Study of Organochlorinated Pesticide Residues and PCBs in Vegetable and Fruit Samples from market in Peja –Kosovo

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Abstract

Organoclorine pesticides (OCP) are the first class of compounds of synthetic pesticides introduced in agricultural and civil uses to counteract noxious insects and insect-born disease. In general they are lipophilic compounds with noticeable chemical and environmental stability. They tend to concentrate in the higher trophic organisms, as they amplify through the food chain. Food is generally recognized as the main source of human intake of pesticides, their metabolites and their residues. Preparation of samples, especially in food samples for quantitative analysis of organochlorined pesticides has an important role in recognizing the real levels. For the analysis of these micro-trace compounds in food samples is a constant search for new analytical methods. The most important steps of their chemical analysis usually are the extraction, purification, fractionation and concentration.

In this study, were analyzed samples of fruit and vegetables from the market of Peja, Kosovo in September 2011. Ultrasonic extraction was used for extracting pesticide residues from samples. Clean-up procedure was performed using firstly sulfuric acid followed a second clean-up procedure in an "open" florisil column. The organochlorine pesticides detected were HCHs (a-, b-, γ- and d-isomers) and the DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), hexachlorobenzene (HCB), heptachlor, heptachlor epoxide, methoxychlor and Aldrine's. Analyses were done with capillary column Rtx-5, 60m long, 0.32mm internal diameter, 0.25 µm film thicknesses on a gas chromatograph Dani 1000, with µECD detector. The found concentrations of the chlorinated pesticides were lower than accepted levels for studied samples.

Key words: Organochlorinated pesticides, Food safety; Food analysis; GC/ECD

1. Introduction

Human exposure to organochlorinated pollutants primarily occurs through food contamination. Fish, meat, fruit, vegetables and other dairy products are the most important dietary sources of pesticides and their metabolites for humans. It is widely accepted that these pollutants will be present in food for many years to come (Lazaro et al, 1996). Safe food and correct nutrition are among the most important environmental factors which affect human health, i.e. the physical development, good mental well-being, productivity at a proper level and ability to absorb information. Great concern was caused by chloroorganic compounds, which proved to be extremely persistent in the environment and accumulative in the food chain (Penttila & Siivinen, 1996; WHO & FAO 1983; Wilhelm et al, 2002). The application of DDT-containing and other chlorinated pesticides has been banned in most countries since the 1970s (Rogan and Chen, 2005). The hopes that it would be possible to clear the environment of the residues of the compound have proved to be futile; despite the passage of time, the monitoring of the environment and food in many countries has confirmed the ubiquity of the compound (Skibniewska et al, 2000). Pesticides applied to the soil and immediately incorporated are protected from photodegradation, volatilization and dew, which can cause hydrolysis (decomposition by reaction with water). The fate of a pesticide applied to soil depends largely on two of its properties: persistence and adsorption (adsorption is inversely related to solubility). Most pesticides in the soil break down or "degrade" over time as a result of several chemical and microbiological reactions.

Gas chromatograph equipped with electron capture detector is the most powerful equipment for determinations of halogenated compounds, also this technique its very efficacy for determination of lower concentrations. Organochlorinated pesticides are generally found in the environment and food matrices from ppm (part per million) to ppb (part per billion) concentrations. Because of these lower concentrations must be a very carefully work in laboratory about clean of glassware and other chemical (must be specify for gas chromatographic grade). At the most of the time samples could not be injected directly to gas chromatograph, they before must pre-treated. Different steps and techniques are used for getting the better results. Extraction, clean-up, concentration and fraction are most used steps. Extraction of the analytes and extract clean-up are the most critical steps in the analytical procedure when it comes to complete recovery of the target substances (Beltran et al, 2000).

2. Materials and Methods

2.1. Sampling of fruits and vegetables samples

Fourteen samples of food (beef, fruit, vegetable and water), food stuff, and environmental (soil, humus, mosses) were taken for this training. The food samples were taken in random mode in supermarket of Peja. Moss and humus samples were taken near Kosovo Institute of Agriculture in Peja.

