

”Ion Ionescu de la Brad”, Iași, Agronomical and Veterinary Science University

Doctoral field: Veterinary Medicine

Specialization: Semiology and Medical Pathology

PhD Student Alina CHELARU (married MUNTEANU)

DOCTORAL THESIS

SCIENTIFIC SUPERVISOR:

Prof. dr. Gheorghe SOLCAN

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*RESEARCH REGARDING THE
DINAMICS OF ORGANOCHLORINE
PESTICIDES IN MILK AND MILK
PRODUCTS IN THE CENTER AREA
OF MOLDOVA*

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ABSTRACT

This study sought to determine the following residues of chloride pesticides in milk and milk products:

- Alpha-hexachlorocyclohexane (α -HCH);
- Beta-hexachlorocyclohexane (β -HCH);
- Gamma-hexachlorocyclohexane (γ -HCH) - Lindane;
- P, p'-dichloro-diphenyl-trichloro-ethane (p, p'-DDT);
- O, p'-dichloro-diphenyl-trichloro-ethane (o, p'-DDT);
- P, p'-dichloro-diphenyl-trichloro-Diethyl (p, p'-DDE);
- O, p'-dichloro-diphenyl-trichloro-Diethyl (o, p'-DDE);
- O, p'-dichloro-diphenyl-dichloro-ethane (o, p'-DDD);
- P, p'-dichloro-diphenyl-dichloro-ethane (p, p'-DDD);
- Heptachlor;
- Aldrin;
- Chlordane;
- Heptachlor epoxide;
- Dieldrin;
- Endrin;
- Hexachlorobenzene (HCB).

During the 3 years of study were examined by gas chromatography 2327 samples of milk and milk products from 40 types: 636 milk samples, 88 milk powder samples, 144 samples of cream, 378 acidic dairy products samples, 127 samples of butter, 162 icecream samples, 724 samples of cheese and 59 samples consisting of by-products from milk processing.

In 2006, out of 131 samples of raw milk material in 93 samples (representing

70.99% of total samples analyzed) were not detected higher values than the method detection limits. The remaining 38 samples recorded higher values than the method detection limits for 2 pesticides (17 samples) and a pesticide (21 samples).

Raw milk of sheep recorded detectable levels above the limits of detection of the method on 19 samples (representing half of sheep milk samples analyzed).

Pasteurized milk samples submitted 2 detectable values for a single compound: one sample with α -HCH and another with total DDT. The samples of milk powder detected 4 samples with values above the limits of detection of the method, all the values obtained for β -HCH.

Out of the 27 samples, 15 samples of fermented cream (55.56% of total samples analyzed) had higher values than the method detection limits.

In 2 cream powder samples, β -HCH was detected with values higher than the detection limit of the method.

In the acidic dairy products from the 38 samples of buttermilk were recorded these values:

- In 22 samples were not detected values above the detection limits of the method;
- In 9 samples were registered higher values of method detection limits for a single compound: 2 samples for α -HCH, β -HCH in 4 samples, one sample for γ -HCH and 2 samples for total DDT;

Of the 43 samples of yogurt, in 32 samples (representing 76.19% of total samples analyzed) were not detected values above the limits of detection of the method, 11 samples recorded higher values of detection limits of the method: 10 samples for a pesticide and 1 for 2 pesticides (for β -HCH and total DDT).

Of the 26 samples of fruit yogurt were detected values above the detection limits of the method for a single parameter in 6 samples (3 samples for α -HCH, 1 for β -HCH and 2 samples for total DDT).

Of the 15 samples from sana on 11 samples (73.34% of total samples analyzed) were not detected higher values of method detection limits.

There were 3 samples that were detected with a single compound higher values of method detection limits: 2 samples for β -HCH and 1 sample for DDT.

In the category of butter out of the 30 samples analyzed, in 23 samples (representing 76.66% of total samples analyzed) were not detected higher values than the method

detection limits. Two samples recorded higher values for the method detection limits for 1 pesticide (β -HCH, total DDT respectively) and for 2 pesticides, 5 samples (3 samples β -HCH and DDT one α -HCH and γ - HCH, and another β -HCH and γ -HCH).

33.33% of block butter samples analyzed had values above the detection limits of method: one sample for a parameter β -HCH.

In the icecream category 4 icecream samples had higher values of method detection limits, but well below the maximum allowed, 3 of them registering for a parameter (α -HCH, γ -HCH and total DDT), and one sample for 2 parameters (γ -HCH and total DDT).

