

Impacts of processing heat treatments on deltamethrin and bifenthrin residues in human breast milk and raw milk from different animals

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(Received October 15, 2017; Accepted November 23, 2017)

Abstract

A total of 163 milk samples (200 ml) human breast milk and (500 ml each) of cows, ewes, goats, buffaloes and camels were collected randomly at weekly intervals (10 samples/week) from Baghdad governorate. Among the total milk samples (138) milk samples were examined during two climatic periods from the beginning of September 2016 to the end of the February 2017 were tested for the occurrence of DMT residues by using the HPLC technique. Besides that, some of the selected positive samples were subjected to one of the commercial heat treatments such as 63°C/30 min, 80°C/5 min and 100°C/5 min to evaluate the efficiency of heat exposure on the degradation of deltamethrin and bifenthrin residues in milk. The results pointed out that milk samples containing the higher fat percentage exhibited significantly ($P<0.05$) the highest concentration of deltamethrin and bifenthrin in summer highest than in winter, increased the fat percentages of milk was being associated with an increased level of deltamethrin residues due to the lipophilic nature of the deltamethrin and bifenthrin pesticide. The current results revealed that milk samples that were collected from buffaloes, ewes and cows recorded the highest deltamethrin and bifenthrin residues in summer season where their mean levels that exceeded the accepted MRLs of 0.05 ppm to milk samples of goats, camels and breast milk the lowest mean levels of deltamethrin and bifenthrin residues. There was a seasonal variation of the deltamethrin and bifenthrin concentrations in milk samples for each animal species where all the milk samples that were collected from buffaloes, ewes, cows, goats, camels and breast milk had higher mean levels of deltamethrin and bifenthrin residues in summer season than in winter season. Data illustrated revealed that there was a seasonal variation in the mean levels of deltamethrin and bifenthrin residues in human breast milk samples for each district village where all the milk samples that were collected from AL-Sader and AL-Karada districts had highest mean levels values in summer than in winter season.

Keywords: High performs liquid chromatography, deltamethrin, bifenthrin, raw milk, Skimmed milk

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تأثير المعاملات الحرارية على متبقيات المبيدات الحشرية الدلتامثرين والبيفنثرين في حليب الانسان وحليب الحيوانات

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فرع الصحة العامة البيطرية، كلية الطب البيطري، جامعة بغداد، قسم الانتاج الحيواني، كلية الزراعة، جامعة سومر، ذي قار، العراق

الخلاصة

تم جمع 163 عينة حليب (200 مل) من حليب الانسان و (500 مل) من حليب الأبقار والنعاج والماعز والجاموس والجمال عشوائياً على فترات أسبوعية (10 عينات / أسبوع) من محافظة بغداد. من بين عينات الحليب تم فحص (138) عينة خلال فترتين مناخيتين من بداية شهر سبتمبر عام 2016 وحتى نهاية شهر فبراير من عام 2017 والتي فحصت بجهاز HPLC لتحديد المتبقيات. وبالإضافة إلى ذلك تم تعريض بعض من العينات التي أظهرت نتائج موجبة لتواجد متبقيات الدلتامثرين، والبيفنثرين إلى إحدى المعالجات الحرارية مثل 63

درجة مئوية لمدة ٣٠ دقيقة و ٨٠ درجة مئوية لمدة ٥ دقائق و ١٠٠ درجة مئوية لمدة ٥ دقائق لتقييم كفاءة التعرض للحرارة على تفسخ متبقيات الدلتا مثرين والبيفنثرين في الحليب. اظهرت النتائج الحليب كامل الدسم فرقاً معنوياً ($P < 0.05$) في احتوائها على المتبقيات في فصل الصيف أكثر من فصل الشتاء. وبعبارة أخرى ان زيادة نسبة الدهون في الحليب لها علاقة طردية مع مستويات متبقيات الدلتا مثرين والبيفنثرين نظراً لكون هذه المبيدات محبة للذابة بالدهون. كشفت نتائج التحليل الإحصائي بان عينات الحليب التي تم جمعها من الجاموس، النعاج والأبقار سجلت وبفارق معنوياً ($P < 0.05$) أعلى ارتفاعاً لمتبقيات الدلتامثرين لكلا الموسمين حيث كان متوسط مستوياتها التي تجاوزت الحدود القصوى المقبولة من (٠,٠٥) جزء في المليون مقارنة لعينات حليب كل من الماعز، الإبل وحليب الانسان والتي سجلت بفارق معنوياً ($P < 0.05$) انخفاضاً في المستويات المتوسطة من متبقيات الدلتامثرين. كان هناك تباين موسمي لتركيزات الدلتامثرين والبيفنثرين في عينات الحليب لكل نوع من أنواع الحيوانات حيث كانت جميع عينات الحليب التي تم جمعها من الجاموس والنعاج والأبقار والماعز والجمال وحليب الانسان أعلى من متوسطات دلتامثرين والبيفنثرين في فصل الصيف مما كانت عليه في فصل الشتاء. اظهرت البيانات الموضحة ان هناك تبايناً موسمياً في المستويات المتوسطة لمخلفات الدلتامثرين والبيفنثرين في عينات حليب البشري لكل قرية حي حيث كانت جميع عينات الحليب التي تم جمعها من منطقتي الصدر والكرادة أعلى القيم المتوسطة في الصيف مما كانت عليه في فصل الشتاء.

