluate was evaporated to a small volume and transferred to a volumetric flask. A portion was injected into a gas chromatograph for qualitative and quantitative analysis. The amount of each residue detected was expressed in relation to fat content and fresh weight of sample.

To analyze for trace elements, the matrix was completely destroyed by heating (600^{o}C). The ash residue was dissolved in hydrochloric acid, and trace elements were determined by AAS. Mercury was determined by a cold-vapor technique after wet digestion. Arsenic was determined spectrophotometrically at 840 nm as a molybdenum blue complex.

The accuracy of the obtained data was estimated by recovery of compounds and elements from spiked samples. Thus, one blank and one spiked sample were analysed with each set of samples.

The aded quantities of chlorinated pesticides and toxic elements were in the range of concentrations expected for the relevant compounds in the analysed samples. The results obtained were corrected for recovery of the corresponding compound or element in the spiked and blank samples. Depending on the compound or element, acceptable recoveries ranged from 70 to 100%. When the recoveries were not within the acceptable range, the results were rejected and the reasons for deviation established and eliminated.

RESULTS AND DISCUSSION

A total of 192 marine fish samples of eight different species (Hake, Dentex, Grooper, Pilchard, Sprat, Gilthead bream, Mackerel, Herring) was examined for residues of chlorinated pesticides. Trace elements (As-arsenic, Cd-cadmium, Hg-mercury, Pb-lead) content was determined in 153 marine fish samples of the same species. The investigated fish included the imported fish species usually consumed in this country. The research was limited to the detection of chlorinated pesticides and some toxic elements in the edible part, i.e. muscle tissue, of the fish.

The national residue limits established for chlorinated pesticides in fish requires expression of the results in relation to fish fresh weight, when the fish species contains less than 10% fat, and on a fat basis, when the fish species

contains more than 10% fat (Pravilnik o količinama...., 1992). Therefore our results for all fish species are presented in both ways. The allowed residue limits in the first case are 0.01 mg/kg for HCB (hexachlorobenzene), α-HCH (-hexachlorocyclohexane), lindane and heptachlorepoxide and 0.1 mg/kg for total DDT. When the results are expresed on a fat basis the residue limits are ten times higher.

The results obtained for chlorinated pesticide residues in imported marine fish, expressed on a fat basis, are presented in Table 1. Table 2 gives the results for pesticide residues detected in the same samples, but expressed in relation to fresh weight. The organochlorine pesticide residues detected were HCB, α-HCH, lindane, heptachlor epoxide, pp'DDT and its metabolites (pp'DDE and pp'DDD), expressed as total DDT. Other chlorinated pesticides such as aldrin, dieldrin, heptachlor and chlordane were not detected.

As can be seen in Table 1. lindane residues were detected in 65.62% of the examined samples, followed by total DDT - 53.65% and its very persistent metabolite pp'DDE, which was detected in 52.08% of the examined samples. Apparently large quantities of lindane were detected in hake (maximum value 101.18; mean value 2.62 mg/kg of fat) and gilthead bream (maximum value 8.91; mean value 1.79 mg/kg of fat). However, taking into consideration the average fat content of these two species of fish (1% for hake and 8.5% for gilthead bream), man's daily intake of lindane would be 8.5 times higher if gilthead bream is consumed compared with an equivalent intake of equally contaminated hake. Generally, because of the fat solubility of chlorinated pesticides, the higher the fat content of the fish species, the greater the intake of pesticide per unit weight of ingested fish. The quantities of other residues detected in the examined fish samples, with the exception of DDT, were negligible. The highest value for DDT (4.41 mg/kg of fat) was detected in mackerel, but the highest mean value was found in Grooper (0.58 mg/kg of fat) and sprat (0.52 mg/kg of fat).

Similar conclusions can be deducted from Table 2. where pesticide residues, are expressed in relation to fish fresh weight. The number of samples assessed as contaminated was of course, much lower than in Table 1. but the most frequently detected pesticides were the same - lindane and DDT in hake, gilthead bream and mackerel. These results are more indicative for evaluation of the actual intake of chlorinated pesticides when consuming different fish species.

The results obtained for the pesticide residues detected in marine fish samples indicate pollution of sea water fish with the worldwide most frequently used and most persistent pesticides - lindane and DDT (Brooks, 1975; Edwards, 1975; Alloway and Ayres, 1984).