2.2. Sample preparation for fruits and vegetables

The samples were homogenized with anhydrous sodium sulphate (Merck, Darmstadt, Germany) and were extracted by ultrasonic bath assisted extraction (1g fresh weight of biota with 30 ml hexane/dichloromethane 3/1, (v/v) (Fluka, Germany, pesticide grade). The extract was purified by shaking with 15g silica gel, impregnated previously with 45% sulfuric acid. A further clean-up of this extract was performed in a open glass column packed with Florisil (particle size 0.063±0.2 μm; Merck, Darmstadt, Germany), deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane/dichloromethane 4/1(v/v) (Spectroscopy grade; Fluka, Germany). The extract was concentrated to 1 ml and analyzed by GC-ECD (Muir & Sverko 2006).

2.3. Gas chromatography analyze

Gas chromatographic analyses were performed with a DANI 1000 gas chromatograph equipped with a 63Ni Electron Capture Detector and a split/splitless injector. The column used was an Optima-5 (low/mid polarity, 5% phenyl methyl siloxane 60 m x 0.33 mm x 0.25μm film). The split/splitless injector and detector temperatures were set at 3000C and 3200C, respectively. Carrier gas was helium at 2 ml/min and make-up gas was nitrogen at 25 ml/min flow. The initial oven temperature was kept at 600C for 4 minutes, than increased to 2000C at 200C/min, and then increased to 2800C at 40C/min. The temperature was finally increased to 3000C, at 100C/min, than held for 7 minutes. Injection volume was 1μl and injections were done in splitless mode. Organochlorine pesticide quantification was performed by external standard method (Nuro et al, 2007).

In table 1 are shown data found for the concentrations of organochlorinated pesticides and PCBs for fruit and vegetable samples analyzed in Kosovo Institute of Agricultural, Peja, Kosovo. Levels of organochlorinated pesticides and PCBs were done in mgkg-1 sample. The higher levels were for Black grape sample (0.96 mgkg-1) and pear sample (0.85 mgkg-1). Apple samples were the "clean" sample with 0.04 mgkg-1.

3. Results and Discussions

Distribution of organochlorinated pesticides were not the same for all samples. Tomato, grape, plumb, carrot pepper and cucumber were the most polluted samples. Apple, cabbage, melon and white grape were the cleanest samples.

In Figure 1 were shown HCHs for fruit and vegetable samples. Total of HCHs were higher for pear samples with 0.196 mg/kg. In the black grape samples were found beta and delta isomers. Epsilon-HCH was found in cabbage samples. Lindane was not found almost for all samples. This fact could be connected with previous application of Lindane and properties of HCH isomers. HCHs levels were lower than acceptable concentration in fruit and vegetable samples.

In Figure 2 were shown DDTs for fruit and vegetable samples analyzed for this study. Carrot (0.17 mg/kg), black grape (0.14 mg/kg), pear (0.96 mg/kg) and pepper (0.68 mg/kg) were most polluted samples. For other samples DDTs were not detected. DDT was not detected for any samples. DDE and DDD, metabolites of DDT were found because of previous use of this pesticide. DDTs levels were lower than acceptable concentration in fruit and vegetable samples.

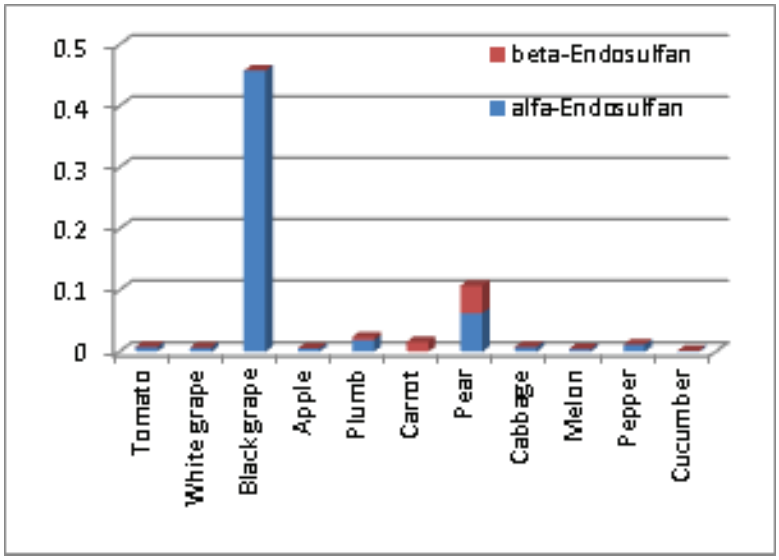
In Figure 3 were shown Heptachlors for fruit and vegetable samples. Pear sample was most polluted with 0.06 mg/kg. Heptachlors were not detected for the main parts of the samples. Heptachlorepoxide A and B (metabolit of Heptachlor) were found because of its previous use. Heptachlor levels were lower than acceptable concentration in fruit and vegetable samples.