The samples of cheese from which determinations were made for 2006 reached the following conclusions:

- In the powder cheese samples were not found higher values of method detection limits;
- Out of the 29 samples of fresh cheese, 24 had lower values of method detection limits, and 5 samples had higher values of method detection limits for only one compound (one sample for α -HCH, 2 samples for β -HCH and one for γ -HCH and total DDT).
- Out of the 12 samples analyzed with cottage cheese, 3 samples had higher values of method detection limits for only one compound (β -HCH, γ -HCH and total DDT) and a sample for 2 compounds (γ -HCH and total DDT).
- 4 samples of cream cheese had higher values of method detection limits for a single compound (one sample for β -HCH, γ -HCH and 2 samples for total DDT).
- fresh curd had 3 samples with values above the detection limits of the method, for only one parameter (one for γ -HCH and 2 samples for total DDT).
- Within the cow salt cheese category 5 samples were detected with higher values of method detection limits, of which 3 samples for one parameter (β -HCH, γ -HCH and total DDT) and 2 samples for 2 parameters (γ -HCH and total DDT).
- 4 samples with values above the detection limits of the method were detected in sheep cheese samples analyzed, 2 samples for one compound (γ -HCH and total DDT) and 2 samples for two compounds (α -HCH and γ -HCH, γ -HCH and total DDT).
- In the goat cheese samples was detected a higher concentration of

organochlorine for a single sample (total DDT).

- The cow feta cheese samples analyzed detected 3 values above the detection limits of the method in 2 samples: one from γ -HCH and the second sample with α -HCH and total DDT.
- In a sample of sheep feta cheese was detected a higher value for total DDT.
- The cheese samples analyzed presented 2 samples with values above the detection limits of the method for a single compound: α -HCH and DDT total respectively.
- Both sheep cheese samples analyzed recorded higher values than the method detection limits for a single parameter (α -HCH and γ -HCH, respectively).
- Cow cheese samples examined had 2 samples with higher values, a sample for a compound (α -HCH) and the other for two compounds (γ -HCH and total DDT).
- Only 5 samples (representing 2.07% of total samples analyzed) of cheese were detected values for α -HCH. B-HCH isomer presented values above the detection limits of the method in 6 samples of cheese analyzed. Mean largest isomer γ -HCH (0.87 mg / kg) was registered on cow cheese, but with a value well below the maximum permissible limit (8 mg / kg product).
- Total DDT was most often determined in samples of cheese, but with averages well below the maximum permissible limit (40 mg / kg product).

In the ensuing years there was a slight tendency to decrease pesticide concentration. Thus, raw cow's milk samples were recorded material values above the detection limits of method: 28 samples for a single parameter: α -HCH in 5 samples, 3 samples β -HCH, γ -HCH in 13 samples and total DDT in 7 samples.

Out of the 45 samples of raw sheep milk 20 samples had values above the limits of detection of the method: 15 samples with values above the detection limits of the method for a single parameter: α -HCH in 1 sample, β -HCH in 3 samples, γ -HCH in 2 samples and DDT in 9 samples.

From the 31 samples of table butter, 5 samples had higher values than the method detection limits. Four samples recorded higher values of method detection limits for a pesticide (2 samples with higher values in γ -HCH, total DDT respectively), and the rest for 2 values (α -HCH and total DDT).

In the icecream category 5 icecream samples had higher values of method detection

limits, but well below the maximum permitted, all of them registering a higher value for each parameter (α -HCH, γ -HCH and total DDT).

In 2008 7 samples were detected above the maximum permissible values for α -HCH, 12 samples for β -HCH, 3 samples for γ -HCH and total DDT in 2 samples. Two of the samples analyzed were detected with higher values for all parameters than the maximum limits and 3 samples were detected above the maximum permitted values with two parameters (α -HCH and β -HCH).

All samples which exceeded the maximum limits came from the same area, in the same period of time (late March) which could indicate an accidental source of pollution. Increasing the frequency of collection of evidence of geographical area and subsequent control of samples from the area showed the classification results in the maximum limits.

In the period January 2006 - December 2008 were analyzed 380 feed samples that were found in the cattle alimentation from which determinations were made of organochlorine in milk and milk products.

For 2006 it is noted a high proportion of contamination organochlorinate corn flour (57.14%), concentrate feed (29.03%) and in hay (26.08%).

At the opposite end stands the absence of organochlorine in soy and sunflower.

For the year 2007 organochlorine are in a high proportion in feed concentrate (28.26%), wheat straw (25%) and in hay (19.04%). At the opposite end stands the absence of organochlorine in oat straw. For the year 2008 is remarkable the high percentage of contaminants in the feed concentrate (20.51%) and hay (15.62%).

On the types and incidence of OCL can conclude the following:

- That in the complex feed, regardless of type, are found practically all compounds shows that one of the components is contaminated. Most likely it is grain, conclusion based on the following considerations:
 - green table feed showed a low pollution;
 - acquisition and accumulation of OCL is much stronger in seeds than in the green plant;
 - complex feed contains various types of crops (maize, triticale) so the effect can be cumulative;
 - the use of imported feed in areas of the globe where OCL use is currently permitted.