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Quantification of the pesticide residues in market pasteurized milk samples using UA-DLLME-SFO method in Kermanshah city, Iran

Quantifizierung von Pestizidrückständen in pasteurisierten Milchproben unter Verwendung der UA-DLLME-SFO-Methode in der Stadt Kermanshah, Iran

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Summary

The widespread application of pesticides by human can result in the accumulation of pesticides in the food and environment which has a serious effect of human and environmental health. This study was conducted to measure residues of 3 widely used pesticides namely diazinon, phosalone and endosulfan in pasteurized milk samples which were collected from different brands in Kermanshah city, Iran. Three milk brands with high distribution were collected from local supermarkets during study period. The selected pesticides were detected in milk samples using HPLC-UV with ultrasound-assisted dispersive liquid-liquid microextraction and solidification of floating organic drop (UA-DLLME-SFO) method. The method detection limit (MDL) was estimated on the basis of the results of 6 replicate analyses of a milk sample spiked with each pesticide standard and was at the range of 1–3 µg/L. Under the optimum conditions, recoveries in milk samples were in the range of 64–72 %. The calibration graphs were linear in the range of 10–800 µg/L and limit of detections (LODs) were in the range of 1–3 µg/L. The mean concentration in the pasteurized milk samples (n = 27) were: 19.43, 3.51 and 3.16 µg/L and the frequency of detection of pesticides in the milk samples were 44.4 %, 11.1 % and 11.1 % for diazinon, phosalone and endosulfan, respectively. Approximately 22.2 % of the samples contained at least one pesticide at detectable level. In conclusion the residues of the detected pesticides were lower than the residue limits set by the FAO/WHO, however, bioaccumulation of these residues is likely to pose health risk to the consumers of milk in Kermanshah city.

Keywords: Pesticides, Monitoring, Organophosphorus pesticides, Pasteurized milk, Endosulfan

Zusammenfassung

Die weitverbreitete Anwendung von Pestiziden kann zur Anhäufung von Pestiziden in der Nahrung und in der Umwelt führen, was zu Auswirkungen auf die Gesundheit von Mensch und Umwelt haben kann. Diese Studie wurde durchgeführt, um Rückstände von drei weit verbreiteten Pestiziden, Diazinon, Phosalon und Endosulfan, in pasteurisierten Milchproben verschiedener Marken aus der Stadt Kermanshah (Iran) zu untersuchen. Drei Milchmarken mit hoher Verbreitung wurden während des Studienzeitraums von lokalen Supermärkten analysiert. Die ausgewählten Pestizide wurden in Milchproben unter Verwendung von HPLC-UV mit Ultraschall-gestützter dispersiver Flüssig-Flüssig-Mikroextraktion und Verfestigung der Methode des schwebenden organischen Tropfens (UA-DLLME-SFO) nachgewiesen. Die Nachweisgrenze wurde auf der Basis der Ergebnisse von 6 Wiederholungsanalysen einer mit jedem Pestizidstandard dotierten Milchprobe ermittelt und lag im Bereich von 1–3 µg/l. Unter optimalen Bedingungen lag die Wiederfindung in den Milchproben im Bereich von 64–72 %. Die Kalibrierungsgraphen waren linear im Bereich von 10–800 µg/l und die Nachweisgrenze (LOD) lag im Bereich von 1–3 µg/l. Die mittlere Konzentration in den pasteurisierten Milchproben (n = 27) betrug: 19,43 µg, 3,51 µg und 3,16 µg/l. Die Häufigkeit des Nachweises von Pestiziden in den Milchproben betrug 44,4 %, 11,1 % und 11,1 % für Diazinon, Phosalon und Endosulfan. Ca. 22,2 % der Proben enthielten mindestens ein Pestizid in nachweisbarer Menge. Zusammenfassend ist festzustellen, dass die Rückstände der nachgewiesenen Pestizide unter den von der FAO/WHO festgesetzten Rückstandshöchstgehalten lagen. Die Bioakkumulation dieser Rückstände ist jedoch wahrscheinlich ein Gesundheitsrisiko für die Verbraucher von Milch in der Stadt Kermanshah.

