


A survey of organochlorine pesticides and PCB concentrations in fatty and non-fatty food samples of Albanian markets

Aurel Nuro^{1,*} , Ilirjana Boci², Oljana Pine², Elda Marku¹, Bledar Myrtaj¹

¹University of Tirana, Faculty of Natural Sciences, Department of Chemistry, Tirana, Albania

²University of Tirana, Faculty of Natural Sciences, Department of Industrial and Environmental Chemistry, Tirana, Albania

*Corresponding author: aurel.nuro@fshn.edu.al

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Abstract

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are used for agricultural and industrial purposes. Characteristic of them are higher stability and toxic effects. Analyses of organochlorine pollutants is a legal requirement to be continuous by respective institutions because human exposure to them primarily occurs through food contamination. Pesticide and PCB analysis were realized in non-fatty food (water, wine, beans, vegetables and dried fruits) and fatty food samples (vegetable oil, butter, meat, chicken and fish) for a five years period (2017-2021) by using gas chromatography technique followed by electron capture detector (GC/ECD). Samples were taken in random mode at different cities of Albania. Organochlorine pesticides (Lindane and its isomers, Heptachlors, DDT and their degradation products, Aldrines and Endosulfanes) and PCB markers were pre-treated and quantify based on EN 12393 and EN 1528 methods. Diversification of samples make this study a valuable guide for analytical laboratories that perform these tests and have limitations on their funds. Modern and costly techniques of GC/MS/MS and LC/MS/MS are recommended for determination of organic pollutants in food samples but GC/ECD technique (a low cost technique) is accepted to be used for organochlorine pollutants analyses because it offers the same limit of detection (ppb) in food samples. Organochlorine pesticides and PCBs were detected almost in all food samples as a result of their previous uses or because of other factors (atmospheric deposition, degradation processes, water irrigation, animal feed, etc.). OCP levels were found in higher level in fish (fatty food samples) and vegetable (non-fatty samples). Pesticide degradation products were found higher than their primary substances because of their previous use. PCB concentrations were found in higher level for chicken (fatty food samples) and wine (non-fatty food samples). Volatile PCBs were found in higher level because of atmospheric deposition. OCP and PCB levels for more than 95% of analysed samples were lower than accepted levels conform EU and Albanian norms but their monitoring must be continuous.

Keywords: food safety, food analyses, organochlorine pesticides, PCB, GC/ECD

Introduction

Organochlorine pesticides (OCPs) were the first class of synthetic pesticides introduced widely for agricultural purposes after Second World War. DDT was the first pesticide (followed by Aldrine, Heptachlors, HCB, Lindane, etc) used effectively for against mosquitos (malaria vector) and other insects that generate serious damages in quantity and quality of agricultural products. In a short time (1940 – 1960) they improved agricultural production [1], but their use was not without danger to environment and human health. OCPs were banned in many countries after 80' due to their persistence and elevated toxicity [2]. Main part of organochlorine pesticides were classified as environmental pollutants and harmful for human health because of their toxic effects [2, 3, 4]. Organochlorine pesticides were used intensively in Albania for against malaria vector and for agricultural purposes for around five decades (1945-1992). The higher quantities of OCPs were applied frequently in the main agricultural areas of the country, located in the West Albania (Lushnja, Fieri, Vlora Durrresi, Lezha, Shkodra, Tirana, etc) but their use was almost in all territory because of agriculture development in different ways (fruits, corns, vegetables, etc.) for different areas. In this period, DDT, Lindane, HCB, Aldrins and Heptachlors were the most used organochlorine pesticides. Lindane was produced in the country for more than 30 years and the other pesticides were imported from other countries

(China, BRSS, Hungary, Bulgaria, etc). Mismanagement of pesticide oddments after 90' in Albania was a source of contamination by pesticides in many areas of the country. Although they have not in use for many years, they have been reported in many areas due to their persistence [5]. Although in many countries these chemicals have been banned since 1980, they were reported to be present in environment (soil, water, air and biota) and food products almost in all countries [1, 2, 3, 4, 5, 6] because of their stability.

