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MONITORING OF SOME PESTICIDE RESIDUES IN THE KAREISH CHEESE SAMPLES COLLECTED FROM KAFR EL-SHEIKH GOVERNORATE, EGYPT.

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ABSTRACT

Monitoring has been conducted to investigate the magnitude of contamination of fresh kareish cheese samples with organochlorines, organophosphates and carbamates pesticide residues from Kafr El-Sheikh governorate, Egypt. Fresh kareish cheese samples were collected monthly for a year period and determined by gas liquid chromatography with an electron capture detector (ECD) for organochlorine and nitrogen phosphorus detector (NPD) for organophosphate and carbamate pesticides.

The results indicated that, all samples either were contaminated with organochlorine pesticides. The residue concentrations of organochlorine pesticides (OCPs) were much lower than maximum residue limits (MRLs) for pesticides in milk which reflects a degree of health safety for human. Residues of organophosphate and carbamate pesticides were below the detection limits for all samples. However, lindane and heptachlor showed higher mean concentrations than other detected compounds.

INTRODUCTION

Pesticide residues and their metabolites represent one of the most harmful issues to human health. As known milk and its products were represent an essential source of human daily food, especially for infants and children all over the world. Dairy products in particular have been shown to have a high incidence of contamination with residues of persistent organochlorine insecticides (Kalra *et al.*, 1983; Kalra and Chawla, 1985; Kannan *et al.*, 1992; Mukherjee and Gopal, 1993; Gupta *et al.*, 1997; John *et al.*, 2001 and Battu *et al.*, 2004).

Feed and fodder offered to animals are often contaminated with pesticide residues (Sandhu, 1980; Raikwar and Nag, 2003) and after feeding, these residues pass through the body systems (Prassad and Chhabra, 2001). The continuous intake of pesticide residues in ruminants is particularly a serious problem in the case of the organochlorines, which are highly liposoluble and deposited in adipose tissues, body fats and remain in situ for a long time. Contamination of milk in both animals and humans by DDT, hexachloro cyclohexane (HCH, commonly known as BHC), aldrin, dieldrin and heptachlor has been reported by researchers in different countries over the last few decades, and the use of most of these chemicals have been banned in certain countries (Williams and Mills, 1964; Kapoor and Kalra, 1988 and 1997; Singhal and Mudgal, 1990; Surendra *et al.*, 1998).

Since about 25 years, the use of DDT and many other organochlorine pesticides in Egyptian agriculture has been banned (Sameeh, 2004). However, these high persistent compounds are still detectable in many different types of environmental samples e.g., water, fish, sediment, vegetables, fruits, milk and foodstuffs (Sandhu, 1980 and Raikwar and Nag,

2003). On the other hand organophosphorus and carbamates pesticide were investigated because of their inclusion through the pesticidal control program in Kafr El-Sheikh.

The present investigation aimed at monitoring the level of pesticides residues in Kareish cheese samples collected from different markets of Kafr El-Sheikh governorate during the year 2006.

MATERIALS AND METHODS

Chemicals, standards

Organochlorine pesticide standards were DDT (dichloro-diphenyl-trichloroethane), DDE (1, 1-(dichloro 2,2 bis (4-clorophenyl) ethane), aldrin, heptachlor and lindane (γ-HCH). Standard solutions were prepared in hexane. Organophosphorus and carbamate pesticide standards were dimethoate, malathion, chlorpyriphos, diazinon, monocrotofos, aldicarb and carbofuran. Standard solutions were prepared in ethyl acetate. The standards were obtained from the Environmental Protection Agency (EPA), USA.

The organic solvents used were acetone, ethanol, ethyl acetate, methanol, methylene chloride and *n*-hexane, analytical grade for residue analysis, anhydrous sodium sulfate and Florisil-PR grade, (60-100 mesh) for column chromatography, obtained from Merck Co., Germany.

