Deltamethrin residues in imported and locally produced butter, cream and soft cheese in the south of Baghdad city

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Summary

A total of 40 imported cream, butter, cheese and yoghurt samples were collected randomly at weekly intervals (1sample/ product/ week) from various supermarkets inside Baghdad province during the summer period. A total of 84 samples of locally produced cream, Butter, soft cheese and yoghurt from buffaloes, cows and ewes were collected randomly at weekly intervals (1 sample/ product/ week) from three different towns (Al-Mahmudiyah, Al-Rasheed and Al-Latifiyah) and were examined on two periods: The first was the period that extended from the beginning of September to the end of November 2015 while the second was the period that extended from the beginning of January to the end of march 2016. Besides that 12 Buffaloș raw whole and skimmed milk samples (6 samples each) and 6 samples of locally produced ewes ghee (Samna) were examined during the summer period. Each dairy product sample was tested for the occurrence of Deltamethrin residues by using the High Performers liquid Chromotography and for fat content by using Gerber method. From the obtained results, data revealed that all of the imported cheese, cream and butter samples were 100% positive and yoghurt samples were 60% positive for the occurrence of Deltamethrin residues during the summer season. The results of this study established the statistically significant ($P<0.05$) influence of the season on the concentrations of the Deltamethrin residues in all of the examined locally produced dairy products where it was found that each of the 7 locally produced dairy products samples (6 samples/ each product) had significantly ($P<0.05$) higher concentrations of Deltamethrin residues in summer than in winter. All the examined locally produced dairy products except yoghurt during summer season presented high contamination levels with Deltamethrin residues and were 100% above the Maximum Residue Limits of 0.05 ppm recommended by the WHO, FAO and European legislation.

Keywords: Yoghurt, Ghee, Deltamethrin, Gerber.

Introduction

Deltamethrin (DMT) is a synthetic pyrethroid pesticide that kills insects through dermal contact and ingestion by rapidly paralyzing the insect nervous system and giving a quick knockdown effect (1). Deltamethrin is formulated in insecticide products as aerosols, sprays, dusts, granules and wettable powders which are some of the most popular and widely used safe insecticides in the world and being sold in many countries for agriculture, public health and livestock applications (2). Deltamethrin is widely sprayed on leafy vegetable like lettuce and spinach and over 98% of the sprayed insecticides reach a destination other than their target species, including non- target species, air, water and soil (3). It is a safe pesticide, if its residual limit in any food material or body is less than the Recommended Maximum Residue Limits (MRLs) set by Environmental Protection Agency (EPA). Higher concentration of DMT than the accepted MRLs can cause a lot of harmful effects in human beings and animals like simple irritation of the skin and eyes, affecting the nervous system, mimicking hormones causing reproductive problems and cancer. In order to avoid this fatal risk to animals and human beings, such type of pesticides should be synthesized and used within limits which are friendly to the environment (4).

The specific objectives of this study were: to evaluate and assess the extent of contamination with DMT residues in imported and locally produced cheese, cream, butter and yoghurt in Baghdad province by using the HPLC technology and to measure the fat contents of all of the examined dairy products to ascertain whether higher DMT residues

were related to their higher fat content and to assess the effect of the butter boiling off on the availability of the DMT residues in the ghee (samna) product.

Materials and Methods

A total of 142 dairy products samples were collected randomly at weekly intervals (5 samples/ week) from various market places in different locations of Baghdad province during the period extended from the beginning of September 2015 to the end March 2016. All the collected dairy products samples were transported to the laboratory of Veterinary Public Health Department at the College of Veterinary Medicine inside the portable ice cooled box. Dairy products samples were examined on two periods; the first was the period that extended from the beginning of September to the end of November 2015 while the second was the period that extended from the beginning of January to the end of March 2016. Each dairy product sample was divided in to two portions where the first portion (100 gm) was used to determine the fat percentage by Gerber method while the second portion (100 gm) was sent to the HPLC analysis to determine the level of DMT residues. This study was designed to determine the level (ppm) of DMT residues in dairy products by using HPLC technique. Dairy product samples were distributed as following: By excluding the kind of season forty imported cream, butter, cheese and yoghurt samples (10 samples/ each product) that were produced by commercial dairy plants were selected from different local supermarkets from the south of Baghdad province that originated from different manufacturing companies, and 84 samples of locally produced ewes' butter, buffalos' cream, cows' soft cheese, buffalos' soft cheese, ewes' soft cheese, buffalos' yoghurt and cows' yoghurt were produced inside the farmers' homes were collected during the two seasons (6 samples/ season) from three different townships which included AL-Mahmuodiyah, AL-Rasheed and AL-Latifiyah markets (2 samples/ township/ season), and by excluding the kind of season, six locally produced ewes' Ghee (samna) samples that were produced by boiling off the butter inside the farmers' homes were collected during the current study period from three different townships which included AL-Mahmudiyah, AL-Rasheed and AL-Latifiyah supermarkets (2 samples/ township). Six locally produced buffalos' skim milk samples that were produced after cream separation inside the farmers' homes and six buffalos' whole milk samples were collected during the current study period from three different townships which included AL-Mahmudiyah, AL-Rasheed and AL-Latifiyah supermarkets.

