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MONITORING OF CERTAIN PESTICIDE RESIDUES IN RAW MILK SAMPLES COLLECTED FROM DIFFERENT MARKETS AT QALUBIA GOVERNORATE, EGYPT

[62]

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ABSTRACT

Monitoring of pesticide residues was carried out in milk samples collected from six markets at Qalubia governorate through four seasons within the year 2001. The detected pesticide residues were including organochlorine pesticides (DDT derivatives, hexachlorocyclohexane and cyclodienes) and non-organochlorine pesticides (organophosphorus, pyrethroids and others). Generally, for the organochlorine pesticide residues, the total mean of *o,p'*-DDE and *p,p'*-DDE in summer samples reached to 0.98 and 1.02 ppm, respectively. In autumn samples, the total mean of *o,p'*-DDE and *o,p'*-DDT reached to 0.57 and 0.84 ppm, respectively. As for hexachlorocyclohexane and/or cyclodiene compounds, milk samples collected at the summer season were the highest samples in their content of such residues, especially, endrin (0.90 ppm) followed by α-HCH (0.37 ppm), aldrin (0.32 ppm) and heptachlor (0.24 ppm). In addition, El-Kanater market followed by Toukh and Qaha were the higher markets that their samples contained the higher residues of organochlorine pesticide residues, especially at the Summer season followed by the autumn. For the non-organochlorine pesticide residues, ten pesticide residues were detected. The milk samples collected at the summer season were containing the higher concentration (as total mean) especially that from markets of Qaha (0.55 ppm) followed by El-Kanater (0.46 ppm),Shoubra (0.28 ppm) and Toukh (0.22 ppm) compared with the other seasons. Generally, the concentrations of the detected pesticide residues were higher than the published Maximum Residue Limits (MRL). In addition, the obtained data showed that hexachlorocyclohexane and cyclodiene compounds exhibited the higher percent of positive frequencies (14.46 %) followed by the non-organochlorine pesticides (11.03 %) while DDT derivatives were the lower frequent compounds (7.90 %) in the collected milk samples.

Key words: Monitoring, Pesticide, Residues, Milk, Egypt

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INTRODUCTION

Actually, large amounts of pesticides enter the environment either directly through the application for pest control or by run-off from the treated agricultural fields. Such pesticides may contaminate both surface and ground water, which in turn the live-stock that drink the contaminated water may have detectable amounts of pesticide residues in their meat and/or milk **(Shibamoto and Bjeldanes, 1993)**. On the other hand, the presence of pesticide residues, especially those belonging to the organochlorine pesticides in the food chain components such as milk is considered as major reason related to their presence in the human breast milk and hence may pose adverse health hazards to breastfed infants **(Solomon & Weiss 2002; Okonkwo & Kampira 2002 and Wong *et al* 2002)**. So that, according to the rolling program of monitoring the pesticide residues on major food commodity groups which was established by different governments **(Arnolds, 1992)**, several authors detected significant amounts of pesticide residues in different foodstuffs such as milk **(Ali, *et al* 1993; Deka *et al* 1995; Dogheim *et al* 1996 and Aman & Bluethgen, 1997)**.

The present investigation aimed to monitor the level of pesticide residues in raw milk samples collected from different markets of Qalubia governorate through four seasons during the year 2001.

MATERIAL AND METHODS

1. Samples Collection and Preparation

Fresh raw milk samples were collected at random from different markets located at Qalyiobia governorate, i.e. Shoubra, Qalyiob, Toukh, Benha, El-Kanater and Qaha during the period from January 2001 to December 2001. Six samples of fresh liquid milk, 1 kilogram each were taken from each market and transferred to the laboratory for the pesticide residue analysis.

2. Pesticide Residue Analysis

2.1. Extraction, Clean-up and GC Determination

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). For the gas chromatographic determination of the extracted organochorine and other pesticide residues from milk samples, GC (Perkin Elmer Autosystem XL Gas Chromatogram) equipped with ECD and NPD detectors was used for separation and identification of the studied pesticides.

Quantification was carried out by the use of pesticide standard solution in acetone (2.5-3.5 mg/5 ml). For identification of the unknown peaks in the samples, chromatograms RRT was compared to the corresponding peaks of the reference standard. A suitable aliquot of standard solution was injected in the mentioned GC under the suitable conditions. The retention time (R.T.), areas under peak, the weight of the studied compounds and separation factors (R) were established as presented in Table (1). In addition, the recovered amounts ranged between 75-85^% for the considered pesticides. The operating conditions for the GC were as follows:

Table 1. The retention time (R.T.), areas under peak, the weight of the studied compounds and separation factors (R) of the separated pesticides on gas chromatography

Compound	RT.	Area/10000	The weight (μg)	Separation factor (R)
α-HCH	4.942	9.3	0.495	2.55
β-HCH	6.455	9.5	0.521	2.66
delta-HCH	7.648	12.7	0.717	1.79
heptachlor	8.427	33.2	1.43	1.12
aldrin	10.433	21.5	0.686	2.45
heptachlor-epoxide	12.820	12.1	0.498	2.89
o,p'-DDE	14.870	36.2	0.873	2.59
cis-chlordane	15.690	6.7	0.323	0.95
p,p'-DDE	17.575	46.3	1.069	2.59
endrin	19.282	32.2	2.028	1.08
o,p'-DDT	20.633	34.7	0.887	1.65
p,p'-DDD	22.100	111.7	2.648	1.40
p,p'-DDT	24.545	19.4	0.496	0.98
thiram	2.513	12.86	1.82	2.14
benefin	2.898	16.26	0.420	1.03
fenitrothion	5.677	22.60	3.00	6.35
parathion	6.320	13.98	0.27	1.84
profenofos	8.975	17.32	2.58	4.39
benalxyl	11.287	25.29	0.83	4.00
fenpropathrin	13.892	27.77	0.73	4.12
pyridaben	15.955	16.55	1.17	3.88
alpha-methin	17.335	26.89	0.83	2.30
etofenprox	21.000	13.27	2.17	3.72

Thirteen organochlorine pesticides were separated on GC column (PE-5, 30 x 0.53 μm ID).
- Detector: ECD
- Temperature: Oven temp. program. 180-250°C (4°C/min).
  Inj. Temp.: 250°C
  Det. Temp. 300°C.
- Carrier gas Helium 4 ml/min.
- Nitrogen make-up 30 ml/min.

