

## EXAMINATION OF ORGANOCHLORINE PESTICIDES IN GOAT'S MILK

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Examination of organochlorine pesticides (OCPs) was performed on samples of goat milk. Typical of OCPs is that they accumulate in the milk fat, for this purpose during the examination analyzed the quantities of OCPs in milk fat, and the quantities of OCPs depending on the temperature and storage time. In samples of raw goat's milk taken from 10 individual farms Pelagonija region, were determined seven OCPs. Value of fat was approximately 2.7%. The milk was kept at a temperature of 4°C for a week till decay. The OCPs was calculated in (w/w %), and was found that most present are Heptachlor average 0,091695, at least Dieldrin with value of 0,034547. Determination was made of the gas chromatograph (GS) from "Agilent Technologies", and calculated analytical yield, R varied in the range of 98,113599 to 101,83674%, which proves that the method is accurate and quantitative.

The maximum value at temperature of 63-65°C is DDT, than Endosulfan heated at a temperature of 71-74°C, while minimum value is Dieldrin at temperature of 89 -100°C. The conclusion of examination is that in our region are still applied insecticides for the protection of plants.

**UDC Number:** 502/504, **DOI:** 10.12955/cbup.2013.59

**Key words:** organochloride pesticides, OCPs, goat milk, milk fat

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### Introduction

Persistent organic pollutants (POPs) are organic compounds that resist photolytic, biological and chemical degradation. A pesticide may be a chemical substance, biological agent (such as a virus or bacteria), antimicrobial, disinfectant or device used against any pest. Pesticides can also be classed as synthetic pesticides or biological pesticides, bio pesticides as classified by Ashnagar (2009). OCPs are being extensively used in tropical countries in malaria control programs and against livestock ectoparasites and agricultural pests, as described by Pandit (2002). They contain carbon, hydrogen and chlorine.

Extensive use of organochlorine pesticides (OCPs) in agriculture and livestock result in environmental contamination. The organochloride pesticides enter the food chain as a result of their lipophilic properties, where the concentration can be increased up to 70,000 times. This causes a potential health risk for consumers (POP's office, 2006). After ingestion, lipophilic pesticides get absorbed from the intestine into the general circulation. Highly lipid soluble pesticides tend to concentrate in tissues with higher lipid contents including adipose tissue, brain, liver, kidneys and in milk. Milk and dairy products are commonly used commodities in almost all the societies of the world and have a pivotal role in human nutrition. The occurrence of pesticides residues in the milk is a matter of public health

concern, so, it is very important to ensure the quality of milk with respect to pesticide residues. In this regard, most of the developed countries have established their maximum residue levels (MRLs) of pesticides in milk and other dairy products, seen from Feqir et al. (2012).

Analyse were conducted for Lindan, Heptachlor, Aldrin, Dieldrin, Endosulfan, Endrin, and DDT for the determination in goat's milk samples. In the group, OCPs include pesticides containing chlorine, for example: Lindan ( $\gamma$ -1, 2, 3, 4, 5, 6 – hexachlorocyclohexane or  $\gamma$ -HCH) is synthetically acquired chlorinated pesticide, and the other two isomers are byproducts of lindane and characterized by high levels of presence in the environment.

p,p,-DDT[1,1,1-trichloro-2,2,-bis-(p-chlorophenyl)ethylene], p,p'- DDE [1,1-dichloro- 2,2,bis(p-chlorophenyl) ethylene], p,p'-DDD[1,1-dichloro-2,2,-bis-(p-chlorophenyl)ethane]. p,p'-DDE and p,p'-DDD occur during chemical transformations of p,p'-DDT, which is the first synthetically acquired pesticide, than Aldrin, Dieldrin, Heptachlor, Endosulfan and Endrin.

## Materials and methods

The research was conducted on raw goat milk and soured-milk products, in a period over three months (December, January and February), from farms located in the Pelagonia region. In this paper research is carried out of qualitative and quantitative determination of milk serum which commonly use non ionized organochlorine insecticides in milk. Chemical analysis was examined for the presence of milk fat. Except for raw milk, research found the presence of OPC in milk warm-up on the temperatures of 63-65<sup>0</sup>C for 30 min, temperature of 71-74<sup>0</sup>C for 15 sec., temperature of 89-100<sup>0</sup>C for 1 sec. Also it was monitored for the presence of organochlorine pesticides in milk kept frozen at a temperature of -18<sup>0</sup>C for 24 hours, milk kept at 4<sup>0</sup>C for 24 hours, and milk kept for one week at 4<sup>0</sup>C.

