

Research Article

Residues of diazinon and chlorpyrifos in potato tuber and their chips

Mahdiyar Saraji¹, Khalil Talebi-Jahromi^{2*}, Mahdi Balali Mood³ and Sohrab Imani¹

1. Department of Plant Protection, Science and Research Branch, Islamic Azad University, Tehran, Iran.

2. Department of Plant Protection, Faculty of Agricultural Science & Engineering, University of Tehran, Karaj, Iran.

3. Medical Toxicology and Drug Abuse Research Centre, Faculty of Medicine, Birjand University of Medical Sciences, Iran.

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 $0.13 \pm 0.042 \mu\text{g.g}^{-1}$, 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; Ouhiti *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

Handling Editor: Saeid Moharrampour

* Corresponding author: khtalebi@ut.ac.ir

Received: 17 October 2021, Accepted: 14 December 2021

Published online: 04 January 2021

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 C₁₈ (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 m² 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.

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 $20 \mu\text{g.g}^{-1}$ tuber of each pesticide, the tubers were sprayed with 80 ml of stock solution of $1000 \mu\text{g.ml}^{-1}$ 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 Heidolph™ 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 ($30 \text{ m} \times 0.32 \text{ mm (ID)} \times 0.25 \mu\text{m}$) 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 $10 \mu\text{g.ml}^{-1}$) separately to potato tuber and chips samples. The standards of each pesticide were used to prepare a stock solution of $1000 \mu\text{g.ml}^{-1}$ 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 $10 \mu\text{g.ml}^{-1}$). 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)

(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.

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

i = Variable i

n = Number of non-missing data points

y = Actual values

\hat{y}_i = 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.