Ten pesticides belong to two fungicides, seven insecticides and one herbicide were also separated on GC column (PE-5, 30 x 0.53 μm ID).
- Detector: NPD
- Temperature: Oven temp. program. 150-300°C (2°C/min).
  Inj/Det. Temp. 250°C.
- Carrier gas: Helium 5 ml/min.

RESULTS AND DISCUSSION

The results of the detected pesticide residues in the milk samples collected from different markets at Qalubia governorate during the year of 2001 are listed in Tables (2, 3, 4, 5, 6 and 7). In addition, the means of the detected amounts of pesticide residues in relation with season and/or market were graphically illustrated in Fig. (1, 2, 3 and 4). However, to facilitate the presentation of the obtained results, it was preferred to discuss the recorded data separately into two categories of the detected pesticide residues, the first, including the organochlorine pesticide residues,i.e. DDT derivatives, hexachlorocyclohexane and cyclodiene residues and the second including the non-organochlorine pesticide residues.

1. Residues of Organochlorine Pesticides

1.1. Residues of DDT

Data in Table (2) and Fig. (1 & 2) show the amounts of the detected pesticide residues expressed as part per million (ppm) in the milk samples collected from the mentioned markets during winter, spring, summer and autumn seasons of the year 2001. As shown in Table (2), the detected residues of *o,p*-DDE, were found in milk samples collected from Toukh at the four seasons, i.e. 0.06, 0.10, 0.90 and 2.46 ppm at winter, spring, summer and autumn, respectively. The same metabolite was found also, in samples collected from Benha but at winter and spring only, i.e. 0.26 and 0.20 ppm, respectively. Also, it was detected in El-Kanater samples collected at winter (0.34 ppm) and summer (4.60 ppm). Milk Samples collected from Qaha contained such metabolite at summer and autumn in concentrations of 0.37 and 0.51 ppm, respectively.

For *p,p'*-DDE metabolite, it was not detected in the milk samples collected at winter season, whereas it was detected at Toukh samples collected at spring and summer seasons, i. e. 0.09 and 0.01 ppm, respectively. Also, El-Kanater samples contained such metabolite at 6.12 and 0.28 ppm in the milk sampes collected at the summer and autumn seasons, respectively. Milk samples collected from Shoubra and Qalyiob in the autumn season, contained the same metabolite at a low concentration, i.e. 0.15 and 0.05 ppm, respectively.

The other metabolite, *p,p'*-DDD was also detected in the collected samples but not at all the selected markets. For example, it was detected at 0.01 and 0.04 ppm in the samples collected from Qalyiob and Benha at winter, while was detected only in the Toukh samples at spring (0.24 ppm). Also, at summer season, the milk samples collected from Shoubra, Qalyiob, Benha and Qaha, contained some residues of such metabolite, i.e. 1.26, 0.39, 0.32 and 0.05 ppm, respectively. In autumn, only the samples collected from Shoubra, EL-Kanater and Qaha contained 0.31, 0.30 and 0.20 ppm of such metablite, respectively.

The *o,p'*-DDT was detected in El-Kanater samples at winter (0.04 ppm), Shoubra and Qalyiob at summer, i.e. 0.29 and 0.18 ppm, respectively, whereas such compound was detected at autumn season in the samples collected from Benha, El-Kanater and Qaha markets at concentration levels of 4.77, 0.21 and 0.07 ppm, respectively. For the *p,p'*-DDT, such compound was detected only in the milk samples collected from Qaha at winter

Table 2. Levels of residues of DDT (ppm) detected in milk sa ples collected from different markets of Qalyiobia governorate during the four seasons of 2001

Season	Market	Detected organochlorine pesticides (ppm)				
		o,p'-DDE	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT
Winter	Shoubra	ND	ND	ND	ND	ND
	Qalyiob	ND	ND	0.01	ND	ND
	Toukh	0.06	ND	ND	ND	ND
	Benha	0.26	ND	0.04	ND	ND
	El-Kanater	0.34	ND	ND	0.04	ND
	Qaha	ND	ND	ND	ND	0.01
Spring	Shoubra	ND	ND	ND	ND	ND
	Qalyiob	0.01	ND	ND	ND	ND
	Toukh	0.10	0.09	0.24	ND	ND
	Benha	0.20	ND	ND	ND	ND
	El-Kanater	ND	ND	ND	ND	ND
	Qaha	ND	ND	ND	ND	ND
Summer	Shoubra	ND	ND	1.26	0.29	ND
	Qalyiob	ND	ND	0.39	0.18	ND
	Toukh	0.90	0.01	ND	ND	ND
	Benha	ND	ND	0.32	ND	0.05
	El-Kanater	4.60	6.12	ND	ND	ND
	Qaha	0.37	ND	0.05	ND	ND
Autumn	Shoubra	ND	0.05	0.31	ND	ND
	Qalyiob	0.49	0.15	ND	ND	ND
	Toukh	2.46	ND	ND	ND	ND
	Benha	ND	0.12	ND	4.77	ND
	El-Kanater	ND	0.28	0.30	0.21	ND
	Qaha	0.51	ND	0.20	0.07	ND

Each value represents the average of six replicates. ND: Not detected under the limit of detection in our laboratory (10 ppb).
Winter date: 20/12-21/3 (1-2-3/2001), Spring date: 21/3-20/6 (4-5-6/2001), Summer date: 20/6-21/9 (7-8-9/2001), and Autumn date: 21/9-20/12 (10-11-12/2001).

and from Benha at the summer season, at concentrations of 0.01 and 0.05 ppm, respectively.

From another viewpoint, when the obtained results of the detected pesticide residues in the collected milk samples were expressed as percent of positive frequencies, (Table, 3), it was found that the metabolite, *o,p'*-DDE exhibited the higher positive frequency percent (12.5%) as total mean during the four seasons, followed by *p,p'*-DDD (10.40%). On contrary, *p,p'*-DDT exhibited the lower positive frequency (3.10%). In addition, the analyzed milk samples showed that the higher positive frequencies were at summer and autumn seasons, i.e. 10.82 and 10.82 %, respectively.

