INCIDENCE AND HYGIENIC SIGNIFICANCE OF ORGANOCHLORINE PESTICIDES IN SOME OF DAIRY PRODUCTS IN BISTRITA-NASAUD COUNTY

Krompaszki Teodora (Oniga)

University of Agriculture Sciences and Veterinary Medicine, Calea Mănăştur 3-5, 400372, Cluj-Napoca; Romania, e-mail: teodora.oniga@yahoo.com

Abstract

Organochlorine pesticides are chemicals used in agriculture due to their toxic action on insects, microscopic fungi, bacteria, plant viruses, parasite herbs and rodents, thus ensuring high and stable yields. Organochlorine pesticides in most cases exert its toxic action on pests and diseases but also on animals and insects and there is a risk that man himself to be affected due to the toxic residues ingested with the food. (Ecke, 1973)Because the presence of an organochlorine pesticide was reported in the county Bistrita-Nasaud in several agricultural structures and in cow's milk, I decided to evaluate in this paper the current status of these residues in some milk products taken from dairy production units in the above mentioned county area. The products were collected and analyzed in two distinct periods, June to August 2009, respectively January to March 2010. The tested samples showed values at and below the maximum permissible residue limit.

Key words: fat dairy products, organochlorine pesticides, dairy units, gas chromatographic method.

INTRODUCTION

Toxic substances in food always concerned the specialists but, in last decades, agriculture chemical treatment, environmental pollution, increasingly industrialization of the nutrition using numerous additives, have created a new dimension to this issue with direct implications to the consumer's health.

The ways in which food is contaminated with pesticides are multiples, beside the direct treatments there are interactions with the atmosphere, hydrosphere and soil. So, the feed can be contaminated as a result of surface treatments during vegetation and storage or by root absorption from the soil. Contaminated feed are consumed by the animals. Entered in the body by different ways, the pesticides can be absorbed by the tissues without any chemical structure or toxicity transformation. Part of it is eliminated by milk, which is detoxification pathway for females. (Banu, 2003)

Organochlorine pesticides have chemical stability and cumulative effect in fat. They accumulate in milk and its derivatives and in cheese products because they are high in fat. (Mihaiu and Cucu, 1998). Until now there is no decontamination method of milk. (Rotaru, 2005)

Because the milk and its derivatives are daily consumed by the children, elderly and adults, it requires a serious monitoring of the presence of pesticide residues in such products, in order to prevent negative effects on the human body.

The Ministry of Agriculture and Rural Development, National Sanitary Veterinary and for Food Safety Authority, also the Ministry of Health has developed a national program for monitoring pesticide residues in fruits, vegetables, grains and foods.

Each component authority develops an independent annual program for controlling pesticide residues in vegetable and animal food for children.

The monitoring program developed by the Ministry of Agriculture and Rural Development is implemented by the Central Laboratory for Pesticide Residues Control in plants and vegetable products, carrying out analysis on products collected by phytosanitary units from each county and from the Municipality of Bucharest.

National legislation in this area includes the Order of the president of the National Sanitary Veterinary and for Food Safety Authority, the minister of Agriculture and Rural Development, the minister of Public Health and the President of National Authority for Consumer Protection no.118/562/1030/313/2007, which sets maximum permissible limits for pesticides in and on fruits, vegetables, grains and other plant products. This Order transposes the Regulation (EC) No. 396/2005 of 23 February 2005.

The NSVFSA Order no. 23 of 01 January 2007 limited the organochlorine pesticides content in raw cow's milk, cream, fresh eggs in shell, eggs and egg yolk and also in meat, meat products, offal or animal fat. The most recent document that limits the content of contaminants is the Commission Regulation (EU) No. 574/2011.

As a member of the European Union, Romania respects the most of the rules imposed by it.

MATERIAL AND METHODS

In order to obtain a more complete picture of dairy's quality from the investigated area, more products collected from the units around the county, have been chosen to be tested, namely: 8 samples fermented cream 20% fat (two types, namely SA1 and SB1, two samples of each type, in the two mentioned periods), 8 samples sweet cream 32% fat (two types, namely SA2 and SC2, two samples of each type, in the two mentioned periods). From cheese products, it have been tested: Dalia cheese 12 samples (three types, namely CDA, CDB and CDC, two samples from each type, in the two mentioned periods), Mozzarella cheese 8 samples (two types, namely MA and MB, two samples from each type, in the two mentioned periods), bellows cheese 12 samples (three types, namely BA, BB and BC, two

samples from each type, in the two mentioned periods). For the confidentiality of the producing units, the collected samples have been coded.

