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Monitoring of Chlorinated Hydrocarbon Pollution of Meat and Fish in Croatia

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Summary

Four hundred and sixty-six fatty tissue samples of beef, pork, poultry and fish were assayed by the gas and liquid chromatography between 1992 and 1996 for chlorinated hydrocarbons: hexachlorobenzene (HCB), α-hexachlorocyclohexane (α-HCH), γ-hexachlorocyclohexane (lindane), DDT and metabolites, and total polychlorinated biphenyls (PCBs). Samples were divided into two groups, meat and fish imported to Croatia, and meat from Croatian farms and fish from the Adriatic Sea. In domestic meat, the levels of pollution with the compounds studied were considerably lower than in imported meats. The differences were most noticeable in lindane and DDT levels in beef, and those of DDT in pork. The average level of lindane in domestic and imported beef was 0.004 and 0.020 mg/kg, respectively. Domestic beef contained on the average 0.013 mg/kg and the imported beef 0.059 mg/kg DDT, respectively. While the average amount of DDT in local pork was 0.014 mg/kg, the average for imported pork was 0.041 mg/kg. Poultry lindane also showed significant differences, an average of 0.012 mg/kg in domestic and 0.034 mg/kg in imported poultry. HCB and α-HCH displayed a statistically significant difference in beef. There was an average level of 0.001 mg/kg of HCB and 0.001 mg/kg of α-HCH. However, imported beef had an average of 0.004 mg/kg of HCB and 0.002 mg/kg of α-HCH. A significant difference was also found in HCB content in poultry; domestic and imported poultry contained an average of 0.001 and 0.003 mg/kg, respectively. As regards the pollution of fish with polychlorinated biphenyls, this was considerably higher in the fish of domestic origin (average of 0.046 mg/kg) than in imported fish (average level of 0.006 mg/kg). Conversely, in both sample groups the pollution of fish with chlorinated pesticides was similar. Compared with meat and fish of the same origin and standing that were analyzed by our laboratory 10 years ago, the pollution of domestic meat and fish with clorinated hydrocarbons showed a trend of noticable decline.

Key words: chlorinated hydrocarbons, pollution, meat, fish, import, domestic, intake

Introduction

The term »chlorinated pesticides« is understood to include the following compounds: DDT and metabolites, hexachlorocyclohexane (HCH) isomers, hexachlorobenzene (HCB), aldrin, dieldrin, endrine, heptachlor, and heptachlor epoxide. Notwithstanding that there is a whole range of other compounds of pesticidal activity with chlorine in their formula, the listed compounds are classed among chlorinated pesticides precisely because of their common chemical characteristics and similar impact on the environment.

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A stable structure of the chlorinated ring makes them all remarkably persistent in the environment, which may result in their insertion into the human food chain and ultimate ingestion by the body. They are lipophilic and liable to slow biodegradation, and therefore chronic exposure to them will lead to their accumulation in the fatty tissue of most diverse organisms.

For these properties and occurrence in the biological material of nontarget organisms, and for the occurrence of insect resistance, a ban on DDT in the USA was imposed in 1972, subsequently following in most other developed countries. Since, however, some tropical countries still use DDT in combating insect-borne diseases, this product could be said to be restricted, but not banned in many countries, especially those in the Southern Hemisphere. Despite the USA ban HCH-based preparations in the 1980s, lindane (a gamma-isomer) is one of the few chlorinated pesticides still currently used world-wide as an ectoparasitocide, as well as in some other limited conditions *(1)*. In the 1970s the use of HCB as fungicide was banned in the USA and some other developed countries. However, it has been introduced in the environment ever since as a waste product in the course of some industrial processes (manufacture of chlorinated solvents, pesticides and similar). HCB is known as a by-product of the HCH biotransformation in mammals. Investigating global technical hexachlorocyclohexane usage and its contamination consequences in the environment from 1948 to 1997, Li *(2)* found that China, Japan and India were the most polluted countries by HCH during different period of time and that in 1990 India was still the country with the highest rate of contamination, and most likely, the most polluted area by technical HCH today.

Polychlorinated biphenyls (PCBs) make up a group of 209 compounds (congeners) with a general formula $C_{12}H_{10-n}Cl_n$ where »n« is the number of chlorine atoms within a range of 1–10. Their physicochemical properties change depending on the number and position of chlorine atoms in the biphenyl structure. Whereas vapor pressure, water solubility and biodegradability decline with the increasing number of chlorine atoms, liposolubility increases. Heating can produce highly dangerous compounds, such as polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and similar *(3)*.