1.2. Residues of hexachlorocyclohexane and cyclodienes

Data in Table (4) show the detected concentrations of pesticide residues, which belong to the hexachlorocyclohexane isomers and cyclodienes compounds in the milk samples.

In the winter season, the hexachlorocyclohexane isomer, α-HCH was detected in all milk samples collected from all the selected markets, except El-Kanater. The detected concentrations ranged between 0.02 ppm in samples of Toukh and increased gradually to 0.15 ppm in samples of Qaha. β-HCH was detected in samples of the three markets only, i.e. Shoubra (0.08 ppm), Qalyiob (0.03 ppm) and Benha (0.11 ppm), whereas delta-HCH was detected only in samples collected from two markets, i.e. Shoubra (0.27 ppm), and El-Kanater (0.16 ppm).

In the same season, the cyclodiene compounds heptachlor residues were found in concentrations ranged between 0.01 ppm in samples of Shoubra to 0.09 ppm in milk samples of Qalyiob, whereas it could not be detected any residues in Toukh samples. In addition, heptachlor-epoxide was detected only in three markets, i.e. Qalyiob, Benha and Qaha at levels ranged between 0.04 to 0.05 ppm. *Cis*-chlordane was detected in higher concentrations 0.08 ppm in samples of Shoubra and 0.13 & 0.12 ppm in samples of Benha and Qaha, respectively. Aldrin and endrin were found only in samples collected from two sites, i.e. Qalyiob and El-Kanater for the former and in Shoubra and El-Kanater for the latter.

In spring season, data clearly show that α-HCH was the most detected isomer which was found in concentrations ranged between 0.03 to 0.37 ppm in collected samples of all the selected markets except El-Kanater. β-HCH was detected only in samples of two markets, i.e. Shoubra (0.37 ppm) and Qaha (0.32 ppm). Delta-HCH was the second isomer detected in the samples collected from the four markets, i.e. Shoubra, Qalyiob, El-Kanater and Qaha in concentrations ranged between 0.04 to 0.33 ppm. The cyclodiene pesticides were detected in a random trend, heptachlor in Toukh and El-Kanater, Heptachlor-epoxide in Qalyiob, Benha and Qaha, aldrin in all markets except Benha and *cis*-chlordane in Shoubra, Benha, El-Kanater and Qaha markets.

The milk samples collected in summer season, showed that the highest content of detected residues (as concentration and positive samples) were delta-HCH, heptachlor, aldrin and *cis*-chlordane. The other compounds and/or

Table 3. The positive frequency percent of the detected residues of DDT derivatives in the collected milk samples through the four seasons

Compound	% Positive frequencies/pesticide and season				Total Mean/pesticide
	Winter	Spring	Summer	Autumn	
o,p'-DDE	12.50	12.50	12.50	12.50	12.50
p,p'-DDE	0.00	4.10	8.30	16.60	7.25
p,p'-DDD	8.30	4.10	16.70	12.50	10.40
o,p'-DDT	4.10	0.00	8.30	12.50	6.23
p,p'-DDT	4.10	0.00	8.30	0.00	3.10
Total Mean/Season	5.80	4.14	10.82	10.82	7.90

Table 4. Hexachlorocyclohexane and cyclodiene pesticide residues (ppm) detected in milk samples collected from different markets of Qalyiobia governorate during the four seasons of 2001

Season	Market	Detected organochlorine pesticides (ppm)							
		α-HCH	β-HCH	Delta-HCH	Heptachlor	aldrin	heptachlor-epoxide	*cis*-chlordane	endrin
Winter	Shoubra	0.03	0.08	0.27	0.01	ND	ND	0.08	0.11
	Qalyiob	0.08	0.03	ND	0.09	0.03	0.05	ND	ND
	Toukh	0.02	ND	ND	ND	ND	ND	ND	ND
	Benha	0.05	0.11	ND	0.03	ND	0.04	0.13	ND
	El-Kanater	ND	ND	0.16	0.08	0.06	ND	ND	0.01
	Qaha	0.15	ND	ND	0.04	ND	0.04	0.12	ND
Spring	Shoubra	0.34	0.37	0.27	ND	0.26	ND	0.12	ND
	Qalyiob	0.23	ND	0.33	ND	0.04	0.05	ND	ND
	Toukh	0.03	ND	ND	0.12	0.06	ND	ND	ND
	Benha	0.04	ND	ND	ND	ND	0.21	0.13	ND
	El-Kanater	ND	ND	0.31	0.30	0.04	ND	0.13	ND
	Qaha	0.37	0.32	0.04	ND	0.05	0.07	0.14	ND
Summer	Shoubra	ND	ND	0.23	0.53	0.04	0.12	0.24	ND
	Qalyiob	1.29	ND	0.15	0.24	0.34	ND	0.46	ND
	Toukh	ND	0.07	ND	0.18	0.24	ND	5.61	ND
	Benha	ND	0.03	0.19	0.31	0.32	ND	0.39	ND
	El-Kanater	0.94	0.15	0.40	ND	0.98	0.40	0.01	0.03
	Qaha	ND	ND	0.17	0.19	ND	0.17	ND	5.38
Autumn	Shoubra	0.41	0.14	0.04	ND	0.36	ND	0.41	0.16
	Qalyiob	ND	0.17	0.21	ND	0.07	0.32	ND	0.22
	Toukh	0.34	0.04	0.22	0.06	0.07	ND	0.25	ND
	Benha	ND	0.24	ND	0.29	0.05	0.28	0.15	ND
	El-Kanater	ND	0.26	0.24	0.41	2.14	ND	0.44	0.11
	Qaha	ND	ND	0.05	0.19	ND	0.17	ND	0.30

Each value represents the average of six replicates. ND: Not detected under the limit of detection in our laboratory (10 ppb).
Winter date: 20/12-21/3 (1-2-3/2001), Spring date: 21/3-20/6 (4-5-6/2001), Summer date: 20/6-21/9 (7-8-9/2001), and Autumn date: 21/9-20/12 (10-11-12/2001).

isomers were found in some milk samples but with a low concentration level ranged between 0.03 to 1.29 ppm, except for endrin which was detected at 5.38 ppm in milk samples collected from Qaha market.

