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Monitoring some pyrethroid pesticides residues in raw cow's and buffalo's milk

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A B S T R A C T

Synthetic pyrethroid pesticides are widely used in animal husbandry and agriculture in Egypt. Excessive use of these pesticides leads to their accumulation in foods of animal origin and causes health problems. Accordingly, the following study was designed to demonstrate the concentrations of some synthetic pyrethroids by HPLC in both cow and buffalo's raw milk samples collected from different local markets and farms at Damanhour, El-Behira governorate, Egypt. The obtained results revealed that Flumethrin, Deltamethrin, Cyhalothrin and Cypermethrin were detected at incidence rate of 17.5 & 22.5; 25& 32.5; 15& 20 and 10 & 12.5% with a mean value of 36.14 ± 7.03 & 41.80 ± 7.91; 40.06 ± 8.71 & 52.70 ± 11.27; 24.65 ± 6.64 & 42.03 ± 8.25 and 89.27 ± 36.51& 121.58 ± 36.95 ppb, in cow and buffalo's milk, respectively. α-cypermethrin could not be detected in any examined raw milk samples. Positive samples for synthetic pyrethroids residues compared with maximum residual limits established by international standards to detect samples below or above these limits. From the results in this study, farm milk was contaminated more than market milk which might be explained by presence of milk farms near to rural area where these synthetic pyrethroids are highly applied. This study would illustrate the risks of presence of synthetic pyrethroids residues in raw milk that threaten consumer health.

Keywords: Raw milk, Flumethrin, Deltamethrin, Cyhalothrin, Cypermethrin, HPLC.

1. Introduction

Pesticide residues are an organic environmental pollutant mostly with lipophilic properties which easily dissolve in milk (Kampire et al. 2011). Pesticide including insecticides, rodenticides, herbicides, and others. The introduction of synthetic insecticides as organophosphate (OP) insecticides, herbicides and pyrethroids contributed mainly for agricultural purposes and pest control (Akhtar et al., 2009). In Egypt, Synthetic pyrethroids pesticide are broadly applied during animal husbandry and in agriculture fields. Accumulation of residues of pyrethroids pesticide in foods especially originated from animals as well as environment is caused by improper use of these pesticides. Continuous exposure to pesticides residues is related with health problems in man and animals (Ritter, 1997). Saleh et al., (2019) reported that presence of chemical hazards in milk have harmful effects on consumer health. Milk could be contaminated with pesticide residues through corn silage, feed, grass, and application on dairy animal environment where humans could acquire these harmful compounds. Between different food products, consumption of milk and its products are the main prompt sources of pesticide residues. (Johansen et al. 2004). Deltamethrin is a synthetic type "II" pyrethroids insecticide. It is considered a basic potent insecticide.

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Moreover, deltamethrin is applied as acaricide in veterinary medicine and to control different insect pests on crops, vegetables, and fruits in the agriculture field (Côté et al., 2014).

Deltamethrin is characterized by high stability in both neutral and acidic solutions and at 40 °C in both light and dark but unstable within alkaline condition (Frank and Gadi, 2015). Salivation, choreoathetosis and hyperexcitability are considered the main toxic effects of deltamethrin (Ray and Forshaw, 2000). These symptoms have fast onset within a short time (Hasibur et al., 2014).

Flumethrin and cypermethrin are synthetic pyrethroids that are commonly applied worldwide on animals to overcome ticks and house flies (Yavuz et al., 2017). Moreover, the containers of those pesticides are used to store animal feed in some farms with the risk of accidental feed contamination. Additionally, accumulation of these pesticides on water, fodder, and feed of dairy animals, might be resulted from volatilization and drift after pesticides spraying on crops near dairy farms (Bedi et al., 2018).

