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Research Article

Residues of diazinon and chlorpyrifos in potato tuber and their chips

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Abstract: Pesticides improve crop yields, but misuse imposes environmental problems and diseases or abnormalities in humans. Based on food security definition, balanced attention to healthy and sufficient products, there is a growing need to pay attention to product health. The present study was aimed to measure the residual levels of chlorpyrifos (CPF) and diazinon (DZN) in potato *Solanum tuberosum* L. cv. Agria and their chips by accurate, rapid, and reliable extraction method (QuEChERS) using gas chromatography equipped with NPD detector (GC-NPD). The samples were analyzed in pre-harvest stages, harvest, and storage. The recovery of DZN was 95.76–99.87% and 82.38–98.05%, and the CPF 90.85–99.07% and 79.4–89.76% in potatoes and chips, respectively. According to the specifications of the European Commission, the relative standard deviation (RSD) of < 11% detected in this study confirms the accuracy of the extraction method. Moreover, the CPF residual level was detected only in the pre-harvest stage; however, the DZN residual levels in the pre-harvest, harvest, and storage stages, and chips were 0.074 ± 0.007, 0.039 ± 0.014, 0.029 ± 0.009, and 0.13 ± 0.042 $\mu g.g^{-1}$, respectively. The residual level in chips and harvest and storage stages was higher than that in the maximum residue level (MRL).

Keywords: pesticide residue, potato, gas chromatography, chlorpyrifos, diazinon

Introduction

After rice, wheat, and maize, Potato *Solanum tuberosum* L. is the fourth major global crop. It is the most consumed food worldwide due to its high nutritional value (Bártová *et al.*, 2015; Aloo *et al.*, 2020; Guchi, 2020). Potatoes are the second major crop in Iran, after wheat. The most important producers of irrigated potatoes are Ardabil, Isfahan, Khorasan, Hamedan, East Azerbaijan, and Fars provinces. The leading producers of rainfed potatoes are Mazandaran, Guilan, and Golestan provinces (Imani Barandagh *et al.*, 2015). Reportedly, up to 60% of potatoes consumed in the daily diet, such as potato chips, French fries, and dehydrated potato products, chilled-peeled potatoes, and canned potatoes, are currently processed in developed countries (Kirkman, 2007). Different segments of the population, particularly children, show great interest in eating snacks, mostly potato chips with especial popularity. Various studies have been reported so far on the side effects and health risks of consuming potato chips, most notably acrylamide being a carcinogen (Pedreschi *et al.*, 2005; Gökmen *et al.*, 2005; Gökmen and Şenyuva, 2006; Rommens *et al.*, 2008; Ouhtit *et al.*, 2014). Due to the need for pest control and the management of potato diseases by pesticides, their residue in potato chips may seriously endanger consumers' health. The accumulation of pesticides in the body, even in small doses, can negatively affect human health

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throughout life (Alavanja *et al.*, 2004; Gökalp Muranli *et al.*, 2015; Nicolopoulou-Stamati *et al.*, 2016). Hence, due to the high consumption of potato chips, especially by children as a sensitive group, it is necessary to evaluate and determine the pesticide residue in the potato chips.

Some previous studies evaluated and confirmed the levels of pesticide residues in potatoes and their products (Martindale, 1988; Tsumura-Hasegawa *et al.*, 1992; Česnik *et al.*, 2006; López-Pérez *et al.*, 2006; Rigueira *et al.*, 2013; Ahmed *et al.*, 2014a; Ahmed *et al.*, 2014b; Ramadan *et al.*, 2020; Reis *et al.*, 2020). Residues of sprout growth inhibitors and fungicides such as thiabendazole, maleic hydrazide, and chlorpropham have also been studied in potato chips and French fries (Lewis *et al.*, 1996; Nagami, 1997; Lentza-Rizos and Balokas, 2001). However, to the best of our knowledge, despite the high consumption of insecticides, no study has been carried out on the pesticide residues in potato chips.