In the autumn season, the milk samples contained a higher concentration of the detected pesticide residues. For example, β and delta-HCH were detected in all samples, except that collected from Qaha market for the β-isomer and Benha for the delta isomer. Also, hepatchlor was detected in Toukh, Benha, El-Kanater and Qaha. Aldrin was detected in all milk samples except that collected from Qaha market, whereas *cis*-chlordane was not detected in milk collected from Qalyiob and Qaha markets. Both of heptachlor-epoxide and endrin were found in samples of three markets, by mean, the former was detected in samples of Qalyiob (0.32 ppm), Benha (0.28 ppm), Qaha (0.17 ppm), while the latter was detected in Shoubra (0.16 ppm), Qalyiob (0.22 ppm), El-Kanater (0.11 ppm) and Qaha (0.30 ppm).

When the detected residues were expressed as positive frequency percent as shown in Table (5), it was very clear that the calculated total mean showed that aldrin was the higher frequent pesticide followed by *cis*-chlordane and heptachlor, i.e. 17.68, 16.68 and 16.63%, respectively. In the same way, when the total mean of the positive frequency was calculated per season, it was found that the analyzed milk samples contained higher frequent pesticides at autumn season followed by summer, i.e. 16.69 and 15.13%, respectively.

Table 5. The positive frequency percent of the detected residues of hexachorocyclohexane and cyclodiene compounds in the collected milk samples through the four seasons

Pesticide	% Positive frequencies/pesticide and season				Total Mean/pesticide
	Winter	Spring	Summer	Autumn	
α-HCH	20.83	20.83	8.30	8.30	14.57
β-HCH	12.50	8.30	12.50	20.80	13.53
Delta-HCH	8.30	16.70	16.70	20.80	15.63
Heptachlor	20.80	8.30	20.80	16.60	16.63
Aldrin	8.30	20.80	20.80	20.80	17.68
Hept-epoxide	12.50	12.50	12.80	12.80	12.65
Cis-chlordane	12.50	16.70	20.80	16.70	16.68
Endrin	8.30	0.00	8.30	16.70	8.33
Total Mean/Season	13.00	13.02	15.13	16.69	14.46

However, according to the plotted histograms in Fig. (1), which expressed the mean of the detected pesticide residues in milk samples in relation with the season, the data clearly indicated that the milk samples collected in the summer season followed by autumn were containing the higher concentrations of DDT residues. In term of figures, the total mean of *o,p'*-DDE and *p,p'*-DDE in summer samples reached 0.98 and 1.02 ppm, respectively. In autumn, the total mean of *o,p'*-DDE and *o,p'*-DDT reached 0.57 and 0.84 ppm, respectively. Such results indicated that the DDE derivative was the higher metabolite present in the collected samples compared with the other derivatives such as *p,p'*-DDD.

In case of the other organochlorine pesticide residues, i.e. hexachlorocyclohexane and/or cyclodiene compounds, the same figure indicated that milk samples collected at the summer season were the highest in their content of such residues, especially, endrin (0.90 ppm) followed by α-HCH (0.37 ppm), aldrin (0.32 ppm) and heptachlor (0.24 ppm).

In addition, Fig. (2) clearly indicated that El-Kanater market followed by Toukh and Qaha were the higher markets that their samples contained the higher residues of organochlorine pesticide residues, especially at the summer season followed by the autumn. In other words, the total mean of such residues reached to 0.91, 0.47 and 0.42 ppm in samples collected at summer season from El-Kanater, Toukh and Qaha respectively. At autumn season, milk samples collected from Benha market contained the higher concentration of organochorine pesticide residues (0.39 ppm) followed by El-Kanater (0.29 ppm) and Toukh (0.23 ppm).

3- Residues of non-organochlorine pesticides

Data shown in Table (6) and graphicaly illustrated in Fig. (3 &4) indicated that the detected non-organochlorine pesticide residues included 10 pesticides. Such compounds could be classified into three groups, i.e. fungicides (thiram and benalaxyl), insecticides (fenitrothion, parathion, profenofos, fenpropathrin, alpha-methrin, etofenprox and pyridaben) and one herbicide (benefin).

Generally, all the mentioned pesticides were detected at the four seasons. The differences between such compounds were in their existence in the milk samples, which were collected from the selected market. For example, thiram was detected in all samples collected from Qaha market during the four seasons, whereas it was not detected in Shoubra samples neither in winter nor in spring season. The detected concentration of each compound was ranged between 0.01 to 0.73 ppm. Also, the same compound was not detected either in Benha at winter, Toukh, El-Kanater at spring or Benha at summer and autumn, respectively.

For the second detected fungicide, (benalaxyl), such compound was detected in the majority of milk samples collected from the most markets at the season of winter with concentrations ranged between 0.05 to 0.10 ppm and summer with a concentration ranged from 0.30 to 1.22 ppm. In addition, such compound was not detected neither in all autumn samples nor in Qalyiob samples at the other seasons.

Various insecticides and/or acaricides were detected in the collected milk samples, in this study. Fenitrothion, was detected in a high concentration in the

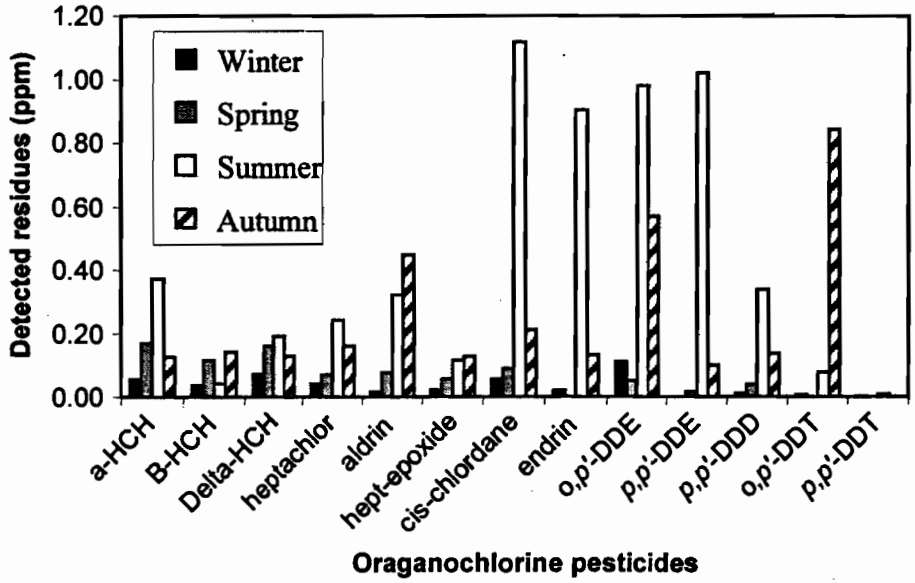

Fig. 1. Mean of the organochlorine pesticide residues (ppm) in milk samples collected from different markets in Qalubia governorate during the four seasons of the year 2001