Variable incidence rate of synthetic pyrethroid pesticide residues, such as deltamethrin, cyhalothrin and cypermethrin was observed in milk samples in previous studies (Bedi et al., 2015). To avoid the risk of milk to be a vehicle of pesticide residues, raw milk samples were collected and analyzed for pesticide content and compared with recommended the maximum residue limit (MRL) and acceptable daily intake in previous studies (Nasef et al., 2019). Saleh et al., (2015) reported that production of organic food would reduce the public health problems caused by improper use of pesticides, antibiotics, and hormones.

The aim of this study was determining the level of some synthetic pyrethroids pesticides such as Flumethrin, Deltamethrin, Cyhalothrin, Cypermethrin and α-cypermethrin in raw milk of cow and buffalo collected from farms and markets at El-Beheria governorate as well as comparing with international standards.

2. Materials and Methods

2.1. Collection of samples

Eighty raw milk samples from cows and buffalos (20 samples from farm and 20 samples from market from both types of milk) were collected randomly from local markets and farms in different districts at Damanhour, El-Behira governorate, Egypt. Samples were transported to the Food Analysis Center, Benha university for detection of synthetic pyrethroids.

2.2. Determination of synthetic pyrethroid pesticides:

2.2.1. Chemicals and reagents:

Synthetic pyrethroid Flumethrin 90%, deltamethrin 98%, Cyhalothrin 95%, cypermethrin and α- Cypermethrin 93% were purchased from Tedia Company (Fairfield, OH, USA). For each pyrethroid pesticide, 60 mg of the pyrethroid was dissolved in acetonitrile and diluting to 100 ml in a volumetric flask to prepare stock standard solution (600 ppm) for each pyrethroid pesticide, working standard solutions were prepared from each stock solution by diluting 0.0625, 0.125, 0.250, 0.500 and 1.0 ml of each pyrethroid stock solution to 50 ml acetonitrile to get 0.75, 1.5, 3, 6 and 12 ppm solutions, respectively, to determine the standard curve linearity for each pyrethroid pesticide. HPLC grade solvents were used.

2.2.2. Technique (Bissacot and Vassilieff, 1997):

Recuperation technique by fortification was used to analyze the quantity of each pyrethroid in the samples. Briefly, addition of standard concentration solutions to samples to obtain different pyrethroid concentrations separately for each pyrethroid within the study. The fortified samples were used to prepare the calibration curves.

2.2.2.1. Extraction and purification:

In an Erlenmeyer flask, 10 ml from each sample were added and acidified with 1N HCl to pH 4, approximately. Then, acetonitrile (50 ml) was added, the closed flask was drastically shaken for 30 minutes. By using Wattman filter paper (No.42), the mixture was filtered in a beaker. The suspended residue within the filter paper was removed and transferred to the Erlenmeyer flask containing 25ml acetonitrile, the flask was mechanically shaken after sealing and for 15 minutes. Another filtration step was applied with the same procedure.

2.2.2.2. Partitioning (AOAC, 2000):

In a separator funnel, the acetonitrile phase (filtrate) in the beaker was mixed with 15ml n-hexan while shaking for a minute. This step was repeated twice, the hexanic phase was discarded and the acetonitrile phases were collected in the beaker. Then, acetonitrile phase (45 ml) was added with approximately 1 minute shaking. Finally, in a beaker containing the first acetonitrile phases, the acetonitrile layer was collected and evaporated under stream of nitrogen in an exhaustion system and heated at 30 oC to dryness.

2.2.2.3. Column Chromatography Cleanup (WHO, 1989):

The dry residue was dissolved in n-hexan (10ml) and eluted in a chromatographic column containing silica gel (4g) with previous activation in an air heater for 5 hours at 130oC followed by cooling and mixing with deionized water (5ml). The silica gel in the chromatographic column, was eluted with 1ml n-hexan: diethyl ether (9: 1). The dry residue was diluted with n-hexan (7ml): diethyl ether (9: 1) and 10ml n-hexan. The eluate was dried in an exhaustion system at room temperature. The diethyl ether was properly purified to remove the possible peroxides before use.