In recent years many developed countries have restricted the use of PCBs to closed systems, banning them in food industry and generally taking many measures to reduce their release into environment.

Chlorinated hydrocarbons are listed as global environmental pollutants. Since they are borne by air, water, and living organisms, DDT and its derivatives have been detected far beyond the point of application and in nearly every environmental medium.

Chlorinated biphenyls can accumulate in the living organisms from the surrounding media and food. While in water organisms ingestion from water is a major source of pollution, in land fauna food is the main source *(4)*.

Human exposure to DDT is mainly via food. Meat, fish, poultry, and dairy produce are the primary sources. Generally, the higher in the food chain organisms are, the higher concentration of the DDT-type compounds they contain.

The discovery of polychlorinated biphenyls (PCBs) in the environment dates from the late 1960s and soon their presence was recorded in almost every component of the global ecosystem *(5)*. Similarly as in chlorinated pesticides, lipophilic properties are the basis of bioaccumulation and biomagnification. The bioconcentration factors amount to 70 000 or higher.

Animal fats, cow milk, and butter and fish are the most important sources of food pollution *(6)*. Because many countries have brought the use and removal of PCBs under control, their introduction into environment has been declining compared to previous tests. However, there is still no clear indication of this possibly being a general trend *(7)*. Due to local contamination, significant amounts of PCBs are still found in fish products, and occasionally in meat and dairy produce.

Recent literature points to a universally major presence of chlorinated pesticide residues in foods, especially those of animal origin (*8–13*).

Since as well as being a meat and fish exporter, Croatia also imports these products from many countries, the present study is set out to compare chlorinated hydrocarbon levels (hexachlorobenzene, α-hexachlorocyclohexane, lindane, DDT and metabolites, and polychlorinated biphenyls (PCBs)) between the imported and domestic meat and fish and to establish whether the previously noted chlorinated hydrocarbon level differences between the two were random or statistically significant.

Another aim was to determine the average daily ingestion of assayed compounds via meat and fish in Croatia and to compare, it with Sweden, a highly developed European country, on which relatively recent literature data is available *(14)*.

Furthermore, to assess the trend of pollution in foods of animal origin with the observed contaminants the findings on chlorinated hydrocarbon-pollution of meat and fish in Croatia of 10 years ago were compared with the 1992–96 findings.

The samples of bovine and porcine fatty tissue, chicken fatty tissue and fish, originated either from imports or from Croatia, submitted from 1992–96 for food safety control to the Croatian National Institute of Public Health were analyzed.

Material and Methods

Samples and sampling

Four hundred sixty-six fatty tissue samples of beef, pork, chicken and the edible parts of fish, originated either from imports or from Croatia, submitted from 1992–96 for food safety control to the Croatian National Institute of Public Health were analyzed. The meat originated from imports and from the livestock farms of inland Croatia. As to fish, it was either imported or fished out of the Adriatic Sea (Table 1).

In the 1992–96 period samples were submitted to the Pesticide Control Laboratory, Health Ecology Ser-

Table 1. Origin and number of samples

Sample	Number	
	Imported	Domestic
Beef	80	122
Pork	72	81
Fish	44	33
Chicken	14	20

vice, Croatian National Institute of Public Health. They were analyzed either freshly arrived or defrosted.

Imported meat came mainly from EU countries, but also from Eastern and Central Europe, as well as China, Australia and New Zealand. Whereas most of the imported fish originated from Argentina, imported chicken came from the neighbouring countries, Slovenia and Hungary.

Submitted domestic meat came mainly from Slavonia, with fish originating from the sea near Rijeka and the environs of Zadar.

Meat samples used in the present work came from the same livestock farms and were assayed at the same laboratory as the samples from 1985/86 *(15).*

Fish samples from central Adriatic were analyzed at the same laboratory as the samples from the period 1984 –88 *(16,17)*.

The following pollutants were examined: hexachlorobenzene, α-hexachlorocyclohexane, γ-hexachlorocyclohexane (lindane), DDT and metabolites, and polychlorinated biphenyls.

Methods

The samples were homogenised, extracted, and purified according to the UNEP/FAO/IAEA-recommended method *(18).* It requires that a given amount of sample (10–30 g) be homogenised with a threefold amount of anhydrous sodium sulphate in a homogeniser for 1–2 min. The extraction of homogenised sample in a Soxhlet apparatus with n-hexane was performed for 8 hours. An aliquot containing 200 mg of fat was transferred to a glass cylinder and purified with concentrated sulphuric acid (to disintegrate fats) by vigorously shaking it for 10 min. The extract had to be clear and colorless. A known amount of purified extract was evaporated to dryness in a stream of nitrogen and then diluted in 1 mL hexane. The amounts of 2–5 μL were injected into a gas chromatograph.