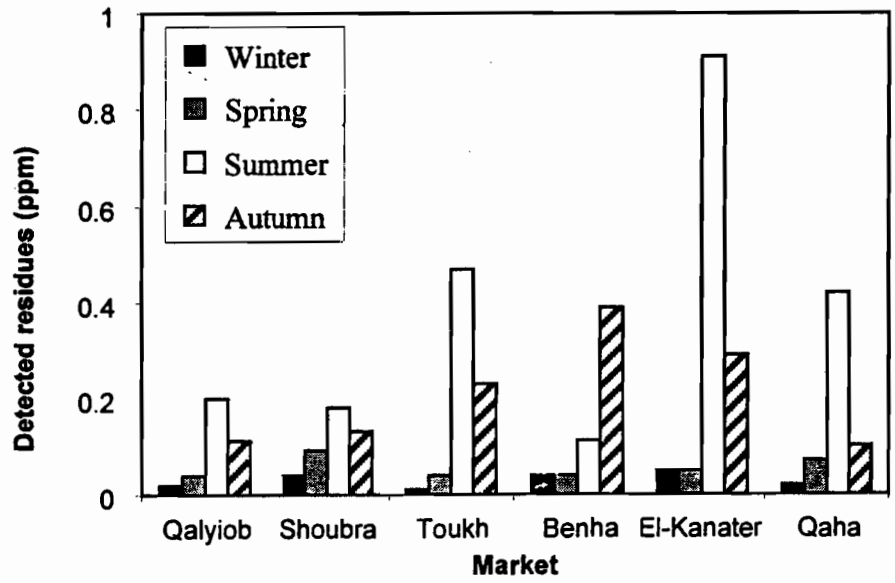

Fig. 2. Mean of the detected orgaochlorine pesticide residues (ppm) in milk samples collected from different markets Qalubia governorate during the four seasons of the year 2001

Table 6. Non-organochlorine pesticide residues (ppm) detected in milk samples collected from different markets of Qalyiobia governorate during the four seasons of 2001

Season	Market	Detected Non-organochlorine pesticides (ppm)				
		Fungicides		Insecticides		
		thiram	benalxyl	fenitrothion	parathion	profenofos
Winter	Shoubra	ND	0.10	0.49	ND	ND
	Qalyiob	0.73	ND	ND	0.12	0.04
	Toukh	0.08	0.09	3.06	ND	0.05
	Benha	ND	0.10	0.12	ND	ND
	El-Kanater	0.12	0.05	0.41	ND	ND
	Qaha	0.04	ND	0.26	ND	0.22
Spring	Shoubra	ND	0.04	0.37	ND	ND
	Qalyiob	ND	ND	ND	0.23	ND
	Toukh	ND	ND	0.21	ND	0.08
	Benha	0.01	0.16	ND	0.56	0.65
	El-Kanater	ND	0.06	0.25	ND	0.47
	Qaha	0.02	ND	ND	ND	0.49
Summer	Shoubra	0.72	ND	0.60	0.30	0.71
	Qalyiob	0.21	ND	ND	ND	ND
	Toukh	ND	1.22	ND	0.31	ND
	Benha	0.01	0.30	ND	0.37	ND
	El-Kanater	0.23	3.50	0.41	0.32	ND
	Qaha	0.15	0.47	ND	3.91	0.61
Autumn	Shoubra	0.51	ND	0.18	ND	0.39
	Qalyiob	0.17	ND	ND	ND	ND
	Toukh	0.01	ND	ND	0.16	ND
	Benha	ND	ND	ND	ND	ND
	El-Kanater	0.07	ND	0.27	0.26	ND
	Qaha	0.01	ND	ND	ND	0.28

Each value represents the average of six replicates. ND: Not detected under the limit of detection in our lab ratory (10 ppb). Winter date: 20/12-21/3 (1-2-3/2001), Springr date: 21/3-20/6 (4-5-6/2001),Summer date: 20/6-21/9 (7-8-9/2001), and Autumn date: 21/9-20/12 (10-11-12/2001).

Table 6. Continued

Season	Market	Detected Non-organochlorine pesticides (ppm)				
		Insecticides				Herbicide
		fenpropathrin	alphamethin	etofenprox	pyridaben	benefin
Winter	Shoubra	0.22	ND	0.16	ND	ND
	Qalyiob	ND	ND	ND	ND	0.02
	Toukh	0.04	ND	ND	0.05	0.02
	Benha	ND	0.25	ND	0.10	0.01
	El-Kanater	0.42	ND	ND	0.13	0.01
	Qaha	0.12	ND	ND	0.22	0.20
Spring	Shoubra	0.13	ND	ND	0.17	ND
	Qalyiob	ND	ND	ND	0.22	ND
	Toukh	ND	0.43	ND	0.21	ND
	Benha	ND	ND	0.42	0.43	ND
	El-Kanater	0.78	ND	0.42	0.10	ND
	Qaha	ND	0.42	ND	ND	ND
Summer	Shoubra	ND	0.44	ND	0.27	ND
	Qalyiob	0.23	0.18	ND	ND	0.65
	Toukh	ND	ND	0.42	ND	0.48
	Benha	0.31	ND	ND	ND	ND
	El-Kanater	ND	ND	ND	0.38	0.21
	Qaha	ND	ND	0.28	0.27	0.36
Autumn	Shoubra	ND	0.30	ND	ND	ND
	Qalyiob	0.12	ND	ND	ND	ND
	Toukh	ND	ND	ND	0.30	ND
	Benha	0.36	ND	ND	ND	0.20
	El-Kanater	0.33	ND	ND	0.39	ND
	Qaha	ND	ND	ND	ND	ND