2.2.2.4. Chromatography:

The dry residue was re-suspended with high grade acetonitrile (1ml), homogenized for few seconds in a shaker. The homogenate was loaded into High Performance Liquid Chromatography (HPLC, Agilent1100). HPLC was equipped with Column: Zorbex SBC 18 (150mm x 4.6mm x 0.5um film thickness); diodearray detector (DAD); Mobile phase: acitonitrile: distilled deionized water (80: 20); Detector: 226nm ultraviolet; Flow rate: 1.0ml/ min.

The homogenate was filtered within the HPLC sample filtering system. Then, the mobile phase used was acetonitrile: distilled deionized water (80: 20) and 1.0 ml/min flow rate under isocratic conditions and the mobile phase was filtered within the solvent filtering system.

2.2.2.5. Quantitative analysis:

The examined pyrethroids residues in each milk sample were analyzed and compared with suitable standard solutions with similar injections. Quantitative analysis of pyrethroids residues was reported by the measurement of each peak area within the chromatogram. The recovery percent of Flumethrin, Deltamethrin, Cyhalothrin, Cypermethrin and α-Cypermethrin in the examined milk samples was 86.1, 97, 91.9, 83.5 and 90.6%, respectively.

3.2. Statistical analysis:

Version 16 of Statistical Package for Social Science, (SPSS 2008) was used for statistical analysis of the results.

3. Results and Discussion

Milk is broadly consumed in the early stages of life, and it is considered an important food for human beings. So, Detection of pyrethroids residues in milk is critical to ensure milk quality and safety (Goulart et al., 2008). Different studies all over the world are focused on pesticide residue analysis in different foods to avoid their harmful effects on the consumer health (Pirsaheb et al., 2018).

Milk contamination with pyrethroids is widely caused by their use in the processing areas or in the barn of dairy animals.

HPLC method is a sensitive technique which detects low content of synthetic pyrethroid residues (cypermethrin, cyhalothrin, flumethrin, and deltamethrin) in raw milk. These pyrethroids are similar in their chemical structures so the same procedures are used for their extraction, purification, and partitioning. HPLC method is practically applied in toxicological assays of pyrethroids residues (Bissacot and Vassilieff, 1997)

Data in Table (1) showed that the incidence of flumethrin pyrethroid in examined farm and market of both cow's and buffalo's milk were 20 &15% and 20 & 25% with mean values of 39.97 ± 10.17 & 32.36 ± 11.22 ppb and 46.07 ± 14.72 &38.38 ± 9.41 ppb, respectively. Generally, Flumethrin was detected with incidence rate of 17.5 and 22.5% in examined samples of cow's and buffalo's milk with a mean value of 36.14 ± 7.03 and 41.80 ± 7.91 ppb, respectively. There was a significant variation ($p<0.05$) between farm and market cow milk as well as buffalo milk. Buffalo's milk was more contaminated with flumethrin residues than cow's milk. Our findings supported by Bissacot and Vassilieff, (1997) study where flumethrin was detected for 28 days in cow's milk after application of flumethrin as a single therapeutic dose. In contrary, Yavuz et al., (2017) reported absence of flumethrin in milk samples collected after 2 days of pour on treatments with flumethrin in Turkey.

The aforementioned results in Table (2) revealed that the percent of positive samples for flumethrin residues was above MRL stated by Commission Regulation (EU), 37/2010 (30 ppb) were 10 and 12.5 % in examined samples of both cow's and buffalo's milk, respectively.

The obtained results in Table (3) declared that deltamethrin residues were detected at the incidence rate of (25& 25%) and (35 & 30%) in examined farm, market cow's and buffalo's milk with mean values of (43.18 ± 13.86 & 36.94 ± 12.02) and (41.70 ± 13.18 & 65.53 ± 18.87 ppb), respectively. There was a significant difference between farm and market samples of cow's and buffalo's milk, also, buffalo's milk more contaminated (32.5%) with deltamethrin residues than cow's milk (25%) this might of higher fat percent in buffalo's milk than cow's milk, this result was supported by LeDoux, (2011) who reported that synthetic pyrethroids bio-accumulated in fatty parts and becoming a possible source of transmission to human by consumption of contaminated foodstuffs.