Schlüsselwörter: Pestizide, Monitoring, Organophosphor-Pestizide, pasteurisierte Milch, Endosulfan

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Introduction

In recent years, exposure to various pesticides by food, water, air and soil through inhalation, ingestion and dermal contact has been increased (Sinha et al., 2011). Food contamination caused by pesticides and heavy metals has increased dramatically in recent years (Adel et al., 2016; Dadar et al., 2017). The use of pesticides can cause an obvious increase in agricultural production and saving human life from diseases but in other hand it results in acute and chronic health problems (Melgar et al., 2010). The widespread use of pesticides has increased the chronic health problems such as increasing in incidences of cancer, chronic kidney diseases, suppression of the immune system, sterility among males and females. Furthermore, pesticides cause endocrine disorders, neurological and behavioral disorders especially among children (Abhilash and Singh, 2009). Organophosphorus pesticides (OPPs) and organochlorines pesticides (OCPs) are among the major groups of pesticides which have been used worldwide and their toxic residues have been reported in various environmental component (Srivastava et al., 2011). OPPs represented 70 % of the total insecticide usage in the United States and around 40% in the world (Nasseri et al., 2018). These pesticides have lipophilic nature and can accumulate in fat-rich substances like milk (John et al., 2001). They enter the human body through the food chain and cause serious health problems. Thus, analysis of pesticide residues in food like milk is essential requirement for consumers, producers, and food-quality control authorities.

Studies have been carried out on pesticide contamination of milk indifferent part of the world (Bedi et al., 2015; Deti et al., 2014; Sajid et al., 2016; Singh et al., 2013) whereas information about OCPs and OPPs contamination of milk in Iran is limited (Bayat et al., 2011; Çok et al., 1999; Shamsipur et al., 2016). About 26,000 tons of pesticides are distributed to farmers in Iran every year. Moreover, the annual usage of pesticides in Iran has been increased dramatically and reached to maximum level of 27000 tons in 2003–2004 (Mostafalou et al., 2013). Nowadays, most countries have restricted or banned the use of OCPs while they may still use in some developing countries. However, due to their physicochemical properties such as lipophilicity, extremely persistent, and high stability, they accumulate in ecosystem and find their ways into the food chain (Zhou et al., 2011). A number of studies conducted during past decadesshows the presence of pesticides residue in different environmental (e.g. water, fish, sediment, butter, pasteurized milk) and human (such as hair and human milk) samples (Mostafalou, et al., 2013). Bayat et al., (2011) reported that the organochlorine pesticides γ-HCH and ß-HCH had the highest concentration of 13.49 ng g^{-1} fat and 11.7 ng g^{-1} fat, in pasteurized and sterilized milk, respectively. However, the survey focused on organophosphorus pesticides is limited. In this study, the residues of two OPPs including diazinon (diethoxy-[(2-isopropyl-6-methyl-4-pyrimidinyl) oxy]-thioxo-phos-phorane) and phosalone (S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-yl-methylO,O-diethyl phosphorodithioate) and one organochlorine pesticide, endosulfan (6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiopin-3-oxide) in pasteurized and homogenized milk samples derived from Kermanshah markets was reported. Key physico-chemical properties of selected pesticides are presented in Table 1.

The present study also includes the application of easy, effective, rugged and less labor-intensive AU-DLLME-SFO method for preconcentration and trace determination of these pesticides in different milk's samples. Monitoring studies to detect pesticide residue levels in milk are very important to determine dietary exposure, so the present work aimed to study the presence of three commonly used pesticides in milk which implied in milk production in Kermanshah city, Iran.

Materials and methods

Chemicals and materials

All reagents were purchased from Merck (Germany) and used without further purification. Diazinon, phosalone and endosulfan standards were procured from Merk (Germany). Stock standard solutions of pesticides were prepared in methanol (HPLC grade, Merck) at 1000 mg/L and were stored at –20 °C. Working standard solutions were daily prepared from the stock standard solution using deionized (DI) water and stored at 4 °C prior to analysis.