Each value represents the average of six replicates. ND: Not detected under the limit of detection in our laboratory (10 ppb). Winter date: 20/12-21/3 (1-2-3/2001), Springr date: 21/3-20/6 (4-5-6/2001),Summer date: 20/6-21/9 (7-8-9/2001), and Autumn date: 21/9-20/12 (10-11-12/2001)

majority of milk samples collected in the winter season (the concentration ranged between 0.12 and 3.06 ppm). At the other seasons, such compound was found only in the samples collected from Shoubra and El-Kanater at the spring, summer and autumn seasons by concentrations of 0.37, 0.25, 0.60, 0.41, 0.18 and 0.27 ppm, respectively. Parathion was found in milk samples collected at summer season, especially that from Qaha (3.91 ppm), whereas the other samples were contained a negligible amounts such as that of Qalyiob at winter and spring (0.12 & 0.23 ppm), Toukh and EL-Kanater at autumn (0.16 & 0.26 ppm).

For profenofos, the majority of such compound was detected in the samples of spring, except that collected from Shoubra or Qalyiob, whereas at winter the residues of such pesticide were detected only in samples of the three markets, i.e. Qalyiob, Toukh and Qaha. Also, such compound was detected only in milk samples collected from Shoubra (0.71 & 0.3 ppm) and Qaha (0.61 & 0.28 ppm) at summer and autumn seasons, respectively.

Fenpropathrin was detected in all seasons but not in all samples. For example, El-Kanater samples contained 0.42, 0.78 and 0.33 ppm at winter, spring and autumn, respectively. Also, the same compound was found in Shoubra samples (0.22 & 0.13 ppm) at winter and spring and that from Qalyiob (0.23 and 0.12 ppm) at summer and autumn, respectively. In addition, the milk samples collected from Benha were contained 0.31 and 0.36 ppm of fenpropathrin at summer and autumn, respectively.

For the other pesticides, alphamethrin and etofenprox, were not detected in all milk samples. On the other hand, Benha, Toukh and Shoubra samples were contained alphamethrin at 0.25, 0.43 and 0.44 ppm at winter, spring and summer, respectively, while it was detected 0.18 and 0.30ppm in Qalyiob and Shoubra samples at Summer and autumn, respectively. Etofeprox, was found in a few samples, i.e. Shoubra at winter (0.16 ppm), Benha and El-Kanater (0.42 and 0.42 ppm) at spring, Toukh and Qaha (0.42 and 0.28 ppm) at summer, while not detected in autumn samples.

For pyridaben, such insecticide/ acaricide was found in the majority of winter samples (0.05-0.22 ppm), except that collected from Shoubra or Qalyiob. Also, it was found that all the samples of spring contained such pesticide in a range of 0.10 to 0.43 ppm, except the Qaha samples which did not contain such compound. However, the other samples related to the season of summer and autumn contained 0.27, 0.38 and 0.27 ppm in samples collected from Shoubra, El-Kanater and Qaha, while samples from Toukh and El-Kanater contained 0.30 and 0.39 ppm at autumn season.

For the herbicide, benefin, such compound was detected in all winter samples, except that collected from Shoubra. The detected concentration ranged between 0.01 to 0.20 ppm. The same compound was not detected in milk samples collected neither at spring nor from Shoubra and Benha at the summer season, while at autumn was detected only in Benha samples.

From another viewpoint, data of the total mean of the positive frequency percent in Table (7), indicated that thiram was the most frequent pesticide in the collected milk samples during the four seasons followed by pyridaben, whereas etofenprox was the lower frequent

Table 7. The positive frequency percent of the detected residues of non-organochlorine pesticides in the collected milk samples through the four seasons

Pesticide	% Positive frequencies/pesticide and season				Total Mean/pesticide
	Winter	Spring	Summer	Autumn	
thiram	16.70	8.30	20.80	20.80	16.65
benalxyl	16.70	12.50	16.70	0.00	11.48
fenitrothion	20.80	12.50	8.30	8.30	12.48
parathion	4.17	8.30	20.80	8.30	10.39
profenofos	12.50	16.70	8.30	8.30	11.45
fenpropathrin	16.70	8.30	8.30	12.50	11.45
alpha-methin	4.20	8.30	8.30	4.20	6.25
etofenprox	4.20	8.30	8.30	0.00	5.20
pyridaben	16.70	20.80	12.50	8.30	14.58
benefin	20.80	0.00	16.70	4.20	10.43
Total Mean/Season	13.35	10.40	12.90	7.49	11.03

compound. The calculated percent of positive frequencies were, 16.65, 14.58 and 5.20 %, respectively. On the other hand, the calculated total mean of whole detected pesticide residues per season showed that milk samples collected at winter contained the higher frequency of pesticides followed by the summer season, while the autumn was the lower season. The calculated percent of positive frequencies, were 13.35, 12.90 and 7.49 %, respectively.

However, when the data were expressed as total mean of the detected non-organochlorine pesticide residues in milk samples in relation with the season (Fig. 3), it was very clear that the milk samples collected at the summer season contained the higher concentrations of such pesticides. For example, at summer season, the total mean of the detected residues reached to 0.91, 0.870.28 and 0.22 ppm for benalaxyl, parathion, benefin and thiram, respectively. The observed exception was fenitrothion residues which reached 0.72 ppm at the winter season.

Data in Fig. (4), clearly indicated that the milk samples collected at the summer season contained the higher concentration of the detected non-oranochlorine pesticide residues (as total mean) especially that from markets of Qaha (0.55 ppm) followed by El-Kanater (0.46 ppm), Shoubra (0.28 ppm) and Toukh (0.22 ppm). The only exception was related to the milk samples collected from Toukh market at winter which contained 0.33 ppm as a total mean of residues of the non-organochlorine pesticides.