Introduction

Presence of persistence and hazardous Agrochemicals in the human diet is an emerging problem in developing countries which encounter poor institutional progress and slow financial development.

Deltamethrin is type II synthetic pyrethroid pesticides that produced in 1974 and first marketed in 1977 and the deltamethrin products are among some of the most popular and widely used insecticides in the world in competing ectoparasites affecting farm animals (1). Bifenthrin is an insecticide used heavily in the control of red imported fire ants, due to its high toxicity to aquatic organisms, it is listed as a restricted use pesticide, although it can be purchased for residential use in lower concentrations and It has a very low solubility in water and tends to bind to soil, which minimizes runoff into water sources (2), The Environmental Protection Agency (EPA) has also identified bifenthrin as a class C carcinogen, meaning that it is a possible human carcinogen (3). The contamination of milk with pesticides is considered as one of the main dangerous aspects in the last few years. Milk has been found to be a very good reference point for monitoring contamination by pesticides (4). To control the presence of pesticide residues in fresh milk and milk products is a big issue for producer, consumer and government due to the potential risk. Human milk as well as animal milk is contaminated through the contaminated food (5). These residues are too much persistent. They accumulate in body fat even in breast milk. Transfers of such pesticide to our body via food of animal origin rich with fat contents such as milk has not been studied till now in Iraq and Since there is no data on the residual levels of deltamethrin and bifenthrin in human breast milk and different animal, this study was conducted to determine the levels of deltamethrin pesticide residues in cow's, ewe's, buffalo's, goat's, camel's milk samples collected from Baghdad province, using High Performance Liquid Chromatography (HPLC).

The aims of current study were to determine the residues of deltamethrin and bifenthrin in Human breast raw milk, cow's, ewe's, goat's, buffalo's and camel's milk samples collected from different areas in Baghdad province, and comparison of the mean levels of this pesticides residues (ppm) between the cow's raw and skimmed milk samples, and assessing the effect of heat treatment on existentially of deltamethrine and bifenthrin residues in raw milk.

Materials and methods

This study was carried out during the period extended from the beginning of September 2016 to the end of the February 2017. A total of 175 milk samples they were of 12 milk samples (200 ml each) of Human breast milk and 163 milk samples (500 ml each) of cows, ewes, goats, buffaloes, camels were collected randomly from Baghdad and at weekly intervals (10 samples / week) in a sterile polyethylene plastic bags from Baghdad governorate.

All the collected milk samples were transported to the laboratory inside portable ice-cooled containers. 175 milk samples were examined on two climatic periods, the first was the summer period that extended from the beginning of September to the end of October 2016 while the second was the winter period that extended from the beginning of January to the end of February 2017. Each milk sample was divided into two portions where the first portion (300 ml) was used to determine the chemical composition of milk such as the specific gravity and the percentages of fat, lactose, protein, solid not fat and minerals by using the Ultrasonic Milk Analyzer. While the second portion of (200 ml) was sent to the HPLC analysis to determine the level of deltamethrine and bifenthrin residues, besides that some of selected positive samples for deltamethrine and bifenthrin residues were subjected to one of the industrial heat treatments such as 63°C /30 min, 80°C /5min and 100°C

/5min to determine the effect of heat treatment on the levels of deltamethrin and bifenthrin residues in milk (1).

Data submitted to statistical analysis by using of variance (ANOVA) and using least significant differences (LSD) to differentiate among the means used spss program (6).