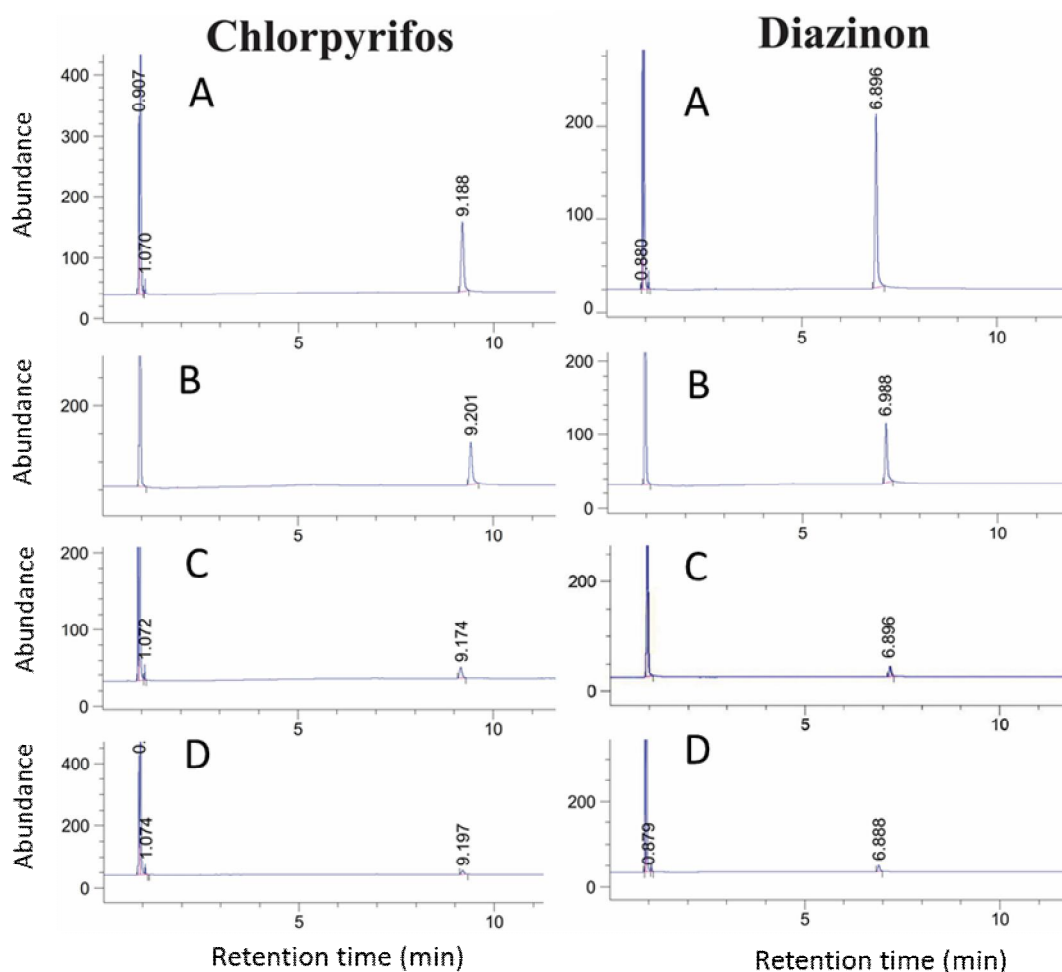


Figure 1 GC-NPD Chromatograms for diazinon and chlorpyrifos standard solutions. A. 10 µg.ml⁻¹; B. 5 µg.ml⁻¹; C. 1 µg.ml⁻¹; D. 0.5 µg.ml⁻¹.

Table 4 shows the results of analyzing the pesticide residues in potato tubers and chips. According to the findings, $0.026 \mu\text{g.g}^{-1}$ of CPF and $0.074 \mu\text{g.g}^{-1}$ DZN was observed in the pre-harvest potato samples. Although 0.039 and $0.029 \mu\text{g.g}^{-1}$ DZN residues were detected in harvest and storage samples, respectively; no CPF was found in either period. No CPF was seen in chips; however, $0.13 \mu\text{g.g}^{-1}$ 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 $3.36 \mu\text{g.g}^{-1}$ of CPF and $2.8 \mu\text{g.g}^{-1}$ of DZN residues in the potato tubers, as well as $2.31 \mu\text{g.g}^{-1}$ of CPF and $1.09 \mu\text{g.g}^{-1}$ of DZN residues in the potato chips. In the second interval, there was $2.8 \mu\text{g.g}^{-1}$ of CPF and $2.01 \mu\text{g.g}^{-1}$ of DZN in the potato tubers, as well as $0.6 \mu\text{g.g}^{-1}$ of CPF and $0.26 \mu\text{g.g}^{-1}$ 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 ($\mu\text{g.g}^{-1}$)	IQL ($\mu\text{g.g}^{-1}$)	EMDL ($\mu\text{g.g}^{-1}$)	EMQL ($\mu\text{g.g}^{-1}$)
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 (µg.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

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 C₁₈ 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