The residues of toxic elements (arsenic, cadmium, lead and mercury) found in the examined species of marine fish are shown in Table 3. The mean values for toxic elements in marine fish are much lower than the residue limits for arsenic, cadmium, lead and mercury (2; 0.1; 1 and 0.5 mg/kg respectively). These residue levels in imported fish have no great direct potential impact on public health. Although data in the literature (Alloway and Ayres, 1984; Bu Olayan and Al Yakoob, 1998) point to biomagnification of arsenic and mercury in higher trophic levels of the marine environment, the results obtained for these two toxic elements do not show a significant difference in relation to the cadmium and lead contents detected.

Table 1. Chlorinated pesticide residues detected in imported marine fish, (mg/kg of fat)

		fish species								total	
		Hake	Dentex	Grooper	Pilchard	Sprat	Gilthead bream	Mackerel	Herring	No	%
	total number of samples	67	10	9	20	25	7	43	11	192	100
	the average fat content, %	1.0	1.5	3.4	7.2	8.2	8.5	16.0	19.0		
Pesticides detected											
	contaminated samples	13	1	0	2	9	1	4	2	32	16.67
HCB	max	0.84	0.07	/	0.02	0.04	0.15	0.02	0.01		
	mean	0.13	0.07	/	0.02	0.03	0.15	0.02	0.01		
	contaminated samples	12	1	0	1	6	0	2	1	23	11.98
αHCH	max	0.80	0.07	/	0.01	0.05	/	0.06	0.04		
	mean	0.20	0.07	/	0.01	0.02	/	0.04	0.04		
	contaminated samples	56	7	4	6	21	6	20	6	126	65.62
Lindane	max	101.18	3.33	2.45	0.67	0.34	8.91	0.28	0.07		
	mean	2.62	0.59	0.67	0.16	0.08	1.79	0.06	0.03		
	contaminated samples	0	0	0	0	0	0	4	1	5	2.60
Heptachlorepoxide	max	/	/	/	/	/	/	0.14	0.02		
	mean	/	/	/	/	/	/	0.04	0.02		
	contaminated samples	21	6	6	11	21	3	24	7	99	51.56
pp'DDE	max	1.23	0.08	1.46	1.36	0.68	0.61	0.29	0.12		
	mean	0.21	0.05	0.56	0.26	0.24	0.23	0.04	0.07		
	contaminated samples	7	4	0	6	19	0	4	2	42	21.88
pp'DDD	max	0.39	0.06	/	0.05	0.43	/	0.08	0.04		
	mean	0.14	0.04	/	0.03	0.14	/	0.03	0.03		
	contaminated samples	6	2	2	3	16	1	5	1	36	18.75
pp'DDT	max	1.66	0.35	0.09	0.13	1.06	0.25	4.41	0.02		
	mean	0.43	0.21	0.08	0.06	0.21	0.25	0.99	0.02		
	contaminated samples	22	6	6	11	21	3	26	7	102	53.12
total DDT	max	2.14	0.37	1.46	1.36	1.50	0.61	4.41	0.16		
	mean	0.36	0.14	0.58	0.28	0.52	0.31	0.24	0.08		

Table 2. Chlorinated pesticide residues detected in imported marine fish, (mg/kg of fresh weight)

		fish species										total	
		Hake	Dentex	Grooper	Pilchard	Sprat	Gilthead bream	Mackerel	Herring			No	%
Pest. det.	No	67	10	9	20	25	7	43	11			192	100
	fat c., %	1.0	1.5	3.4	7.2	8.2	8.5	16.0	19.0				
HCB	cont. s.	1	0	0	0	0	1	0	0			2	1.04
	max	0.01	/	/	/	/	0.01	/	/				
	mean	0.01	/	/	/	/	0.01	/	/				
αHCH	cont. s.	1	0	0	0	0	0	1	1			3	1.56
	max	0.01	/	/	/	/	/	0.01	0.01				
	mean	0.01	/	/	/	/	/	0.01	0.01				
Lindane	cont. s.	15	2	1	2	7	5	11	2			45	23.44
	max	1.01	0.05	0.08	0.05	0.03	0.76	0.05	0.01				
	mean	0.10	0.03	0.08	0.03	0.02	0.18	0.02	0.01				
H.h.e.	cont. s.	0	0	0	0	0	0	1	0			1	0.52
	max	/	/	/	/	/	/	0.02	/				
	mean	/	/	/	/	/	/	0.02	/				
pp'DDE	cont. s.	2	0	6	9	18	2	12	6			55	28.65
	max	0.01	/	0.05	0.10	0.06	0.05	0.05	0.02				
	mean	0.01	/	0.02	0.02	0.02	0.02	0.01	0.01				
pp'DDD	cont. s.	0	0	0	0	10	0	1	1			12	6.25
	max	/	/	/	/	0.04	/	0.01	0.01				
	mean	/	/	/	/	0.02	/	0.01	0.01				
pp'DDT	cont. s.	1	0	0	1	11	1	5	0			19	9.90
	max	0.02	/	/	0.01	0.09	0.02	0.71	/				
	mean	0.02	/	/	0.01	0.02	0.02	0.16	/				
tot. DDT	cont. s.	4	0	6	9	21	2	14	7			63	32.81
	max	0.02	/	0.05	0.10	0.12	0.05	0.71	0.03				
	mean	0.01	/	0.02	0.03	0.04	0.04	0.07	0.02				