The determination of chlorinated compounds was made using a Perkin Elmer Sigma 300 gas chromatograph with ^{63}Ni electron capture detector and capillary column with unpolarized CP SIL-5 stationary phase. The length of column was 25 m, internal diameter of the capillary 0.22 mm, and thickness of the film 0.12 μm.

The following operating conditions were set for chromatography: column temperature 200 °C, temperature of the injector 250 °C, temperature of the detector 300 °C, carrier gas (argon) flow 0.92 mL/min.

The identification of chlorinated compounds in the samples was made by comparing the retention time of compounds in the standard mixture. The concentrations of chlorinated hydrocarbons were determined in samples by using the external standard method comparing the heights of peaks for compounds with a known concentration in the standard solution with heights of the same peaks in the samples.

The quantification of polychlorinated biphenyl residues was made by comparing the sum of heights of certain peaks with the sum of heights of these same peaks in the standard mixture with a known concentration of Aroclor 1254 and Aroclor 1260.

Made periodically, the percentage of recovery ranged from 95–108 % for chlorinated pesticides and from 88–90 % for PCBs. The limit of detection of chlorinated pesticides varied between 0.001 and 0.01 ng, for polychlorinated biphenyls being 0.05 ng. Table 2 illustrates the sensitivity values for individual analytes.

The method used *(18)* specifies that the accuracy of analytical procedure is satisfactory if the relative standard deviation (in μg of analyte) per 1 kg sample (ppb) in five successive pollutant level determinations in the same basic sample does not exceed 20 % of the average value. In the assays mentioned, the relative standard deviation was 8.5 % of the average, which meets the required accuracy criteria.

Table 2. Sensitivity thresholds of the samples

	Meat (mg/kg) calculated per fat content	Fish (mg/kg) calculated per edible part
HCB	0.001	0.0001
α-HCH	0.001	0.0001
Lindane	0.001	0.0001
DDT and metabolites	0.001	0.0001
PCBs	0.01 (calculated per edible part)	0.01

»Blind« probes were made periodically to check the purity of laboratory glass and chemicals.

In statistical analysis values below the sensitivity threshold of the determination method were entered as »0«.

The existence of difference between the two sample groups was established by using the t-test based at significance levels of 95 and 99 % *(19).*

Results and Discussion

Appearing in international trade as a food exporter, Croatia, like any modern country, at the same time also imports foods from many countries. It is possible to establish the trends of pollution with individual pollutants by monitoring over years the observation of legally set food safety criteria. This was the main objective of the present investigation covering the monitoring of chlorinated hydrocarbon levels in meat and fish samples. Chlorinated hydrocarbons were selected for their known properties of persistence, liposolubility and bioaccumulation on species at higher trophic levels. Meat and fish were selected as good indicators of food pollution with these compounds.

The investigation included three sample groups: samples from Croatia, imported samples, and samples examined in the same laboratory 10 years before. In all, 166 samples of imported meat, 44 of imported fish, as well as 223 samples of domestic meat and 33 of domestic fish were assayed (Table 1). It should be added that they were all intended for market, *i.e.* for wide consumption and can thus be used in calculating the average intake of chlorinated hydrocarbons through meat and fish. Such sample classification was used in order to reach some of the objectives of this study. First, we aimed to establish whether the domestic meat, as has been observed through long-standing investigation, is in fact less polluted than imported meat. In addition, the present study was intended to show what the pollution trend with chlorinated hydrocarbons might be in relation to the period of 10 years ago as well as whether all compounds examined displayed the same trend. In contrast to the use of DDT, HCB and HCH having been banned or very strictly limited for more than 20 years, lindane still continues to be used. As evident from the literature many chlorinated pesticides are both used and found even most recently in many countries from which we import meat (*e.g.* Australia, China).

Percentages of positive results of described examinations are presented in Table 3.