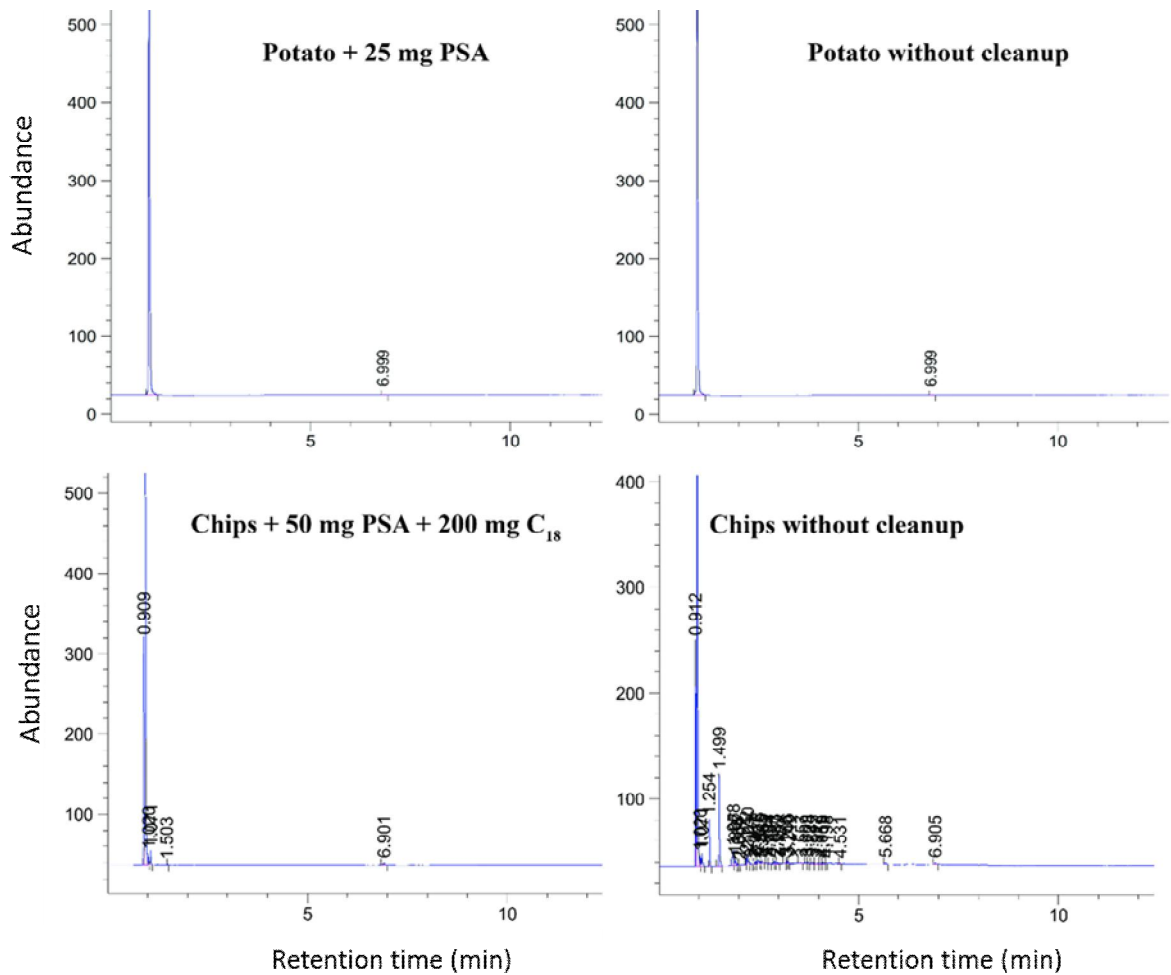


Figure 2 Comparison of the effect of adsorbents application in the cleanup stage on the matrix' samples.

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 $\mu\text{g}\cdot\text{g}^{-1}$, respectively, and in chips by 0.13 $\mu\text{g}\cdot\text{g}^{-1}$ 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 $\mu\text{g}\cdot\text{g}^{-1}$ 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

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.

Acknowledgment

This study was financially and technically supported by the Islamic Azad University, Science and Research Branch, Tehran, Iran.

