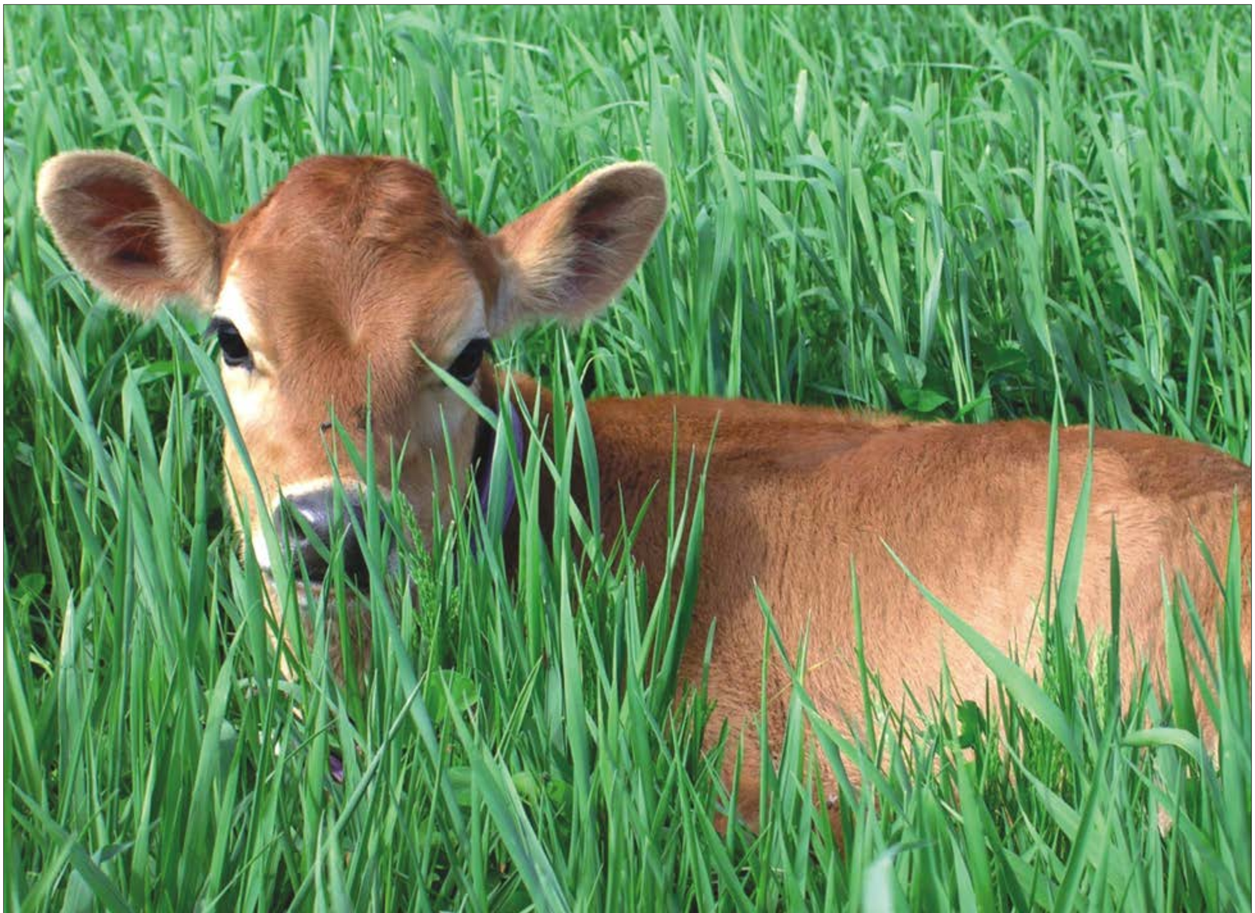

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Research Article
Reduction of Pesticide Residues in Egyptian Buffalo Milk by Some Processing Treatments

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Abstract
This study was designed to evaluate the pesticide residues in Egypt. Buffalo milk was collected from Sharkia, Dakhlia and Giza provinces. The effect of pasteurization, sterilization, fermentation and coagulation on some organophosphorus (dimethoate and malathion) pesticides spiked in buffalo milk was studied. The obtained results showed that the sampling time and method of analysis may be behind the remarkable effect on dimethoate and malathion content of milk samples. All treatments had significant effects on the reduction of pesticides level. The pesticides degradation percentage was improved by fermentation. Pasteurization however removed malathion completely and reduced dimethoate level to a great extent.