The mean concentrations of examined pesticides are presented in Tables 4–7. As customary in the regulations of many countries, pollutant levels were expressed in mg/kg of fat contained in meat, and in mg/kg of the edible parts of fish *(20).*

Hexachlorobenzene (HCB)

The presence of HCB was more common in imported than domestic samples (Table 4). In contrast to 52, 39 and 43 % of samples, respectively, found in imported beef, pork and poultry, the respective percentages in domestic beef, pork and poultry were 19, 16 and 25 % (Table 3). Imported beef also had higher average values, this also being true for maximum values. In beef, the differences between imported and domestic meat were statistically significant ($p<0.001$), as well as in poultry ($p<0.05$); in pork, however, the difference did not reach the level of significance. HCB was present in 25 % of imported and 27 % of domestic fish. In imported fish, the average was barely above the threshold of the sensitivity method, being 0.0004 mg/kg. It was

Table 3. Percentage (%) of positive* results of determinations

Sample		HCB	α-HCH	lindane	DDT	PCB's
Beef	– import 1992–96	52	35	75	81	0
	– domestic 1992–96	19	8	35	50	0
	– domestic 1985/86	33	25	63	92	8
Pork	– import 1992–96	39	21	85	82	0
	– domestic 1992–96	16	12	44	41	0
	– domestic 1985/86	7	20	57	80	27
Poultry	– import 1992–96	43	21	93	50	0
	– domestic 1992–96	25	10	70	55	0
Fish	– import 1992–96	25	25	95	91	7
	– domestic 1992–96	27	48	91	100	30
	– domestic 1985/86	–	–	–		77

* the results higher than sensitivity thresholds of the method are considered as positive results

Table 4. Hexachlorobenzene in meat and fish

	HCB in beef mg/kg of fat				HCB in pork mg/kg of fat		
	import 1992–96	domestic 1992–96	domestic 1985/86		import 1992–96	domestic 1992–96	domestic 1985/86
N	80	122	63	N	72	81	75
mean	0.004	0.001	0.001	mean	0.002	0.001	0.000
median	0.001	0.000	0.000	median	0.000	0.000	0.000
min	0.000	0.000	0.000	min	0.000	0.000	0.000
max	0.043	0.018	0.009	max	0.025	0.024	0.010
SD	0.008	0.003	0.002	SD	0.004	0.003	0.001

	HCB in poultry mg/kg of fat			HCB in fish mg/kg of edible portion	
	import 1992–96	domestic 1992–96		import 1992–96	domestic 1992–96
N	14	20	N	44	33
mean	0.003	0.001	mean	0.0004	0.0000
median	0.000	0.000	median	0.0000	0.0000
min	0.000	0.000	min	0.0000	0.0000
max	0.012	0.003	max	0.0064	0.0003
SD	0.005	0.001	SD	0.0012	0.0001

even less in local fish. Unlike in imported fish, where 0.0064 mg/kg was the largest amount of HCB, in domestic fish this was 0.0003 mg/kg. The difference between the two groups is not statistically significant. Compared with the period of 10 years ago, the present HCB values are even higher (though not statistically significant), which is probably a consequence of intensified industrial production processes in which HCB is released as a by-product *(21)*.

α-*hexachlorocyclohexane (HCH)*

As regards the presence of HCH, namely its α-isomers in investigated samples, we found that 35 % of imported beef had α-HCH levels higher than threshold sensitivity of the determination method (0.0001 mg/kg). This was true for only 8 % of domestic beef. α-HCH was found in 21 % of imported and 12 % of domestic pork, as well as in 21 % of imported and 10 % of local poultry (Table 3). Average values were low (Table 5), varying round threshold sensitivity in all positive samples, with the difference between imported and domestic meat statistically significant in beef only ($p<0.05$). In fish, there were α-HCH averages of 0.0004 mg/kg and 0.0001 mg/kg in domestic and imported fish, respectively. One sample of imported fish contained 0.0128 mg/kg α-HCH, exceeding the maximum allowance of 0.01 mg/kg. However, the difference between imported and domestic fish did not reach the level of statistical significance. Compared with the period of 10 years back, there was no significant difference between beef and pork regarding α-HCH levels. It should be stressed that in over 50 % of the samples the levels did not go above the sensitivity threshold of the determination method even when the average values were equal to the sensitivity threshold.

Lindane

Lindane, the gamma-isomer of the hexachlorocyclohexane, was far more interesting than the previous two pollutants. In Croatia, like in many other European countries and in the Americas, the use of lindane is under no ban. Consequently, there are no significant differences regarding lindane among samples analyzed 10 years ago and recent samples. However, as it is shown in Table 6, imported beef had higher average (0.020 mg/kg) and maximum (0.116 mg/kg) lindane values than domestic beef with an average of 0.004 mg/kg and a maximum of 0.067 mg/kg. The difference is statistically significant ($p<0.0001$). In addition, the average lindane values in pork were higher in the imported than domestic meat, but they were not statistically significant. In poultry, lindane levels were greater in the imported than domestic samples, showing statistically significant difference ($p<0.005$). The average value in imported and domestic samples was 0.034 mg/kg and 0.012 mg/kg, respectively. In imported poultry, the maximum recorded lindane level of 0.079 mg/kg contrasts with 0.040 mg/kg in domestic poultry. Closely similar levels of lindane, mutually not statistically different, were found in the fish of domestic and foreign origin.