Reference

- Ahmed, M. A. I., Khalil, N. S. and Abd El Rahman, T. A. E. 2014a. Carbamate pesticide residues analysis of potato tuber samples using high-performance liquid chromatography (HPLC). *Journal of Environmental Chemistry and Ecotoxicology*, 6(1): 1-5.
- Ahmed, M. A. I., Khalil, N. S. and Abd El Rahman, T. A. E. 2014b. Determination of pesticide residues in potato tuber samples using QuEChERS method with gas chromatography. *Australian Journal of Basic and Applied Sciences*, 8(3): 349-353.
- Alavanja, M. C. R., Hoppin, J. A. and Kamel, F. 2004. Health Effects of Chronic Pesticide Exposure: Cancer and Neurotoxicity. *Annual Review of Public Health*, 25(1): 155-197.
- Aloo, B. N., Mbega, E. R., Makumba, B. A., Hertel, R. and Daniel, R. 2020. Molecular identification and in vitro plant growth-promoting activities of culturable potato (*Solanum tuberosum* L.) Rhizobacteria in Tanzania. *Potato Research*, 64(1):67-95.
- Anastassiades, M., Lehotay, S. J., Štajnbaher, D. and Schenck, F. J. 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *Journal of AOAC International*, 86(2):412-431.
- Andrade, G. C. R. M., Monteiro, S. H., Francisco, J. G., Figueiredo, L. A., Rocha, A. A. and Tornisielo, V. L. 2015. Effects of types of washing and peeling in relation to pesticide residues in tomatoes. *Journal of the Brazilian Chemical Society*, 26: 1994-2002.
- Andrašćiková, M., Hrouzková, S. and Cunha, S. C. 2013. Combination of QuEChERS and DLLME for GC-MS determination of pesticide residues in orange samples. *Food Additives and Contaminants: Part A*, 30(2): 286-297.
- Aysal, P., Ambrus, Á., Lehotay, S. J. and Cannavan, A. 2007. Validation of an efficient method for the determination of pesticide residues in fruits and vegetables using ethyl acetate for extraction. *Journal of Environmental Science and Health, Part B*, 42(5): 481-490.
- Bártová, V., Bárta, J., Brabcová, A., Zdráhal, Z. and Horáčková, V. 2015. Amino acid composition and nutritional value of four cultivated South American potato species. *Journal of Food Composition and Analysis*, 40: 78-85.
- Česnik, H. B., Gregorčič, A., Bolta, Š. V. and Kmecl, V. 2006. Monitoring of pesticide residues in apples, lettuce and potato of the Slovene origin, 2001-04. *Food Additives and Contaminants*, 23(2): 164-173.
- Chavarri, M. J., Herrera, A. and Ariño, A. 2005. The decrease in pesticides in fruit and vegetables during commercial processing. *International Journal of Food Science and Technology*, 40(2): 205-211.
- Corley, J. 2003. Best practices in establishing detection and quantification limits for pesticide residues in foods. *Handbook of Residue Analytical Methods for Agrochemicals*, 1: 0471491942-4.
- Cunha, S. C., Lehotay, S. J., Mastovska, K., Fernandes, J. O., Beatriz, M. and Oliveira, P. P. 2007. Evaluation of the QuEChERS sample preparation approach for the analysis of pesticide residues in olives. *Journal of Separation Science*, 30(4): 620-632.
- European Commission. 2019. Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed. Report Number: SANTE/12682/2019.
- European Commission. 2020. EU. Pesticides. Maximum Residue Levels: Annexes II, III,

- IV, VII, Regulation 396/2005/EC. Available from: <https://echa.europa.eu> [Accessed 15th December 2020].
- FAO 1997. Diazinon (022). In: FAO and WHO (Eds.), *Pesticide Residues in Food*. Food and Agriculture Organization of the United Nations. 157-296.
- FAO. 2020. Codex alimentarius, international food standards-Potato. Available from: <http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/commodities-detail/en/?lang=en&id=347> [Accessed 22th November 2020].
- Ghotbadini-Bahraman, N., Sheibani, A. and Reza Shishehbore, M. 2017. Off-line coupling of QuEChERS sample preparation to ion mobility spectrometry for the determination of chlorpyrifos residue in pistachio oil. *International Journal for Ion Mobility Spectrometry*, 20(1): 41-45.
- Gökalp Muranli, F. D., Kanev, M. and Özdemir, K. 2015. Genotoxic effects of diazinon on human peripheral blood lymphocytes. *Arhiv za Higijenu Rada i Toksikologiju*, 66(2): 153-158.
- Gökmen, V. and Şenyuva, H. Z. 2006. Study of colour and acrylamide formation in coffee, wheat flour and potato chips during heating. *Food Chemistry*, 99(2): 238-243.
- Gökmen, V., Şenyuva, H. Z., Acar, J. and Sarıoğlu, K. 2005. Determination of acrylamide in potato chips and crisps by high-performance liquid chromatography. *Journal of Chromatography A*, 1088(1): 193-199.
- González-Curbelo, M. Á., Hernández-Borges, J., Ravelo-Pérez, L. M. and Rodríguez-Delgado, M. Á. 2011. Insecticides extraction from banana leaves using a modified QuEChERS method. *Food Chemistry*, 125(3): 1083-1090.
- Guchi, E. 2020. Disease management practice on potato (*Solanum tuberosum* L.) in Ethiopia. *World Journal of Agricultural Research*, 3(1): 34-42.
- Hazer, O., Akkik, M., Demir, D. and Turhan, Y. 2017. Determination of carbendazim and Chlorpyrifos in selected fruits and vegetables samples using QuEChERS. *Eurasian Journal of Analytical Chemistry*, 12(2): 17-30.
- Heshmati, A., Hamidi, M. and Nili-Ahmadabadi, A. 2019. Effect of storage, washing, and cooking on the stability of five pesticides in edible fungi of *Agaricus bisporus*: A degradation kinetic study. *Food Science and Nutrition*, 7(12): 3993-4000.
- Heshmati, A., Nili-Ahmadabadi, A., Rahimi, A., Vahidinia, A. and Taheri, M. 2020. Dissipation behavior and risk assessment of fungicide and insecticide residues in grape under open-field, storage and washing conditions. *Journal of Cleaner Production*, 270: 122287.
- Imani Barandagh, M., Mousavi, N., Kazemi, A. and Hoseinzadeh, S. 2015. Economic Analysis of Strategic Potato Crop. *International Conference on Applied Research in Agriculture*. 22 May 2015, Tehran, pp. 1-11. Available from: <https://civilica.com/doc/414812>. [Accessed 11th April 2020].
- Keikotlhaile, B. M., Spanoghe, P. and Steurbaut, W. 2010. Effects of food processing on pesticide residues in fruits and vegetables: A meta-analysis approach. *Food and Chemical Toxicology*, 48(1): 1-6.
- Kirkman, M. A. 2007. Global markets for processed potato products. In: Vreugdenhil, D., Bradshaw, J., Gebhardt, C., Govers, F., Mackerron, D. K. L., Taylor, M. A. and Ross, H. A. (Eds.), *Potato Biology and Biotechnology*. Elsevier Science B.V.
- Koesukwiwat, U., Lehotay, S. J., Mastovska, K., Dorweiler, K. J. and Leepipatpiboon, N. 2010. Extension of the QuEChERS method for pesticide residues in cereals to flaxseeds, peanuts, and doughs. *Journal of Agricultural and Food Chemistry*, 58(10): 5950-5958.
- Lentza-Rizos, C. and Balokas, A. 2001. Residue levels of chlorpropham in individual tubers and composite samples of postharvest-treated potatoes. *Journal of Agricultural and Food Chemistry*, 49(2): 710-714.

