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Evaluation of Organochloro Pesticides in Chicken Meat in Tirana Market, Albania

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The study included the analyses of food samples taken from chicken meat with different origin collected between December 2007 and March 2008 in Tirana market (Albania). The detected organochloro pesticides were HCHs (α-, β-, γ-, δ-isomers), aldrine, endrine, dieldrine and DDT-related chemicals (*o,p*'-DDE; *p,p*'-DDE; *p,p*'-DDD; *p,p*'-DDT). The analysis was performed by gas chromatography electron capture detection. All the results were expressed on a fresh weight basis. The concentrations of organochloro pesticides in all samples were far below the EC regulation (2375/2001/EC) limits. Organochloro pesticides patterns from two types of chicken samples (imported and village chicken feed up in natural conditions) were compared using principal component analysis and were correlated with the organochloro pesticides patterns from two different potential contamination sources, industrial meat and growed up in natural condition meat. Moreover, three origin indices (concentration ratios of organochloro pesticide isomer pairs) were used to evaluate the suitability of these compounds as tracers to distinguish between the contamination arising from different sources. The evaluation of contaminant patterns permits the conclusion that the organochloro pesticides present in these samples are of different origin.

Key Words: Organochloro pesticides, Chicken meat, Principal components analysis, Chemical analysis.

INTRODUCTION

Synthetic pesticides have been used since early to mid-twentieth century, when insecticidal properties of DDT were discovered. Over 800 pesticide active ingredients are formulated in about 21000 different commercial products. The modern history of pesticides dates back to World War II when for the first time the insecticidal properties of DDT were recognized. *p,p′*-Dichloro diphenyl trichloroethane (DDT) was first introduced on a large scale to fight fleas, lice, flies and mosquitoes and reduce the spread of insect borne diseases, such as malaria and yellow fever. Many public health benefits have been realized by the use of pesticides, but their potential impact on the environment is substantial too[1]. Organochloro 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. Organochloro pesticides are used extensively as insecticides, sterilizes and herbicides. In particular, those used as insecticides are extremely toxic to living bodies. Most OCPs have been progressively restricted and then banned in the 1970s in most industrialized countries. A widespread environmental pollution has resulted from their use in agriculture and civil uses. Human exposure to organochlorinated pollutants primarily occurs through food contamination. Fish, meat and diary products are the most important dietary sources of OCP for humans and it is widely accepted that these pollutants will be present in food for many years to come[2,3].

Principal components analysis (PCA) is used for interpretation of present results, as a technique for simplifying a multi-dimensional data set, by reducing it to lower dimensions for analysis[4,5].

EXPERIMENTAL

Sampling procedure: This study included the analyses of 28 chicken meat samples, collected between December 2007 and March 2008 in different points of Tirana market (Albania). There were 16 village chicken meat samples (feed up in natural conditions) and 12 imported chicken meat samples (feed up in industrial conditions).

The method used was based on EN 1258/1/2/3/4[6] for determination of OCP and PCBs in food samples. The samples, represented from chicken meat tissues, were stored at -10 ºC.

Analysis procedure: The samples were homogenized with anhydrous sodium sulphate (Merck, Darmstadt, Germany) and was extracted by water bath assisted extraction (1 g fresh weight of chicken tissue with hexane/dichloromethane 4/1, (v/v) (Fluka, Germany, pesticide grade). The internal standard PCB 29 was added to each sample prior to extraction. The extract was purified by shaking with 15 g silica gel, impregnated previously with 45 % sulfuric acid. After filtration, the extract was concentrated in Kuderna Darnish to 5 mL volume. A further clean-up of this extract was performed in a column packed with Florisil (particle size 0.063 ± 0.2 µm; Merck, Darmstadt, Germany), deactivated with 5 % water. The organochlorine compounds were eluted with 15 mL of hexane/dichloromethane 5/1 (v/v) (spectroscopy grade; Fluka, Germany). The extract was concentrated again to 1 mL and analyzed by GC-ECD[5,7].