PCB mixtures were used worldwide, for more than 50 years, starting from 1929 to 1980 when they production were banned [6]. Note that their use was continued for some other years until they were replaced by other compounds. PCB mixtures were produced by chlorination of biphenyl. Depending on the percentage of chlorine, different mixtures of PCBs were produced (e.g. Arochlor 1248, Arochlor 1256, Arochlor 1260, etc). Their use was mainly for industrial applications (dielectric fluids in capacitors and transformers, and as heat exchange fluids). They are chemically highly stable, lipophilic compounds and resist microbial, photochemical, chemical and thermal degradation. Unfortunately, the same properties which make PCBs interesting for industrial use make them harmful harmful to the environment and organisms [7, 8]. PCBs cause adverse effects on reproduction, development, and endocrine function including thyroid hormone homeostasis and estrogen-responsive tissues [9, 10]. PCBs were not in use before 90' in Albania. After 90', they were used as electric transformer oil in a limited number of imported equipments. The profile of PCBs in Albania is built mostly by volatile PCBs because of their atmospheric deposition [5], however year after year their profile changed to the most heavy PCBs [6, 7, 8, 9] because of punctual sources.

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 pollutants for entire population. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are first compounds introduced in persistent organic pollutants (POPs) list [11] because of their long-life in environment and their elevated toxicity. Organochlorine pollutants resist chemical, biological and photolytic degradation. Their degradation process is very slowly. They are characterized by low solubility in water and high solubility in fats leading their bioaccumulation in fatty tissues. Some of them can evaporate easily so they can move in long distances in the atmosphere before deposition occur. This characteristic has shown the presence of these compounds throughout the world, even in regions where they are never used [3, 4, 8, 10]. Today, unfortunately, facing a problem of the past, because many tones of POP compounds were used in large amounts almost in all countries include Albania.

On the one hand, analyses of organochlorine pollutants in food samples is a legal requirement to be continuous by respective institutions because human exposure to them primarily occurs through food contamination but in the other hand analyzes of OCPs and PCBs in food samples is complicated because their levels are quiet low (from ppt to ppm level). Allowed level of these pollutants in food samples generally are in ug/kg (ug/l) or ppb level. Several methods have been published for the determination of organochlorine pesticides and PCBs in fatty and non-fatty food samples. Most analytical methods based on the extraction of the chlorinated pollutants with organic solvent, clean-up with solvent-solvent partition and/or adsorption chromatography, followed by determination of the residues by gas chromatography (GC) coluped with electron capture detection (ECD) or mass spectrometry (MS) detection [2, 3, 4, 5, 10, 11]. GC/MS/MS and LC/MS/MS techniques are primary recommended for determination of organic pollutants in food samples but GC/ECD technique (a low cost technique) is accepted to be used for rutine analyses of organochlorine pollutants. It offers the same limit of detection (ppb) for organochlorine pollutants in food samples. This technique can be introduced in laboratories that perform these tests but have limitations on their funds. The aim of this study is to show data of OCPs and PCBs in food samples of Albanian markets by using GC/ECD technique.

Materials and Methods

Sampling of food samples from Albanian markets

Fatty-food products (vegetable oil, olive oil, butter, meat, chicken and fish) and non-fat food products (water, wine, beans, and dried fruits) were collected for a 5 years period (2017-2021) from the Albanian markets. The samples were taken in random mode in order to be as representative as possible to the food products that are marketed in our country (12, 14, 19). The samples origin were from Albania and other countries. Water,

wine, beans, dried fruit, fruit-vegetable, vegetable oil, olive oil and butter samples were stored and transported at +4°C while meat, chicken and fish samples were transported and stored at -4°C before analysis.