- Lewis, D. J., Thorpe, S. A. and Reynolds, S. L. 1996. The carry-through of residues of thiabendazole, tecnazene and chlorpropham from potatoes following manufacture into potato crisps and jacket potato crisps. *Food Additives and Contaminants*, 13(2): 221-229.
- Li, J., Sun, M., Chang, Q., Hu, X., Kang, J. and Fan, C. 2017. Determination of pesticide residues in teas via QuEChERS combined with dispersive liquid-liquid microextraction followed by gas chromatography-tandem mass spectrometry. *Chromatographia*, 80(9): 1447-1458.
- López-Pérez, G. C., Arias-Estévez, M., López-Periago, E., Soto-González, B., Cancho-Grande, B. and Simal-Gándara, J. 2006. Dynamics of pesticides in potato crops. *Journal of Agricultural and Food Chemistry*, 54(5): 1797-1803.
- Machado, I., Gérez, N., Pistón, M., Heinzen, H. and Cesio, M. V. 2017. Determination of pesticide residues in globe artichoke leaves and fruits by GC-MS and LC-MS/MS using the same QuEChERS procedure. *Food Chemistry*, 227: 227-236.
- Martindale, R. W. 1988. Determination of residues of a range of fungicides, anti-sprouting agents and (organochlorine and organophosphorus) insecticides in potatoes by gas-liquid and high-performance liquid chromatography. *Analyst*, 113(8): 1229-1233.
- Nagami, H. 1997. Residues of maleic hydrazide and chlorpropham in potato chips. *Bulletin of Environmental Contamination and Toxicology*, 58(5): 764-768.
- Nicolopoulou-Stamati, P., Maipas, S., Kotampasi, C., Stamatis, P. and Hens, L. 2016. Chemical pesticides and human health: the urgent need for a new concept in agriculture. *Frontiers in Public Health*, 4: 148. Available from: doi: 10.3389/fpubh.2016.00148. [Accessed 10th September 2020].
- Niell, S., Pareja, L., Geis Asteggianti, L., Cesio, M. V. and Heinzen, H. 2010. Comparison of extraction solvents and conditions for herbicide residues in milled rice with liquid chromatography-diode array detection analysis (LC-DAD). *Food Additives and Contaminants: Part A*, 27(2): 206-211.
- Ouhtit, A., Al-Sharbaty, M., Gupta, I. and Al-Farsi, Y. 2014. Potato chips and childhood: What does the science say? An unrecognized threat?. *Nutrition*, 30(10): 1110-1112.
- Pareja, L., Cesio, V., Heinzen, H. and Fernández-Alba, A. R. 2011. Evaluation of various QuEChERS based methods for the analysis of herbicides and other commonly used pesticides in polished rice by LC-MS/MS. *Talanta*, 83(5): 1613-1622.
- Pedreschi, F., Moyano, P., Kaack, K. and Granby, K. 2005. Color changes and acrylamide formation in fried potato slices. *Food Research International*, 38(1): 1-9.
- Pizzutti, I. R., de Kok, A., Hiemstra, M., Wickert, C. and Prestes, O. D. 2009. Method validation and comparison of acetonitrile and acetone extraction for the analysis of 169 pesticides in soya grain by liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*, 1216(21): 4539-4552.
- Polgár, L., Kmellár, B., García-Reyes, J. F. and Fodor, P. 2012. Comprehensive evaluation of the cleanup step in QuEChERS procedure for the multi-residue determination of pesticides in different vegetable oils using LC-MS/MS. *Analytical Methods*, 4(4): 1142-1148.
- Rai, S., Singh, A. K., Srivastava, A., Yadav, S., Siddiqui, M. H. and Mudiam, M. K. R. 2016. Comparative evaluation of QuEChERS method coupled to DLLME extraction for the analysis of multiresidue pesticides in vegetables and fruits by gas chromatography-mass spectrometry. *Food Analytical Methods*, 9(9): 2656-2669.
- Ramadan, M. F., Abdel-Hamid, M., Altorgoman, M. M., AlGaramah, H. A., Alawi, M. A., Shati, A. A., Shweeta, H. A. and Awwad, N. S. 2020. Evaluation of pesticide residues in vegetables from the Asir Region, Saudi Arabia. *Molecules*, 25(1): 205. Available from: doi :10.3390/molecules25010205. [Accessed 11th October 2020].
- Reis, D., Silva, P., Perestrelo, R. and Câmara, J. S. 2020. Residue analysis of insecticides in