Pest. det.-pesticide detected; No-total number of samples; fat c.-the average fat content;
cont. s.-contaminated samples; H.h.e.-heptachlorepoxide; tot. DDT-total DDT

Table 3. Toxic elements detected in imported marine fish, (mg/kg of fresh weight)

		fish species								
		Hake	Dentex	Grooper	Pilchard	Sprat	Gilthead bream	Mackerel	Herring
total number of samples		50	10	11	20	24	5	25	8
toxic elements detected									
Arsenic (As)	max	0.60	0.47	0.19	0.40	0.38	1.49	0.33	0.90
	mean	0.09	0.24	0.06	0.15	0.12	0.57	0.08	0.49
Cadmium (Cd)	max	0.10	0.06	0.08	0.05	0.09	0.13	0.06	0.09
	mean	0.02	0.02	0.01	0.02	0.03	0.06	0.01	0.02
Lead (Pb)	max	0.92	0.43	0.43	0.40	0.51	0.65	0.29	0.05
	mean	0.11	0.12	0.09	0.16	0.14	0.31	0.03	0.01
Mercury (Hg)	max	0.032	0.040	0.040	0.032	0.027	0.050	0.025	0.028
	mean	0.017	0.019	0.019	0.014	0.018	0.023	0.013	0.024

Since marine fish is used throughout the world for production of fish meal, residues of chlorinated pesticides and toxic elements from marine fish can enter and accumulate in the animal body through animal feeds. Furthermore the residues might enter the human food supply. From that standpoint the determined residues can be of public health concern.

The ban or restriction concerning the use of chlorinated pesticides in industrialised countries, as well as the prevention and control of any kind of environmental contamination, will undoubtedly contribute to reduction of global pollution and, consequently of contamination of marine food.

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OSTACI ORGANOHLORNIH PESTICIDA I TOKSIČNIH ELEMENATA U NEKIM VRSTAMA MORSKE RIBE

SPIRIĆ AURELIJA, SAIČIĆ SNEŽANA, JANKOVIĆ S i RADIČEVIĆ TATJANA

SADRŽAJ

Upotreba mnogih hemikalija u poljoprivredi i industriji zahteva procenu njihovih koncentracija u okolini i u lancu ishrane, u cilju zaštite zdravlja ljudi. Među ovim hemikalijama, zbog njihove toksičnosti i bioakumulacije, najviše se proučavaju organohlorni pesticidi i toksični elementi (AS, Pb, Cd, Hg). Rezidui ovih jedinjenja u morskoj ribi mogu na dva načina da utiču na ljudsko zdravlje: konzumiranjem ribe ili preko ribljeg brašna koje kao komponenta stočne hrane može biti faktor unosa rezidua u telo životinja. Konzumiranjem mesa čovek je indirektno izlo'en organohlornim pesticidima i toksičnim elementima. Imajući ovo u vidu, cilj našeg rada je bio da se ispitaju količine organohlornih pesticida i toksičnih elemenata u nekim vrstama morske ribe iz uvoza, kao pokazatelji stepena ljudske izlo'enosti.

Količine organohlornih pesticida i toksičnih elemenata određivane su u osam vrsta morske ribe iz uvoza. Hlorovani pesticidi su ispitani u 192 a toksični elementi u 153 uzorka ribe. Ispitivanja su se odnosila na vrste riba koje se najviše konzumiraju u zemlji. Od svih organohlornih pesticida, rezidui lindana su detektovani u najvećem broju ispitanih uzoraka (65.62%) i u najvećim količinama (srednja vrednost 2.62 mg/kg). Totalni DDT je detektovan u 52.08% uzoraka ribe, sa najvećom srednjom vrednošću od 0.58 mg/kg masti. Rezidui drugih hlorovanih pesticida koje smo detektovali u ispitanim uzorcima ribe bili su od manjeg značaja. Rezultati dobijeni za toksične elemente ukazuju da količina toksičnih elemenata u ispitanim uzorcima morske ribe ne predstavljaju rizik po zdravlje potrošača.