Gas chromatographic analyses were performed with an HP 6890 Series II gas chromatograph equipped with a ^{63}Ni Electron capture detector and a split/splitless injector. The column used was a HP-5 (low/mid polarity, 5 % phenyl methyl siloxane 25 m × 0.33 mm × 0.25 µm film). The split/splitless injector and detector temperatures were set at 280 and 320 ºC, respectively. Carrier gas was helium at 19.8 mL/min and make-up gas was nitrogen at 10.2 mL/min flow. The initial oven temperature was kept at 60 ºC for 4 min, than increased to 200 ºC at 20 ºC/min and then increased to 280 ºC at 4 ºC/min. The temperature was finally increased to 300 ºC, at 10 ºC/min, than held for 7 min. Injection volume was 2 µL and injections were done in splitless mode. Organochloro pesticide quantification was performed by internal standard method[8,9].

RESULTS AND DISCUSSION

The statistical data of the concentrations of OCPs found in the village chicken and imported chicken meat samples are presented, respectively in Tables 1 and 2.

The organochloro pesticides distribution profile appears similar for village chicken and imported chicken samples (Fig. 1). The imported chicken samples contained higher concentrations for most of the investigated organochlorine pesticides, like: 4,4'-DDT and its metabolites, aldrine, endrine and dieldrine. The 4,4'- DDE/4,4'-DDT ratio is higher than in the imported chickens suggesting that 4,4'-DDT in Albania (where the chickens has been feed) has been used longer than the countries of origin for the imported chickens.

The total concentration of the investigated OCPs was lower in Albanian village chicken meat samples (48.58 ng/g f.w.) than in the imported chicken meat samples (65.70 ng/g f.w.). However, the relative contributions of OCPs are similar in both types of samples (Fig. 2). ΣDDTs is the most predominant for both types of samples[10,11].

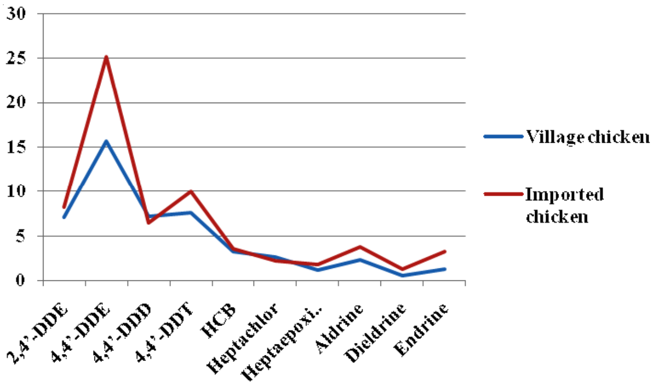

Fig. 1. Distribution of OCP's mean concentrations (ng/g f.w.)

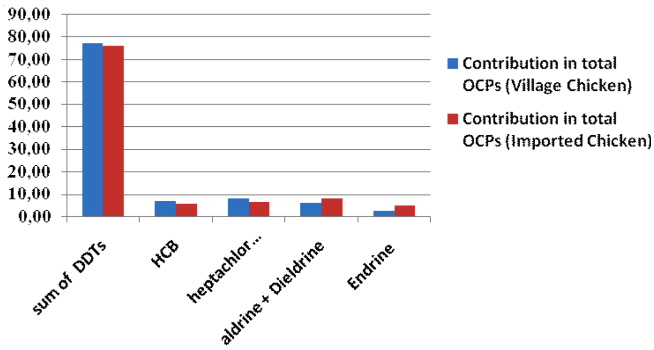

Fig. 2. Relative contributions to total sum of OCPs in the village and imported chicken meat

In Albania, chicken meat is widely used and represents an important part of Albanian diet. ADI and daily intake values as percentage of ADI for Albanian man with high poultry consumption (150 g/day) are presented in Table-3. It is obvious that all the investigated chicken samples taken in the Albanian market, were sanitary safe[6,12].