Chlorpyrifos (CPF) and diazinon (DZN) are two widely used pesticides in potato cultivation against the pests active in the soil, such as *Agriotes* sp. and *Phthorimaea operculella* Zeller in Iran. The use of CPF can control losses caused by *P. operculella* during storage. The present study aimed to identify and measure the levels of DZN and CPF residues in potato chips. Thus, the levels of DZN and CPF residues from farm to factory were measured to assess changes in the residual levels of these pesticides in potato and potato chips.

Materials and Methods

Reagents and chemicals: Anhydrous magnesium sulfate, sodium chloride, and ethyl acetate GC grade were from Merck (Germany). PSA (Primary Secondary Amine) and C_{18} (Octadecyl) were obtained from Agilent Technologies, Inc. (the USA), and the technical materials of CPF and DZN (with 98% and 96% purity, respectively) from Kimia Gohar Khak (Iran).

Study area: The studied farm with an area of one hectare is located in Chakaneh village in Neyshabur city, Khorasan Razavi province, Iran (36°49′04″N 58°30′15″E). In this farm, Mancozeb, Avant, Confidor, Abamectin, DZN, and CPF have been used to control pests. DZN (EC 60%) and CPF (EC 40.8%) at 4 ml/l with irrigation water until mid-August, and diazinon were sprayed at a concentration of 2.5 ml/l up to early September to control pests.

Sampling: The samples of potato tubers were collected in three steps: 1) 20 days pre-harvest, 2) at the same time as harvest, and 3) one month after storing in cold storage. An area of 100 m^2 of isolated land on the farm was left unsprayed as control. The sampling route of the potatoes was considered to be hypothetically the letter Z in the whole field studied. Then an entire plant was harvested every ten meters and transferred to a polyethylene bag. At the end of the sampling, one tuber was selected randomly from each bag and placed in another bag. Finally, three kilograms of the tuber samples were randomly selected from the last bag and delivered to the laboratory in a labeled bag. At harvest time, the bags containing potatoes sampled from different parts of the study farm were marked and cold-stored in a separate room. Moreover, one month after the product storage period, 200 kg of the mixed tubers were randomly selected from 40 tons of harvested potatoes, 3 kg of which was then randomly assigned to measure pesticide residue and transported to the laboratory in a labeled bag. The potatoes were transferred to the Topis complex (Mashhad, Iran) to be processed into potato chips. The first input of the potatoes was marked, and the rest of the production process was done according to the factory procedure to distinguish the chips of interest from the previous batch. Of the potato chips produced, 1 kg of products was randomly sampled and sent to the laboratory labeled polyethylene bag.

Preparations: During the testing process, each potato tuber was first divided into approximately four equal parts. A quarter of each tuber was completely homogenized inside a blender pitcher (model: Waring ™ 700S/700G). The potato chips were ground using a laboratory batch mill (model: IKA™). Part of the homogenized samples immediately underwent extraction, and the rest was then transferred to glass containers and stored after labeling and sealing at −20 °C.

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Study of pesticides residue in homemade potato chips: This section was performed following obtaining the results of the analysis of the pesticides residue in the chips. This inquiry aimed to compare the differences in the level of pesticides residue in chips versus potatoes after washing and peeling and homemade preparing of chips. For this purpose, four kilograms of potatoes were purchased from a market. Potatoes were sprayed with DZN and CPF to notice the difference in residual levels between chips and potatoes. To obtain 20 $\mu g.g^{-1}$ tuber of each pesticide, the tubers were sprayed with 80 ml of stock solution of 1000 $\mu g.ml^{-1}$ of DZN and CPF prepared in ethyl acetate. Sprayed potatoes were stored at room temperature. The potato samples and chips prepared from them were then analyzed to identify and measure the levels of pesticide residues at two intervals: a) three days after spraying and b) one week after spraying. At each phase, 1 kg of potatoes was randomly selected. Each tuber was then divided into two equal parts, half of which were transferred to the blender pitcher to measure pesticide residue in the samples, and the other half was used to produce the chips.