Collection of milk samples

Fresh pasteurized and homogenized milk samples from three widely used dairy commercial brands (A, B and C) were collected from local markets in Kermanshah city, Iran in year 2016. Samples of these three brand were analyzed in triplicate (n=9). Each sample of homogenized and pasteurized milk was packaged in carton bags and the samples were transported in cooling boxes containing ice packs (4 °C) to the laboratory and immediately stored in a freezer at –20 °C until further analysis.

Extraction and analytical method

All samples were extracted and analyzed according to the previous established method (Ahmadi-Jouibari et al., 2013; Pirsaheb et al., 2013) with some modifications as follow; for the preparation of milk samples, in a 100-ml Erlenmeyer flask, 20 ml of milk was diluted with DI water. Then, 1.0 ml of Carrez solution A (containing potassium hexacyanoferrate (II) trihydrate, 15 % w/v in water) was added and mixed thoroughly. The next step, 1.0 ml of Carrez solution B (containing zinc sulfate heptahydrate, 30 % w/v in water) was added and mixed thoroughly. The contents of the Erlenmeyer flasks were transferred to 100-ml volumetric flasks, and were filled with DI water quantitatively. Subsequently, the solution was filtered through a Whatman No. 1 filter paper (Whatman Inc., Clifton, NJ, USA). An aliquot of 5 ml of the resulting solution was subjected to the UA-DLLME-SFO. UA-DLLME-SFO is a simple, reliable,

TABLE 1: *Key physico-chemical properties of endosulfan, diazinon and phosalone (Kim et al., 2015; Weber et al., 2010).*

Pesticides	Molecular formula	Molec. weight (g/mol)	Solubility (in water) (mg/L)	log Kow	Vapor Pressure (mm Hg)	ADI[a] (mg/kg bw/day)
Endosulfan	$C_9H_6Cl_6O_3S$	406.904	<1	4.94	1×10^{-5}	0.006
Diazinon	$C_{12}H_{21}N_2O_3PS$	304.345	<1	3.69	0.0001	0.0002
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	367.8	3.05	4.38	4.54×10^{-8}	0.01

[a]: Acceptable daily intake

inexpensive, and environmentally friendly method based on ultrasound-assisted dispersive liquid-liquid microextraction and solidification of floating organic drop (UA-DLLME-SFO). This was followed by high performance liquid-liquid chromatography-ultraviolet detector (HPLC-UV) which was developed for the simultaneous determination of selected pesticides in milk samples (Majlesi et al., 2016). For this, at first step, analytical portion of 1.0 g milk sample spiked or unspiked with pesticides was transferred into a 10-ml centrifuge tube. Then, 5.0 ml of acetone (as extractant) were added and extracted by ultrasonic bath within 30 min at room temperature. 1.0 ml of disperser solvent which is acetone mixed with 30.0 µl of 1-undecanol a microextraction solvent in DLLME, was rapidly injected into above extracted sample using a 1.0-ml syringe (Gastight, Hamilton, USA). A cloudy solution from the dispersion of the fine droplets of 1-undecanol in the aqueous sample was formed in the test tube. The mixture was centrifuged for 4 min at 5000 rpm and the organic solvent was separated from the solution due to density difference. The test tube was then transferred into an ice bath for cooling. After 5 min, the extraction solvent solidified and was then transferred into a conical vial, where it melts quickly at room temperature. Finally, 25 µl of this organic phase was injected into the Knauer HPLC (Germany).