Milk fat was examined with the Acidobutirometric method by Gerber, which is based on the dissolution of all ingredients from milk with sulfuric acid, except milk fat which separates on the surface. Fat separation is facilitated by adding amyl alcohol that reduces surface tension, and is accelerated by centrifugation; for the determination of milk fat a graduated butyrometer was used to show the percentage of fat and appropriate centrifuge.

In order to check the accuracy of the method used above, the milk from each region was exactly added of the known quantities of p,p 'DDT, which previously made the determination of OCP. Validation of the accuracy of the method was done by the value of the analytical yield (R). The apparatus that was used to determinate the concentration organochlorine pesticides in milk is a gas chromatograph from "Agilent Technologies", the model GC 7890N equipped with appropriate software system.

## Results and discussion

OCPs are made of chromatographic analysis present in raw goat milk from the Pelagonia region, and was monitored on their amounts and calculated in %, during a period of the three months (December 2009, January and February 2010). Their quantities are measured (w/w %) for OCPs in milk depending on content of fat milk content. They are also measured on w/w% for all OCPs in raw goat milk, depending on the applied temperature, temperatures adequately applicable for standardisation and pasteurisation of milk and their storage time. The following temperatures were applied: 4<sup>0</sup>C for 24 hours, 63-65<sup>0</sup>C for 30 minutes, 71-74<sup>0</sup>C for 15 seconds, 89-100<sup>0</sup>C for 1 second; milk was kept at a temperature of -18<sup>0</sup>C for a time of 24 hours.

The content of the pesticides in the milk all decreased as the treatment time progress indicating degradation of the pesticides by Li-Ying (2011). Sterilization process had an efficient role on the degradation or elimination of pesticide residues from Abou Donio (2010). In order to increase the accuracy of the values obtained for the tested parameters, they are presented in tables and graphs below. Values in Table 1 are average values of three repetitions.

Table 1: Quantity (w/ w%) of OCP depending on the applied temperature and milk fat in raw goat milk from the Pelagonia region						
Name of pesticide	Milk fat (%)	w/w% of t = 4°C 24 hours	w/w% of t = 63-65°C 30 min.	w/w% of t = 71-74 °C 15 sec.	w/w% of t =89-100°C 1 sec.	w/w% of t = - 18°C 24 hours
Lindan	2.7	0.075100	0.123602	0.056572	0.031176	0.065946
Heptachlor	2.7	0.068348	0.119892	0.083758	0.058480	0.061842
Aldrin	2.7	0.028410	0.038994	0.036244	0.010762	0.013834
Dieldrin	2.7	0.024726	0.018682	0.048374	0	0.022036
Endosulfan	2.7	0.052784	0.081025	0.170824	0.010222	0.036455
Endrin	2.7	0.050450	0.055890	0.036618	0.016494	0.041714
DDT	2.7	0.036432	0	0.050708	0.023384	0.038040
X	2.7	0.048035	0.073014	0.069014	0.025086	0.039981
SD	2.7	0.0193071	0.042949	0.0476479	0.018193	0.019048
Source: Author						

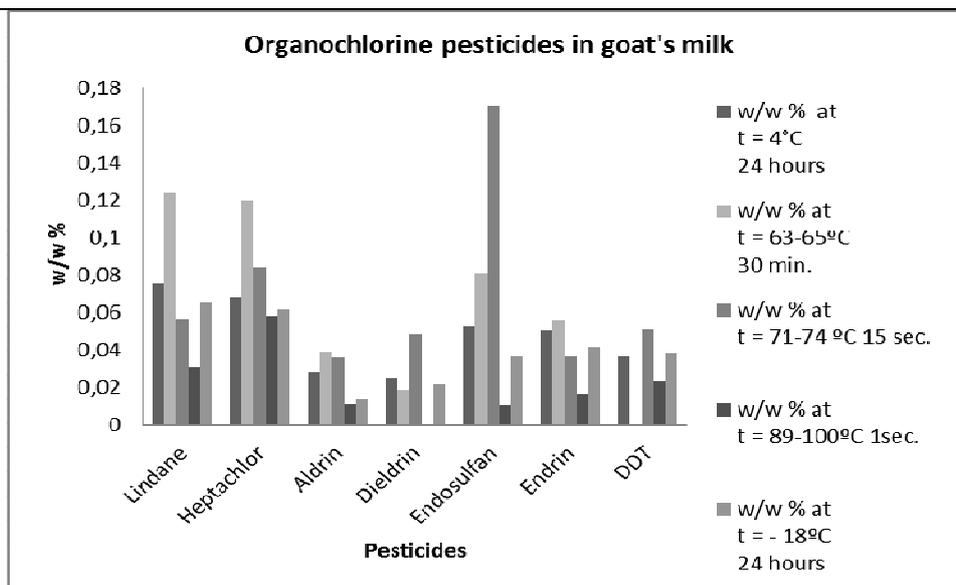
As seen from the data presented in Table 1, highest mean OCP value is 0.073014 on heating milk at a temperature of 63-65°C for 30 min, while the minimum OCP value is 0.025086 on heating milk at a temperature of 89-100°C for 1 second.