Extraction and analysis: Immediately after sampling and preparing, the samples were extracted and cleaned up using the QuEChERS method (Anastassiades *et al.*, 2003) modified by Torabi *et al.* (2017). First, 5 g of the homogenized sample was transferred to a 50-ml centrifuge tube (1.5 ml of deionized water was added to the potato chips samples). Then 7 ml of ethyl acetate GC grade was poured into the sample and shaken vigorously for 1 min via a vortex (model: IKA VX4). Next, 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride were added and shaken strenuously on the vortex for 1 min, followed by centrifugation at 6000 rpm for 5 min. After separating the layers, 1 ml of the obtained supernatant was transferred to a 1.5-ml microtube containing 25 mg of PSA and 150 mg of anhydrous magnesium sulfate (200 mg of C_{18} + 50 mg of PSA for potato chips samples). The samples were vigorously vortexed for 1 min and centrifuged at 4500 rpm for 10 min. Finally, 700 µl of the supernatant was transferred to a balloon of the HeidolphTM rotary evaporator (model: Laborota 4002 control) using a micropipette. After completely evaporating the solvent at 40 °C, to avoid damage caused to GC column due to water content of the injection samples, the residues were dissolved in 700 µl of ethyl acetate and transferred to a GC vial using the micropipette. Additionally, to compare the effect of cleanup mediated by PSA and C_{18} adsorbents on the sample components, one potato control sample and potato chips were prepared and injected into the GC according to the modified QuEChERS method in two procedures, one cleanup with PSA (and C_{18} for potato chips) and another without cleanup.

The concentrations of pesticide residues were measured by Gas Chromatography (Agilent 7890B) equipped with nitrogen-phosphorus detector (NPD) using HP-5 capillary column (30 m × 0.32 mm (ID) × 0.25 µm) coated with 5% Phenyl Methyl Siloxane and the carrier gas of nitrogen (99.999%) at a flow rate of 4 ml/min. The injection volume was 1 µl in splitless inlet mode. The temperature program used for analysis was as follows: the initial temperature was 80 °C, held for 1 min, raised to 160 °C at 20 °C /min and held for 1 min, then increased to 280 °C at 5 °C /min and held for 2 min and the injector temperature was 220 °C.

Method validation: The study method was validated for apparent recovery, linearity, and quantitation limit. The method's accuracy was estimated using a recovery test by spiking four standard DZN and CPF concentrations (0.5, 1, 5, and 10 $\mu g.ml^{-1}$) separately to potato tuber and chips samples. The standards of each pesticide were used to prepare a stock solution of 1000 $\mu g.ml^{-1}$ for each pesticide in ethyl acetate. The linearity of the method was assessed by drawing standard and matrix-matched calibration curves for each pesticide (0.5, 1, 5, and 10 $\mu g.ml^{-1}$). All experiments were performed in triplicate. The reproducibility of the method was assessed by calculating the relative standard deviation (%RSD). The sensitivity of the process was evaluated by calculating the instrument detection limit (IDL), instrument quantification limit (IQL), estimated method detection limit (EMDL) and estimated method quantification limit (EMQL) using the root mean square error (RMSE)

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(Equation 1) as well as the slope of the calibration curve (Corley, 2003; Torabi *et al.*, 2017). IDL, IQL, EMDL, and EMQL were calculated based on the matrix-matched calibration curve to consider the matrix effects in the samples. Microsoft Excel 2010 software was employed to compute the equations and parameters. Mean comparison test was performed by Tukey and LSD methods using Minitab 19 software.