HPLC condition:

The extracts were separated on FLC (Fast liquid chromatography) columns, C-18 DB, 2.7 µm Particle size (50 × 4.6 mm ID).

Mobile phase: 0.1% acetic acid in deionized water (solvent A) and acetonitrile (solvent B) (20: 80, v/v).

Detection: UV spectrophotometer detector set as 275 nm.

Flow rate: 1.5 ml/min.

Temperature: 30 ºC.

Dairy product samples extraction and separation procedure for DMT quantification in dairy product samples

100 gm sample were taken in a conical flask, 10 gm of zink acetate were added in it to remove the fats. Milk filtrate was added in a separating funnel. To extract DMT from this extract, 150 ml of n-hexane were added in a separating funnel. After shaking of n-hexane with the sample for 4 min., organic layer containing DMT was separated and further 50 ml of n-hexane were added to the aqueous layer to remove the possible traces of DMT. The filtrate (organic layer) was transferred to 250 ml separating funnel and partitioned by 100 ml acetonitrile; the above mixture was shaked for 3 min. and acetonitrile layer was collected separately. 10 gms of anhydrous Na2SO4 were added to the acetonitrile layer to remove the water contents, at the end, the DMT extract was cleaned by passing on silica column (200 × 5 mm I.D) using 50 ml n-hexane followed by 50 ml ether as mobile phase, the DMT fraction was subjected to stream of nitrogen to evaporate the solvent, the final residues were dissolved in 2 ml of the separating mobile phase. The extract was filtered on disposable minister filters 0.2um (Supelco Company cat NO 16534K) then 20 µl were injected on HPLC column. The

concentration for each compound was quantitatively determined by comparison the peak area of the standard with that of samples. Data subjected to analysis using One-way ANOVA. Means were compared using least significant differences. P<0.05 considered significant.

Results and Discussion

Results illustrated in (Table, 1), It was found that all of the imported cheese samples had significantly (P<0.05) the highest concentration of DMT residues (0.1406 ppm) followed by the imported butter and cream samples where their mean levels were 0.12889 and 0.06808 ppm respectively whereas the yoghurt samples had significantly (P<0.05) the lowest concentration of DMT residues (0.01676 ppm) which was within the permissible limit established by the WHO and FAO. It is obvious that all of the examined imported cheese, cream and butter samples had levels of DMT residues above the permissible MRLs that established by the WHO and FAO during the summer season which could be related to several reasons including: Using of DMT in non-appropriate dose (over dose), Farmer were not well educated and did not use the veterinarians guidelines, besides their usage of deteriorate fruits and vegetables as a source of feed for their animals. Similar finding was reported by (5 and 6) who confirmed the presence of DMT residues in the fruits and vegetables.

Data illustrated in (Table, 2) revealed that the mean levels of DMT residues in all of the examined six locally produced Ewes' Ghee (samna) samples that were collected from the three different townships during the September -November was 0.0761 ppm and failed to conform to the standard MRLs of 0.05 ppm that recommended by WHO and FAO (2015). Processes involving heat treatment can increase volatilization, hydrolysis or other chemical degradation and thus reduce the pesticides residual levels (7). The production of ghee (samna) from buffalos' and cows' butter reduced the levels of pesticide residues where the reduction levels of Hexachlorobenzene (HCB) Lindane, Aldrin, Heptachlor epoxide, Chlordane and DDT in samna from contaminated buffalos and Cows butter were (29.2% and 25%), (46.2% and 31.3%), (38.1% and 35.7%), (31% and 33.3%), (43.8% and 40%) and (31.8% and 35) respectively. This reduction may be attributed to the heat treatment during butter boiling off as well as the precipitate of the residues with the by-product (8). Similar findings were reported by the (9 and 10) reported that heat treatment such as sterilization showed the efficient role on the degradation of pesticide residues in the dairy products.