Key words: Pesticide residues, organophosphorus, heat treatments, fermentation, coagulation

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The widespread occurrence in the environment of any foreign chemical like pesticides is a matter of public health concern. Pesticides are poisons of course, they are used to control insects, rodents and other undesirable animals and plants. The possible harmful effect to the general population from intake of small amounts of these pesticides chemicals as residues in crops, water and air or from cattle (fat tissue and/or milk) fed on crops by-products treated with pesticides (Iftikhar *et al*., 2014) was considered by many researchers. In determining the overall effect on public health, the health benefits of pesticides must also be considered (Rychen *et al*., 2008). Durham (1971) reported that, pesticides promote health directly through control of insect vector borne diseases and indirectly through increased and improved agriculture production of food and fiber.

Pesticides may classify according to their chemical nature and structure to four main classes; organochlorine, organophosphorus, carbamates and pyrethroids. Organophosphorus pesticides (OPPs) are esters, amides or thiol derivatives of phosphoric acid (Shaker and Elsharkawy, 2015). They are widely used in agriculture and for household plant care, mainly as insecticides, due to their broad spectrum of action and shorter persistence in the environment than organochlorine pesticides. However, organophosphorus can be concentrated throughout the food chain. Lactating animals can absorb these compounds by all routes (inhalation, ingestion and dermal absorption) and thus can secrete contaminated milk (Gazzotti *et al*., 2009).

Because of the special place of milk in the diet of infants, children and also adults, the presence of significant amounts of residues is undesirable (Shaker and Elsharkawy, 2015). Consequently residues limits for milk and dairy products tend to be more severe than those for other food stuffs. The annual reports of the WHO and FAO committee group represents tolerance level and limits for individual pesticides in different food commodities including milk and dairy products (FAO and WHO., 2008).

Pesticide residues in milk and dairy products and the effect of various treatments on those residues have been reported and studied by several investigators (Pagliuca *et al*., 2005, 2006; Abou Donia *et al*., 2010; Bo and Zhao, 2010; Bo *et al*., 2011; Bajwa and Sandhu, 2014). With the above in view, this study has been carried out and the results obtained are recorded to evaluate the naturally occurred pesticide residues in egyptian buffalo milk collected from different locations and to study the effect of some processing treatments on organophosphorus (dimethoat and malathion) pesticides spiked in buffalo milk.

MATERIALS AND METHODS

Materials: Two composite fresh buffalo milk samples collected from different locations at Sharkia and Dakhlia (rural zone) were obtained from the Dairy Technology Unit, Dairy Science Department, Faculty of Agriculture, Cairo University. Another composite fresh buffalo milk sample was obtained from the herd of the Faculty of Agriculture, Cairo University (urban zone).

As for the conditions of herds it was as the following:

- All herds had been kept indoors and fed wheat straw *ad libitum*, adequate amount of concentrate, silage and green cornstalk (drawa)
- Yogurt starter culture Yc-280 (Chr. Hansen Laboratory, Copenhagen, Denmark) was used
- Rennet solution (0.08 N) prepared in the Dairy Technology Unit, Dairy Science Department, Faculty of Agriculture, Cairo University was used
- Dimethoat was obtained from Ministry of Agriculture, Giza, Egypt
- Malathion adwia (50%) was obtained from the Pesticides Laboratory, Faculty of Agriculture, Cairo University

Methods of analysis: Buffalo milk samples were analysed for total solids, fat and acidity contents according to AOAC (1999) methods. Pesticide residues were determined. In the pesticides division of Principal Central Laboratory, Faculty of Agricultural, Cairo University, Pagliuca *et al*. (2005) method was used for organophosphorus pesticides determination in buffalo milk samples collected during the first week of August, 2011. However, the QUECHERS method described by Anastassiades *et al*. (2003) was used in the Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Ministry of Agriculture, Agriculture Center for determination of different classes of pesteside residues in samples collected during the first week of December, 2011.