Minimum OCP value of the standard deviation (SD) on heating milk is 0.018193 at a temperature of 89-100°C for 1 second, while the maximum OCP value of the standard deviation is 0.0476479 on heating milk at a temperature of 71-74°C for a period of 15 seconds. From Figure 1 we can see that all OCP in goat milk was treated at different temperatures with different heating time. Pesticides from the group Endosulfan had a maximum quantity 0.170824 heated at a temperature of 71-74°C, while the minimum values are proven in pesticides from the group Dieldrin heated at a temperature of 89-100°C and pesticide from the group DDT heated at a temperature of 63-65°C.

The fat-soluble knowing of Organochlorine pesticide graphically represents pesticide dependence of the fat, as presented in Figure 2.

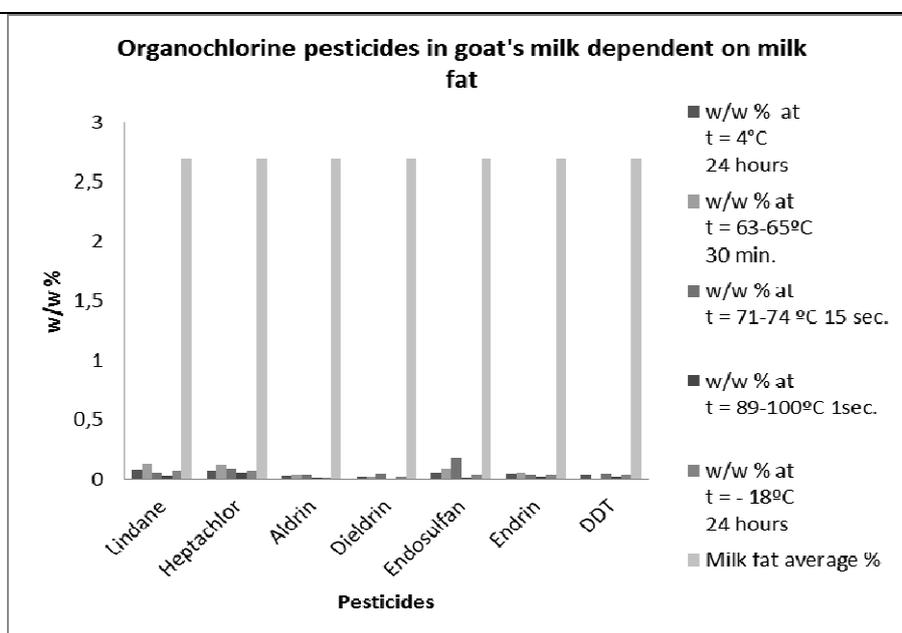
In all samples of goat milk fat percentage has the same value around 2.7, the presence of pesticides in the ppm, but it is seen that although there is a small presence in the ppm, they are fat-soluble. Compared with Feqir et al. (2012) all pesticides residues (cyhalothrin, endosulfan, chlorpyrifos and cypermethrin) under study except endosulfan showed a positive correlation of all the pesticide residues under study with respect to the percentage fat. This finding is in accordance to the findings of Abou Donia (2010), who reported the accumulation of a high level of pesticide residues in high fat milk as compared to low fat milk.

Figure 1: OCP depending on the applied temperature and milk fat in raw goat milk from the Pelagonia region



Source: Author

Figure 2: OCP depending on milk fat in raw goat milk from the Pelagonia region



Source: Author

Measurement was done w/w % OCP in raw goat's milk which was kept in the refrigerator at a temperature of 4°C during one week until it's used by date as presented in Table 2. In terms of days of storage a statistical processing of the results was used by applying the mean value and standard deviation.