Lower incidence of deltamethrin in raw milk was revealed by Dallegrave et al., (2018) who found that the incidence of deltamethrin in raw milk in Brazil was 13% with median value of 0.04 $\mu g L^{-1}$. In addition, Nasef et al., (2019) found that the incidence of deltamethrin in raw milk samples collected from three different districts within Alexandria, Egypt was7.5, 6.66 and 3.33% with mean values of 0.111 ± 0.052, 0.115 ± 0.037 and 0.016 ± 0.0 ppm, respectively. In contrast, deltamethrin could not be detected in cows' fresh milk which were collected within Gharbia governorate from different locations (Nasr et al., 2007) and in buffalo's milk collected from Kafr Elsheikh governorate (Ismail and Elkassas 2016).

Our findings revealed that deltamethrin was the most synthetic pyrethroids found in examined milk samples, these findings were supported by Neelam et al., (2013) who reported that deltamethrin was significantly present in milk samples more than other examined pesticide residues. Goodarzi et al., (2010) reported that the residues of deltamethrin were recovered at different levels from feed and water samples until the first three days of application. This might be related to bad biosafety procedures such as absence of specific area for pesticides spraying, drinker not frequently changed after spraying and lack of precautions during pesticides spraying process.

The abovementioned results in Table (4) revealed that the percent of positive samples for deltamethrin residues above MRL stated by Codex Alimentarius Commission (CAC, 2018) (30 ppb) were 15 and 17.5 % in examined samples of cow's and buffalo's milk, respectively. Nasef et al., (2019) reported that 11.66% of examined raw milk samples at Alexandria governorate exceeding the permissible limits of Deltamethrin (0.05 ppm) established by European Commission. Deltamethrin can develop neurotoxicity in humans although its safe use (Pulaman, 2011).

The presented data in Table (5) showed that cyhalothrin was detected in farm and market cow's milk with incidence rate 15 and 15% with mean values of 21.66 ± 8.04 and 26.63 ± 12.14 ppb, respectively. While, in farm and market buffalo's milk was detected at incidence 25 and 15% with mean values of 42.34 ± 10.69 and41.50 ± 15.93 ppb, respectively. No significant difference at ($p<0.05$) between farm and market samples of cow's milk and buffalo's milk, buffalo's milk more contaminated within 20 % with cyhalothrin residues than cow's milk (15%).

Higher rate of incidence of cyhalothrin was reported in raw milk analyzed by Dallegrave et al., (2018) who found that the incidence rate of cyhalothrin residue in raw milk in Brazil was 76%. In addition, El-Asuoty et al., (2017) could detect Lambda-cyhalothrin at incidence rate of 56.7% in examined raw milk samples collected from El-Beheria governorate with a mean value of 0.0156 ppm. Lower incidence was obtained by Nasef et al., (2019) who reported that the incidence of cyhalothrin samples of raw milk collected from three districts within Alexandria governorates were 5, 3.33 and 3.33% with a mean value of 0.033 ± 0.015, 0.072 ± 0.0 and 0.093 ± 0.0 ppm, respectively.

According to MRL of cyhalothrin (50 ppb) stated by EU, (2010), only one sample (5%) of market cow's milk was above this limit while in farm and market buffalo's milk, there was 10 and 5 % of examined samples above established limits, respectively, Table (6).

Illustrated data in Table (7) elucidated that cypermethrin was detected in only in one sample (5%) of farm cow's milk with a level of 122.40 ppb, and 3 samples (15%) of market cow's milk with mean values of 78.23 ± 49.20 ppb. In addition, cypermethrin was detected at incidence rate of 15 and 10% in examined farm and market buffalo's milk with mean values of 125.40 ± 52.93 and 115.85 ± 72.05 ppb, respectively. There was a significant variation between farm and market samples of cow and buffalo milk. Also, buffalo's milk is more contaminated (12.5%) with cypermethrin residues than cow's milk (10%).