Statistical analysis: Data are expressed as the Mean±SD. Date were analyzed one-way analysis of variance (ANOVA), followed by assessment of differences by HSD *post-hoc* test. All statistical calculations were performed using by SPSS Inc. (2007) statistical package. Results were considered statistically significant at $p<0.05$.

Experimental procedures

Evaluation of pesticide residues in collected samples: Three composite samples of fresh raw buffalo milk (3 kg each) collected from the previously mentioned locations were obtained. Five hundred milliliters raw milk from each sample was mixed thoroughly for preparation of the fourth sample. All samples were analyzed for detection of some pesticide residues.

Effect of processing on some organophosphorus pesticides spiked in buffalo milk: Equal amounts of raw buffalo milk from each source were mixed thoroughly and treated to study the effect of pasteurization, sterilization, fermentation and coagulation on distribution of pesticides among milk. Briefly, the first part was spiked with malathion at level of 4 mg/100 g milk. While, the other part was spiked with dimethoat level of 4 mg/100 g milk. Spiked milk samples were then shake vigorously to ensure complete absorption and distribution among milk. Each part of contaminated samples was then divided into five portions. The first portion was left as control, the second portion was pasteurized (72°C/15 sec) and immediately cooled, the third portion was sterilized (121°C/15 min) in an autoclave and then rapidly cooled, the fourth portion was fermented by yogurt starter culture (0.05 g L^{-1}) at 43°C/2.5 h) and immediately cooled and the fifth portion was coagulated by animal rennet (2 mL L^{-1}) at 40°C till complete coagulation then the curd was cutting and the whey was draining. Finally, malathion and dimethoat were then extracted and determined in both treated and untreated samples.

RESULTS AND DISCUSSION

Organophosphorus and organochlorines are widely used in many agroindustrial areas of modern agriculture in Egypt as they are considered economically important for high yield production. Although pesticides provide effective and practical control of disease vector bearing and crop destroying insects, the necessity of using these toxic materials on human or his immediate environment has created potential hazards that are of great public health significance (Shaker and Elsharkhawy, 2015).

Therefore, preliminary trails were made in cooperation with the Pesticides Division of Principal Center Lab, Faculty of Agriculture, Cairo University and the Central Lab of Residue Analysis of Pesticides and Heavy Metals in Food, Ministry of Agriculture, Agriculture Center, in order to distinguish the occurrence of the predominant pesticide residues in Egypt, buffalo milk collected from different locations on one hand and follow the effect of some processing on some pesticides spiked in buffalo milk on the other hand.

Evaluation of naturally occurred pesticide residues in Egypt, buffalo milk collected from different locations: Fat, total solids and acidity contents of milk collected from Sharkia, Dakhlia and Giza provinces were determined. All samples have normal composition as shown in Table 1. Reports obtained from the Pesticides Division of Principal Center Lab, Faculty of Agriculture, Cairo University, showed organophosphorus pesticide contamination in buffalo milk samples collected from different locations in Egypt.

Dimethoate was found in the range of 0.000-0.493 mg/100 g, while malathion was in the range of 0.022-0.040 mg/100 g milk as shown in Table 2 and Fig. 1. In this respect, Mallatou *et al*. (1997) investigated thirty eight samples of bovine milk and found that eleven milk samples contained organophosphorus pesticide residues with contents below the maximum permitted amount and the contents in two samples were 43 and 280 mg kg^{-1}.

Table 1: Composition of raw buffalo milk collected from different locations

Province	Fat (%)	Total solids (%)	Acidity (%)
Sharkia (A)	6.80	17.23	0.18
Dakhlia (B)	7.10	17.59	0.18
Giza (C)	7.00	17.47	0.18
Bulk (D)	6.90	17.35	0.18

Table 2: Pesticide residues naturally occurred in egyptian buffalo milk collected from different locations[a]

Compounds	Province	Concentration (mg/100 g)
Dimethoate	A	0.493
	B	0.000
	C	0.396
	D	0.200
Malathion	A	0.038
	B	0.040
	C	0.022
	D	ND[b]

[a]Determined in the Pesticides Division of Principal Central Laboratory, Faculty of Agriculture, Cairo University, [b]ND: Not detected