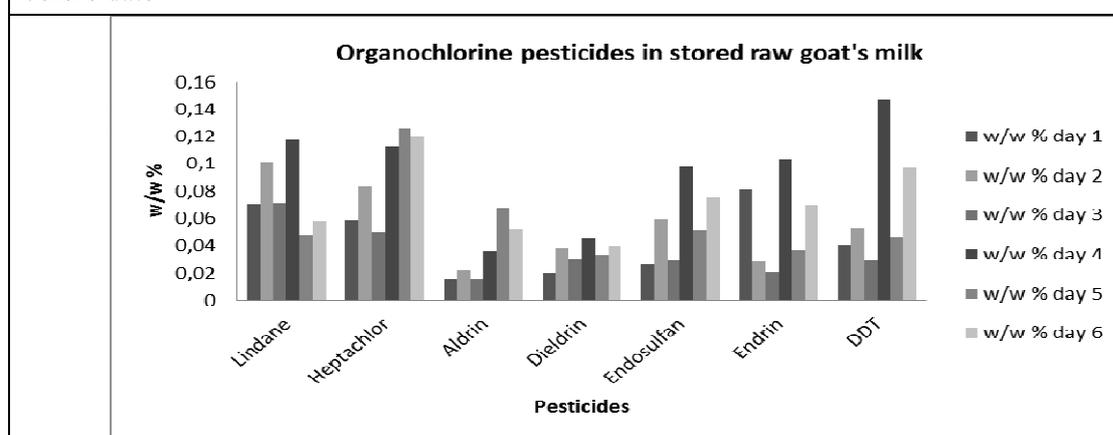
Table 2: Statistical processing of the results OCP in raw goat's milk kept in the refrigerator at a temperature of 4°C

No. of days	Lindan w/w%	Heptachlor w/w%	Aldrin w/w%	Dieldrin w/w%	Endosulfan w/w%	Endrin w/w%	DDT w/w%
1	0.070522	0.058354	0.015454	0.020456	0.026269	0.080866	0.040324
2	0.100864	0.083102	0.022006	0.038174	0.059406	0.027954	0.053114
3	0.071176	0.050270	0.015732	0.030306	0.028944	0.020862	0.028934
4	0.117240	0.112920	0.036048	0.045206	0.098472	0.103296	0.147294
5	0.047322	0.126044	0.067626	0.033692	0.051204	0.036780	0.045880
6	0.058236	0.119482	0.051837	0.039449	0.074838	0.070038	0.096587
$\bar{x}$	0.077560	0.091695	0.034783	0.034547	0.056522	0.056632	0.068688
SD	0.026440	0.032569	0.021311	0.008579	0.027595	0.032986	0.044955

Source: Author

As seen from the data presented in Table 2, highest mean OCP value in raw goat milk kept for a week at a temperature of 4°C in refrigerator reach group pesticide Heptachlor 0.091695, and the minimum value were pesticide group Dieldrin 0.034547. Minimum value of the standard deviation (SD) group has pesticides Aldrin 0.021311, while the maximum value has pesticide's group DDT with 0.044955 presented in Figure 3.

Figure 3: OCP in raw goat's milk kept in the refrigerator at a temperature of 4°C until it reaches best before date



Source: Author

From the data in Figure 3 for pesticides of group Lindan minimum quantity is 0.047322% which is determined on the fifth day of its storage in the refrigerator, while the maximum amount of 0.117240% is determined on the fourth day during storage of raw goat's milk. Pesticides from the group Heptachlor minimum quantity is 0.050270% proven on the third day, while the maximum amount is proven fifth day 0.126044% of it's scaling in the refrigerator at a temperature of 4°C. Pesticides from the group Aldrin minimum quantity is 0.015454% proven on the first day, while a maximum quantity 0.067626% is proven on the fifth day during storage of raw milk. Pesticides from the group Dieldrin minimum quantity is 0.020456% proven on the first day, while the maximum

quantity 0.045206% is proven fourth day during storage of milk. Pesticides from the group Endosulfan minimum quantity is proven first day 0.026269% while maximum quantity is 0.098472% proven on fourth day during storage of milk. Pesticides from the group Endrin minimum quantity 0.020862% is proven third day, while the maximum quantity 0.103296% fourth day during storage milk in the refrigerator. Pesticides from the group DDT and all OCP pesticides in goat milk were proven with the maximum quantity of 0.147294% on the fourth day during storage of milk, while the minimum quantity 0.028934% is proven third day during storage of milk.

## Conclusion

A Gas chromatography method for determining OCPs in milk and dairy products has been developed, which may be used for routine analysis in everyday laboratory practice. The acquired values of the analytical yield R, with which the accuracy of the method is tested, are within the limits from 98.113599% to 101.83674%. This appoints to the fact that the method is quantitative and accurate. From the tested OCPs in raw goat's milk from the Pelagonia region, most present is Heptahlor and least present is Dieldrin. In raw goat's milk, kept at 4°C for one week until spoiled, also most present is Heptahlor with average value of 0.091695. Least present is Dieldrin with average value of 0.034547. All OCP in goat's milk were treated with different temperatures and with different heating time, the maximum quantity is 0.170824 group pesticide Endosulfan heated on temperature of 71-74°C, while the minimum quantity group pesticide Dieldrin heated on temperature of 89 -100°C and the DDT pesticide heated on temperature of 63-65°C. From examination of the seven OCPs can be concluded that in our Pelagonia region still apply insecticides for the protection of plants, mostly present DDT.

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