Table 1. Sampling data for fatty and non-fatty foods from Albanian markets (2017-2021)

	Sample type	Sample number	Year of sampling	Sampling areas of Albania
Non-Fatty samples (limited on fat) Method 12393	Water	46	2017, 2018, 2020, 2021	Tirane, Fier, Lushnje, Burrel
	Wine	14	2018	Tirane, Durres, Lushnje, Kolonje
	Bean	26	2018, 2020	Lushnje, Korce, Kolonje, Kavaje, Berat, Lezhe
	Dry fruits	16	2019	Tirane, Durres, Lushnje, Kolonje, Korce, Importi
	Fruit and vegetables	52	2017, 2018, 2020, 2021	Tirane, Durres, Lushnje, Korce, Kolonje, Elbasan
Fatty food samples Method 1528	Vegetal oil	12	2020	Tirane
	Olive oil	20	2017, 2018	Tirane, Lushnje, Berat, Vlore, Importi
	Butter	26	2018, 2020	Tirane, Durres, Lushnje, Korce, Kolonje, Fushe-Kruje, Importi
	Meat and by-products	34	2017, 2018, 2019, 2020, 2021	Tirane, Durres, Lushnje, Kolonje, Permet, Tepelene, Gjirokaster, Importi
	Chicken and by-products	38	2017, 2018, 2019, 2020, 2021	Tirane, Durres, Lushnje, Korce, Kavaje, Importi
	Fish	44	2017, 2018, 2019, 2020, 2021	Vlore, Durres, Shkoder, Lezhe, Pogradec

Preparation of fatty food samples for pesticide and PCB analyzes

Solid samples: The extraction method for determination of OCPs and PCBs in fatty solid matrices (butter, meat, chicken, fish) was based on EN 1258/1 Method. About 2-10 g of fresh sample was homogenized in a mortar with anhydrous sodium sulfate (5 times higher than mass sample) and after that it was put into a flask when 50 ml of n-hexane/dichloromethane (3/1) was added. The samples were extracted for 60 min in ultrasonic bath. The sample was spiked with internal standard (PCB 29) before extraction. 40 g of silicagel with 45% acid sulphuric (m/m) were added for lipid hydrolyze. For a second clean-up procedure were used a florisil column and 15 ml of hexane/dichloromethane (4/1) for column elution. Extracts were concentrated to approximately 2 ml and finally were analyzed using GC/ECD technique [12, 13, 14, 15, 16, 17, 18].

Liquid samples: Treatment steps for determination of organochlorine pollutants in liquid samples with high percentage of fat was based on EN 1258/1/2/3/4 method. About 5 g of vegetable or olive oil was weighed into a flask in which 5 g of sodium sulfate, 25 g silicagel with 45% acid sulphuric (m/m) and 30 ml acetone were added. The sample was spiked with internal standard (PCB 29), and was extracted in ultrasonic bath for 60 min. For clean-up procedure was used a florisil column and 10 ml of hexane/dichloromethane (4/1) for column elution. Extract was evaporated to approximately 1 ml followed by GC/ECD analyze [12, 13, 14, 15, 16, 17].

Preparation of non-fatty food samples for pesticide and PCB analysis

Solid samples: Firstly, 5-10g fresh solid samples with low percentage of fat (bean, dry fruits and fruit-vegetable samples) were homogenized with anhydrous sodium sulfate (1:2 to 1:5 in mass) and after that were extracted by ultrasonic bath assisted by 50 ml hexane/dichloromethane 3/1, (v/v) as extraction solvent. 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 an open glass column packed with Florisil, deactivated with 5% water. The organochlorine compounds were eluted with 10 ml of hexane/dichloromethane 4/1(v/v). The extract was concentrated to 2 ml and analyzed by GC-ECD [19, 20, 21].