- potatoes by QuEChERS-dSPE/UHPLC-PDA. *Foods*, 9(8): 1000. Available from: doi:10.3390/foods9081000. [Accessed 11th October 2020].
- Rigueira, L. M. B., Ribeiro, K. D. L., de Queiroz, M. E. L. R., Neves, A. A., Zambolim, L. and Oliveira, R. M. 2013. Determination of chlorpyrifos and thiamethoxam in potato tuber (*Solanum tuberosum* L.) and soil of Brazil using solid-liquid extraction with low temperature partitioning (SLE/LTP). *Journal of the Brazilian Chemical Society*, 24: 2042-2049.
- Romero-González, R., Frenich, A. G. and Vidal, J. L. M. 2008. Multiresidue method for fast determination of pesticides in fruit juices by ultra performance liquid chromatography coupled to tandem mass spectrometry. *Talanta*, 76(1): 211-225.
- Rommens, C. M., Yan, H., Swords, K., Richael, C. and Ye, J. 2008. Low-acrylamide French fries and potato chips. *Plant Biotechnology Journal*, 6(8): 843-853.
- Soliman, K. M. 2001. Changes in concentration of pesticide residues in potatoes during washing and home preparation. *Food and Chemical Toxicology*, 39(8): 887-891.
- Talebi, K. and Torabi, E. 2018. *Analysis of Pesticide Residues in Agricultural Products (Principles and Methods)*. University of Tehran.
- Tiryaki, O. 2016. Validation of QuEChERS method for the determination of some pesticide residues in two apple varieties. *Journal of Environmental Science and Health, Part B*, 51(10): 722-729.
- Torabi, E., Talebi, K., Pourbabae, A. and Ahmadzadeh, M. 2017. Evaluation of a modified QuEChERS method for extraction of diazinon and edifenphos from two paddy soils using HPLC-UV. *Plant Pest Research*, 17(1): 13-28.
- Tsumura-Hasegawa, Y., Tonogai, Y., Nakamura, Y. and Ito, Y. 1992. Residue levels of dichlorvos, chlorpropham, and pyrethrins in postharvest-treated potatoes during storage or processing into starch. *Journal of Agricultural and Food Chemistry*, 40(7): 1240-1244.
- Varela-Martínez, D. A., González-Curbelo, M. Á., González-Sálamo, J. and Hernández-Borges, J. 2019. Analysis of multiclass pesticides in dried fruits using QuEChERS-gas chromatography tandem mass spectrometry. *Food Chemistry*, 297: 124961. Available from: doi: 10.1016/j.foodchem.2019.124961. [Accessed 23th October 2020].
- Yang, T., Doherty, J., Zhao, B., Kinchla, A. J., Clark, J. M. and He, L. 2017. Effectiveness of commercial and homemade washing agents in removing pesticide residues on and in apples. *Journal of Agricultural and Food Chemistry*, 65(44): 9744-9752.