Gas chromatographic determination of organochlorine pesticide residues in food products is conducted in the following main stages of work: extraction, passage through the column with anhydrous sodium sulfate, purification, gas chromatographic determination, calculation and interpretation of results. (Hura, 1995)

Analyses have been performed according to STAS SR EN ISO 1528, using a gas chromatograph Perkin Elmer model Auto System XL, at the Sanitary Veterinary and for Food Safety Laboratory Bistrita-Nasaud.

Organochlorine pesticide residues have been extracted from the sample using petroleum ether and acetonitrile, have been purified by passage through a florisil column and then eluted with a mixture of ethyl ether and petroleum eter. Next, the eluates have been concentrated and then determined quantitatively the organochlorine pesticide residues by gas chromatography.

RESULTS AND DISCUSSION

The results of quantitative determinations of investigated cream samples are listed in Table 1. Toxic concentrations, both the LMA value, as well as the value found in samples are expressed in mg POC/kg fat (ppm).

Table 1

Quantitative determination of organochlorine pesticide residues in cream samples

No.*	POC in sample	LMA, ppm	Concentration found in sample			
			SA1	SB1	SA2	SC2
06-08.2009 (n=8)						
1	αHCH	0.004	0.0011		0.0021	0.0027
2	HCB	0.01	0.0032	0.0045	0.0038	0.0047
3	βHCH	0.003	0.0010	0.0012	0.0007	
4	γHCH	0.008	0.0043	0.0055	0.0040	0.0021
8	Clordan[1]	0.002			0.0007	
11	Endrin	0.0008	0.0007	0.0006	0.0005	0.0008
12	Endosulfan[2]	0.004	0.0015	0.0020	0.0008	0.0025
13,14	DDT	0.04	0.0118	0.0211	0.0220	0.0115
01-03.2010 (n=8)						
1	αHCH	0.004	0.0025	0.0019	0.0027	0.0020
2	HCB	0.01	0.0046	0.0031	0.0040	0.0038
3	βHCH	0.003	0.0015	0.0011	0.0022	0.0023
4	γHCH	0.008	0.0051	0.0038	0.0040	0.0035
11	Endrin	0.0008	0.0004	0.0007	0.0008	0.0006
12	Endosulfan	0.004	0.0019	0.0022	0.0021	0.0018
13,14	DDT[3]	0.04	0.0226	0.0101	0.0184	0.0200

Legend: (*) - refers to the elution order of compounds in samples, namely in standard; LMA, the maximum permissible limit, 1 - sum of cis and trans isomers and oxychlordan,

expressed in Chlordane, 2 - sum of alpha- and beta-isomers and endosulfan sulfate, expressed as Endosulfan, 3 - sum of DDT, DDE and DDD isomers, expressed as DDT).

While analyzing the table it appears that the isomers α, β, γ HCH present residues concentrations lower with on order of magnitude to the LMA value, the γ HCH isomer appears in all tested samples, α, β HCH isomers appear randomly, as period and assortment, in 75%, respectively 87,5% of the tested samples. Chlordane isomer is present only in one type of sample (SA2) and it has four times lower concentration than LMA value. Organochlorine compounds HCB and DDT (alone or with its isomers) showed lower concentration than LMA, but the same order of magnitude. In 25% of samples the Endrin residues concentration was equal to LMA, in 25% concentration was lower by one than the LMA and the rest ra ranged between 0.0004 mg/kg – 0.0006 mg/kg.

