MONITORING OF ORGANOCHLORINE PESTICIDE RESIDUES IN MILK PRODUCTS

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Abstract

Fifty four random samples (27 milk samples, 12 cream samples, 11 karish (Skim milk) cheese samples and 4 yoghurt samples) were collected from Agriculture Research Station of Kafer El-Sheikh. All collected samples were subjected to extraction and clean up procedure for multi-residue detection of pesticides. The results demonstrated that p,p-DDE was the only and most frequent organochlorine residue contaminates milk and cheese samples. Storage process caused a significant decrease of p,p-DDE residues in cheese samples after 15 days storage. Pasteurization process doesn't cause any decrease in p,p-DDE residue. p.p-DDE and p,p-DDD residues were detected in higher concentrations in case of cream samples compared with milk samples. p,p-DDD was the only residue that detected in yoghurt samples. None of the milk or milk product samples exceeded the Codex Alimentarius residue limits for DDT complex in milk.

INTRODUCTION

There is a growing awareness and alarm regarding the possible hazards and economic losses to the ever increasing number of toxic substances that enter the food chain. Many of the contaminant enter food directly or indirectly as a result of human activities, like agriculture, food technological processing, etc. Much of the public concern is focused on the residues of the organochlorine compounds. Some of the most detected pesticides residues of this group are DDT, aldrin, dieldrin, lindane (gamma HCH) and heptachlor. Such chemicals are characterized by their great tendency to accumulate and persist in animal tissues as they are all fat soluble pesticides Fries et al. (1972). Although organochlorines had been curtailed from agricultural use since the early 1970's they are highly persistent in environment and still contaminate food from animal origin Dogheim et al. (1990).

The present study was conducted to investigate the levels of organochlorine pesticide residues in buffaloes and cattle milk, cream, cheese and yoghurt samples collected from Agricultural Research Station at Kafr El-Sheikh from Dec. 1995 to Feb. 1996.

Various buffalo milk types (raw, ripened, skim and pasteurized), cream, cheese and yoghurt samples were analyzed to detect chlorinated hydrocarbon pesticide residues.

Methods described in FDA Pesticide Analytical Manual "PAM" (1968) and Suzuki et al., (1979), which had been adopted in previous work by Dogheim et al. (1988, 1990, 1991 and 1996) were also followed in this study.

MATERIALS AND METHODS

Sampling & Sample Preparation

Fifty four random samples (twenty seven milk samples 19 raw milk, 5 ripened milk, 1 skim milk, and 2 pasteurized milk) lL each, twelve cream samples, eleven karish (skim milk) cheese samples and four yoghurt samples were collected from Agriculture Research Station at Kafer El-Sheikh from Dec. 1995 to Feb. 1996. Milk samples were collected by supervised manual expression into laboratory cleaned jars with aluminum-lined caps to be examined for the presence of pesticide residues.

Milk and Yoghurt: Each sample of milk or yoghurt was throughly mixed and a subsample of 10 ml. was measured in small glass container with screw Teflon capped stopper and kept deeply frozen at-20^{o}C for pesticide residues analysis.

Karish (skim milk) Cheese: Twenty five gm of each cheese sample was thoroughly mashed with 50 ml of distilled water in clean dry blender, then 10 ml from each prepared sample was measured into small glass containers with screw Teflon stoppers and kept deeply frozen at-20^{o}C for analysis.

Cream: Thirty gm of each sample was added to 150 ml of n-hexane then blended and filtered. The sample was subjected to centrifugation for 2 min. at 2000 rpm. followed by evaporation of n-hexane phase after separation. Three gm from each prepared sample (about 18 gm of fat produced) was weighed for pesticide residues analysis.

tween petroleum ether and acetonitril. The combined petroleum ether extract was concentrated to 5 ml, FDA (1995). Cream samples were subjected to further clean up procedure using florisil column chromatography according to Suzuki et al. (1979).

Gas Chromatography Determination

Aldrin was selected as internal standard and used in quantitation after checking its absence from all samples by GC-MS.

Columns 1 & 2 were used to quantitate and confirm organochlorine pesticide residues, respectively. Twelve organochlorine compounds were subjected to the analysis with limit of quantitation ranged from 0.005 to 0.01 mg/kg and recoveries rates >90%. Data for milk samples were calculated on a whole milk basis. Data for cream samples were calculated on lipid content basis.