1) $$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(y - y_2)^2}{n}}$$

i = Variable i
n = Number of non-missing data points
y = Actual values
y_1= Predicted values

Results

The retention times of pesticides were determined after injecting the standard solution into the GC three times (Fig. 1). Standard and matrix-matched calibration curves were plotted using the area under the curve of each concentration. The linearity of the method was confirmed by the regression equation obtained and the calibration curves of DZN and CPF standards, and the calibration curves of matrix-matched properties obtained from the average of three replications (Table 1). The values of IDL, IQL, EMDL, and EMQL for DZN and CPF and the recovery test results and %RSD are shown in Tables 2 and 3, respectively.

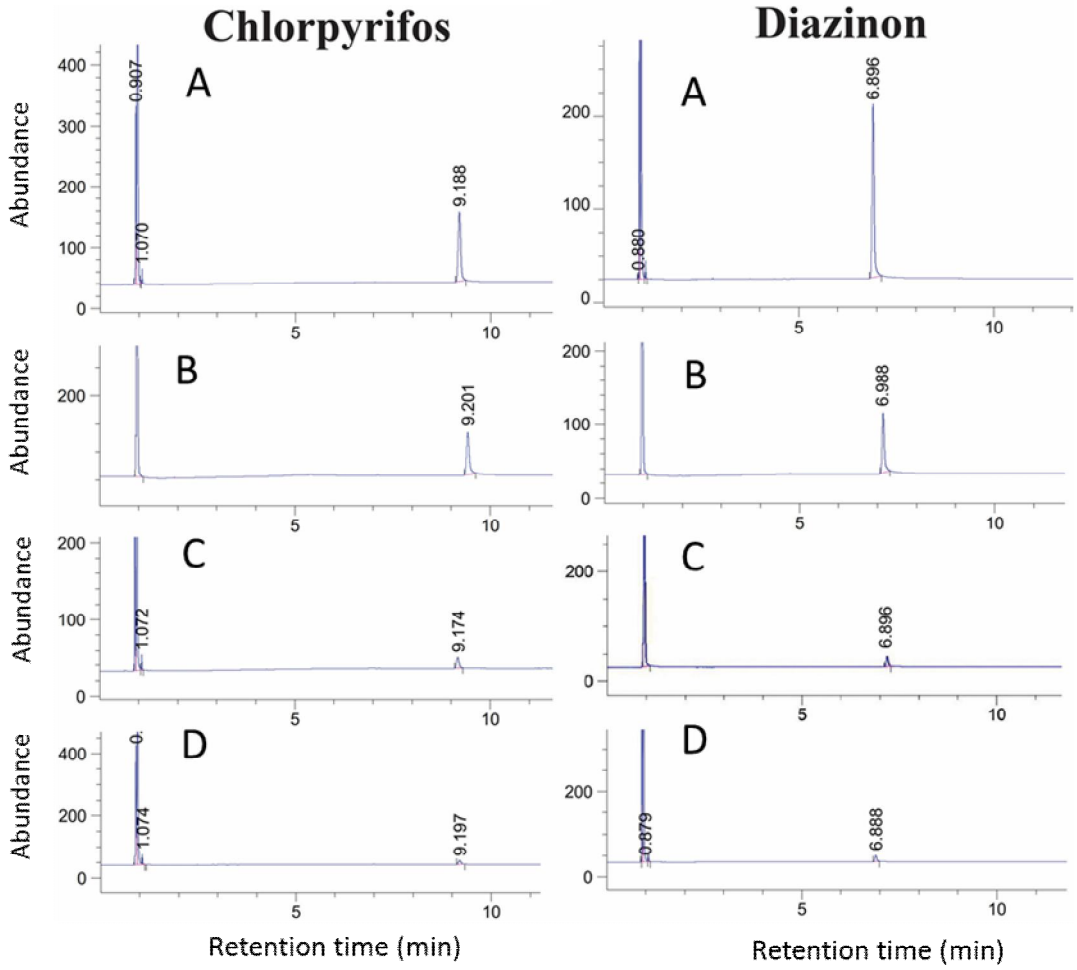

Figure 1 GC-NPD Chromatograms for diazinon and chlorpyrifos standard solutions. A. 10 µg.ml^{-1}; B. 5 µg.ml^{-1}; C. 1 µg.ml^{-1}; D. 0.5 µg.ml^{-1}.