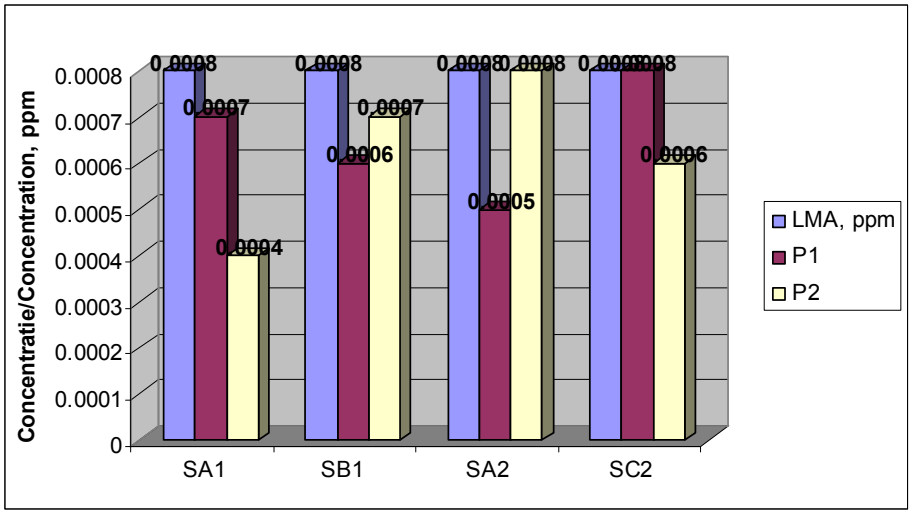

Figure 1- Comparison of calculated concentrations for Endrin in cream samples
Legend: LMA, maximum permissible limit; P1: 06-08.2009; P2: 01-03.2010

In the county Bihor, in 2008, was found cream samples 25% fat which not showed organochlorine pesticide residues concentrations higher than maximum permissible by sanitary legislation. (Macicaş, 2008).

Endosulfan was found in concentrations between 0.0008 mg/kg-0.0025 mg/kg, i.e. between 20 and 62.5% of the limit permissible by sanitary legislation.

The results of quantitative measurements for cheese samples obtained in the two studied periods are shown in Tables 2 and 3.

Table 2

Quantitative determination of organochlorine pesticide residues in sample of Dalia Cheese (n=6)

Nr.*	POC in sample	LMA, ppm	Concentration found in the sample, ppm					
			06-08.2009 (n=6)			01-03.2010 (n=6)		
			CDA	CDB	CDC	CDA	CDB	CDC
1	αHCH	0.1	0.0011			0.0002		0.0003
2	HCB	0.25	0.0001	0.0012		0.0010	0.0009	0.0007
3	βHCH	0.075		0.0112		0.0300	0.0412	0.0255
4	γHCH	0.2	0.0002	0.0008	0.0001	0.1000	0.0011	0.0007
11	Endrin	0.02	0.0125	0.0111	0.0114	0.0100		0.0119
12	Endosulfan	0.1	0.0451	0.0654	0.0561	0.0671	0.0687	0.0099
9,13,14	4,4'DDT	1	0.4115	0.3110	0.2223	0.4357	0.5528	0.2354

Table 3

Quantitative determination of organochlorine pesticide residues in sample of Mozzarella cheese and bellows cheese (n=10)

Nr.*	POC in sample	LMA, ppm	Concentration found in the sample, ppm				
			MA	MB	BA	BB	BC
06-08.2009 (n=10)							
1	αHCH	0.1	0.0007			0.0004	
2	HCB	0.25		0.0120		0.0140	0.0012
3	βHCH	0.075	0.0212	0.0318	0.0400	0.0115	0.0200
4	γHCH	0.2	0.0007	0.0003			0.0005
5,7	Heptaclor1)	0.1	0.0005			0.0004	0.0001
11	Endrin	0.02	0.0111	0.0100	0.0111	0.0200	0.0114
12	Endosulfan	0.1	0.0689	0.0110	0.0100	0.0798	0.0657
9,13,14	DDT2)	1	0.0451	0.1110	0.4001	0.5147	0.1145
01-03.2010 (n=10)							
1	αHCH	0.1	0.0010	0.0012	0.0021	0.0031	
3	βHCH	0.075	0.0215		0.0111	0.0254	
4	γHCH	0.2	0.1101	0.1045			0.0009
11	Endrin	0.02	0.0115		0.0110	0.0112	0.0111
12	Endosulfan	0.1	0.0508	0.0607			0.0701
9,13,14	DDT	1	0.4545	0.2378	0.4055	0.3488	0.6778

Legend: tables 2 and 3: (*) – refers to the elution order of compounds in samples, respectively in standard; LMA- maximum permissible limit; 1) 2) – sum of isomers.