DDT

DDT is the best indicator of the differences between imported and domestic meat (Table 7). Both imported beef and imported pork exhibited significantly higher DDT levels than corresponding domestic meats ($p<0.0001$ for beef and $p<0.001$ for pork). In addition, eighty-one percent of imported beef and 50 % of domestic beef were DDT-positive (levels above the sensitivity threshold) as well as 82 % of imported pork and 41 % of domestic pork and 50 % of imported and 55 % of domestic poultry, respectively (Table 3).

Regarding fish, the DDT levels in imported and domestic fish did not differ significantly. A sample of imported and domestic fish each had DDT levels above the maximum allowances (0.1698 mg/kg in imported and 0.1590 mg/kg in domestic fish). While in fish the aver-

Table 5. α-HCH in meat and fish

	α-HCH in beef mg/kg of fat				**α-HCH in pork mg/kg of fat**		
	import 1992–96	**domestic 1992–96**	**domestic 1985/86**		**import 1992–96**	**domestic 1992–96**	**domestic 1985/86**
N	80	122	63	N	72	81	75
mean	0.002	0.001	0.001	mean	0.001	0.000	0.001
median	0.000	0.000	0.000	median	0.000	0.000	0.000
min	0.000	0.000	0.000	min	0.000	0.000	0.000
max	0.029	0.027	0.010	max	0.015	0.009	0.025
SD	0.005	0.003	0.002	SD	0.002	0.001	0.004

	α-HCH in poultry mg/kg of fat			**α-HCH in fish mg/kg of edible portion**	
	import 1992–96	**domestic 1992–96**		**import 1992–96**	**domestic 1992–96**
N	14	20	N	44	33
mean	0.001	0.000	mean	0.0004	0.0001
median	0.000	0.000	median	0.0000	0.0000
min	0.000	0.000	min	0.0000	0.0000
max	0.009	0.004	max	0.0128	0.0021
SD	0.002	0.001	SD	0.0020	0.0004

Table 6. Lindane in meat and fish

	Lindane in beef mg/kg of fat				**Lindane in pork mg/kg of fat**		
	import 1992–96	**domestic 1992–96**	**domestic 1985/86**		**import 1992–96**	**domestic 1992–96**	**domestic 1985/86**
N	80	122	63	N	72	81	75
mean	0.020	0.004	0.009	mean	0.019	0.012	0.013
median	0.010	0.000	0.001	median	0.013	0.000	0.001
min	0.000	0.000	0.000	min	0.000	0.000	0.000
max	0.116	0.067	0.115	max	0.152	0.152	0.082
SD	0.025	0.009	0.023	SD	0.023	0.025	0.023

	Lindane in poultry mg/kg of fat			**Lindane in fish mg/kg of edible portion**	
	import 1992–96	**domestic 1992–96**		**import 1992–96**	**domestic 1992–96**
N	14	20	N	44	33
mean	0.034	0.012	mean	0.0022	0.0020
median	0.039	0.006	median	0.0016	0.0010
min	0.000	0.000	min	0.0000	0.0000
max	0.079	0.049	max	0.0139	0.0102
SD	0.026	0.016	SD	0.0024	0.0025

Table 7. Total DDT in meat and fish

	Total DDT in beef mg/kg of fat				**Total DDT in pork mg/kg of fat**		
	import 1992–96	**domestic 1992–96**	**domestic 1985/86**		**import 1992–96**	**domestic 1992–96**	**domestic 1985/86**
N	80	122	63	N	72	81	75
mean	0.059	0.013	0.051	mean	0.041	0.014	0.052
median	0.029	0.001	0.018	median	0.015	0.000	0.009
min	0.000	0.000	0.000	min	0.000	0.000	0.000
max	0.427	0.157	0.571	max	0.265	0.235	0.626
SD	0.081	0.027	0.097	SD	0.059	0.038	0.112