Distribution of OCPs using principal component analysis: Principal component analysis (PCA) was used to compare the OCP distribution in two types of chicken samples (imported

TABLE-1
STATISTICAL DATA OF THE ANALYTICAL RESULTS OF VILLAGE CHICKEN MEAT (N = 16) (ng/g FRESH WEIGHT)

Index	2,4'-DDE	4,4'-DDE	4,4'-DDD	4,4'-DDT	HCB	Heptachlor	Heptachlor epoxide	Aldrine	Dieldrine	Endrine
Mean	7.08	15.7	7.157	7.57	3.21	2.58	1.19	2.26	0.52	1.21
Median	6.13	14.96	5.17	7.39	2.73	1.59	0.66	1.94	0	0.5
STDEV	3.72	9.54	7.93	6.09	2.21	3.35	1.28	2.24	1.03	1.77
Variance	13.84	90.93	62.94	37.09	4.88	11.26	1.65	4.99	1.06	3.13
Min	3.62	1.34	0	0	0.42	0	0	0	0	0
Max	15.68	37.2	23.49	16.49	7.67	14.25	4.64	7.03	3.12	5.02

TABLE-2
STATISTICAL DATA OF THE ANALYTICAL RESULTS OF IMPORTED CHICKEN MEAT (N = 12) (ng/g FRESH WEIGHT)

Index	2,4'-DDE	4,4'-DDE	4,4'-DDD	4,4'-DDT	HCB	Heptachlor	Heptachlor epoxide	Aldrine	Dieldrine	Endrine
Mean	8.22	25.12	6.44	10	3.6	2.22	1.83	3.77	1.29	3.21
Median	6.95	23.24	1.975	6.145	2.16	1.29	1.185	1.89	0.25	1.57
STDEV	4.92	12.75	14.74	15.82	4.66	2.62	1.79	4.19	2.25	4.62
Variance	24.16	162.64	217.36	250.17	21.75	6.89	3.23	17.58	5.07	21.35
Min	3.9	10.9	0	0	0.79	0.5	0.34	0	0	0
Max	19.4	60.4	52.55	56.37	17.32	9.83	6.08	12.53	6.88	15.14

TABLE-3
ADI AND DAILY INTAKE FOR AN ALBANIAN MAN WITH HIGH POULTRY CONSUMPTION (150 g/day)

-OCP group	ADI* (ng)	Village chicken		Imported chicken	
		Mean concentration in chicken meat (ng/g f.w.)	Daily intake as percentage of ADI	Mean concentration in chicken meat (ng/g f.w.)	Daily intake as percentage of ADI
ΣDDTs	1400000	77.21	0.83	75.77	0.81
HCB	42000	6.61	2.36	5.48	1.96
Heptachlor + heptachlorepoxide	7000	7.76	16.63	6.16	13.21
Aldrine + dieldrine	7000	5.93	12.70	7.70	16.50
Endrine	14000	2.49	2.67	4.89	5.23

*ADIs are normalized for a 70 kg body weight (UNEP/FAO 1990)[13,14].

and village chicken feed up in natural conditions) collected from different market points in Tirana (Albania). The result was performed on data standardized to the total OCP concentration of each sample. The principal component analysis represents the patterns by arranging the variables (OCPs) and factors along axes (principal components), which are assumed to represent basic relationships.

Two different types of OCP distribution were found for two types of chicken meat (Fig. 3). The village chicken meat, the first principal component (4,4'-DDD and 4,4'-DDD) describes the maximum amount of variation of the data and subsequent calculated principal components (heptachlor epoxide, 4,4'-DDT, 2,4'-DDE and aldrine) describe the remaining variation of the data in decreasing order of importance. It is shown too, most important components are positively correlated to each other.