RESULTS AND DISCUSSION

Public concern of health and environmental hazards from the use of agricultural chemicals had been increased dramatically in recent years. Some of the most prominent pesticides of this group include DDT, aldrin, dieldrin, lindane (gamma HCH) and heptachlor's. It is well known that the widespread use of organochlorine compounds has caused serious problems to man due to their bioaccumulation in several organisms. The majority of these compounds are toxic in high levels and a few, are carcinogenic in small laboratory animal tests. They reach man through the food chain and accumulate in various organs, but mainly in fatty tissues (Acker et al. 1975). According to other studies carried out in Egypt, Dogheim et al. (1988, 1990, 1991 and 1996) the pesticides most commoniy found in various animal food stuff are lindane, the isomers of BHC (HCH), DDT and derivatives (DDE and DDD), dieldrin and heptachlor epoxide.

Raw milk: Table 1 shows that p,p'-DDE was the only organochlorine residue compound detected in raw milk in relatively low avarage amount (0.012) mg/kg compared to the previous monitoring data of organochlorine compounds in buffalo milk samples collected from Fayoum and Beni-Suef governorates in 1986. However, the mean values of total p,p'DDT detected in buffalo milk samples collected from Beni-Suef governorate were 3.4 mg/kg, and 0.61 mg/kg (Dogheim et al. 1988 and Dogheim et al. 1990), respectively. In Fayoum governorate, greater amounts of DDT

Table 1. Organochlorine pesticide residues in ppm detected in milk processed milk samples collected from 28 Dec. 1995 to 25 Feb. 1996.

Code No.	Type of milk	DDE-p,p`	Mean
1	milk	0.014	
2	milk	0.013	
3	milk	0.016	
4	milk	0.014	
5	milk	0.013	
6	milk	0.014	
7	milk	0.015	
8	milk	0.013	
9	milk	0.010	
10	milk	0.012	0.012
11	milk	N.D	
12	milk	N.D	
13	milk	0.012	
14	milk	0.010	
15	milk	0.012	
16	milk	0.014	
17	milk	0.010	
18	milk	0.010	
19	milk	0.020	
20	ripened milk	N.D	
21	ripened milk	0.005	
22	ripened milk	0.017	0.01
23	ripened milk	0.007	
24	ripened milk	0.016	
25	skim milk	0.004	0.004
26	pasteurized milk	0.013	
27	pasteurized milk	0.010	0.012

The results are calculated on whole volume basis.
Codex MRL = 0.05 based on whole milk volume.
N.D = not detected
No. of samples = 27

complex residues were detected due to the high amount of p,p'-DDT with the mean value 4.24 mg/kg, (Dogheim et al. 1990).

Skim milk: Table 1 shows that the avarage of p,p'-DDE residue amounts detected in skim milk samples were less than that detected in raw, ripened and pasteurized milk samples.

Pasteurized milk: It was noted that pasteurization process doesn't show any decrease in p,p'-DDE residue which is the main contaminat traced in Pasteurized milk samples. This is in agreement with the conclusion of China et al. (1978). They studied the effect of heating on HCH, DDT and DDe contents of milk. It was found that repeated pasteurization of milk didn't affect total HCH content (0.08-0.11) mg/kg and p,p'-DDE content (0.006 mg/kg).

Ripened milk: In case of ripened milk samples, p,p'-DDE was detected in concentrations ranged between 0.005-0.017 mg/kg depending on the efficiency of fat separation process from milk.

All data obtained confirm the fact that the p,p'-DDE is the most frequently contaminant which is attributed to the bioaccumulation character of such metabolites detected but not in higher amounts (Acker et al., 1975). These data might indicate the old use of p,p'-DDT and o,p'-DDT. Aging of DDt stored in food chain results in higher p,p'-DDE concentration as derivatives. It is the most persistent of DDT derivatives. Fries et al (1972) and Hayes (1975) reported that DDE is more resistant to metabolic degradation than DDT in animals and man. Also DDE is found in almost all the living organisms because of its strong affinity for body fat (Jensen and Jansson, 1976).

Cream milk samples: DDE-p,p' and DDD-p,p' were detected in higher concentrations compared to milk samples which could be attributed to the high fat content of cream samples, Tables 1 & 2. Such chemicals are characterized by their great tendency to accumulate and persist in animal tissues resulting in being stored in body fat (Spence et al., 1990). Storage process has a slight effect on decreasing both residue derivatives which reached a maximum loss of (44%) in sample D3 after 8 days storage.