In Figure 4 were shown Aldrines for fruit and vegetable samples. Aldrines were found in higher concentrations than other pesticides. Pear samples with mean value of 0.27 mg/kg were the most polluted samples. Aldrine, Isodrine and Endrin were found for black grape, carrot and pear samples in higher concentration than other Aldrines. Aldrines levels were lower than acceptable concentration in fruit and vegetable samples. Aldrines could be in use cover in other commercial names.

Table 1. Concentrations of organochlorinated pesticides and PCBs in fruit and vegetable samples analyzed in Kosovo Institute of Agriculture , Peja, Kosovo

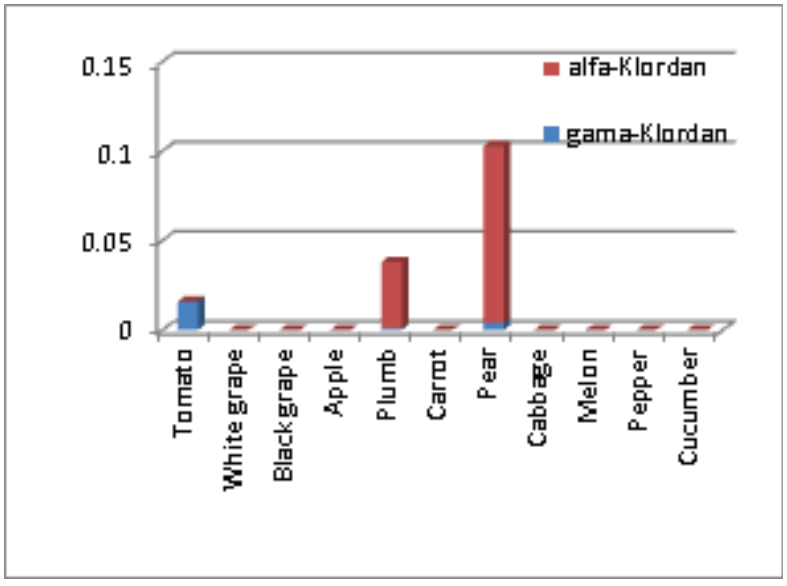
Compound Name	Reten. Time [min]	Tomato	White grape	Black grape	Apple	Plumb	Carrot	Pear	Cabbage	Melon	Pepper	Cucumber
alfa-HCH	34.267											
HCB	34.63	0.012	0.005	0.039	0.002	0.009	0.008	0.004	0.004	0.004	0.004	0.006
beta-HCH	35.413	0.015	0.006	0.039		0.005	0.005		0.006	0.007	0.004	0.011
Lindan	35.85					0.003	0.005	0.02				0.003
delta-HCH	36.95			0.056	0.002	0.002				0.001		0.008
epsilon-HCH	37.42					0.011		0.179				
PCB 28	37.967											
Heptaklor	38.34											
PCB 52	39.193					0.009		0.037				
Aldrina	39.68		0.013				0.125	0.078	0.012	0.013	0.004	0.014
Isodrin	40.947	0.008	0.004	0.064	0.004	0.003	0.014	0.009	0.007	0.003	0.006	0.004
HeptaklorepoksidB	42.173		0.002			0.009		0.038	0.002	0.003	0.002	
oxy-Klordan	42.513		0.002			0.002		0.004				0.005
HeptaklorepoksidA	42.72		0.002		0.005	0.006		0.022				0.003
2.4' DDE	43.5		0.001	0.14	0.023	0.007	0.009	0.016	0.002	0.001		0.004
gama-Klordan	44.12	0.016				0.001		0.004				
PCB 101	44.42						0.126	0.058			0.031	
4,4'-DDE	44.687	0.008	0.003					0.007			0.042	0.005
alfa-Endosulfan	45.17	0.008	0.007	0.458	0.006	0.019		0.063	0.008	0.005	0.012	0.002
alfa-Klordan	46.127					0.037		0.099				
2.4 DDD	46.36										0.014	
Dieldrin	46.583	0.003	0.003			0.007		0.016			0.018	0.003
44'-DDD	46.893					0.016	0.163	0.055			0.013	
beta-Endosulfan	47.27					0.005	0.016	0.045				
24'-DDT	47.587											
Endrin	47.93	0.017	0.025	0.161		0.052		0.173		0.013		
44'-DDT	48.487							0.019				
PCB 153	48.8						0.034	0.007				
PCB 138	51.19	0.166	0.14	0.498	0.131	0.41		1.475	0.108	0.103	0.101	
Metoksiklor	51.693											
PCB 180	52.59						0.01	0.006				
Mirex	55.43						0.02					
OCP Sum		**0.087**	**0.073**	**0.957**	**0.042**	**0.194**	**0.365**	**0.851**	**0.041**	**0.050**	**0.119**	**0.068**
PCB Sum		**0.166**	**0.140**	**0.498**	**0.131**	**0.419**	**0.170**	**1.583**	**0.108**	**0.103**	**0.132**	**0.000**