Results and discussion

Comparison of the mean levels of deltamethrin and bifenthrin residues between the full fat and skimmed milk samples

The results illustrated in Table 1 revealed that in raw milk and skimmed milk with fat from 3.29% to 1.064% the deltamethrin residues were from 0.113 and 0.00 ppm and

bifenthrin residues from 0.134 and 0.00 ppm. The current results established the statistically significant ($P<0.05$) influence of the fat percentage on the concentration of the deltamethrin and bifenthrin residues in milk samples. In the USA, Australia and Canada the skim milk is made when all the milk fat is removed from the raw milk by using a separator (7). The results of the current study were in agreement with (8). Who reported that skimming of buffaloes and cow's milk lead to a slight reduction in the analyzed pesticide concentration in skim milk. In addition, it was in agreement with (9) Pyrethroids range from non-polar to low-polarity lipophilic compounds. Owing to their metabolism in animals, they tend to bio-accumulate in lipid compartments, becoming a potential source of human exposure through foodstuffs (8).

Table 1: Comparison of the mean levels of deltamethrin and bifenthrin residues (ppm) between the cow's raw and skimmed milk samples collected from the Abu-Ghraib dairy plant

Source of samples	No. of xamined samples	Fat% Mean	Deltamethrin (ppm) Mean \pm S.E	Bifenthrin (ppm) Mean \pm S.E	%violation MRLs 0.05
Whole milk	5	3.29	0.113 \pm 0.22 A	0.134 \pm 0.31 a	100%
Skimmed milk	5	1.064	0.0 \pm 0.0 B	0.0 \pm 0.0 b	NV*

The effect of different industrial heat treatments on the degradation of the deltamethrin and bifenthrin residues (ppm) in cow's milk

Exposure of raw milk samples to one of the industrial heat treatments such as 63C°/30 min, 80C°/5 min, and 100C°/5 min caused a significant ($P<0.05$) reduction in the concentrations of deltamethrin residues at the rate of 15%, 35% and 78% respectively (Table 2). Boiling of the raw milk samples for 5 minutes offered an effective approach since it greatly reduced the levels deltamethrin residues to less than the MRLs that recommended by the USA and European legislations (10-12). The degradation of the

deltamethrin and bifenthrin residues in milk depends on both the time and degree of temperature treatment. The work of (13) revealed that high temperature of the food processing leads to the large reductions in pesticide levels in the milk product. Deltamethrin and bifenthrin were decreased in pasteurized raw milk samples and pasteurization was proved to be the least effective on the degradation or elimination of pesticide residues (8). Pasteurization has been reported to have very little effect on the Dichlorodiphenyltrichloroethane (DDT) levels in milk (14).

Table 2: The effect of different industrial heat treatments on the degradation of the deltamethrin and bifenthrin residues (ppm) in cow's milk

Heat treatment	N0.of samples per product	Fat % mean \pm SE	Deltamethrin (ppm) mean \pm SE	Bifenthrin (ppm) Mean \pm S.E	% Reduction
Room temp. (30°C)	3	4.85	0.180 \pm 0.003 A	0.182 \pm 0.010 a	0%
63°C/30 min	3	4.85	0.147 \pm 0.005 B	0.152 \pm 0.006 b	15%
80°C/5 min	3	4.85	0.119 \pm 0.015 C	0.114 \pm 0.017 c	35%
100°C /5 min	3	4.85	0.040 \pm 0.003 D	0.043 \pm 0.004 d	78%

Deltamethrin and bifenthrin residues in raw milk samples of different animal species

The one way analysis of variance (ANOVA) revealed that there was a significant ($P<0.05$) seasonal variation of the deltamethrin and bifenthrin concentrations in milk samples for each animal species. All the milk samples

collected from buffaloes, ewes, cows, goats and camels had significantly ($P<0.05$) higher mean levels of deltamethrin residues in summer season (0.174, 0.142, 0.133, 0.045 and 0.032 ppm respectively) and bifenthrin concentrations in milk samples for each animal species where all the milk samples that were collected from buffaloes, ewes, cows,

goats and camels had significantly ($P < 0.05$) higher mean levels of Bifenthrin residues in summer season (0.152, 0.124, 0.117, 0.043, 0.038 ppm respectively) than in winter season levels of deltamethrin residues in buffaloes, ewes, cows, goats and camels (0.009, 0.012, 0.012, 0.005 and 0.002 ppm respectively) and levels Bifenthrin residues in winter season in buffaloes, ewes, cows, goats and camels (0.013, 0.017, 0.014, 0.006, 0.005 ppm respectively). From obtained results in this study, it is obvious that all of the examined milk samples from buffaloes, ewes and cows in summer season were failed to conform to the standard MRLs as they exceeded the accepted MRLs of 0.05 ppm (100% violation) that recommended by the WHO and FAO for the deltamethrin and bifenthrin residues in milk samples as shown in table 3. From the obtained results, it was clearly obvious that the detectable concentrations of the deltamethrin were higher in buffalo's and ewe's milk

samples than those found in cow's, goats and camels. The results could be attributed to the higher fat content of Buffalo's and Ewe's milk than the other animals as well as the lipophilic nature of the deltamethrin and bifenthrin (15,16). Ashry et al. (17) reported that the pesticides residues were higher in Buffalo's milk than cow's milk since the fat contents of Buffalo's milk was on average twice as higher as that of cow's milk (18).