	Total DDT in poultry mg/kg of fat			**Total DDT in fish mg/kg of edible portion**	
	import 1992–96	**domestic 1992–96**		**import 1992–96**	**domestic 1992–96**
N	14	20	N	44	33
mean	0.022	0.017	mean	0.0087	0.0103
median	0.003	0.004	median	0.0016	0.0041
min	0.000	0.000	min	0.0000	0.0002
max	0.088	0.089	max	0.1698	0.1590
SD	0.032	0.028	SD	0.0274	0.0272

age DDT values varied around 10 % maximum residue limit (MRL) *(22)*, in meat they were only just above 1 % MRL, which confirms the fact that fish is the food item through ingestion of which the body receives the highest intake of chlorinated pesticides. Considering that the Adriatic is a closed-type sea, and additionally small and warm, the fact that results on domestic and imported (mainly of oceanic origin) fish are similar could be said to be satisfactory. One should emphasize that the average DDT values for imported meat are in excellent agreement with the simultaneously published results in the countries from which we import it *(8)*. Whereas average DDT values in the meat assayed and analyzed in this work ranged from 0.041–0.059 mg/kg, the values published in literature are 0.052 mg/kg. Domestic meat samples had an average DDT value of 0.013–0.014 mg/kg, even less than the average in some West European countries *(23)*. The presence of individual metabolites in samples is also important for DDT contamination (Table 8).

Table 8. Presence of DDT metabolites in examined samples

	Beef		**Pork**	
	domestic	**import**	**domestic**	**import**
DDE, %	47	76	35	75
DDT (*o,p′* + *p,p′*), %	16	49	16	46
DDD, %	0	14	3	13

Whereas DDE was present in 34.57–46.72 % of domestic samples, in foreign samples 75–76.25 % were recorded. DDE showed the largest presence of all DDT metabolites. This is a result not only of the long use of DDT as a pesticide, but also of pollution with DDE as the primary pollutant *(24).* Interestingly, in contrast to North America where lindane was much more widespread *(25)*, the average values of DDT in Croatia in the 1985–86 period were much higher than those of lindane.

The pollution of meat with chlorinated pesticides in Croatia now compared to that of 10 years ago undeniably exhibits a declining trend. The differences observed were most significant for DDT. In pork and beef the average decreased to one fourth so that currently 50 % of pork is DDT-free. While in 1985/86 the DDT median for pork was 0.009 mg/kg, it is below 0.001 mg/kg now. In 1985/86, the median for DDT in beef amounted to 0.018 mg/kg compared with the current 0.001 mg/kg.

It is important to stress that no sample of domestic or imported meat had the examined chlorinated pesticides at levels exceeding the maximum allowances. While in imported meat there was a DDT level of 42.7 % MRL, in domestic meat this was 23.5 %, with other pollutants reaching even lower values.

Polychlorinated biphenyls (PCBs)

The pollution of pork and beef with PCBs in the period between 1992–1996 can be said to be satisfactory (Table 3). In no single sample were the levels greater than the sensitivity threshold of the method (0.01 mg/kg). In the tests run 10 years ago beef and pork contained 8 and 27 % of polychlorinated biphenyls respectively, which was even then within the prescribed limits. The literature suggests that the situation in most other countries was similar. In the 1980s, the average levels of polychlorinated biphenyls in meat ranged from 0.05 to 0.4 mg/kg. Subsequently they mainly fell below the threshold of sensitivity (*26–28*).

Nonetheless, the presence of polychlorinated biphenyls is much greater in domestic than imported fish (Table 9).

Table 9. Polychlorinated biphenyls in fish

	Import fish 1992–96	**Domestic fish 1992–96**	**Domestic fish 1984–88**
N	44	33	46
mean/(mg/kg)	0.006	0.046	0.059–0.287
positive samples/%	7	30	77
maximum/(mg/kg)	0.167	0.117	2.303

Whereas the percentage of positive samples of domestic fish was fourfold more than of imported fish, the average values were nearly eight times higher. The average of 0.006 mg/kg in imported fish contrasts with 0.046 mg/kg in domestic fish. Nonetheless, in view of the aforementioned characteristics of the Adriatic Sea and of the high values obtained at some locations in northern and eastern Europe as well as in the Mediterranean *(29)*, we can be satisfied. Compared with the results on polychlorinated biphenyl levels in the Adriatic fish from 1984–88, a marked reduction in the pollution is noticeable. While in that period the polychlorinated biphenyl average for fish ranged from 0.059–0.287 mg/kg (depending on catch site), the present value in domestic fish is 0.046 mg/kg.

Intake of chlorinated hydrocarbons

Based on annual national consumption of meat and fish per member of a household in Croatia (Table 10) and on individual contaminant averages in a given group of samples, the average daily intake of the pollutants are calculated (*30, 31*).