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Table 4 shows the results of analyzing the pesticide residues in potato tubers and chips. According to the findings, 0.026 $\mu g.g^{-1}$ of CPF and 0.074 $\mu g.g^{-1}$ DZN was observed in the pre-harvest potato samples. Although 0.039 and 0.029 $\mu g.g^{-1}$ DZN residues were detected in harvest and storage samples, respectively; no CPF was found in either period. No CPF was seen in chips; however, 0.13 $\mu g.g^{-1}$ of DZN was present in chips samples. The mean comparison with Tukey's test revealed no significant difference (P = 0.06) in DZN residue levels between the chips samples and the three studied periods of potato tubers. However, the studied steps were classified into different groups based on the LSD method (Table 4).

In the first interval, there was 3.36 $\mu g.g^{-1}$ of CPF and 2.8 $\mu g.g^{-1}$ of DZN residues in the potato tubers, as well as 2.31 $\mu g.g^{-1}$ of CPF and 1.09 $\mu g.g^{-1}$ of DZN residues in the potato chips. In the second interval, there was 2.8 $\mu g.g^{-1}$ of CPF and 2.01 $\mu g.g^{-1}$ of DZN in the potato tubers, as well as 0.6 $\mu g.g^{-1}$ of CPF and 0.26 $\mu g.g^{-1}$ of DZN residues in the potato chips. According to the sprayed potatoes and homemade chips analysis, pesticide residues in both intervals were higher in the sprayed potatoes than in the chips produced.

Table 1 Calibration curve properties for chlorpyrifos and diazinon.

Pesticide	Calibration type	Commodity	Regression equation	r^2
Diazinon	Standard		y = 65.698x - 0.6709	1
	Matrix-matched	Potato tuber	y = 62.721x + 1.3206	1
		Chips	y = 65.168x + 1.0634	1
Chlorpyrifos	Standard		y = 60.733x + 0.6441	1
	Matrix-matched	Potato tuber	y = 60.201x - 0.8107	1
		Chips	y = 55.102x + 8.6305	0.999

Table 2 Extraction method sensitivity for diazinon and chlorpyrifos.

Pesticide	Commodity	IDL ($\mu g.g^{-1}$)	IQL ($\mu g.g^{-1}$)	EMDL ($\mu g.g^{-1}$)	EMQL ($\mu g.g^{-1}$)
Diazinon	Potato	0.01	0.06	0.002	0.009
	Chips	0.02	0.08	0.003	0.012
Chlorpyrifos	Potato	0.06	0.20	0.009	0.030
	Chips	0.11	0.38	0.020	0.060

Table 3 Validation of the analytical method for diazinon and chlorpyrifos.

Pesticide	Commodity	Spiking level ($\mu g.ml^{-1}$)	Recovery (Mean ± SE) (%)	RSD (%)
Diazinon	Potato	0.5	99.87 ± 6.28	10.9
		1	99.35 ± 4.14	7.21
		5	96.08 ± 1.4	2.52
		10	95.76 ± 1.66	3.01
	Chips	0.5	82.38 ± 3.96	8.34
		1	88.05 ± 2.37	4.66
		5	96.69 ± 6.08	10.89
		10	98.05 ± 0.73	1.29
Chlorpyrifos	Potato	0.5	90.85 ± 2.46	4.70
		1	99.71 ± 2.52	4.37
		5	98.23 ± 3.47	6.13
		10	98.96 ± 2.01	3.52
	Chips	0.5	80.77 ± 1.94	4.16
		1	79.40 ± 1.24	2.70
		5	89.76 ± 2.73	5.27
		10	89.61 ± 1.57	3.04

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The chromatogram from the injection of control potato tubers and potato chips with/without cleanup in Fig. 2 shows that although the use or non-use of PSA in potatoes was not different, the use of PSA and C_{18} are fruitful in eliminating the matrix effect of chips.