Figure 1. Endosulfanes for fruit and vegetable samples



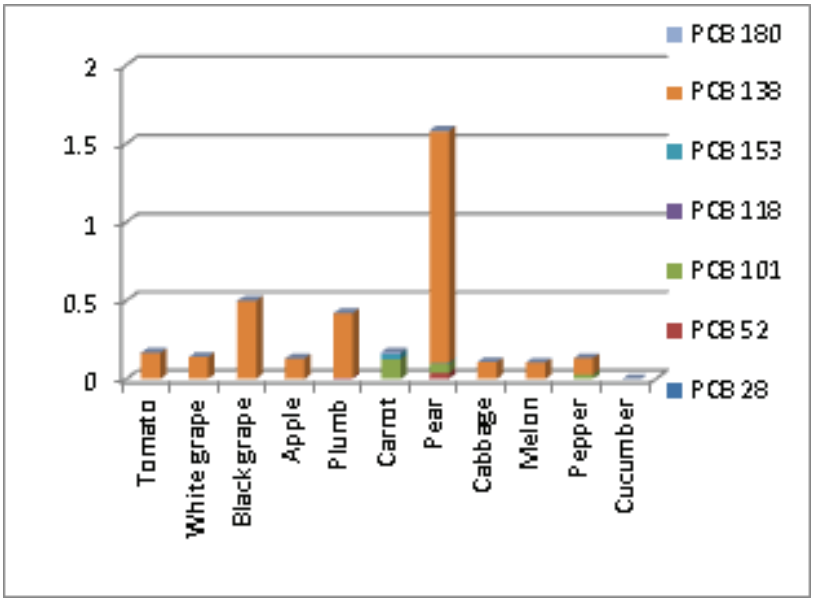
Source: Own data from Analytical laboratory of KIA , Peje Kosovo

Figure 2. Klordan for fruit and vegetable samples



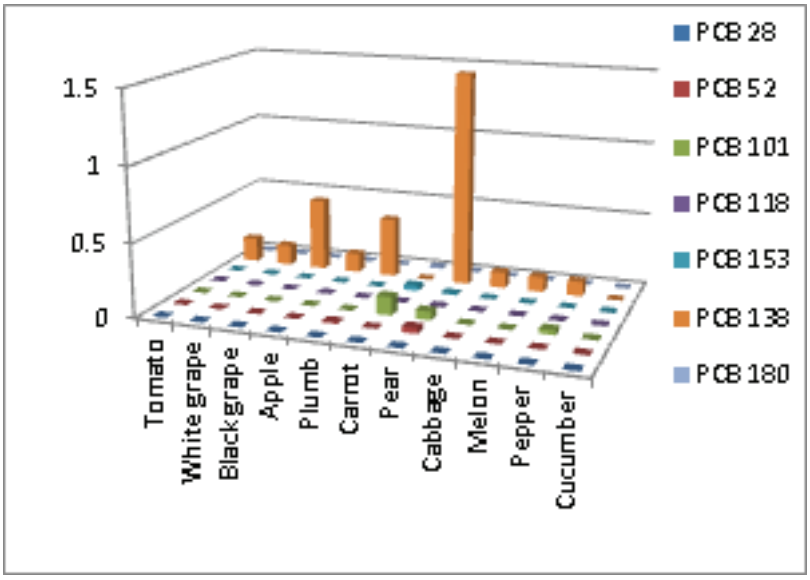
Source: Own data from Analytical laboratory of KIA , Peje Kosovo