The concentration of the three isomers of HCH in tested cheese products is non-homogenous, which seems to indicate the use of other sources for the production of certain cheese assortments. There is the possibility that sheep cheese fraudulently used to be contaminated by private producers, using some veterinary products forbidden by law, such as Lindavet. γHCH isomer appears in all cheese samples, except for two samples of bellows cheese. Official use of Lindane until recently in the EU (2002) and until last year in RO, justifies its accumulation mainly in fatty foods. HCB and Heptachlor pesticides are present only in cheese samples

tested in the first period, with concentrations below the permissible limits of sanitary legislation. Endrin presented to 12.05% of samples values equal with LMA and for the remaining samples have been calculated concentrations between 0.0100 mg/kg-0.0115 mg/kg, below the LMA.

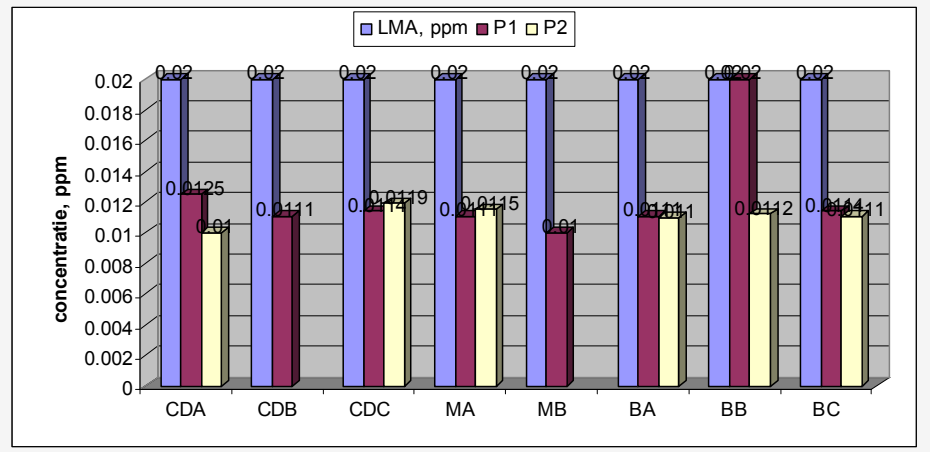

Figure 2 – Comparison of concentrations for Endrin in cheese samples
Legend:LMA- maximum permissible limit; P1-period 06.-08.2009, P2-period 01.- 03.2010

The Endosulfan ranged from 0.0099 mg/kg (CDC) to 0.0798 mg/kg (BB) and DDT ranged from 0.0451 mg/kg (MA) to 0.0798 mg/kg (BC).

For all the studied cheese assortments the organochlorine pesticide residues level was below the permissible limit values by the sanitary legislation, with one exception, (BB) where Endrin concentration was equal to the maximum permissible limit.

CONCLUSIONS

HCH isomers appear in all investigated sample in different combination of isomers. This is determined by using this product for over 30 years, which led to strong spread in environmental factors. Endosulfan has the lowest fat solubility of organochlorine compounds under sanitary veterinary surveillance, but is transported by environmental factors and will still be found in higher concentration than other compounds, because it had been used until 2008. Although Endosulfan was forbidden since 01.01.2008, however it is found in the studied products, especially in the first period 06-08.2009. Endrin is an Aldrin and Dieldrin stereoisomer form and was banned in the same period with Dieldrin. Its incidence is high in the studied products, because it has a great capacity to maintain and accumulate in the soil, where it can be resumed by the feed. DDT alone or as sum of isomers is a pesticide that was used on a massive scale and even though is no longer used since the same period as technical HCH, is found in all environmental factors, even in food, due its high bioaccumulation capacity. In addition it is still used in Asia to control of tropical diseases, which contributes to its maintenance in the environment.

From the presented data it can be observed that there is a contamination by organochlorine pesticides in the dairy products and even is not exceeded the maximum permissible limits set by the sanitary legislation in force, it requires an analysis of the causes of their presence and the start of a program to eliminate them.

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