Liquid samples: 1000 ml drinking water or 500 ml wine samples were extracted by liquid-liquid extraction assisted with 30 ml hexane as extracting solvent. The extract was purified by shaking with 2 gr anhydrous sodium sulphate and 10 g silica gel, impregnated previously with 45% sulfuric acid. A further clean-up of this extract was performed in an open glass column packed with Florisil, deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane/dichloromethane 4/1(v/v). The extracts were concentrated to 2 ml and after that were analyzed by GC-ECD [19, 20, 21, 22].

Apparatus and chromatography

Gas chromatographic analyses were performed with a Varian 450 GC equipped with a ^{63}Ni electron capture detector and PTV injector. The column used was Rtx-5 [low/mid polarity, 5% (phenyl methyl siloxane)] (30 m x 33 mm I.D., x 25 mm film). The injector and detector temperatures were set at 280°C and 300°C, respectively. Carrier gas was He at 1 ml/min and make-up gas were nitrogen at 24 ml/min. The initial oven temperature was kept at 60°C for 4 min, which was increased, to 200°C at 20°C/min, held for 7 min, and then increased to 280°C at 4°C/min for 20 min. The temperature was finally increased to 300°C, at 10°C/min, held for 7 min. Injection volume was 2 μl . Pesticide quantification was performed by internal standard method using PCB 29 as internal standard compound. The following organochlorine pesticides: Hexachlorocyclohexanes (alpha-, beta-, gamma- and delta-HCH isomers), Heptachlors (Heptachlor and Heptachlor epoxide), DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT and Methoxychlor), Aldrines (Aldrine, Dieldrin, Endrin, Endrin keton and Endrin aldehyde), Endosulfanes (Endosulfane I, Endosulfane II and Endosulfan sulfate) and 7 PCB markers (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) were detected simultaneously in all fatty and non-fatty food samples. Method evaluation was done before the analysis of organochlorine pesticides and PCBs in the GC/ECD apparatus in order to get the optimal working parameters for the qualitative and quantitative analysis of organochlorine pollutants. Parameter validation was done for recovery, reproducibility, repeatability, correlation coefficient, LOD, LOQ, etc. (LOD for each individual chlorinated compounds was 0.5 ppb). IAEA 435 tuna sample was used for method evaluation. Calibration curves of each pesticide were done by using EPA 8081 pesticide standard and PCB markers solutions at concentrations of 1, 2.5, 5, 10, 25, 50, and 100 ppb. The working solution with a concentration of 25 ppb was used to determine the retention times of the each individual analyte [12, 17, 21].

Results and Discussion

Levels of organochlorine pesticides, their metabolites and polychlorinated biphenyls were analyzed in fatty and non-fatty food samples from Albania markets. Different types of food samples were analyzed in a five years period (2017-2021). EN 1528/1/2/3/4 protocols were used for isolation and quantification of chlorinated compounds in fatty food samples and EN 12393/1/2/3 Method was used for their analyze in non-fatty food samples. Organochlorine pollutants were detected using capillary gas chromatography with ECD technique. Data of organochlorine pesticides and PCB markers in food samples were shown in Table 2. Levels of pesticides and PCBs in solid samples were reported in $\mu\text{g}/\text{kg}$ sample or ppb while in liquid samples in $\mu\text{g}/\text{L}$ or ppb. Organochlorine pollutants were found in all analyzed food samples. The average concentration of organochlorine pesticides for fat samples was 1.51 ppb and for non-fat samples 0.79 ppb. It seems clear that fat favors their bioconcentration due to their moderate polarity. The highest value of pesticides and PCBs were found in fishes > chicken > fruit-vegetables > meat. Note that in more than 95% of analyzed samples, the total concentrations of pesticides were lower than the accepted level of total pesticides (50 ppb). The presence of pesticides in food samples may be due to previous use of organochlorine pesticides for agricultural purposes. Other factors such as the persistence of pesticides, their degradation processes, their mobility (in soil, in water, in food chain), geology and hydrogeology are the main factors that affect the level of pesticides in different types of samples. The presence of organochlorine pesticides is mainly due to their previous uses because in most of the samples at higher levels were found pesticide residues and not the primary active substances used as pesticides. PCB in food samples could be mainly because of their atmospheric deposition. Some punctual sources are not excluded. The origin of the samples

is also another factor that significantly affects the found levels for OCPs and PCBs at the same type of sample.

