

## **INCIDENCE AND HYGIENIC SIGNIFICANCE OF ORGANOCHLORINE PESTICIDES IN PRODUCTS SUSPECTED OF BEING INFECTED BY TRACEABILITY, FEED, IN BISTRITA-NASAUD COUNTY**

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### **Abstract**

*The increased food needs due to the growth of world's population, led to an increased use of chemicals, especially fertilizers and pesticides. In addition to the beneficial role of increasing agricultural production and also of animal production, some pesticides have been shown to have negative effects on human health through bioaccumulation. Feeding the animals with feed containing low doses of organochlorine pesticides determines a significant accumulation of the residues within 1-2 months. Monitoring the organochlorine pesticides residues is a current concern in the European Union's countries, so that in addition of environmental factors monitoring, the studies also refer to feed. In this paper I studied the incidence and the significance of organochlorine pesticides under sanitary veterinary surveillance in green mass feed samples and complex feed samples, collected in Bistrita-Nasaud County. The samples have been collected between June-September 2010, showing values below the maximum permissible limit.*

**Key words:** green mass feed, complex feed, organochlorine pesticides, maximum permissible limit of residues

### **INTRODUCTION**

Modern pesticides are synthetic chemicals such as inorganic and organic. The discovery of actually used pesticides began during and especially after the Second World War, caused by the increased widespread production of organochlorine and organophosphorus insecticides. Pesticide's practical importance is underlined by its production dynamics: at the beginning of this century, world production was insignificant (about 56,000 tons in 1916), and today has exceeded 20 million tons / year.

The widespread use of organochlorine pesticides had and still has multiple advantages, but also some inconveniences. Organochlorine compounds have low degradability, both chemical and biological in living organisms and in the environment, as a result of a very high bioconcentration potential, which characterizes many of the compounds. It results a continuous load of the soil, vegetation and water, caused by the regular and repeated treatments and by their increasing accumulations. Ingested by animals (through treated or contaminated feed), they are retained in the fatty tissue (being fat-soluble) or they are excreted in milk and eggs.

This way, they cause a general pollution of food which is maintained for a long time because of their stability.

A study by Bai et al., 2006, in China, believes that the use of organochlorine pesticides in agriculture and to control diseases leads to a high incidence of HCH and DDT residues in the tested food samples. Thus 80% of the tested samples have been tested positive for these contaminants. (Bai et al., 2006)

EFSA experts at the European level have drawn synthetic studies on HCH, Endosulfan, Endrin and DDT isomers, as undesirable substances in animal feed. The identified difficulty refers to how the results are reported, respectively as “total samples” of which “positive”. For this reason, the concrete values at disposal were limited. (EFSA, a, 2005 - EFSA, b, 2006) Then in terms of composition, feed is different from country to country. The situation of tested feed is comparable with that on the European level, considering the different periods until these compounds have been used in our country than in other countries of the European Union.

#### **MATERIAL AND METHODS**

Green mass feed (coded as FV) have been tested, also complex feed used in the farms from Bistrita-Nasaud County, coded as TRM1 (complex feed for lactating cows) and TRM2 (green feed for cows with resting breast).

Of the methods described in the literature for fat-free products was chosen the method with acetonitrile extraction (alone or mixt with the water) liquid-liquid partition with petroleum ether and purification on florisil® column (SR EN 12393-1, 2, 3, 2003) To determine the concentration value of the organochlorine pesticide residues from feed, it was used a gas chromatograph Perkin Elmer model Auto System XL, at the Sanitary Veterinary and for Food Safety Laboratory Bistrita-Nasaud.

Data have been reported in LMA values – maximum permissible limit for organochlorine pesticide residues in vegetable food included in the Order ANSVSA/MAPDR/MS/ANPC no.12/173/286/1/124/2006. The maximum permissible limits for the feed are also mentioned in the Order no.18/2007, Regulation (EC) no.299/2008 and more recently in Regulation (EC) no.574/2011, but there is no change to the order of 2006.

The legislation doesn't provide any special categories of vegetable food as “Feed”, but given the type of samples evaluated, it had been taken from the legislation the maximum permissible values for contaminants type POC in vegetable food, which can be found in green feed and also in complex feed.

## RESULTS AND DISCUSSION

The content of organochlorine pesticides (in ppm or mg / kg) of feed samples tested is shown in Tables 1 and 2.