Results illustrated in (Table, 3) revealed that there was a significant (P<0.05) difference in the mean levels of DMT residues between the Buffalos' whole and skimmed milk samples where the Buffalos' whole milk samples had significantly (P<0.05) the highest concentration of DMT residues overall the other skimmed milk samples with the mean values of 0.1476 and 0.0682 ppm respectively. The results further demonstrated that all of the Buffalos whole and skimmed milk samples for both seasons were 100% above the MRLs of 0.05 ppm that recommended by the WHO and FAO (2015).

The skimming of Buffalos' and cows' milk led to slight reduction in the analyzed pesticides concentration in skim milk where the reduction levels in Buffalos' and Cows' milk were (3.4 and 4.3%), (8.1% and 8.3%), (12.5% and 8.3%), (9.5% and 16.7%), (13.0% and 8.3%) and (12.9% and 16%) for HCB, Lindane, Aldrin, Heptachlor epoxide, Chlordane and DDT respectively, (8). These results coincide with those reported by (9) who found that skimming of milk led to slight reduction in ß-HCB, Lindane and DDT. In contrast, higher reduction levels in Lindane and DDT by skimming were reported by (11) these differences in the reduction levels may be attributed to the skimming process and the higher losses of fat in the skim milk. Residues of some pesticides removed with skim milk and butter milk due to the association of residues with the phospholipids in milk (12).

Data illustrated in (Table, 4) revealed that there was a significant (P<0.05) differences in the average mean levels of DMT residues between both the Buffalos' cream samples and Ewes' soft cheese and other products where both the Buffalos' cream and Ewes' soft cheese recorded significantly (P<0.05) the highest

concentrations of DMT residues during summer season where their mean levels were 0.13258 and 0.1647 ppm respectively, in comparison to Ewes' butter, Cows' soft cheese and Buffalos' soft cheese that had significantly (P<0.05) lower concentrations of DMT residues where their mean levels were 0.05560, 0.05821 and 0.0863 ppm respectively whereas both Buffalos' and Cows' yoghurt had significantly (P<0.05) the lowest concentration of DMT residues where their mean levels were 0.0752 and 0.04884 ppm respectively. From the obtained results, it's obvious that all of examined locally produced dairy products except the yoghurt in summer season failed to conform to the standard MRLs as they exceeded the accepted MRLs of 0.05 ppm (i.e. 100% violation) that recommended by WHO and FAO (2015). The hot temperature during the September-November leads to more animal sweating, vasodilatation and higher absorption of pesticides (13). The farmers that working for the foreign commercial dairy companies are usually reared their animals in closed farms. Higher faeces and mud in the grounds of the closed farms act as the best media for the growth of ticks and other insects and lead the farmers to spray all the places inside the farm with DMT more than three times during the summer season which in turn contaminates the feed and feedlots of the farm. In such case the DMT transferred to the animal body via both the consumption (ingestion) of the contamination feed and the inhalation of the contaminated air due to the bad ventilation inside the crowdy closed farms which in turn excreted in milk through the blood stream. (14 and 15). Showed that the amount of pesticides applied in spring and summer season were much higher than that in other seasons and the levels of pesticides in the soil environment in spring and summer season were much higher than that in other seasons (16).

Table, 1: Comparison of the mean levels of DMT residues between different imported dairy products during the summer season.

Type of products	No. of examined samples	Fat % Mean	DMT residues Ppm Mean ± SE	Violation% MRLS= 0.05
Cheese	10	24.40	0.1406± 0.0389 A	100%
Cream	10	26.40	0.0680± 0.0092 C	100%
Butter	10	80.00	0.1288±0.0178 B	100%
Yoghurt	10	4.36	0.0167± 0.0058 D	NV

LSD=0.03
Different capital letters in a column revealed significant (P<0.05) differences in the mean levels of DMT residues (ppm) between different dairy products.
SE: Standard Error.
NV: No Violation.

Table, 2: Occurrence of DMT residues and its concentration in locally produced ewes' ghee (Samna) samples collected from different townships during the summer season.

Source of samples	No. of examined samples	Fat% Mean	DMT residues Ppm Mean ± SE	Violation% MRLS= 0.05
AL- Mahmudiyah	2	99%	0.0443±0.0320 B	NV
AL- Rasheed	2	99%	0.085±0.0600 A	100%
AL- Latifiyah	2	99%	0.099± 0.0749 A	100%
Total	6	99%	0.0761	100%

LSD= 0.02. Different capital letters in a column revealed significant (P<0.05) differences in mean levels of DMT residues (ppm) between townships.