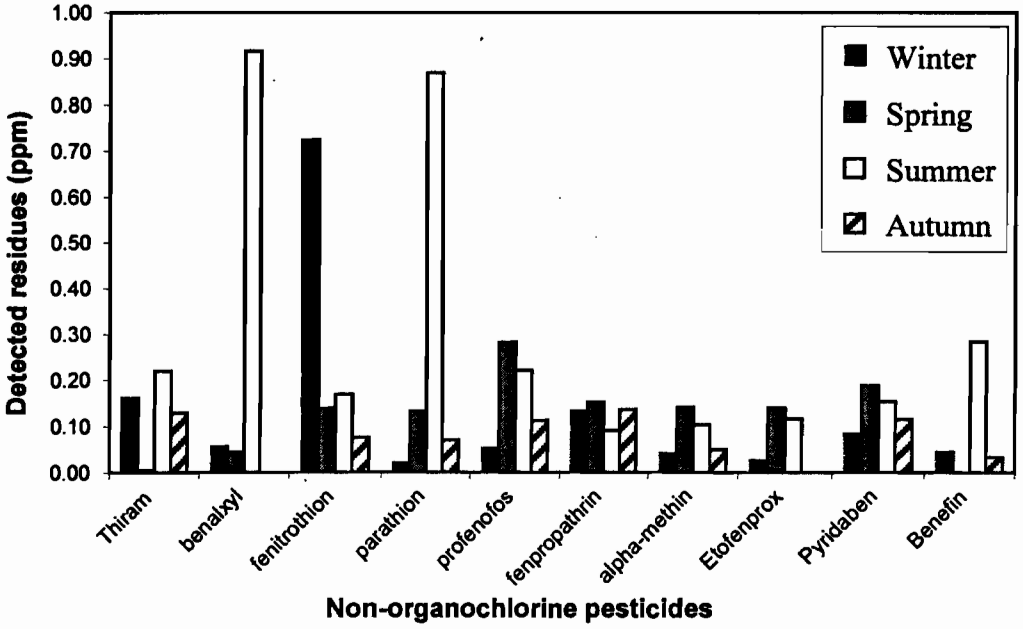

Fig. 3. Mean of the non-orgaochlorine pesticide residues in milk samples collected from different markets in Qalubia governorate during the four seasons of the year 2001

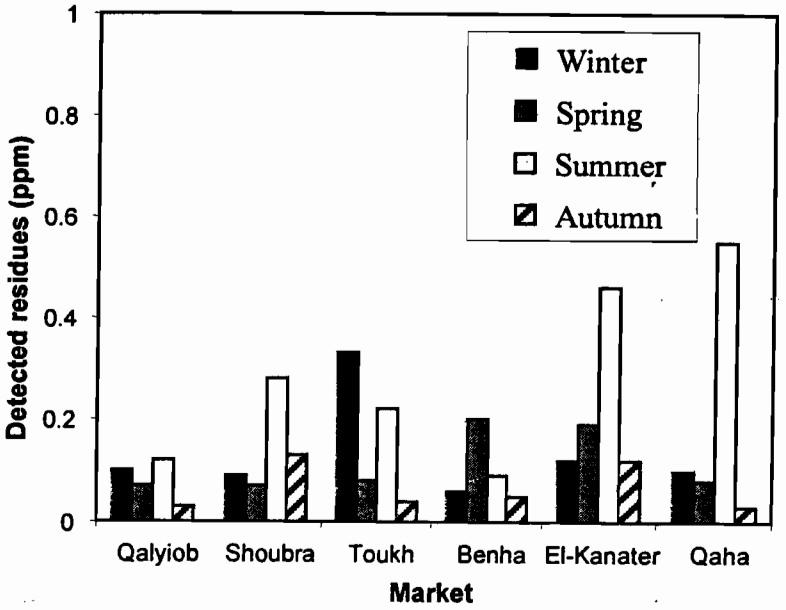

Fig. 4. Mean of non-organochloroine pesticide residues (ppm) in milk samples collected from different markets of Qalubia governorate during the four seasons of the year 2001

Generally, it was found that the majority of the detected concentrations of pesticide residues in the collected milk samples were higher than the published Maximum Residue Limits of pesticides in milk **(Alimentarious Commission, 1999)**. For example, the Maximum Residue Limits of aldrin, chlordane, DDT, fenitrothion, fenpropathrin, heptachlor, and profenofos in milk are 0.006, 0.002, 0.02, 0.002, 0.1, 0.006 and 0.01 ppm, respectively.

In spite of the majority of the organochlorine and some organophosphorus pesticides such as parathion were banned from use in Egypt since 1980's, the presence of the detected pesticide residues (either organochlorine or non-organochlorine) in the collected milk samples is expected. There are several reasons behind the existence of such residues in the collected milk samples, such as the illegal use of the banned pesticides and hence the producer animals of milk, i.e. cows or buffalo's are feeding on the contaminated fodder and hence enter the food chain. Similar explanation was described by **(Wong and Lee 1997)** who reported that DDT and HCH have been banned in China since 1983, whereas residues of such compounds are still persist in the environment and cause contamination through the food chain. Also, according to the fact that the majority of the pesticides are lipophilic compounds which lead to accumulate in the lipid tissues of mentioned animals. Moreover, the existence of the detected pesticide residues in milk samples may be explained by the transfer and movement of pesticides from treated area to water resources and hence reach to the animals through drinking of the contaminated water **(Shibamoto and Bjeldanes, 1993)**.

In addition, from the toxicological viewpoint, the presence of the mentioned pesticide residues is expected since that the secretion of milk is one of many routes to eliminate the pesticide residues from the mammalian body **(Matthews, 1979)**.

However, the obtained data are in agreement with other results recorded by other investigators (either in Egypt or from other countries). For example, **Dogheim *et al* (1996)** showed that several organochlorine and organophosphorus pesticides residues were monitored in animal and human milk during the Multiresidue analysis program. From those detected, beta-HCH residues showed an increasing pattern, especially in human milk samples from Cairo, Egypt. In case of milk samples collected from animals, the results showed that the detected residues approached the extraneous residue limits of the Codex Committee on Pesticide Residues.