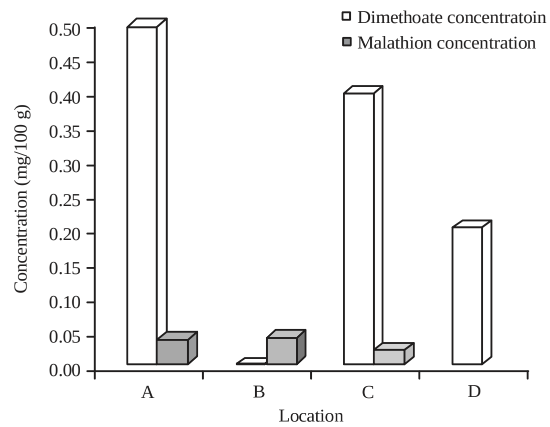

Fig. 1: Pesticide residues naturally occurred in Egypt, buffalo milk collected from different locations

Table 3: Recovery of dimethoate and malathion pesticides spiked in raw buffalo milk[a]

Pesticides	Spiked (mg/100 g)	Determined	Recovery[b] (%)
Dimethoate	4	3.852	96.3
Malathion	2	1.695	84.75

[a]Determined in the Pesticides Division of Principal Central Laboratory, Faculty of Agriculture, Cairo University, [b]Recovery (%) = (mg determined/mg spiked)×100

Pagliuca *et al.* (2006) also found that among one hundred and thirty five raw milk samples analyzed, thirty seven samples were positive for traces and ten samples showed organophosphorus pesticide contamination in the range of 5-18 mg kg^{-1}.

Reports obtained from the Central Lab of residue analysis of pesticides and heavy metals in food, Ministry of Agriculture, Agriculture Center indicated that buffalo milk samples collected from different locations (December, 2011) were free from four hundred and two of different classes of pesticides including dimethoate and malathion. The Limited Of Quantification (LOQ) of the different classes of pesticides was in the range of 0.01-0.05 mg kg^{-1} milk. Egyptian standards in 2010 indicate that the Maximum Residue Limits (MRL) of the different classes of pesticides for raw milk should be in the range of 0.01-0.1 mg kg^{-1}.

Data obtained are agreed with those illustrated in the report of FAO and WHO (2008). Abou Donia *et al.* (2010) on the other hand analyzed buffaloes and cows milk for pesticide residues and found that, none of the raw milk revealed the presence of any organophosphorus pesticides including dimethoate and malathion.

Comparing the results of the Pesticide Division of Principal Central Laboratory, Faculty of Agriculture, Cairo University and the Central Laboratory of Residue Analysis of Pesticides, one can say that the differences between the results obtained may be due to the sampling time or the sensitivity of the method of analysis. These results are in accordance with those of Pagliuca *et al.* (2006) who reported that the organophosphorus resedues in milk may influence by the season.

Effect of processing on some organophosphorus pesticides spiked in buffalo milk: Fresh buffalo milk was spiked with the desired pesticides to follow the effect of pasteurization, sterilization, fermentation and coagulation on the degradation and disappearance of pesticide residues. The pesticides used were dimethoate and malathion.

The recovery of dimethoate and malathion was 96.3 and 84.75% as shown in Table 3. Data obtained showed some loss in the added pesticides. This loss may be due to the loss during handling, extraction or purification of the pesticides. Pesticides loss during the extraction or purification steps was previously recorded by Braun and Tstanek (1982), Abou-Arab (1987) and Abd-Rabo *et al.* (1989).