ارزیابی باقی مانده دیازینون و کلرپایریفوس در سیب زمینی *Solanum tuberosum* رقم آگریا و چیپس سیب زمینی تهیه شده از آن

مهدی یار سراجی^۱، خلیل طالبی جهرمی^{۲*}، مهدی بلالی مود^۳ و سهراب ایمانی^۱

۱- گروه گیاه پزشکی، واحد علوم و تحقیقات، دانشگاه آزاد اسلامی، تهران، ایران.

۲- گروه گیاه پزشکی، دانشکده علوم و مهندسی کشاورزی، دانشگاه تهران، کرج، ایران.

۳- مرکز تحقیقات مسمومیت ها و سوء مصرف مواد، دانشکده پزشکی، دانشگاه علوم پزشکی و خدمات درمانی بیرجند، ایران.

پست الکترونیکی نویسنده مسئول مکاتبه: khtalebi@ut.ac.ir

دریافت: ۲۵ مهر ۱۴۰۰؛ پذیرش: ۲۳ آذر ۱۴۰۰

چکیده: اگرچه استفاده از سموم دفع آفات نباتی باعث بهبود عملکرد محصولات کشاورزی شده اند، اما استفاده نادرست از آن ها سبب بروز مشکلات زیست محیطی و ایجاد بیماری ها و ناهنجاری هایی در انسان می شود. همچنین براساس تعریف امنیت غذایی (توجه متوازن به تولید محصول کافی و سالم)، لزوم توجه به سلامت محصولات بیش از پیش نمایان می شود. این تحقیق با هدف اندازه گیری میزان باقی مانده کلرپایریفوس (CPF) و دیازینون (DZN) در سیب زمینی *Solanum tuberosum* L. cv. Agria و چیپس سیب زمینی با روش استخراج دقیق، سریع و قابل اعتماد (QuEChERS) و با استفاده از دستگاه کروماتوگرافی گازی مجهز به شناساگر NPD انجام شد. سیب زمینی در سه مرحله قبل از برداشت، برداشت و سردخانه مورد بررسی قرار گرفت. درصد بازیابی DZN در سیب زمینی و چیپس به ترتیب ۹۵/۷۶-۹۹/۸۷٪ و ۸۲/۳۸-۹۸/۰۵٪ و درصد بازیابی CPF در سیب زمینی و چیپس به ترتیب ۸۵/۹۰-۹۹/۰۷٪ و ۷۹/۴-۸۹/۷۶٪ بود. براساس مشخصات کمیسیون اروپا، انحراف استاندارد نسبی (RSD) کمتر از ۱۱ به دست آمده در این تحقیق، صحت و دقت روش استخراج را تأیید می کند. همچنین CPF تنها در مرحله قبل از برداشت شناسایی شد، اما میزان باقی مانده DZN در مرحله قبل از برداشت، برداشت، سردخانه و چیپس های تهیه شده به ترتیب 0.007 ± 0.074 ، 0.014 ± 0.039 ، 0.009 ± 0.029 و 0.042 ± 0.13 میکروگرم بر گرم بود. مقدار باقی مانده در چیپس، مراحل برداشت و سردخانه بالاتر از بیشینه مجاز باقی مانده سموم بود.

واژگان کلیدی: باقی مانده آفتکش، سیب زمینی، کروماتوگرافی گازی، کلرپایریفوس، دیازینون