Sample Preparation

Fresh kareish cheese samples (2 kg from each place) were collected monthly from three regions in Kafr El-Sheikh governorate (Kafr El-Sheikh, Seedy Salem and Abo-Zyada) during the period from January 2006 to December 2006. After collection, all the samples were stored at 4°C until the extraction was done.

Extraction and clean-up procedures

Extraction of pesticide residues was carried out using ethanol-ethyl acetate (5:95 v/v), whereas the clean-up was done on florisil column with methanol- methylene chloride (7:93 v/v) as described by Bennet *et al.*, (1997). After cleanup, the final extracts were evaporated to dryness using rotatory vacuum evaporator. The dried material was dissolved in 2 ml ethylacetate for gas chromatograph (GC) analysis. One-microliter aliquot was injected into GC. The Organophosphorus and carbamate insecticides were extracted and cleaned up according to Hill *et al.*, (1967) and Rangaswamy *et al.*, (1976) respectively.

Gas chromatograph (HRGC-ECD and NPD)

Residues of the monitored pesticides were analyzed by using a gas chromatograph (GC) model HP-5890 equipped with a tritium electron capture detector (^{3}H-ECD) for detection of chlorinated pesticides. A nitrogen phosphorus detector (NPD) was employed to determine the organophosphorus and carbamate pesticides. Megabore column Hp- 608 part No. 190955-023; (30m x 0.53 mm id, 0.25 µm film thickness) was used. Split injection (0.8 min. hold) was applied with temperature at 220°C. For ^{3}H-ECD the carrier gas used was helium at a flow rate of 2.5 ml/min, the make up gas was nitrogen at 35 ml/min., anode purge, nitrogen at 4 ml/min., temperature was 280 °C. The initial oven temperature was 80°C (1 min) →

(30°C/min) 170°C → (10°C/min) 300°C hold 10 min. For the NPD, the carrier gas used was hydrogen at a flow rate of 4 ml/min. and the make up gas was helium at 30 ml/min with temperature at 225 C. Initial oven temperature was 80°C (1 min) → (25°C/min) 190°C → (2°C/min) 225°C → (5°C/min) 280 hold 20 min.

Calibration, qualitative and quantitative analysis were carried out in addition to recovery experiments at concentration level of 1µg/L by fortification. The percentage recovery of the studied pesticides on kareish cheese ranged from 83% to 90%.

RESULTS AND DISCUSSION

Fresh kareish cheese samples analyzed for pesticide residues revealed that all samples were contaminated with organochlorine pesticides, DDE (1, 1-(dichloro 2,2 bis (4-clorophenyl) ethane) aldrin, heptachlor and lindane (γ-HCH). On the other hand, dimethoate, malathion, chlorpyriphos, diazinon, monocrotofos, aldicarb and carbofuran were below the detectable level in all samples.

The concentration of the detected pesticide residues from Kafr El-Sheikh during sampling time are listed in Table 1. The mean concentrations of the detected organochlorine compounds in Kafr El-Sheikh governorate are illustrated in Figures 1.

The data presented in Tables (1) revealed, that the mean concentrations of heptachlor ranged approximately between 13.33-1.01, 5.43-0.55 and 13.19-1.13 for Kafr El-Sheikh, Seedy Salem and Abo-Zyada, respectively. As shown in Table (1) DDE was detected at Kafr El-Sheikh and Seedy Salem with total concentration 0.31 and 0.74 ng/kg respectively. On the other hand, DDE was below the detectable level in Abo-Zyada.

The results reflected that, Heptachlor and lindane were highly accumulated in kareish cheese samples and the total concentration were 48.03-22.00, 12.46-3.73 and 52.94-10.65 ng/kg in Kafr El-Sheikh, Seedy Salem and Abo-Zyada, respectively. On the other hand, Aldrin and DDE had the lowest values of accumulation in all samples.