Deltamethrin and bifenthrin is fat soluble and either stored in adipose tissues or secreted in milk fat where residues of particularly organochlorine pesticides tend to accumulate in the body fat or enter to milk fat while the less lipophilic compounds and their metabolites may be excreted in the urine (19). The results of this study is similar to the study of Jackson Ombui (20) and a Sara and Najim (1).

Table 3: Seasonal variation of the mean levels of deltamethrin and bifenthrin residues (PPM) in raw milk samples of different animal species collected from Abu-Ghraib village.

Source of milk samples	No. Of examined samples	Summer					Winter				
		Fat %	Deltamethrin residues Mean±SE	Bifenthrin residues Mean±SE	% violation MRLs 0.05	Fat %	Deltamethrin residues Mean±SE	Bifenthrin residues Mean±SE	% violation MRLs 0.05		
Buffaloes	5	6.85	0.174±0.003 Aa	0.152±0.002 Ca	100%	7.17	0.009 ±0.003 B	0.013±0.006 Da	NV*		
Ewes	5	6.34	0.142±0.029 Ab	0.124±0.013 Cb	100%	5.95	0.012 ±0.003 B	0.017±0.004 Da	NV*		
Cows	5	3.81	0.133±0.013 Ab	0.117±0.006 Cb	100%	3.3	0.012 ±0.003 B	0.014±0.001 Da	NV*		
Goats	5	2.82	0.045±0.009 Ac	0.043±0.003 Cc	NV*	2.56	0.005 ±0.003 B	0.006±0.004 Db	NV*		
Camels	5	2.54	0.032±0.013 Ac	0.038±0.009 Cc	NV*	2.33	0.002±0.003 B	0.005±0.001	NV*		

Seasonal variation of the mean levels of deltamethrin and bifenthrin residues (ppm) in breast milk sample collected from al-sader and al-karada districts

The data/ illustrated in the Table 4 was shown the mean levels of deltamethrin residues in the Breast milk samples that were collected from both AL-Sader and AL-Karada districts during the two climatic periods (3 samples/ district/ season). Overall, one way analysis of variance (ANOVA) revealed that there was a significant ($P < 0.05$) differences between the mean levels of deltamethrin residues in milk samples that were collected from AL-Sader and AL-Karada districts during the summer season, where milk samples that were collected from AL-Sader district which recorded significantly ($P < 0.05$) during the summer season.

According to the season, the results showed that the statistically significantly ($P < 0.05$) were influence by the concentrations of the deltamethrin residues in Breast milk samples. Data illustrated in Table 4 revealed that there was

a seasonal variation in the mean levels of deltamethrin residues in breast milk samples for each district village where all the milk samples collected from AL-Sader and AL-Karada districts had significantly ($P < 0.05$) the higher mean levels values of deltamethrin residues in summer season were (0.024 and 0.020 ppm respectively) while, in winter season were (0.0 and 0.0 ppm respectively). The bifenthrin residues in summer season were (0.0231 and 0.0153 ppm respectively). While, in winter season were (0.0 and 0.0 ppm respectively). because most farmers used the pesticides during the summer season much more than the other seasons (21).

Generally the results further demonstrated that all of the examined breast milk samples from the above mentioned two districts in summer season did not exceed the accepted MRLs of 0.05 ppm that recommended by the WHO and FAO (18).

Table 4: Seasonal variation of the mean levels of deltamethrin and bifenthrin residues (PPM) in Breast milk sample collected from AL- Sader and AL-Karada districts.

Source of milk samples	No. of examined samples per season	Summer				Winter			
		Fat %	Deltamethrin residues Mean±SE	Bifenthrin residues Mean±SE	% violation MRLs 0.05	Fat %	Deltamethrin residues Mean±SE	Bifenthrin residues Mean±SE	% violation MRLs 0.05
AL-Sader district	6	2.75	0.024±0.002 Aa	0.0231±0.003 Ca	NV*	2.60	0.0 B	0.0 D	NV*
AL-Karada district	6	2.85	0.020±0.003 Ab	0.0153±0.007 Cb	NV*	2.75	0.0 B	0.0 D	NV*
Total	12	2.8	0.022	0.0192	NV*	2.67	0.0	0.0	NV*

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