Higher incidence of cypermethrin in raw milk samples was reported by Dallegrave et al., (2018) who found that the incidence of cypermethrin residue in raw milk samples in Brazil was 92%, Also, El-Asuoty et al., (2017) found that the incidence of cypermethrin in examined raw milk collected from El-Beheria governorate was 60 % with mean value of 0.0253±0.0040 ppm. In addition, Ismail and Elkassas (2016) reported that the mean values of cypermethrin in buffalo's milk collected from kafr El-sheikh governorate was 0.1985±0.022 ppm. In contrast, cypermethrin could not be detected in fresh cow's milk samples collected at Gharbia governorate from different locations (Nasr et al., 2007).

Cypermethrin is reported as a prohibited pesticide by the Environmental Protection Agency due to its high toxicity. In Egypt, it is still used in veterinary and agriculture sectors to overcome a broad spectrum of pests. It is also used for pests' control in buildings and at home (Extoxnet, 1996). Roothwell et al. (2001) were quantified cypermethrin residues and found that milk was contaminated with a mean value of 15 µg Kg-1 in dairy cattle. They found that contaminated diet is considered as the main source of cypermethrin excretion in milk. In addition, Alvarez et al. (2010) found that cow's milk collected from urban farms was found to be contaminated with cypermethrin.

Our findings revealed that α-cypermethrin could not be detected in any examined samples of cow's and buffalo's milk. According to CAC, (2018) which reported that MRL of cypermethrin in raw milk was 100 ppb, only one sample of each farm and market cow's milk exceeded this limit. In farm and market buffalo's milk, there was 10 and 5% of the examined exceeding this limit, respectively. El-Asuoty et al., (2017) reported that cypermethrin concentrations that found in examined raw milk samples at El-Beheria governorate were not exceeded the permissible limits at (0.05 ppm) established by EU, (2014).

4. Conclusion

In conclusion, buffalo's milk is more contaminated with the investigated synthetic pyrethroids than cow's milk, especially farm milk which was contaminated more than market's milk as milk farms were nearest to rural area where these synthetic pyrethroids are applicable in agriculture and animal husbandry. Therefore, it is critical to monitor the level of synthetic pyrethroids in milk and dairy products to achieve the optimal level of food safety and safeguard the health of consumers.

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Table (4): Distribution of examined raw cow's and Buffalo's milk samples contaminated with Deltamethrin residues in relation to the maximum residue limit (MRL)human health under organic broiler production. Global Veterinaria, 14(3), pp.409-417.
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Table (1): Incidence and mean values of Flumethrin residues (ppb) in examined raw cow's and buffalo's milk samples.

Source of milk	No of examined samples	Cow milk (n=40)			Buffalo milk (n=40)		
		Positive sample		Mean ± SEM	Positive sample		Mean ± SEM
		No	%		No	%	
Farm milk	20	4	20	39.97 ± 10.17a	4	20	46.07 ± 14.72a
Market milk	20	3	15	32.36 ± 11.22b	5	25	38.38 ± 9.41b
Total	40	7	17.5	36.14 ± 7.03	9	22.5	41.80 ± 7.91

Means carrying different superscript are significantly different (P<0.05), SEM= standard error of the mean.

Table (2): Distribution of examined raw cow's and Buffalo's milk samples contaminated with Flumethrin residues in relation to the maximum residue limit (MRL)

Source of milk	No of examined samples	MRL of Flumethrin in raw milk (EU (37/2010) (ppb)*	Cow milk (n=40)		Buffalo milk (n=40)	
			Samples above MRL		Samples above MRL	
			No	%	No	%
Farm milk	20	30	2	10	3	15
Market milk	20	30	2	10	2	10
Total	40	30	4	10	5	12.5

* MRL recommended by EU (37/2010)

Table (3): Incidence and mean values of Deltamethrin residues (ppb) in examined raw cow's and buffalo's milk samples.