The situation was different at imported chicken meat samples, where most important components are negatively correlated to each other. The first principal component of this group of samples was 4,4'-DDD, which describes the maximum amount of variation of the data and subsequent calculated principal components, 4,4'-DDT describes the remaining variation of the data in decreasing order of importance, followed from endrine, aldrine, heptachlor, heptachlor epoxide[15]. The number of principal components in this case is higher than the number of principal components found for village chicken meat (based on Kaiser criterion), signifying that the number of OCP pollutants were higher in the imported chicken meat feed up in industrial condition. Each OCP was found to be orthogonal to the previous one. Data were modelled by PCA MINITAB software: Principal Component Factor Analysis of the Correlation Matrix; Rotated Factor Loadings and Communalities; Varimax Rotation.

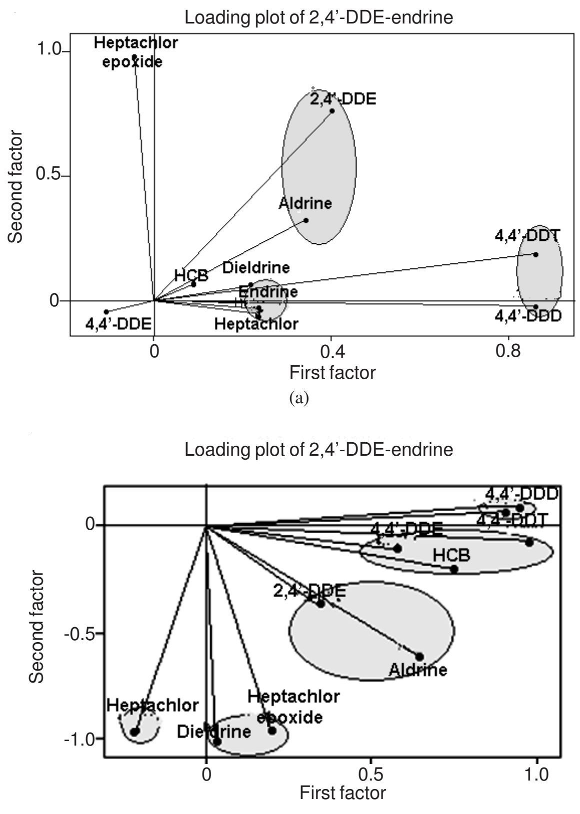

Fig. 3. Load plot of 2,4'-DDE-endrine (a) village chicken and (b) imported chicken

Organochlorine pesticides patterns: In order to determine the nature of OCP pollution, we compared the OCP patterns of village and imported chicken meat. The relative concentrations of OCPs in samples were analyzed by principal component analysis. The data were modeled by MINITAB software: cluster analysis of variables, correlation coefficient distance and average linkage. The results are shown in Fig. 4.

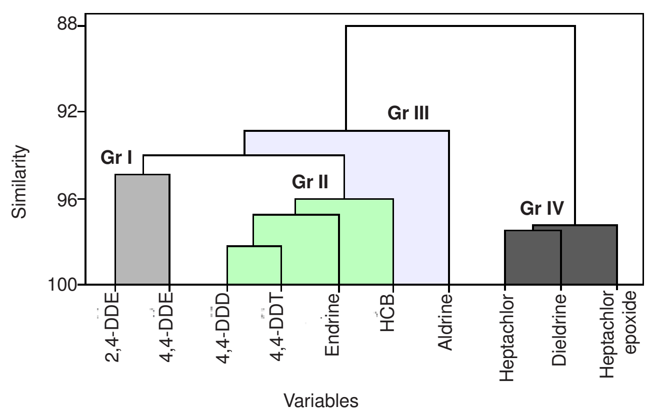

Fig. 4. Cluster analysis of variables (a) village chicken and (b) imported chicken

Different group's classification of OCP variables were found for village and imported chicken meat related with different sources of contamination being evident in present chicken samples. From an inspection of the cluster analysis of variables, the chlorinated pesticides are separated in four clusters, according to their molecular weight or liophilicity. The first cluster contains two DDE isomers which have the same molecular weight and similar liophilicity. The second cluster contains 4,4'-DDT, its metabolite 4,4'-DDD, endrine and HCB. Most of OCPs falling in the first two clusters are members of dichlorodiphenylmethane derivatives' family, with lower polarity[16]. Chlorinated cyclodiene pesticides (with a different chemical structure) like heptachlor, heptachlor epoxide, aldrine, dieldrine, *etc*., fall in the third and fourth cluster. This indicates that the bioaccumulation ability of chlorinated pesticides can be attributed either to their hydrophobicity or to their chemical structure.