*Table 1*

Quantitative determination of POC residues in green fodder samples, (n=4)

No. (*)	Organochlorine compound found in sample	LMA (ppm)	Concentration in sample (ppm)	
			FV1	FV2
1	$\alpha$ HCH	0.01	0.0020	0.0030
2	HCB	0.01	0.0050	0.0060
3	$\beta$ HCH	0.01	0.0030	0.0030
4	$\gamma$ HCH	0.2	0.0080	0.0020
5	Heptachlor (sum of Heptachlor and Heptachlor Oxide, expressed as Heptachlor)	0.01	0.0004	0.0002
11	Endrin	0.01	0.0005	0.0048
12	$\alpha$ Endosulfan	0.1	0.0019	0.0025
13	4,4'DDE (DDT sum of DDT, TDE and DDE isomers, expressed as DDT)	0.05	0.0005	0.0006

Legend: (\*) - refers to the elution order of compounds in samples, namely in standard;  
LMA- the maximum permissible limit; FV1, FV2- green fodder 1, 2

*Table 2*

Quantitative determination of POC residues in combined fodder samples, TRM1 (n=4) and TRM2 (n=4)

No. (*)	Organochlorine compound found in sample	LMA, ppm	Concentration in sample, ppm	
			TRM1	
			(1)	(2)
1	$\alpha$ HCH	0.02	0.0022	0.0031
2	HCB	0.01	0.0040	0.0055
3	$\beta$ HCH	0.01	0.0035	0.0029
4	$\gamma$ HCH	0.2	0.0103	0.0124
5,7	Heptachlor (sum of Heptachlor and Heptachlor Oxide, expressed as Heptachlor)	0.01	0.0003	0.0001
6,10	Aldrin (simple or combined, expressed as Dieldrin)	0.01	0.0011	0.0013
8	Chlordane(sum of cis and trans isomers and of oxichlordan, expressed as chlordane)	0.01-0.02	0.0016	0.0005
9,13,14	DDT (sum of DDT, TDE and DDE isomers, expressed as DDT)	0.05	0.0044	0.0053

11	Endrin	0.01	0.0025	0.0011
12	$\alpha$ Endosulfan	0.1	0.0077	0.0029
No. (*)	Organochlorine compound found in sample	LMA, ppm	Concentration in sample, ppm	
			TRM2	
			(1)	(2)
1	$\alpha$ HCH	0.02	0.0020	0.0011
2	HCB	0.01	0.0039	0.0020
3	$\beta$ HCH	0.01	0.0022	0.0019
4	$\gamma$ HCH	0.2	0.0037	0.0030
5,7	Heptachlor (sum of Heptachlor and Heptachlor Oxide expressed as Heptachlor)	0.01	0.0013	0.0006
6,10	Aldrin (simple or combined, expressed as Dieldrin)	0.01	0.0021	0.0011
8	Chlordane(sum of cis and trans isomers and of oxichlordane, expressed as chlordane)	0.01-0.02	0.0014	0.0004
9,13,14	DDT (sum of DDT, TDE and DDE isomers, expressed as DDT)	0.05	0.0055	0.0039
11	Endrin	0.01	0.0031	0.0050

Legend: (\*) - refers to the elution order of compounds in samples, namely in standard; LMA- the maximum permissible limit; (1), (2) - series of samples.

A first observation that that can be made after analyzing the tables is that quantitatively the feed types tested are different. The organochlorine pesticides identified as positive in green fodder, present residue values below the maximum permissible value (LMA), the differences being of the order of magnitude. This is due to the short period of "live" of the green mass and also to the short period of contact with the soil and water through which it can be contaminated.

The values found are very similar to those found in a study of vegetation located in the mountains of Asia. Thus, in 2006, Wang et al., found in grasses located at altitudes between 4700-5620 m, concentrations ranging from 0.0003 to 0.0078 ppm for HCH isomers and between 0.0001 to 0.0031 ppm for Endosulfan. In this study, concentrations of HCH isomers have been found between 0.0020 to 0.0080 ppm and of endosulfan between 0.0019 to 0.0025 ppm. The DDT concentrations found in the mountains of Asia ranged from 0.0011 to 0.0069 ppm, reflecting the continued use of DDT in this part of the globe. In this paper was found only 4,4'DDE isomer of DDT, at a concentration between 0.0005 to 0.0006 ppm. This proves once again the effect of the air transport of pesticides, especially of those administered in powder form, as DDT in Asia. (Martens, P., et al., 1971)

The concentration values calculated for DDT in feed type TRM1, between 0.0044 ppm and 0.0053 ppm, i.e. 8.8% respectively 10.6% of LMA, can be explained by its persistence in the environment, along with massive scale usage in the past. However, the sources can be accidental, as it happened in 2002 in Germany, where some feed samples tested (flour type "eco") have shown high DDT contamination between 11-180 ppb, values that have been attributed to the warehouse where the feed have been stored and that was previously used for pesticides. (EFSA, b, 2006)

Besides, the presence of DDT was reported in Bistrita-Nasaud County in cow's milk, because many producers have been used these chemicals to disinfect the cattle, after that they have been faced with serious damages, caused by the refusal of the industrial plants to collect contaminated milk.