The sequence of organochlorine compounds, depending on their concentration level in all samples from Kafr El-Sheikh governorate was heptachlor > lindane > aldrin > DDE. The concentration of the detected pesticides ranged from 13.33 to 0.14 ng/kg (Table 1). The results in Fig. 1 showed that, the heptachlor and lindane had a higher mean concentration levels than the other detected pesticides in all sampling areas. However, these concentrations were below the FAO maximum residue level in milk (FAO 1993).

The results in Table 1 showed that, heptachlor and lindane were the most detected compounds in all sampling areas; the mean concentrations were 4.0 and 1.83 ng/kg in Kafr El-Sheikh, 1.04 and 0.31 in Seedy Salem and 4.41 and 0.89 in Abo-Zyada respectively. Moreover aldrin and DDE were the lowest detected compounds during the study period at all sampling areas.

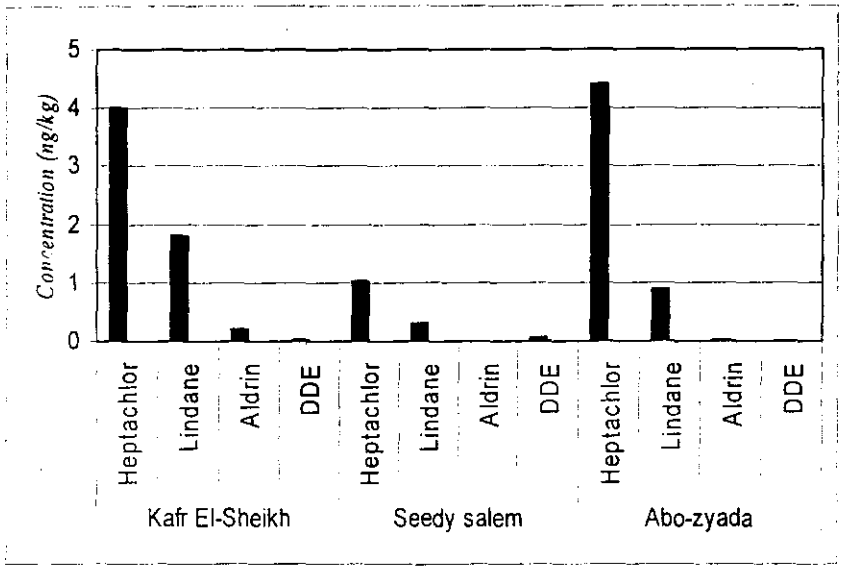

Fig. 1: Mean concentration of pesticide residues in fresh kareish cheese samples during different months in kafr El-Sheikh governorate.

The obtained data are in agreement with results recorded by other investigators. Amr (1999) reported that pesticides residues of DDT, HCH and dieldrin were detected among 130 milk, cheese, butter, yoghurt and milk powder samples collected from different market in Egypt. Bentabol and Jodral (1995) developed a multiresidue technique for the analysis of 17 organochlorine compounds in cheese. By such technique, different organochlorine pesticide residues in the collected cheese samples from different markets in Spain were found. The detected compouds were alpha-hexachlorocyclohexane (alphaHCH), beta-HCH, gamma-HCH, deltaHCH, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, chlordane, o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'DDE, p,p'-DDE, and the fungicide hexachlorobenzene. Also, Mallatou *el al* (1997) found that 32.1 % of the collected cheese samples from Greece during 1991-1992 contained residues of one or more of alphaBHC, p,p'-DDE, lindane and aldrindieldrin. The range of concentrations were 0.8 to 2 ng/- for lindane, 4 to 10 ng/g for alpha-BHC, 20 to 70 ng/g for p,p'-DDE and 0.2 ng/g for aldrin. All mean concentrations found were below the maximum limits permitted by the European Union. More recently, Pandit *el al* (2002) showed that trace levels of DDT and HCH were detected in the milk and dairy product including cheese samples of various brands collected from different cities in Maharashtra, India. All levels of organochlorine pesticide residues in milk and milk products were below the maximum permissible limits given by the FAO/WHO.