Source of milk	No of examined samples	Cow milk (n=40)			Buffalo milk (n=40)		
		Positive sample		Mean ± SEM	Positive sample		Mean ± SEM
		No	%		No	%	
Farm milk	20	5	25	43.18 ± 13.86a	7	35	41.70 ± 13.18b
Market milk	20	5	25	36.94 ± 12.02b	6	30	65.53 ± 18.87a
Total	40	10	25	40.06 ± 8.71	13	32.5	52.70 ± 11.27

Means carrying different superscript are significantly different (P<0.05), SEM= standard error of the mean.

Table (4): Distribution of examined raw cow's and Buffalo's milk samples contaminated with Deltamethrin residues in relation to the maximum residue limit (MRL)

Source of milk	No of examined samples	MRL of Deltamethrin in raw milk CAC (2018) (ppb)*	Cow milk (n=40)		Buffalo milk (n=40)	
			Samples above MRL		Samples above MRL	
			No	%	No	%
Farm milk	20	30	4	20	3	15
Market milk	20	30	2	10	4	20
Total	40	30	6	15	7	17.5

* MRL recommended by CAC (2018)

Table (5): Incidence and mean values of Cyhalothrin residues (ppb) in examined raw cow's and buffalo's milk samples.

Source of milk	No of examined samples	Cow milk (n=40)			Buffalo milk (n=40)		
		Positive sample		Mean ± SEM	Positive sample		Mean ± SEM
		No	%		No	%	
Farm milk	20	3	15	21.66 ± 8.04[a]	5	25	42.34 ± 10.69[a]
Market milk	20	3	15	26.63 ± 12.14[a]	3	15	41.50 ± 15.93[a]
Total	40	6	15	24.65 ± 6.64	8	20	42.03 ± 8.25

Means carrying different superscript are significantly different (P<0.05), SEM= standard error of the mean.

Table (6): Distribution of examined raw cow's and Buffalo's milk samples contaminated with Cyhalothrin residues in relation to the maximum residue limit (MRL)

Source of milk	No of examined samples	MRL of Cyhalothrin in raw milk EU (37/2010) (ppb)*	Cow milk (n=40)		Buffalo milk (n=40)	
			Samples above MRL		Samples above MRL	
			No	%	No	**%**
Farm milk	20	50	0	0	2	10
Market milk	20	50	1	5	1	5
Total	40	50	1	2.5	3	7.5

* MRL recommended by EU (37/2010)

Table (7): Incidence and mean values of Cypermethrin residues (ppb) in examined raw cow's and buffalo's milk samples.

Source of milk	No of examined samples	Cow milk (n=40)			Buffalo milk (n=40)		
		Positive sample		Mean ± SEM	Positive sample		Mean ± SEM
		No	%		No	%	
Farm milk	20	1	5	122.40± 0.00[a]	3	15	125.40 ± 52.93[a]
Market milk	20	3	15	78.23 ± 49.20[b]	2	10	115.85 ± 72.05[b]
Total	40	4	10	89.27 ± 36.51	5	12.5	121.58 ± 36.95

Means carrying different superscript are significantly different (P<0.05), SEM= standard error of the mean.

Table (8): Distribution of examined raw cow's and Buffalo's milk samples contaminated with Cypermethrin residues in relation to the maximum residue limit (MRL)

Source of milk	No of examined samples	MRL of Cypermethrin in raw milk CAC (2018) (ppb)*	Cow milk (n=40)		Buffalo milk (n=40)	
			Samples above MRL		Samples above MRL	
			No	%	No	%
Farm milk	20	100	1	5	2	10
Market milk	20	100	1	5	1	5
Total	40	100	1	2.5	3	7.5

* MRL recommended by CAC (2018)