Figure 3. PCB markers for fruit and vegetable samples (Prepared by Authors)



Source: Own data from Analytical laboratory of KIA , Peje Kosovo

Figure 4. Distribution of PCB markers for fruit and vegetable samples (Prepared by Authors)



Source: Own data from Analytical laboratory of KIA , Peje Kosovo

In Figure 5 was shown HCB concentration for fruit and vegetable samples. Black grape samples were most polluted with 0.04 mgkg-1 HCB levels were lower than acceptable concentration in fruit and vegetable samples. HCB can be in use because was detected almost for all samples.

In Figure 6 was shown Mirex concentration for fruit and vegetable samples. Mirex was detected only in carrot sample with 0.02 mgkg-1 Mirex levels were lower than acceptable concentration in fruit and vegetable samples.

In Figure 7 were shown total of alfa and beta Endosulfan for fruit and vegetable samples. Black grape samples with mean value 0.45 mg/kg and pear samples with mean value of 0.1 mg/kg. Endosulfan could be in use cover in other commercial names. Its levels were lower than acceptable concentration in fruit and vegetable samples.

In Figure 8 were shown alfa and gama Klordan for fruit and vegetable samples. Pear samples were most polluted with 0.10 mgkg-1 lower than acceptable concentration in fruit and vegetable samples. For the main part of samples Klordan were not detected.

In Figure 9 were shown total of PCB markers for fruit and vegetable samples. PCBs were detected for all samples. Pear samples with 1.53 mgkg-1 were most polluted. This sample has level higher than acceptable concentration in fruit and vegetable samples. In Figure 10 were shown distribution of PCB markers for fruit and vegetable samples. PCB 138 was found in higher concentration for all samples. Other PCBs were not detected. Other samples have levels lower than acceptable concentration in fruit and vegetable samples.

4. Conclusions

Determination of organochlorinated pesticides and PCBs for fruit and vegetable samples were realized in Kosovo Institute of Agricultural, Peja, Kosovo. Organochlorinated pesticides and PCBs were determining conform EU protocols in fruit and vegetable samples. The higher levels of organochlorinated pesticides were for Black grape sample and pear sample. Apple samples were the "clean" sample. Distribution of organochlorinated pesticides were not the same for all samples.

In the black grape samples were found beta and delta isomers. Epsilon-HCH was found in cabbage samples. Lindane was not found almost for all samples. This fact could be connected with previous application of Lindane and properties of HCH isomers. DDT was not detected for any samples. DDE and DDD, metabolites of DDT were found in carrot, bleck grape, pear and pepper samples because of previous use of this pesticide. Heptachlors were not detected for the main parts of the samples. Heptachlorepoxide A and B (metabolit of Heptachlor) were found because of its previous use. Aldrines were found in higher concentrations than other pesticides. Aldrine, Isodrine

and Endrin were found for black grape, carrot and pear samples in higher concentration than other Aldrines. Aldrines levels were lower than acceptable concentration in fruit and vegetable samples. Aldrines could be in use cover in other commercial names. HCB can be in use because was detected almost for all samples. Mirex was detected only in carrot samples. Endosulfan could be in use cover in other commercial names because their level for some of analyzed samples. For the main part of samples Klordan were not detected. This could be owing to last usage for agricultural purposes or/and because of pesticide and their metabolites chemistry (their stability, solubility, ect,.). The main factor for concentrations (in low concentrations) in analyzed samples could be because their before use of pesticides in respective agricultural areas. Organochlorinated pesticide levels were lower than acceptable concentration in fruit and vegetable samples. PCBs were detected for all samples. Pear sample has level higher than acceptable concentration in fruit and vegetable samples. Other samples have levels lower than acceptable concentration in fruit and vegetable samples.PCB 138 was found in higher concentration for all samples. Other PCBs were not detected.

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