Validation studies of the analytical method

To evaluate the practical applicability of the proposed UA-DLLME-SFO, validation parameters were obtained under the most favorable conditions using spiked milk sample (Pirsaheb and Fattahi, 2018). Mean recovery (as a measure of trueness), intra- and inter-assay precision, calibration curve suitability, and sensitivity and the limit of quantification (LOQ) were characterized and evaluated. For validating a method, mean recoveries of 60–110 % with a repeatability RSD ≤ 10% are considered acceptable. The mean recoveries were determined from spiked pasteurized milk samples, which previously analyzed to ensure the absence of pesticide residues. This was repeated for five times at two different concentrations (10 and 100 µg/L). The limit of quantification (LOQ) was considered as the lowest tested concentration. The limit of detection (LOD) was determined with signal to noise ≥3, whereas the instrument limit of quantification (LOQ) for S/N = 10. LOD and LOQ were determined by analyzing spiked extracts of pasteurized milk. Repeatability of data was assessed using five consecutive analyses under identical condition on the same day. Linearity was determined by assessing the signal responses of target analyses in the standard over a concentration range from 5–800 µg/L. The precision of the method was determined based on repeatability (or inter-day precision) and by calculating the analyzed concentrations inequality control samples, prepared at three levels (each five replicates) for five consecutive days (Eslami et al., 2015). These results indicate the feasibility and reliability of the UA-DLLME-SFO method for detecting target pesticides in milk samples.

Statistical analysis

Statistical analysis of experimental data was carried out by using SPSS Analysis Software Version 16 and Microsoft excels 2007. Each assay was performed in triplicate.

Results

Analytical method validation

The linearity of calibration plots was obtained over the range of 5–800 µg/L with high coefficient of determinations (r^2) which was greater than 0.9966 for all tests (Table 2). Repeatability and reproducibility, both presented as relative standard deviations (RSDs), and were lower than 6.1 % and 8.2 %, respectively (Table 1). The limits of detection (LODs), was calculated as three times the baseline noise (S/N = 3), was in the range of 1–3 µg/L. The limit of quantification (LOQ) for each analyte was determined at S/N = 10 and ranged from 3.5–9.5 µg/L. The broad linear dynamic range combined with the low detection limit suggested a high potential for monitoring residues of pesticides in various samples by applying the proposed UA-DLLME–SFO method.

Occurrence of pesticides in pasteurized milk samples

Two OPPs (diazinon and phosalone) and one OCP (endosulfan) content of collected milk samples were analyzed. The mean and frequencies of pesticides residues are presented in Table 3. It was found that 44.4, 11.1 and 11.1 % of the collected samples contain diazinon, phosalone and endosulfan, respectively. In general, in 44.4 % of the samples one pesticide have been detected. Average concentrations of detected pesticides were 19.43, 3.51 and 3.16 µg/L for diazinon, phosalone and endosulfan, respectively.

TABLE 2: *Average recoveries (%) (n = 5), RSDs, limits of detection (LODs) and limits of quantitation (LOQs) of 3 standard pesticides in pasteurized milk.*

Analyte	ER[a] (%)	RSD[b] % (intra-day)	RSD% (inter-day)	LR[c] (µg/L)	r^{2d}	LOD[e] (µg/L)	LOQ[f] (µg/L)
Diazinon	67	4.8	5.6	10–600	0.9966	3	9.5
Phosalone	72	3.7	4.3	5–800	0.9976	1	3.5
Endosulfan	64	6.1	8.2	10–600	0.9971	3	9.5

[a]: ER, extraction recovery. [b]: RSD at concentration of 100 µg L^{-1} of pesticides. [c]: LR, linear range. [d]: r^2, coefficient of determination. [e]: LOD, limit of detection for S/N = 3. [f]: LOQ, limit of quantification for S/N=10.

TABLE 3: *Mean, medians, range (µg/L) and detection frequency (%) of pesticide residues in milk samples.*

Pesticides	Milk brands	Mean[a] (µg/L) ± SD[b]	Median	Range	Frequency of detection (%)
Diazinon	A	24.533 ± 42.49	bdl[c]	bdl – 73.6	
	B	17.967 ± 18.41	17.1	bdl – 36.8	44.4 %
	C	15.8 ± 1.3	27.36	bdl – 47.4	
Phosalone	A	bdl	bdl	0	
	B	bdl	bdl	0	11.1 %
	C	10.533 ± 18.24	bdl	bdl – 31.6	
Endosulfan	A	9.5 ± 16.45	bdl	bdl – 28.5	
	B	bdl	bdl	0	11.1 %
	C	bdl	bdl	0	

[a]: Mean was calculated from positive quantifiable samples only. [b]: SD = standard deviation of the mean. [c]: bdl = below detection limit.