Kariesh (Skim milk) Cheese: Table 3 demonstrated that DDE-p,p'was the only residue detected in cheese samples. It was observed that storage process caused a significant decreasing of DDE-p,p' residue after 15 days storage.

Table 2. Storage effect on Organochlorine pesticide residues in ppm detected in milk cream samples collected from 30 Dec. 1995 to 8 Jan. 1996.

Code No.	Storage period (days)	DDE-p,p`	DDD-p,p`	Total	Reduction %
A1	---	0.194	0.028	0.222	---
A2	3	0.257	0.029	0.286	increased (128%)
A3	8	0.224	0.017	0.241	increased (108%)
B1	---	0.240	0.030	0.270	---
B2	3	0.237	0.031	0.268	0.7
B3	8	0.228	0.013	0.241	10.7
C1	---	0.213	0.002	0.215	---
C2	3	0.213	0.003	0.216	increased (100%)
C3	8	0.176	0.002	0.178	17.2
D1	---	0.274	0.032	0.306	---
D2	3	0.246	0.031	0.277	9.5
D3	8	0.139	0.032	0.171	44.1

The results are calculated on fat content basis.
No. of samples = 12

Table 3. Storage effect on Organochlorine pesticide residues in ppm detected in Kariesh (skim milk) cheese samples collected from 4 Jan. to 25 Feb. 1996.

Code No.	Storage Period (days)	DDE-p,p`	Reduction %
KG1	---	0.015	---
KG2	5	0.012	20
KG3	10	0.010	33.3
KG4	15	0.006	60
K1	---	0.010	---
K2	5	0.012	increased (120%)
K3	10	0.008	20
K4	15	0.008	20
KC1	8	0.013	---
KC2	10	0.014	increased (107%)
KC3	12	0.012	7.6

The results are calculated on fat content basis.
No. of samples = 11

Yoghurt samples: Table 4 shows that DDE-p,p' was the most frequent residue detected in yoghurt samples. However DDD-p,p' was detected in only one sample.

Table 4. Organochlorine pesticide residues in ppm detected in yogurt samples collected from 8 Jan. to 14 Jan. 1996.

Code No.	DDE-p,p`	DDD-p,p`	Total
YG1	0.019	N.D	0.019
YG2	0.016	N.D	0.016
YG3	0.022	N.D	0.025
YG4	0.014	N.D	0.014

The results are calculated on fat content basis.
No. of samples = 4

CONCLUSION

The experimental data indicated that no organophosphorous, carbamate, pyrithroid residues were detected in analyzed milk or milk product samples. No violation was observed in any analyzed sample. The MRL's of total DDT derivatives is 1.25 ppm calculated on fat basis and 0.05 ppm on whole volume (Codex 1996). However, it should be mentioned that p,p,-DDE residues inspite of their low concentrations reaching the levels below the MRL they are still higher than in other developed countries in milk and milk product samples especially cream.

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تقصى مستويات متبقيات المبيدات الكلورينية فى منتجات الألبان

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تم جمع عدد ٥٤ عينة عشوائية من منتجات الألبان المختلفة وذلك بإشراف محطة البحوث الزراعية بكفر الشيخ وبياناتها كالتالى : ٢٧ عينة لبن، ١٢ عينة قشدة ، ١١ عينة جبن قريش، ٤ عينات زبادى. تم استخلاص وتقدير المركبات الكلورينية بطريقة Multiresidue . أوضحت النتائج أن مركب p,p'-DDE هو المركب الوحيد الأكثر وجوداً فى كل عينات اللبن والجبن. كما لوحظ أن عملية تخزين الجبن تؤدى إلى تقليل ملحوظ لمتبقى مركب p,p'-DDE فى حين أن عملية البسترة لم تؤثر فى كميات متبقى مركب p,p'-DDE . وجدت متبقيات المركبين p,p,'-DDD,p,p'-DDE بتركيزات عالية نسبياً فى عينات القشدة مقارنة بالكميات التى وجدت فى عينات اللبن.

أما بالنسبة لعينات الزبادى فقد وجد متبقى مركب p,p'-DDD. لم تتعد أى من العينات الحدود المسموح بها فى اللبن والتى وضعتها لجنة الكودكس العالمية.