Table 4 Residual value (Mean ± SE) of diazinon and chlorpyrifos in the samples.

Commodity	Stage	Diazinon (µg.g^{-1})	MRL (µg.g^{-1})	Chlorpyrifos (µg.g^{-1})	MRL (µg.g^{-1})
Potato	Pre-harvest	0.074 ± 0.007^{ab3}	0.01$^{1\&2}$	0.026 ± 0.001	2^{1} and 0.01^{2}
	Harvest	0.039 ± 0.014^{b}		ND^{4}	
	storage	0.029 ± 0.009^{b}		ND	
Chips	-	0.130 ± 0.042^{a}	< 0.01^{1}	ND	-

1 FAO codex
2 EU commission codex
3 LSD; (α = 0.05)
4 Non detectable

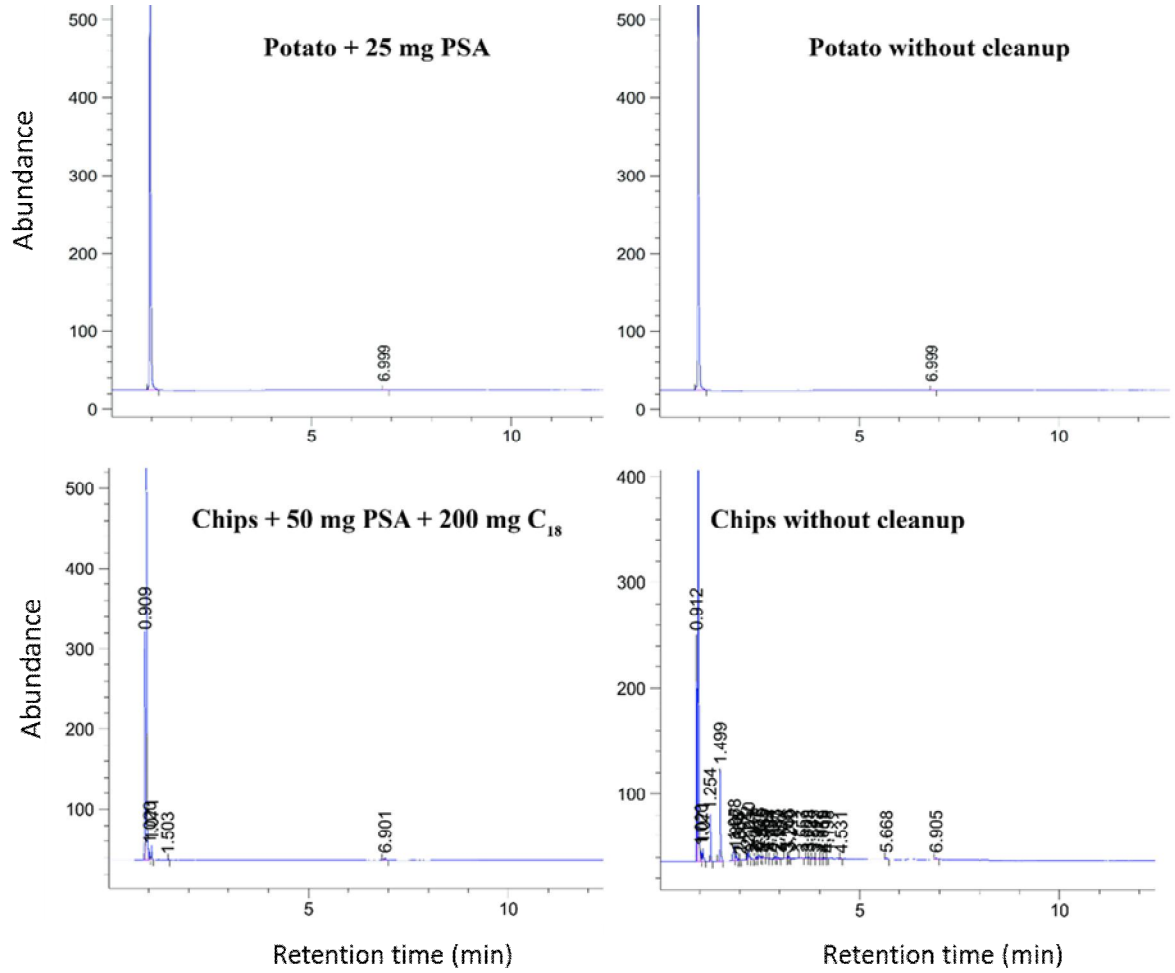

Figure 2 Comparison of the effect of adsorbents application in the cleanup stage on the matrix' samples.

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Discussion

So far, DZN and CPF have been extracted using various solvents in crops such as apples, oranges, bananas, dried fruits, peanuts, vegetables, tea, potato, and vegetable oils using the QuEChERS method (Anastassiades *et al.*, 2003; Cunha *et al.*, 2007; González-Curbelo *et al.*, 2011; Andraščíková *et al.*, 2013; Ahmed *et al.*, 2014b; Rai *et al.*, 2016; Tiryaki, 2016; Ghotbadini-Bahraman *et al.*, 2017; Hazer *et al.*, 2017; Li *et al.*, 2017; Machado *et al.*, 2017b; Varela-Martínez *et al.*, 2019; Reis *et al.*, 2020). In this study, acetonitrile was replaced with ethyl acetate as a solvent in the original QuEChERS method because of the greater toxicity and high cost, and incompatibility with GC, especially NPD detectors (Talebi and Torabi, 2018; Aysal *et al.*, 2007). Previously, Aysal *et al.* (2007) and Torabi *et al.* (2017) reported successful results using ethyl acetate solvent in the QuEChERS method for the extraction of DZN and 23 other pesticides from tomatoes, apples, and frozen green beans, as well as DZN and edifenphos from the soil, respectively. High precision, sensitivity, and efficiency of extraction method via ethyl acetate solvent in line with the European Commission specifications (European Commission, 2019) were confirmed regarding the extraction method with 95.76−99.87% and 82.38−98.05% recovery rates for DZN in potato tubers and chips and 90.85−99.07% and 79.4−89.76% for CPF in potato tubers and chips, respectively, and with an RSD of less than 11%.