The concentration of Lindane and its isomers were found at higher levels in fatty food samples (fish, chicken and meat). The average level of HCHs for the fatty samples was 2.24 ppb while for the non-fatty food samples their average was 0.94 ppb. The highest levels of HCHs were found for fish (5.01 ppb), chicken (4.53 ppb), wine (4.01 ppb) meat (3.48 ppb) and fruit-vegetable (3.27 ppb) samples. The lowest level was found in water, bean and olive oil samples. The presence of HCHs in food products is related to the past use of Lindane as an insecticide. The concentration of Lindane was lower compared to other isomers due to their physical properties such as its stability, degradation time, solubility, etc. Beta-HCH was found more abundantly for fatty samples while delta-HCH was found higher in non-fatty samples. Total of HCH isomers were lower than allowed level for HCHs in Codex Alimentarius (0.01 mg/kg or 10 ppb) almost for all analyzed samples [23, 24]. Exception was for two carrot samples (Lushnje) and a vegetable sample (Tirana).

Heptachlor's were found at higher levels for fatty food samples. Their average level for fatty samples was 1.22 ppb while for non-fatty food samples their average was 0.51 ppb. The highest levels of Heptachlor and its metabolite were found for fish, chicken and meat samples. The lowest level was found in wine, dry-fruits, water, and olive oil samples where these compounds were not detected (below LOD) for more than 50% of analyzed samples. Heptachlor epoxide (degradation product) was found in higher level than Heptachlor (active pesticide). Their concentrations come mainly from the degradation of Heptachlor in the past as an insecticide for agro-agricultural purposes. Heptachlor levels in all samples were lower than the permitted levels based on Codex alimentary (0.02 mg/kg or 20 ppb) almost for all analyzed samples [23, 24].

Aldrin's were found at higher levels in high fat content samples especially in fish and chicken samples. Their average level for fatty samples was 1.72 ppb while for non-fatty food samples their average was 0.98 ppb. The highest levels of Aldrin were found for fish (6.14 ppb) and chicken (4.17 ppb) samples. The lowest level was found in butter, wine, olive oil and water samples. For all analyzed samples higher levels of Aldrin degradation products (Dieldrin, Endrin and Endrin aldehyde) was noted. Their concentrations come mainly from the degradation of Aldrin used earlier for agro-agricultural purposes. Aldrin levels for almost all samples were lower than allowed levels (0.1-0.2 mg/kg or 100-200 ppb) based on Codex Alimentary Commission limitations [23, 24]

DDT was the least frequently found pesticide compared to other groups of pesticides. This is also because its use has been discontinued in our country for a long time. Their average level for fatty samples was 1.95 ppb while for non-fatty food samples their average was 0.18 ppb. The highest levels of DDT were found for fish and meat samples. DDTs was not detected in water, wine and dry-fruits. These contaminants are found due to previous uses of DDT. DDT metabolites (DDE and DDD) were found more abundantly because of their physical properties. The levels of DDTs in all samples were lower than the permitted levels based on Codex Alimentarius norms (0.1-0.3 mg/kg or 100-300 ppb) for all analyzed samples [23, 24].

Endosulfans were found at higher levels for samples with high fat content. Their average concentration for fatty samples was 3.64 ppb while for non-fatty food samples their average was 1.08 ppb. The highest levels of Endosulfans were found for fish, chicken, fruit-vegetables, butter and dry-fruit samples. The lowest level was found in wine, water and vegetable oil samples. Different by other pesticides, Endosulfane, the active substance used as pesticide was found in higher level compare to its metabolites. This pesticide may still be in use under falsified labels or may be found as an impurity in some permitted pesticides. Punctual sources of this pesticide are not excluded. Almost in all samples, total of Endosulfanes were lower than the permitted levels based on Codex Alimentarius norms (0.03-0.5 mg/kg or 30-500 ppb) [23, 24]. Their total was found above the permitted level in a chicken sample (Tirana) and five fruit-vegetable samples (Tirana, Lushnja, Fieri, Korca).