Regarding the effect of different processes on dimethoate and malathion degradation, it could be note that all treatments had significant effects on the reduction of pesticides (Table 4 and Fig. 2). Table 4 shows that the degradation of dimethoate was 73.42% as a result of pasteurization, while malathion was completely destructed and not detected in milk sample. Sterilization process on the other hand, had a significant effect on the dimethoate and malathion content. The percent of reduction was 75.72% for

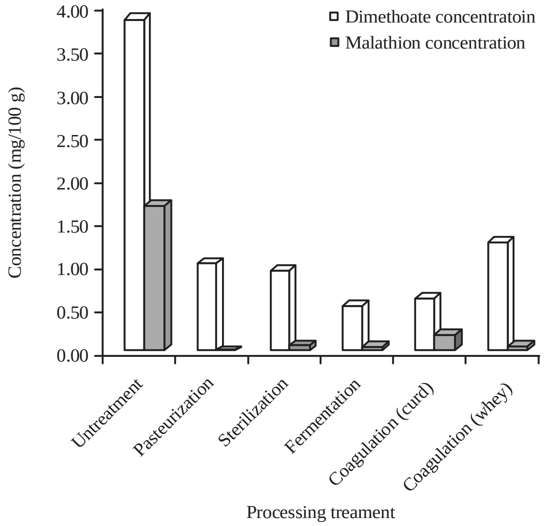

Fig. 2: Effect of different processes on degradation of dimethoate and malathion spiked in buffalo milk

Table 4: Effect of different processes on degradation of dimethoate and malathion spiked in buffalo milk

	Concentration (mg/100 g)		Degradation[a] (%)	
Process	Dimethoate	Malathion	Dimethoate	Malathion
Un-treatment	3.852±0.001[a]	1.695±0.001[a]	-	-
Pasteurization	1.024±0.001[c]	0.000±0.000[f]	73.42	100.00
Sterilization	0.935±0.003[d]	0.068±0.000[c]	75.72	95.99
Fermentation	0.520±0.017[f]	0.048±0.001[e]	86.50	97.17
Coagulation curd	0.618±0.001[e]	0.193±0.001[b]	50.96	85.02
Whey	1.271±0.003[b]	0.061±0.001[d]		

[a]Degradation (%): 100 (mg treated mg^{-1} untreated×100), Means in the same column with different superscript letters differ significantly

dimethoate and 95.99% for malathion. As shown in Table 4 it could be note that fermentation had a considerable effect. The concentration of dimethoate reduced from 3.852-0.520 mg/100 g and that of malathion from 1.695-0.048 mg/100 g. In other words, the pesticides degradation percentage was improved being 86.5% for dimethoate and 97.17% for malathion as compared with the other processes.

Data obtained in Table 4, also show that the degradation of malathion was greater than that of dimethoate. These results are in agreement with those found by Bo and Zhao (2010) and Zhao and Wang (2012), they mentioned that dimethoate and methyl parathion were more stable but malathion was the most labile.

Regarding the effect of heat treatments and fermentation process, Bogialli *et al*. (2005) and Ozbey and Uygun (2007) mentioned that the organophosphorus pesticides in foods were affected by fermentation, heat treatment and drying. The work of Kaushik *et al*. (2009) revealed that the food processing leads to large reduction in pesticide levels in most cases. On the other hand, Zhang *et al*. (2006) mentioned that the manufacturing technology of yogurt, including heat treatments (pasteurization and sterilization) and the action of microorganisms during storage can result in reduction of pesticide levels in yogurt. The results of Bo and Zhao (2010) revealed that the growth of lactic bacteria in bovine milk could reduce the residue levels of some organophosphorus pesticides and might decrease the safety risk of the products. The work of Bo *et al*. (2011) also revealed that two direct vat set starters enhanced organophosphorus degradation in whole milk in different extents.

As for the effect of coagulation process, data obtained showed that the degradation percentage of dimethoate and malathion of the curd was decreased as compared with the other treatments which may be attributed to binding of small amount of pesticide to the rennet enzyme (Abdou *et al*., 1983) or to the chemical nature of the pesticide (Pagliuca *et al*., 2006).

CONCLUSION

The Egypt government had banned the use of organophosphorus and organochlorine pesticides since

1980s. Although, our reports showed residues of dimethoate (0.000-0.493 mg/100 g) and malathion (0.022-0.040 mg/100 g) in buffalo milk samples collected from Sharkia, Dakhlia and Giza province in Egypt to be less than maximum limit accepted by the egyptian standards in 2010 for malathion but higher for dimethoate. As the milk processing treatment, we can conclude that the fermentation was the most effective process, which reduced the concentration of dimethoate and malathion pesticides to a great extent. Pasteurization however removed malathion completely and reduced the concentration of dimethoate.

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