Several reports have confirmed the reduction of pesticide residue after peeling and washing (Soliman, 2001; Chavarri et al., 2005; Keikotlhaile et al., 2010; Ahmed et al., 2014b; Andrade et al., 2015; Yang et al., 2017; Heshmati et al., 2019; Heshmati et al., 2020). According to the Codex established by the FAO and the EU Commission (FAO, 1997; FAO, 2020; European Commission, 2020), the level of DZN residue in potato tubers during the harvest and storage periods with 0.039 and 0.029 $\mu g.g^{-1}$, respectively, and in chips by 0.13 $\mu g.g^{-1}$ of DZN was higher than that of MRL. Martindale (1988) and Česnik et al. (2006) reported no DZN and CPF residues in potato samples. According to Ahmed et al. (2014a), washed potato tubers had no residue, and unwashed samples had 0.009−0.04 $\mu g.g^{-1}$ of CPF, lower than the MRL determined by FAO. Further, Rigueira et al. (2013) and Reis et al. (2020) found CPF residue in potatoes lower than MRL. The data obtained from the analysis of pesticide residues in the homemade preparation method in both intervals showed that the residual amount of DZN and CPF in chips was less than that of potatoes.

Although some studies excluded adsorbents due to the partial removal of pesticide residues (Niell *et al.*, 2010; Pareja *et al.*, 2011), reduced selectivity and minor changes in the matrix effects (Romero-González *et al.*, 2008; Pizzutti *et al.*, 2009), deletion of the cleanup step in samples with the complex matrix can adversely affect the results of pesticide detection and recovery testing (Fig. 2). Therefore, the effect of the use or non-use of adsorbents on processed foods needs further investigation.