PCBs were found higher in samples with high fat content. Their average level for fatty food samples was 3.55 ppb while for non-fatty food samples was 1.81 ppb. The highest levels of PCB markers were found in fish, butter, fruit-vegetables, chicken and olive oil samples. The lowest level was found in water, vegetable oil and meat samples. Profile for PCBs in fatty food samples were: PCB118 > PCB 138 > PCB 153 > PCB 28. PCB 138 and PCB 153 congeners have higher solubility in fats compare to others. Their presence was higher in fatty food samples. PCB 28 and PCB 52 were found higher in non-fatty food samples. These

congeners are representative of volatile PCBs, which means that their origin could be because of atmospheric deposition. The levels of PCB markers (their total) were lower than permitted level in all food samples based in national and international norms [25, 26].

Table 2. Organochlorine pesticides and PCB data (ppb or ug/kg or ug/L) in food samples from Albanian markets (2017-2021)

		Fatty food samples						Non-fatty food sample				
		Liquid sample		Solid sample				Liquid sample		Solid sample		
		Vegetal oil	Olive oil	Butter	Meat and by-products	Chicken and by-products	Fish	Water	Wine	Bean	Dry fruits	Fruit / Vegetables
HCHs	Average	1.82	1.32	0.61	3.48	4.53	5.01	N.D.	4.01	0.91	1.57	3.27
	Median	0.47	0.14	0.58	0.77	1.16	1.40		1.03	0.19	0.44	0.91
	Minimum	0.00	0.00	0.00	0.00	0.00	0.51		0.25	0.12	0.18	0.20
	Maximum	0.88	1.05	1.11	1.94	2.22	1.70		1.70	0.42	0.52	1.25
	STDV	0.40	0.48	0.51	0.96	1.08	0.53		0.73	0.13	0.15	0.49
Heptachlors	Average	0.88	0.00	1.07	1.37	2.24	2.54	N.D.	0.18	0.82	N.D.	0.88
	Median	0.44	0.20	0.54	0.69	1.12	1.27		0.09	0.41		0.44
	Minimum	0.26	0.12	0.45	0.40	0.70	1.22		0.06	0.08		0.11
	Maximum	0.62	0.27	0.62	0.97	1.54	1.32		0.12	0.74		0.77
	STDV	0.25	0.11	0.12	0.40	0.59	0.07		0.04	0.47		0.47
DDTs	Average	1.20	0.85	1.31	3.51	1.94	4.69	N.D.	N.D.	0.00	N.D.	1.25
	Median	0.37	0.11	0.30	1.52	0.40	1.34			0.09		0.19
	Minimum	0.32	0.00	0.00	0.00	0.22	1.03			0.04		0.05
	Maximum	0.51	0.74	1.01	1.99	1.32	2.32			0.13		0.96
	STDV	0.10	0.40	0.52	1.04	0.59	0.67			0.05		0.49
Adrins	Average	1.54	0.28	N.D.	N.D.	4.17	6.14	0.85	N.D.	1.88	2.16	1.81
	Median	0.22	0.05			0.93	1.32	0.00		0.14	0.40	0.38
	Minimum	0.00	0.00			0.67	1.04	0.00		0.11	0.20	0.32
	Maximum	1.11	0.18			1.64	2.47	0.85		1.49	1.16	0.73
	STDV	0.52	0.09			0.46	0.65	0.43		0.68	0.43	0.19
Endosulfans	Average	0.68	2.06	4.42	2.76	6.98	8.45	0.68	N.D.	3.24	4.30	5.09
	Median	0.14	0.58	1.35	0.95	1.74	3.03	0.00		0.98	1.83	1.48
	Minimum	0.13	0.10	0.71	0.00	0.57	2.13	0.00		0.14	0.44	0.32
	Maximum	0.41	1.38	2.36	1.81	4.67	3.29	0.68		2.12	2.03	3.29
	STDV	0.16	0.65	0.83	0.91	2.11	0.61	0.39		0.99	0.87	1.50
PCB markers	Average	1.03	2.55	3.12	1.34	2.92	7.31	N.D.	1.97	1.84	2.19	3.42
	Median	0.00	0.12	0.00	0.00	0.00	1.36		0.12	0.12	0.19	0.20
	Minimum	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
	Maximum	0.76	1.25	2.91	0.94	2.22	2.22		0.70	0.77	0.98	1.28
	STDV	0.29	0.54	1.09	0.36	0.84	0.88		0.29	0.35	0.34	0.55