According to the Codex Alimentarius Commission, the acceptable daily intake (ADI) of heptachlor, lindane and aldrin are given as 0.0005, 0.008 and 0.0001 mg/kg body wt/ day, respectively (F.D.A. 1993 and Commonwealth of Australia 2005). Depending on the mean concentration

level of detected pesticides in all samples and average consumption compared with the estimated intake for pesticide residues, it was realized that, it was remained within safe limits during this study period. Interestingly, none of the samples analyzed showed the presence of commonly used organophosphorus or carbamate compounds.

Table (1): Mean average of some pesticides residues in fresh kareish cheese (ng/kg) in Kafr El-Sheikh governorate

Time of samples	Kafr El-Sheikh				Seedy Salem				Abo-Zyada			
	H	L	A	D	H	L	A	D	H	L	A	D
January	N.D	4.54	N.D	N.D	0.62	0.14	N.D	0.23	1.13	1.66	N.D	N.D
February	1.04	N.D	N.D	N.D	0.64	0.45	N.D	0.217	13.19	0.65	N.D	N.D
March	N.D	0.276	N.D	N.D	N.D	0.276	N.D	N.D	N.D	0.167	N.D	N.D
April	1.01	2.402	N.D	N.D	N.D	0.26	N.D	N.D	7.31	0.52	N.D	N.D
May	4.31	4.03	N.D	N.D	0.55	0.43	N.D	0.29	6.21	0.44	N.D	N.D
June	4.7	N.D	N.D	N.D	2.73	N.D	N.D	N.D	2.07	N.D	N.D	N.D
July	3.39	N.D	N.D	N.D	2.49	N.D	N.D	N.D	1.80	N.D	N.D	N.D
August	6.01	N.D	N.D	N.D	N.D	N.D	N.D	N.D	2.07	N.D	N.D	N.D
September	13.33	1.52	2.25	N.D	N.D	N.D	N.D	N.D	9.93	1.24	N.D	N.D
October	8.67	1.54	N.D	N.D	N.D	N.D	N.D	N.D	4.63	4.15	N.D	N.D
November	N.D	2.79	N.D	0.309	5.43	2.172	N.D	N.D	2.35	N.D	0.61	N.D
December	5.566	4.90	N.D	N.D	N.D	N.D	N.D	N.D	2.25	1.82	N.D	N.D
Total Conc.	48.03	22.00	2.25	0.31	12.46	3.73	--	0.74	52.94	10.65	0.61	--
Mean Conc.	4.00	1.83	0.19	0.03	1.04	0.31	--	0.06	4.41	0.89	0.05	--

H= Heptachlor, L= Lindane, A= Aldrin, D= DDE and N.D = Not detected, organophosphorus and carbamate pesticides were below the detectable level

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تتبع متبقيات المبيدات فى عينات الجبن القريش التى تم تجميعها من محافظة كفر الشيخ

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هذه الدراسة اجريت للتعرف وتتبع متبقيات المبيدات الكلورنية والفوسفورية العضوية والكارباماتية فى الجبن القريش فى ثلاث مواقع فى محافظة كفر الشيخ (كفر الشيخ-سيدى سالم-ابوزيادة) فى جمهورية مصر العربية. تم جمع عينات الجبن القريش شهريا ولمدة سنة كاملة وتحليلها بجهاز الـ GC باستخدام كشاف الـ ECD للمركبات الكلورنية والـ NPD للمركبات الفوسفورية والكارباماتية.

ولقد اوضحت النتائج ان جميع عينات الجبن القريش فى محافظة كفر الشيخ كانت ملوثة بالمركبات الكلورنية العضوية. وكان متوسط تركيز المبيدات الكلورينية المكتشفة اقل بكثر من اقصى متبقى للمبيد موصى به فى اللبن مما يعكس درجة الامان العالية على الصحة العامه للانسان. فى حين انه لم يتم اكتشاف اى من المركبات الفوسفورية العضوية والكارباماتية. وكان لكل من اللندين والهبتاكلور اعلى متوسط تركيز بين المركبات المكتشفة