Table, 3: Comparison of the mean levels of DMT residues between the buffalos' whole and skimmed milk samples collected from different townships during the summer season.

Source of samples	No. of examined sample per product	Whole milk			Skimmed milk		
		Fat % Mean	DMT Ppm Mean ± SE	%violation MRLs 0.05	Fat % Mean	DMT Ppm Mean ± SE	% violatin MRLs 0.05
AL- Mahmudiyah	2	6.88	0.16335± 0.0468 A	100%	1.12	0.0650± 0.0050 B	100%
AL- Rasheed	2	6.85	0.14627± 0.0051 A	100%	1.10	0.0640± 0.0080 B	100%
AL- Latifiyah	2	6.72	0.13323± 0.0090 A	100%	1.14	0.0758± 0.0048 B	100%
Total	6	6.82	0.14761	100%	1.12	0.06826	100%

•Horizontal different capital letters revealed significant (P<0.05) differences in mean levels of DMT residues (ppm) between whole and skimmed milk samples.

Table, 4: Seasonal variation of the mean levels of DTM residues in the locally produced butter, cream, soft cheese and yoghurt collected from three different townships.

Source of samples	No. of examined samples per season	Summer season			Winter season		
		Fat % Mean	DMT Ppm Mean ± SE	%violation MRLs 0.05	Fat % Mean	DMT Ppm Mean ± SE	%violation MRLs 0.05
Ewes' butter	6	80 %	0.05560± 0.0088 Aa	NV	80 %	0.01163± 0.0114 B	NV
Buffalos' cream	6	60%	0.13258± 0.0949 Ab	NV	60%	0.070216± 0.0100 B	100%
Cows' soft cheese	6	22%	0.05421± 0.0101 Aa	NV	22%	0.039583± 0.01161 B	NV
Buffalos' soft cheese	6	8%	0.0863± 0.0134 Aa	100%	8%	0.0399±0.0053 B	NV
Ewes' soft cheese	6	14.3%	0.1647± 0.01824 Ac	100%	14.33%	0.02510± 0.0121 B	NV
(Buffalos' yoghurt)	6	4%	0.0752± 0.0074 Aa	100%	4%	0.03246± 0.0084 B	NV
cows' (yoghurt)	6	6%	0.04884± 0.0132 a	NV	6%	0.0204±0.0102	NV

• Mean in a column not followed by the same small letters revealed significant (p< 0.05) differences between dairy products.
• Horizontal different capital letters revealed significant (P<0.05) differences in the mean levels of Deltamethrin (DMT) residues (ppm) between seasons.

References

1. Haug, G. and Hoffman, H. (1990). Chemistry of Plant Protection 4: Synthetic Pyrethroid Insecticides: Structures and Properties. Springer Verlag. Berlin, Heidelberg, New York. (eds).
2. Thomson, W. T. (1992). Agricultural chemicals book I-insecticides, acaricides and ovicides. Agricultural chemicals book I-insecticides, acaricides and ovicides.
3. Miller, G.T. (2004). Sustaining the Earth, 6th Ed. Thompson Learning, Inc. Pacific Grove, California. Chapter 9, Pp:211-216.
4. Ali, Z.; Gilani, R.; Hussain, H. and Hussain, I. (2013). Quantitative determination of Deltamethrin in milk, blood and urine of domestic animals. IOSR J. Appl. Chem. (IOSR-JAC) e-ISSN: 2278-5736. 5(1):51-56.
5. Perveen, Z.; Riazuddin, I. S.; Khuhro, M. I.; Bhutto, M. A., and Ahmed, M. (2012). Monitoring of multiple pesticide residues in some fruits in Karachi, Pakistan. Pakistan J. Botany, 43:1915-1918.
6. Bempah, C. K.; Asomaning, J. and Boateng, J. (2012). Market basket survey for some pesticides residues in fruits and vegetables from Ghana. J. Microbiol., Biotechnol. Food Sci., 2(3):850.
7. Holland, P. T.; Hamilton, D.; Ohlin, B.; and Skidmore, M. (1994). Pesticides report 31: Effects of storage and processing on pesticide residues in plant products (technical report). Pure Appl. Chem., 66(2): 335-356.
8. Abou Donia, M.; Abou-Arab, A.; Enb, A.; El-Senaity, M. and Abd-Rabou N. (2010). Chimical composition of raw milk and the accumulation of pesticide residues in milk production. Global Veterinary. 4(1): 6-14.
9. Abou-Arab, A. A. K. (1999). Effect of processing and storage of dairy products on lindane residues and metabolites. Food Chemistry. (64):467-473.
10. Zhang, H. B.; Luo, Y. M.; Zhao, Q. G.; Wong, M. H. and Zhang, G. L. (2006). Residues of organochlorine pesticides in Hong Kong soils. Chemosphere. 63(4):633-641.
11. El-Alfy, M. B. S. (1981). Studies on the residues of insecticides in some foods. M.Sc., Fac. Agric., Moshtohor, Zagazig Univ.
12. Hugunin, A. G. and R. L. Bradley (1971). Distribution of organochlorine pesticides among some milk components. 1 Dairy Sci., 54:355.
13. Stroud, M. A. (2003). Enviromental extremes – heat. Oxford textbook of medicine. 4th Ed. Oxford: OUP. Pp:966-967.
14. Kalantzi, O. I.; Alcock, R. E.; Johnston, P. A.; Santillo, D.; Stringer, R. L.; Thomas, G. O. and Jones, K. C. (2001). The global distribution of PCBs and organochlorine pesticides in butter. Environm. Sci. Technol., 35(6):1013-1018.