Table 10. Annual per person consumption of meat and fish in Croatia

	1986	**1990**
m(pork)/kg	16.1	19.6
m(beef)/kg	15.1	13.6
m(poultry meat)/kg	15.1	13.7
m(fish)/kg	6.4	5.7

As the amounts of chlorinated hydrocarbons in meats were expressed per fat content, to calculate average intake of definite pollutant by meat we expressed the obtained pollutant concentrations in fat as the concentrations in meat using the nutritional tables data about the average levels of fat in beef, pork, and poultry *(32).* The average weight of a human was taken to be 60 kg.

Analyzing the intake of individual chlorinated hydrocarbons by beef, pork and poultry consumption (Table 11), we found their levels in imported meat to be several times higher than in domestic meat. Thus, the average daily intake of hexachlorobenzene via imported beef is quadrupled compared to the intake made through domestic meat; the intake via imported pork is twice as high as the intake through domestic meat. The situation with the intake of lindane, as well as of DDT, is similar. In fish, however, the status is different. The chlorinated pesticide intake in Croatia through domestic and imported fish is roughly the same, but we do ingest as much as eight times more PCBs, that is 2.5 times more than the Swedes did in 1990 (Table 12).

Because of the low fish consumption in Croatia, the chlorinated pesticide intake here is by far smaller than in Sweden. For example, the average daily intake of lindane through imported fish amounts to 0.6 ng/kg body weight/day. Through domestic fish, this amounts to 0.5 ng/kg body weight/day whereas in Sweden in 1990 this was 5 ng/kg body weight/day. Our daily DDT intake via imported and domestic fish is 2.3 and 2.6, respectively, against 16 ng/kg body weight/day in Sweden in 1990. While with domestic meat and fish (total intake) we receive almost identical amounts of lindane as the Swedes did in 1990, our DDT intake is 2.5 times less than in Sweden. In contrast, via imported meat and fish (total intake) we ingest nearly identical amounts of DDT as the Swedes, and twice as much lindane as they did in 1990.

Comparing the average daily intake of examined chlorinated hydrocarbones to the FAO/WHO recommended quantities, it is evident that all samples, whether imported or domestic, were sanitary safe. For example, the hexaclorobenzene intake through imported meat and fish reaches only 0.24 % of the acceptable daily quantity, that of lindane and DDT through imported meat and fish were 0.15 and 0.12 %, respectively.

Table 11. Average daily intake of chlorinated hydrocarbons

Sample	**HCB** average daily intake ng/kg of body mass/day			
	import 1992–96	domestic 1992–96	domestic 1985/86	Sweden
Beef	0.5	0.1	0.1	
Pork	0.6	0.3	0.3	0.9
Poultry	0.2	0.1		
Fish	0.1	0.0		1
Total intake	1.4	0.5		1.9
% ADI*	0.24	0.08		0.32
FAO ADI	600			
Sample	**Lindane** average daily intake ng/kg of body mass/day			
	import 1992– 96	domestic 1992–96	domestic 1985/86	Sweden
Beef	2.5	0.5	1.2	
Pork	5.9	3.7	3.3	0.9
Poultry	2.7	1.0		
Fish	0.6	0.5		5
Total intake	11.7	5.7		5.9
% ADI	0.15	0.07		0.07
FAO ADI	8000			
Sample	**DDT** average daily intake ng/kg of body mass/day			
	import 1992–96	domestic 1992–96	domestic 1985/86	Sweden
Beef	7.3	1.6	7.0	
Pork	12.8	4.4	13.4	9
Poultry	1.8	1.3		
Fish	2.3	2.6		16
Total intake	24.2	10.0		25
% ADI	0.12	0.05		0.12
FAO ADI	20000			

*ADI = acceptable daily intake

Table 12. Average daily intake of polychlorinated biphenyls (PCBs) by fish

Sample	**Average daily intake ng/kg of body mass/day**			
	import 1992–96	**domestic 1992–96**	**domestic 1984–88**	**Sweden 1990.**
Fish	1.6	12.0	17.2– 83.9	4.7
% ADI	0.06	0.48	0.69– 3.35	0.19
FAO ADI	2500–3000			
US FDA recommended maximum intake	1000			

Conclusion

The above data allow the following conclusions:

– In the 389 meat samples assayed in the present study the maximum quantity permitted by the Croatian law was not exceeded. In 1 sample of domestic and 44 samples of imported fish these regulations were violated.

– Meat from domestic farms had lower, mostly statistically significantly lower, values than imported meat.