Conclusion

The organochlorine pesticides distribution profile appears similar for village chicken and imported chicken samples. The imported chicken samples contained higher concentrations for most of the investigated organochlorine pesticides, like: 4,4'-DDT and its metabolites, aldrine, endrine and dieldrine. The 4,4'-DDE/4,4'-DDT ratio is higher in the imported chickens suggesting that 4,4'-DDT in Albania (where the chickens has been feed) used longer than the countries of origin for the imported chickens. The OCP distribution profile appears similar for village chicken and imported chicken samples (Fig. 1). The imported chicken samples contained higher concentrations for most of the investigated organochlorine pesticides, like: 4,4'-DDT and its metabolites, aldrine, endrine and dieldrine. The 4,4'-DDE/4,4'-DDT ratio is higher than in the imported chickens suggesting that 4,4'-DDT in albania has been used longer than the countries of origin for the imported chickens.

The total concentration of the investigated OCPs was lower in Albanian village chicken meat samples than in the imported chicken meat samples. The relative contributions of OCPs are similar in both types of samples. ΣDDTs was the most predominant for both types of samples. In Albania, chicken meat represents an important part of Albanian diet. Taking into account ADI and daily intake values as percentage of ADI for Albanian man with high poultry consumption resulted that all the investigated chicken samples taken in the Albanian market, were sanitary safe.

Principal component analysis (PCA) was used to compare the OCP distribution in two types of chicken samples (imported and village chicken feed up in natural conditions) collected from different market points in Tirana (Albania). The result was performed on data standardized to the total OCP concentration of each sample. Two different types of OCP distribution were found for two types of meat samples. For the village chicken meat samples, the first principal component (4,4'-DDD and 4,4'-DDD) describes the maximum amount of variation of the data and subsequent calculated principal components (heptachlor epoxide, 4,4'-DDT, 2,4'-DDE and aldrine) describe the remaining variation of the data in decreasing order of importance. Most important components are positively correlated to each other. The situation was different at imported chicken meat samples, where most important components are negatively correlated to each other. The first principal component of this group of samples was 4,4'-DDD, which describes the maximum amount of variation of the data and subsequent calculated principal components, 4,4'-DDT describes the remaining variation of the data in decreasing order of importance, followed from endrine, aldrine, heptachlor, heptachlor epoxide. The number of principal components in this case is higher than the number of principal components found for village chicken meat, suggesting that the number of OCP pollutants were evidently higher in the imported chicken meat feed up in industrial condition. The relative concentrations of OCPs in samples were analyzed by cluster analysis of variables. Different group's classification of OCP variables were found for village and imported chicken meat related with different sources of contamination being evident in our samples. From an inspection of the cluster analysis of variables, the chlorinated pesticides were separated in four clusters, according to their molecular weight or liophilicity. The first cluster contained two DDE isomers which have the same molecular weight and similar liophilicity. The second cluster contains 4,4'-DDT, its metabolite 4,4'-DDD, endrine and HCB. Most of OCPs falling in the first two clusters were members of dichlorodiphenylmethane derivatives' family, with lower polarity. Chlorinated cyclodiene group pesticides like heptachlor, heptachlor epoxide, aldrine, dieldrine, *etc*., falled in the third and fourth cluster. This indicates that the bioaccumulation ability of chlorinated pesticides can be attributed either to their hydrophobicity or to their chemical structure.

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