15. Semeena, V. S.; Feichter, J. and Lammel, G. (2005). Impact of the regional climate and substance properties on the fate and atmospheric long-range transport of persistent organic pollutants? examples of DDT and HCH. Atmospheric Chemistry and Physics Discussions. 5(6):12569-12615.

16. Hongjun, L.; Hongwei Pana, B. and Beidou, Xi. (2014). Pesticides pollution characteristics in the soil-groundwater system of vegetable greenhouse cultivation in eastern China. J. Chem. Pharmaceut. Res., 6(6):369-373.

متبقيات الدلتامثرين في منتجات الزبد والقيمر والجبن الطري المستوردة والمحلية في مدينة بغداد

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الخلاصة

جمعت 40 عينة من القشدة والزبدة والجبن واللبن المستورد بشكل عشوائي على مدد أسبوعية (1 عينة/ منتج/ أسبوع) من محلات السوبر ماركت المختلفة داخل محافظة بغداد في موسم الصيف. جُمع نحو 84 عينة من كريم، الزبدة، جبن الجاموس وجبن الابقار وجبن النعاج الطري ولبن الجاموس والأبقار المنتجة محليا على فترات أسبوعية (1 عينة/ المنتج/ أسبوع) من ثلاث نواحي مختلفة (المحمودية، الرشيد واللطيفية) و فحصت في حقبتين، الحقبة الأولى خلال موسم الصيف والتي امتدت من بداية أيلول وحتى نهاية شهر تشرين الثاني عام 2015، فيما كانت الثانية في موسم الشتاء والتي امتدت من بداية كانون الثاني وحتى نهاية آذار 2016. فضلاً عن 12 عينة من حليب الجاموس الخام ومنزوع الدسم (6 عينات لكل منهما) و 6 عينات من دهن الحر للنعاج المنتج محليا (سمنا) فُحصت في موسم الصيف. وفحصت كل عينة لمنتجات الألبان لكشف متبقيات الدلتامثرين باستعمال كروموتوغرافي السوائل عالي الأداء و فحص محتوى الدهون باستعمال طريقة جربر. من النتائج التي تم الحصول عليها، كشفت البيانات أن جميع عينات الجبن والقشدة والزبدة المستوردة كانت 100٪ عينات موجبة و 60٪ من عينات اللبن كانت موجبة لتواجد متبقيات الدلتامثرين خلال موسم الصيف. أثبتت نتائج هذه الدراسة وجود تاثير معنوي ($P<0.05$) للموسم على نسبة متبقيات الدلتامثرين في منتجات الألبان المنتجة محليا حيث وجد أن كل 7 من عينات منتجات الألبان المنتجة محليا (6 عينات/ منتج) كانت أعلى تركيزاً في الصيف مما كانت عليه في موسم الشتاء. اظهرت كل منتجات الألبان المنتجة محليا المفحوصه باستثناء اللبن خلال موسم الصيف مستويات تلوث عالية مع متبقيات الدلتامثرين وكانت 100٪ أعلى من الحدود القصوى من 0.05 جزء في المليون التي أوصت بها منظمة الصحة العالمية والفاو والتشريعات الأوروبية.

الكلمات المفتاحية: اللبن، الدهن الحر، الدلتامثرين، كربر.