– Differences were most evident in beef, being far smaller in pork and especially poultry, which was probably due to a different way of feeding.

– A larger *p,p'*-DDT presence in imported meat indicates the likelihood of continuous use of DDT in the countries from which we import meat.

– Domestic meat compared to the situation 10 years ago, shows a clear decline of DDT pollution. The same comparison showed no significant change in the levels of lindane and HCB, which is the consequence of continuous use of lindane and of the development of industries where HCB is made as a by-product. Nor was there a significant change in HCH levels; it should be stressed that they were very low 10 years ago as well.

– Fish is the prime source of human contamination with chlorinated pesticides as corroborated by the fact that while in fish the DDT mean value amounts to 10 % of MRL, in meat it does not exceed 1 %.

– Compared with imported fish mainly of oceanic origin, the Adriatic fish does not contain significantly larger amounts of chlorinated pesticides.

– Owing to the very low fish consumption in Croatia, the amounts of chlorinated pesticides ingested are severalfold lower than in countries with higher fish consumption, *e.g.* Sweden.

– Polychlorinated biphenyls were present neither in domestic nor imported meat in amounts larger than the sensitivity threshold of the method.

– While no fish sample contained polychlorinated biphenyls in amounts greater than permitted, the domestic fish contained them in significantly greater amounts than the imported fish. Thus, in contrast to a polychlorinated biphenyl mean value of 0.046 mg/kg in domestic fish, there was a mean value of 0.006 mg/kg in imported fish. Notwithstanding the low fish consumption, the average daily polychlorinated biphenyl intake was 2.5 times higher than in Sweden in 1990.

– In comparison with the period of 10 years ago, the falling trend of fish pollution with polychlorinated biphenyls may also be seen in the fact that 77 % of positive samples from that period decreased to 30 % positive in the present investigation.

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Praćenje onečišćenja mesa i ribe kloriranim ugljikovodicima u Hrvatskoj

Sažetak

U razdoblju od 1992. do 1996. godine plinskom i tekućinskom kromatografijom ispitivan je udjel kloriranih ugljikovodika: heksaklorbenzena (HCB), α-heksaklorcikloheksana (α-HCH), lindana, DDT-a i metabolita te ukupnih polikloriranih bifenila u 466 uzoraka masnog tkiva goveda, svinja, peradi i ribe. Uzorci su podijeljeni u dvije skupine: meso i riba uvezeni u Hrvatsku te meso s domaćih farmi i riba iz Jadranskoga mora. Uzorci mesa domaćeg podrijetla puno su manje onečišćeni ispitivanim spojevima od uvoznih. Razlike su najuočljivije u udjelu lindana i DDT-a u govedini i DDT-a u svinjetini. Prosječna količina lindana u domaćoj govedini bila je 0,004 mg/kg, a u uvoznoj 0,020 mg/kg. Domaća govedina sadržavala je prosječno 0,013 mg/kg, a uvozna 0,059 mg/kg DDT-a. Svinjetina domaćeg podrijetla imala je prosječno 0,014 mg/kg DDT-a, a uvozna 0,041 mg/kg. Razlika je značajna i u udjelu lindana u peradi; prosječni udjel u domaćim uzorcima bio je 0,012 mg/kg, a u uvoznoj peradi 0,034 mg/kg. Statistički značajna razlika utvrđena je i pri udjelu HCB i α-HCH u govedini; u domaćim uzorcima nađeno je prosječno 0,001 mg/kg HCB i 0,001 mg/kg α-HCH. U uvezenoj govedini bilo je 0,004 mg/kg HCB i 0,002 mg/kg α-HCH. Značajne razlike nađene su također za udjel HCB u peradi; domaća perad sadržavala je 0.001 mg/kg, a uvozna 0,003 mg/kg. Međutim, domaća je riba puno više onečišćena polikloriranim bifenilima (prosječno 0,046 mg/kg) od uvozne ribe (prosječno 0,006 mg/kg), dok je onečišćenje kloriranim pesticidima za obje skupine uzoraka bilo slično. Niti jedan uzorak mesa nije sadržavao klorirane ugljikovodike iznad maksimalno dopuštene količine, dok su po jedan uzorak ribe iz Jadrana i uvozne ribe imali vrijednost iznad maksimalno dopuštene. Uspoređujući udjel ispitivanih kloriranih ugljikovodika u uzorcima analiziranim 10 godina prije u istom laboratoriju, uočena je tendencija smanjenja onečišćenja namirnica animalnog podrijetla kloriranim ugljikovodicima.