The remaining compounds identified, namely Heptachlor (sum of Heptachlor and heptachlor Oxide, expressed as Heptachlor), Aldrin, Chlordane (sum of isomers) and Endrin present concentrations significantly lower than maximum permissible limit of sanitary legislation in force. Pesticide HCB was found in both green fodder and complex feed in concentrations between 0.0020 ppm (TRM2) to 0.0060 ppm (FV2), representing 20% respectively 60% of LMA value. HCB is a chemical compound obtained by substituting hydrogen atoms of benzene with chlorine atoms, used to combat common bunt of wheat. Specific provisions for hexachlorobenzene (HCB) are specified in Directive 76/464/EEC, where along with aldrin, dieldrin, endrin, isodrin, hexachlorobutadiene also the chloroform should be covered by the Directive 86/280/EEC.

Differences between the degree of contamination presented by the two types of complex feed TRM1 and TRM2 are reflected on the compounds Lindane and Endrin. Lindane presents higher values of residue concentrations in the complex fodder TRM1 (0.0103 to 0.0124 ppm, 5.15% -6.2% of LMA) and in fodder TRM2 (0.0037 to 0.0030 ppm, 1.85% -1.5% of LMA). Referring to Endrin, the situation is reversed, namely concentrations are lower for TRM1 fodder (0.0025 to 0.0011 ppm, 2.5% - 11% of LMA), as opposed to the fodder type TRM2, which has higher concentration values (0.0031 to 0.0050 ppm, i.e. 31% respectively 50% of LMA). These situations are illustrated in Figures 1 and 2.

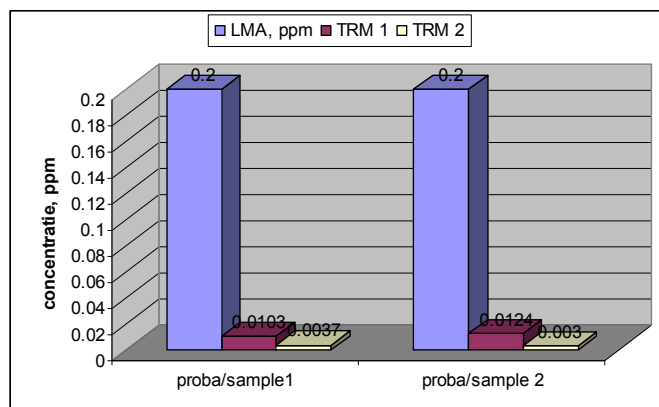


Figure 1- Quantitative determination of  $\gamma$ HCH in combined feed TRM1 and TRM2

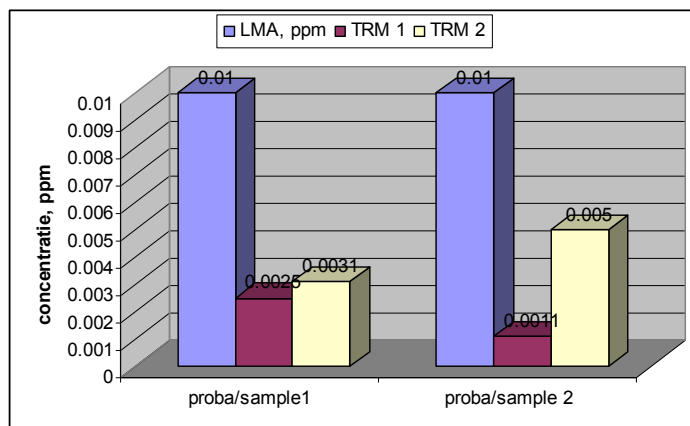


Figure 2- Quantitative determination of Endrin in combined feed TRM1 and TRM2

Green fodder samples have a much lower contamination than combined fodder. Compounds identified in green fodder are: HCH, HCB isomers, Endrin and DDT isomers. In this case there are two types of pesticides, namely those used until recently ( $\gamma$ HCH and Endosulfan) and organochlorine compounds with very large capacity of accumulation in the soil (Endrin).

The fact that in the complex feed, regardless of its type, are found practically all the compounds under sanitary veterinary surveillance could mean that one component is contaminated. It could be the cereals, because the green mass of fodder showed a low impurification and organochlorine pesticides penetration and accumulation in grains is stronger than in the green part of plants. Combined feed also contains various types of grains

(corn, triticale) so the effect can be cumulative. Another explanation could be that imported feed is used from some areas of the world where organochlorine pesticide use is currently permitted.

## **CONCLUSIONS**

After analyzing the results obtained in this study it can be concluded that: both in green fodder and in complex feed type TRM1 and TRM2 all compounds have been identified in large numbers, with values of residue concentrations lower than the maximum limit permissible by sanitary legislation in force, explained by agro-technical treatments performed during the period in which samples were collected.

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8. \*\*\*Ordinul ANSVSA/MAPDR/MS/ANPC nr.12/173/286/1/124/2006-privind stabilirea limitelor maxime admise de reziduuri de pesticide în și pe fructe, legume, cereale și alte produse de origine vegetală;
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