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Discussion

Comparative concentrations of detected pesticides show that highest residue concentration of diazinon and endosulfan was observed in milk brand A whereas phosalone was present in milk brand C. Diazinon was present in all brands. However, the mean residue concentration in milk brand A was above the maximum residue limit of international organizations (0.02 mg/kg fat milk), FAO/WHO (FAO/WHO, 2000). The presence of OP pesticide residues over the maximum residue limit (MRL) and Acceptable daily intake (ADI) values could be a possible risk to consumer's health, especially children (Salas et al., 2003). Based on Bluthgen and Heeschen's study (1997), the metabolic breakdown of OP pesticideis was rather quick and there was only a littlechance to monitor their residues in milk. However, diazinon was detected and measured in all milk samples in the present study. The mean levels of diazinon of pasteurized milk which was observed in this study is in accordance with previous studies such as Salas, et al. (2003) (0.013 ppm), and Bourne and Arthur(1967) (0.023 ± 0.011 ppm) whereas higher than the value reported by Fagnani et al. (2011a) (not detectable) and Shamsipur et al. (2016) (not detectable). The residue concentrations of phosalone in two brands (A and B) were below detected level and this was 10.53 ± 18.24 mg/Lin milk sample of brand C. The low level of phosalone residue could be attributed to the low daily intake of phosalone by animal. Moreover, heat treatments (pasteurization, boiling and sterilization) of milk and also storage period could reduce pesticides levels (Abou-Arab, 1999). However, phosalone was not detected in studies like Fagnani et al. (2011b), Sheridan and Meola (1999) and Tsiplakou et al. (2010) whose monitored pesticides residues in milk. Finally, endosulfan as an organochlorine pesticide was the only pesticide found in the milk sample from brand and the mean concentration was 9.5 ± 16.45 µg/L. This value of endosulfan is much lower than the MRL of 0.003 mg/kg (FAO/WHO, 2006). Darko and Acquaah (2008) found 0.09 µg/kg endosulfan residue in bovine milk samples in Ghana. Organochlorine pesticides are not readily degradable in the environment and have lipophilic nature with a tendency to bioaccumulate, therefore they can be presented at high concentrations in fatty food like milk (Lozowicka et al., 2014).

In general, the number of sample exceeds the MRL established by FAO/WHO was one (milk A by diazinon). Several factors are contributed in dairy product contamination with pesticides residues which including: animal feeds contamination with pesticides residues, environmental contamination, application of pesticides on farm animals for ectoparasite removal and accidental spills. The best way of controlling the contamination of milk from pesticides residues is to prevent contamination of feed. Finally, it would be necessary for dairy industries, milk producers and health authorities to collaborate to try to reduce toxic residues in such an important food like milk. However, this work was conducted in local area and it would be necessary to perform it at regional and national scales to discuss more about the fate of OPPs and OCPs in the environment.

Conclusion

The simple, precise, rapid and reproducible UA-DLLME-SFO method was used for determining pesticides residue in milk samples. The samples were selected from three brands of pasteurized milk. The method had the LOD and LOQ of 1–3 and 3.5–9.5 µg/L, respectively. The obtained results indicated that the 22.2 % of the samples contain at least one detectable pesticide. However, only diazinon had the mean concentration above MRL, 0.02 mg/kg fat milk. More attention should be given on the usage of diazinon in farm and cattle feed to reduce the residue of diazinon. Dairy and specially milk are important food item and proper care should be taken to use safe pesticide for preventing potential risk to human. Monitoring of the pesticide residue level could assist the supervising program to establish a planned and more controlled application of pesticides.

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Author Contribution

All authors have contributed to the manuscript.

Significance statement

- This study discovers the effectiveness of UA-DLLME-SFO method as a preconcentration and extraction method for optimizing and detection and quantification of three selected pesticides.
- This study discovers that approximately 22.2 % of the samples contained at least one pesticide at detectable residues level.
- This study will help the researcher to further investigate the pesticides contamination in food and environment.

Conflict of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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