N.D. – Not Detected or lower than Limit of Detection (LOD = 0.5ppb)

Conclusion

Levels of organochlorine pesticides, their metabolites and polychlorinated biphenyls were analyzed for five years period (2017-2021) in food samples from Albanian markets. Samples were classified as fatty and non-fatty food samples based on their fat percentage. EN 1528/1/2/3/4 and EN 12393/1/2/3 protocols were used for determination of chlorinated compounds respectively in fatty and non-fatty food samples, recommended to be followed as national standards in Albania. The qualitative and quantitative analysis of pesticides was carried out by gas chromatography followed by electron capture detector. This technique is recommended to be used for routine analyzes of organochlorine pollutants because the detection levels of these pollutants are in ppb level, due to specificity of ECD for halogenated compounds. Note that, GC/ECD is cheaper technique than GC/MS/MS, which is suggested as the most reliable technique.

The presence of organochlorine pesticides and their residues is observed almost in all samples. The average concentration of organochlorine pesticides for fatty samples was greater than for non-fatty samples. Adipose tissue and fat favor the bioconcentration of these pollutants due to their moderate polarity. The highest value of pesticides was found in fish samples. In more than 95% of the analyzed samples, the total amount of pesticides (each individe) was less than the allowed level. Higher levels were found in some fish samples, chicken samples, carrot samples, etc. These levels may be due to punctual sources of these pollutants. The presence of pesticides in food samples may be due to previous use of organochlorine pesticides for agricultural purposes. Other factors such as the persistence of pesticides, their degradation processes, their mobility, geology and hydrogeology are the main factors that affect the level of pesticides in different types of samples. The origin of the samples is also another factor that significantly affects the levels found for the same type of sample analyzed. Note that the presence of organochlorine pesticides is mainly due to their previous uses because in most of the samples (about 87%) at higher levels pesticide residues were found and not the primary active substances used for agricultural purposes. Presence of PCB markers in food samples of Albanian markets could be mainly because atmospheric depositions but punctual sources are not exluded. Their physic-chemical properties (boiling point, water/fat solubility, etc.) affect their concentrations in food samples. Presence of OCPs and PCBs in food samples (reported data from this study) must encourage the responsible institutions in Albania to monitor pesticides and other organic pollutants in food and feed samples not only because it is a legal obligation but because it is related with health of population.