Pesticides improve crop yields, but misuse imposes environmental problems and human poisonings with complications in different body organs. Diazinon and chlorpyrifos are the commonly used agricultural pesticides in Iran. Despite the use of DZN at the recommended concentration (2.5-4 ml/l) and the observance of the pre-harvest interval, the DZN residue in potato tubers and chips was higher than MRL. These findings confirm the importance of replacing DZN with short-lived pesticides. Due to the potential for the accumulation of pesticides in the human body and their side effects, consuming minimal potato chips in sensitive groups such as children and pregnant women is recommended.

Due to the peeling and frying in oil that has not been used before, the homemade chips had less residues than potatoes. In contrast, commercially produced chips had more residue than homemade. In the commercial production of potato chips, repeated use of oil may dissolve some non-polar and semi-polar pesticides in the oil. Thereby, the pesticide residue may be

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transferred from the oil to the potatoes produced under rigorous monitoring without any unauthorized residues. In addition, water loss during processing may motivate the condensation of the residue level.

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ارزیابی باقی‌مانده دیازینون و کلرپایریفوس در سیب‌زمینی *Solanum tuberosum* رقم آگریا و چیپس سیب‌زمینی تهیه شده از آن

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چکیده: اگرچه استفاده از سموم دفع آفات نباتی باعث بهبود عملکرد محصولات کشاورزی شده‌اند، اما استفاده نادرست از آن‌ها سبب بروز مشکلات زیست‌محیطی و ایجاد بیماری‌ها و ناهنجاری‌هایی در انسان می‌شود. هم‌چنین براساس تعریف امنیت غذایی (توجه متوازن به تولید محصول کافی و سالم)، لزوم توجه به سلامت محصولات بیش‌از پیش نمایان می‌شود. این تحقیق با هدف اندازه‌گیری میزان باقی‌مانده کلرپایریفوس (CPF) و دیازینون (DZN) در سیب‌زمینی *Solanum tuberosum* L. cv. Agria و چیپس سیب‌زمینی با روش استخراج دقیق، سریع و قابل‌اعتماد (QuEChERS) و با استفاده از دستگاه کروماتوگرافی گازی مجهز به شناساگر NPD انجام شد. سیب‌زمینی در سه مرحله قبل از برداشت، برداشت و سردخانه مورد بررسی قرار گرفت. درصد بازیابی DZN در سیب‌زمینی و چیپس به‌ترتیب ۹۵/۷۶-۹۹/۸۷٪ و ۸۲/۳۸-۹۸/۰۵٪ و درصد بازیابی CPF در سیب‌زمینی و چیپس به‌ترتیب ۹۰/۸۵-۹۹/۰۷٪ و ۷۹/۴-۸۹/۷۶٪ بود. براساس مشخصات کمیسیون اروپا، انحراف استاندارد نسبی (RSD) کم‌تر از ۱۱ به‌دست آمده در این تحقیق، صحت و دقت روش استخراج را تأیید می‌کند. هم‌چنین CPF تنها در مرحله قبل از برداشت شناسایی شد، اما میزان باقی‌مانده DZN در مرحله قبل از برداشت، برداشت، سردخانه و چیپس‌های تهیه شده به‌ترتیب ۰/۰۰۷ ± ۰/۰۷۴، ۰/۰۱۴ ± ۰/۰۳۹، ۰/۰۰۹ ± ۰/۰۲۹ و ۰/۰۴۲ ± ۰/۱۳ میکروگرم بر گرم بود. مقدار باقی‌مانده در چیپس، مراحل برداشت و سردخانه بالاتر از بیشینه مجاز باقی‌مانده سموم بود.

واژگان کلیدی: باقی‌مانده آفتکش، سیب‌زمینی، کروماتوگرافی گازی، کلرپایریفوس، دیازینون

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