In case of the other countries, **Maitre *et al* (1994)** found that almost all pasteurised milk samples collected from Santa Fe City, Argentina showed the presence of organochlorine pesticide residues. The most frequently detected residues were heptachlor and its epoxide (98%) and hexachlorocyclohexane, HCH (alpha and gamma isomers), aldrin, dieldrin, chlordane, endosulfan (I and II) and DDT (*o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD). Also, **Waliszewski *et al* (1997)** found that HCH levels were 0.094 mg/kg on fat basis in collected cow's milk samples from the central region of Veracruz state, Mexico. The mean DDT levels was 0.159 mg/kg. **Wong and Lee (1997)** found that 42 of 252 milk samples (pasteurized, fresh, and raw milk) collected from different markets of Hong Kong

contained organochloride pesticide residues at levels exceeding the Extraneous Maximum Residue Limits of the Codex Committee on Pesticide Residues especially for DDE and HCH isomer levels. In addition, **Kalra *et al* (1999)** showed that DDT and its metabolites (DDE and *p,p'*- dichlorodiphenyldichloroethane [DDD]), isomers of hexachlorocyclohexane HCH, heptachlor and its epoxide and aldrin were detected in more than 80% of dairy milk samples collected from rural and urban areas of 12 states representing different geographical regions of India. The detected concentrations of DDT residues, alpha-HCH, beta-HCH, gamma-HCH and delta-HCH exceeded their maximum residue limits prescribed by the Ministry of Health and Family Welfare of the Indian Government. Similar finding was reported by **John *et al* (2001).**

More recently, **Ciscato *et al* (2002)** reported that 0.76% of raw milk samples collected from Sao Paulo City, Brazil were contaminated with HCH (alpha isomer) and 10.60% with endosulfan (alpha and beta isomers). In addition, **Cressey and Vannoort (2003)** reported that residues of *p,p'*-DDE were found in seven of 20 milk-based infant formulae weaning foods in New Zealand at concentrations ranging from 0.03 to 0.5 mg/kg while residues of *p,p'*-DDT were found in one imported milk-based infant formula at 0.7 mg/kg.

From another viewpoint, the obtained results exhibited that there are some variations in the detected pesticide residues especially in relation with the selected markets or with the season. Such variation may be due to the variation in the distribution of agricultural area treated by such pesticides, especially those included the animals fodder's. Similar finding was reported by **Kalra *et al* (1999)** who found that the detected pesticide residues showed significance variation in the incidence as well as level of the detected pesticide residues in milk samples collected from different regions of India.

Moreover, the obtained results showed that pesticide residues were found in more numbers and levels in milk samples collected at summer season. Such observation may be due the high rate of pesticide application in summer more than winter or other season. However, such finding was in agreement with that obtained by **(John *et al* 2001)**.

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مجلة اتحاد الجامعات العربية للدراسات والبحوث الزراعية ، جامعة عين شمس ، القاهرة ، ١١(٢) ، ٨٦٥ - ٨٨٤ ، ٢٠٠٣

الكشف عن متبقيات بعض المبيدات فى عينات اللبن التى تم جمعها من الأسواق المختلفة بمحافظة القليوبية، مصر

[٦٢]

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إستهدفت الدراسة إستكشاف تواجد مخلفات بعض المبيدات فى عينات اللبن الخام التى تم جمعها من ستة أسواق بمحافظة القليوبية اثناء الأربعة مواسم من عام ٢٠٠١. ولقد تبين أن ما تم الكشف عنه من متبقيات كانت تابعة لمبيدات الكلورينية العضوية (مشتقات مركب الددت ومشابهات الهكساكلوروسيكلوهكسان والسيكلودايين) وكذلك مبيدات غير كلورينية عضوية والتى إشتملت على مبيدات فوسفورية عضوية وبيريثرويدز وغيرها.

بصفة عامة، لقد أظهرت النتائج المتحصل عليها من خلال ما تم حسابه من المتوسط العام لمتبقيات المبيدات التى تم الكشف عنها أن متبقيات المشتقات (*o,p'*-DDE) وكذلك (*p,p'*-DDE) فى عينات اللبن التى تم جمعها فى فصل الصيف قد وصلت إلى تركيز قدره ٠,٩٨و ١,٠٢ جزء فى المليون على التوالى. وفى فصل الخريف، فإن المتوسط العام للمشتق (*o,p'*-DDE) والمشابه (*o,p'*-DDT) قد وصل إلى ٠,٥٧ و٠,٨٤ جزء فى المليون على التوالى. وبالنسبة لمركبات الهكساكلوروسيكلوهكسان والسيكلودايين، فإن عينات اللبن التى تم جمعها بموسم الصيف كانت من أكثر العينات إحتواءاً على متبقيات تلك المركبات خاصة الإندرين الذى وصلت متبقياته إلى ٠,٩٠ جزء فى المليون ويتبعه المشابه الفا-هكساكلوروسيكلوهكسان (٠,٣٧ جزء فى المليون) والألدرين (٠,٣٢ جزء فى المليون) والهبتاكلور (٠,٢٤ جزء فى المليون). إضافة إلى ذلك، فإن عينات اللبن التى تم جمعها من أسواق القناطر ويليها طوخ وقها كانت من أكثر العينات إحتواءاً على متبقيات المبيدات الكلورينية خاصة فى فصل الصيف والخريف .

وفيما يتعلق بمتبقيات المبيدات غير الكلورينية، فقد أمكن الكشف عن متبقيات لعشرة مبيدات. فقد أظهرت نتائج التحليل أن عينات اللبن التى جمعت بموسم الصيف كانت تحتوى على أعلى التركيزات (كمتوسط عام) خاصة فى العينات التى جمعت من أسواق قها (٠,٥٥ جزء فى المليون) يليها القناطر (٠,٤٦ جزء فى المليون) وشبرا (٠,٢٨ جزء فى المليون) وطوخ (٠,٢٢ جزء فى المليون) وذلك بالمقارنة بالأسواق الأخرى.

عموماء قد تبين أن تركيزات متبقيات المبيدات التى تم الكشف عنها كانت أعلى من الحدود القصوى لمتبقيات المبيدات والتى تم نشرها من خلال الهيئات الدولية. إضافة إلى ذلك ، فإن النتائج المتحصل عليها أظهرت أن مركبات الهكساكلوروسيكلوهكسان والسيكلودايين أظهرت أعلى نسبة موجبة للتكرارية (١٤,٤٦ %) يليها المتبقيات التابعة للمبيدات غير الكلورينية (١١,٠٣%) بينما مشتقات الددت كانت الأقل تكرارية (٧,٩٠%) فى عينات اللبن التى تم جمعها.

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