References

- [1] Muco A. (1999) Organochlorine, Pyrethrin and Pyrethroid Insecticides: Single class, Multiresidue Analysis of. Pesticides. Pp. 6384-6414
- [2] Nshimiyimana FX., El Abidi A., Fekhaoui M., Benbakhta B., Barakate N., Hami H. and Soulaymani A. (2014) Analysis Method for Pesticide Residues in Biological Matrices: Gas Chromatography-mass Spectrometry, Journal of Life Sciences, Vol. 8, No. 6, pp. 489-495 ISSN 1934-7391.
- [3] Skibniewska K., Smoczynski S. (2000) Modern looks on the residues chloroorganic insecticide in food. Żyw.Czlow.Metab.Vol. 27 (supl). Pp. 279-281.
- [4] Penttila P.L., Siivinen K., (1996) Control and intake of pesticide residues during 1981-1993 in Finland Food Additives & Contaminants: Part A, Volume 13, Issue 6, Pp. 609 – 621.
- [5] Nuro A., Koci K., Marku E. (2007) Occurrence of Persistent Chlorinated Contaminants using Butter as an Integrative Matrix., Journal of Environmental Protection and Ecology 8,No 3, 544-555.
- [6] <https://www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls-pcbs>
- [7] Erickson, M.D. (2001). Introduction: PCB properties, uses, occurrence, and regulatory history. In: Robertson, L.W., Hansen, L.G. (Eds.), PCBs: Recent Advances in Environmental Toxicology and Health Effects. The University Press of Kentucky, Lexington, Kentucky, Pp. 131–152.
- [8] Bernard, A., Hermans, C., Broeckaert, F., Depoorter, G., De Cock, A., Houins, G., (1999) Food contamination by PCBs and dioxins. Nature 401, Pp. 231–232.
- [9] ATSDR, 2000. Toxicological profile for polychlorinated biphenyls (PCBs). US department of health and human services, Public health service, Agency for toxic substances and disease registry, Atlanta, Georgia.

- [10] Takekuma M., Saito K., Ogawa M., Matumoto R., Kobayashi S. (2004) Levels of PCDDs, PCDFs and Co-PCBs in human milk in Saitama, Japan, and epidemiological research. *Chemosphere*, (54): 127–135.
- [11] Wilhelm M., Schrey P., Wittsiepe J., Heinzow B. (2002) Dietary intake of persistent organic pollutants (POPs) by German children using duplicate portion sampling. *Int. J. Hyg. Environ. Health*. Vol. 204. Pp. 359-362.
- [12] Corcia A. (1999) Pesticides Analysis: Introduction. *Pesticides*. Pp.6111-6113
- [13] Beltran J., Lopez F.J., Hernandez F. (2000) Solid-phase micro-extraction in pesticide residue analysis. *Journal of Chromatography A*, 885
- [14] EN 1528-1 (1996) Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 1: General
- [15] EN 1528-2 (1996) Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 2: Extraction of fat, pesticides and PCBs, and determination of fat content
- [16] EN 1528-3 (1996) Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 3: Clean-up methods
- [17] EN 1528-4 (1996) Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 4: Determination, confirmatory tests, miscellaneous
- [18] Yoon H.R., Lee E.J, Park M.K., Park J.H. (1998) Sulfuric Acid Pretreatment for Simultaneous GC Screening of Organochlorine and Organophosphorus Pesticides in Herbal Essential Oils. *Cromatographia*. Vol 47. No 9/10.
- [19] EN 12393-1 (1998) Non-fatty foods – Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 1: General considerations
- [20] EN 12393-1 (1998) Non-fatty foods – Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 2: Methods for extraction and clean-up
- [21] EN 12393-1 (1998) Non-fatty foods – Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 3: Determination and confirmatory tests
- [22] EN 16693 (2015) Water quality - Determination of organochlorine pesticides (OCP) in whole water samples - Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)
- [23] Codex Alimentarius, Volume II-Pesticide Residues in Food. 2010
- [24] Lazaro R., Herrera A., Arino A., Pilar Conchello M., Bayrri S. (1996) Organochlorine pesticide residues in total diet samples from Aragon (Northeastern Spain). *J.Agric.Food Chem*. Vol. 44. Pp. 2742-2747.
- [25] Focant J.-F., Pirard C., De Pauw E.. (2004) Levels of PCDDs, PCDFs and PCBs in Belgian and international fast food samples. *Chemosphere* (54): 137–142
- [26] Papadopoulos A., Vassiliadou I., Costopoulou D., Papanicolaou C., Leondiadis L. (2004) Levels of dioxins and dioxin-like PCBs in food samples on the Greek market. *Chemosphere* (57): 413–419