Arab Universities Journal of Agricultural Sciences
(2025) 33 (1) 110-121
Website: http://ajs.journals.ekb.eg

Monitoring Multiple Pesticide Residues in Potato Tubers and Associated Health Risks

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https://doi.org/ 10.21608/ajs.2025.352951.1592

Received 14 January 2025; Accepted 22 April 2025

Keywords:

Monitoring,
Risk assessment,
Pesticides residues,
Potato tubers,
Organophosphate,
Neonicotinoids

Abstract: This research aimed to establish a reliable analytical procedure for monitoring pesticides in fresh potato tubers. A total of 466 pesticides from various chemical groups, including organophosphates, neonicotinoids, conazoles, chloronitriles, carbamates, acylamino acids, and phenylureas, were examined in thirty-three potato samples collected from local markets in Cairo and Giza governorates in Egypt between 2021 and 2022. Pesticide residues of chlorothalonil and chloropropham were detected using GC-MS/MS, while emamectin, imidacloprid, and pencycuron were analyzed via LC-MS/MS; others (chlorpyrifos, difenoconazole, and metalaxyl) were determined using both methodologies. Recovery percentages and the limit of quantification (LOQ) were established, ranging from 70-120% and 0.01-0.05 mg kg^{-1}, respectively. Overall, the average residue values in the targeted potato samples from the two aforementioned governorates varied from 0.01-5.63 and 0.01-3.28 mg kg^{-1}, respectively. All detected pesticides were present at levels below the MRLs, except for chlorothalonil, emamectin, and imidacloprid. The lowest percentages of acute risk (%ARfD), chronic risk (%ADI), and daily intake (EDI) of pesticide residues by adult consumers were also calculated for all detected pesticides to assess their impact on consumer health.

1 Introduction

Potatoes are widely recognized as a vital root crop. They are cultivated in over 125 countries and serve as a daily dietary staple for more than a billion people. More than 5,000 distinct varieties exist worldwide, approximately 4000 of which are indigenous, primarily found in the Andes region of South America. Potatoes are a fundamental food resource across diverse cultures and nations, from Ireland to India (FAO 2016).

Potatoes are a key export crop on which many producers and consumers depend. Therefore, monitoring pesticide residues and concentrations in vegetables and fruits is crucial to the consuming and exporting system. Potatoes are one of the crops most susceptible to diseases, especially fungal diseases, which require high concentrations and frequencies of pesticides. This causes an increased risk of crop contamination with pesticide residues higher than maximum residue levels (MRLs) (Jardim and Caldas 2012, Ahmed et al 2013).

The impact of pesticide contamination on food has been extensively studied in regions such as North America, Japan, and various European countries. However, there remains a lack of information regarding pesticide residues in developing nations, particularly concerning ready-to-eat products available in markets. Therefore, ensuring the swift and accurate detection and measurement of pesticides in both unprocessed and processed food items is essential for protecting consumer health, making it a priority for regulators, producers, and consumers (El-Sheikh et al 2022, 2023).

Pesticide residues were extracted using the analytical technique QuEChERS (Anastassiades et al 2003), and qualitative as well as quantitative analyses were performed by GC-MS/MS and/or LC-MS/MS (Frenich et al 2008, Lehotay 2011). Most findings indicated detectable levels of pesticides in potatoes, often exceeding or varying from the established permissible thresholds (Belitz et al 2009, Salim et al 2019).

Various pesticides contaminate the entire ecosystem, either directly or indirectly, leading to significant health risks for all living organisms (Sharma et al 2019). The evaluation of pesticide health risks involved measuring the total pesticide residues found in analyzed samples and comparing them to the acceptable daily intake (ADI) standards for specific pesticides. Residues exceeding the (MRL) in raw vegetables and fruits pose potential health risks to humans. Health risks were assessed in vegetable and fruit samples with pesticide residues, revealing potential consumer exposure when %ARfD (acute reference dose) or %ADI (acceptable daily intake) levels exceed 100% (El-Sheikh et al 2022, 2023).

Pesticide residues in potato tubers present significant health concerns for consumers, emphasizing the need for regular monitoring by national authorities prior to export or import. This study examined pesticide residues found in potato samples collected from various markets in the Cairo and Giza governorates between 2021 and 2022.

2 Material and Methods

2.1 Pesticide standards and chemicals

Standards for pesticides (466 pesticides) were >98% pure and purchased from Augsburg, Germany (Dr. Ehrenstorfer GmbH). Standard solution Stocks were prepared in suitable solvents according to their polarity and solubility. Each pesticide standard solution was created with a concentration (1000 µg ml^{-1} using 10 ml of toluene). To prepare working solutions of 0.02, 0.1, 0.5, and 2.50 µg ml^{-1}, the stock solutions were diluted by methyl alcohol and then kept at 4 °C. The extraction kits were purchased from Supelco® Analytical Products and/or Agilent Technologies (USA). Acetonitrile, ethyl acetate and methanol were acquired from (CARLO ERBA), whereas toluene and acetone were obtained from (Merck). Deionized water (DIW) with a resistivity of 17.6 Ω cm was produced using Milli-Q water as a purification system, a product of Millipore.

2.2 Sampling

A total of 33 fresh potato samples, one kilogram each were collected from commercial markets at Cairo (18) and Giza (15) governorates during 2021-2022. The specimens were contained in sterile polyethylene bags and delivered to the lab using an ice chest. Following this, they were thoroughly blended and cut into small pieces using a high-speed electrical blender. Subsequently, three 10 g sub-samples from each specimen were preserved at -20°C for pesticide residue inspection.

2.3 Extraction and clean-up of pesticide residues

Using the QuEChERS technique, 466 pesticide residues were extracted and purified (Anastassiades et al 2003). Qualitative and quantitative determinations were performed using GC-MS/MS and LC-MS/MS. Approximately 10 grams of potato samples were homogenized and placed into a 50 mL polypropylene tube. Then, 0.1% acidified acetonitrile (MeCN, 10 mL) was added, and the tube was vortexed for 3 minutes at its maximum speed (4500 rpm). Four grams of anhydrous $MgSO_4$ and one gram of NaCl were added and vortexed for one minute. After 30 seconds of mixing with 50 µL of the internal standard solution (triphenyl phosphate/TPP), the extracts underwent centrifugation for 10 minutes at 4500 rpm. After that, 1 mL of the solvent layer (acetonitrile) (MeCN) was transferred to a 15 mL cleanup tube that contained 150 mg of anhydrous MgSO4 and 25 mg of PSA (primary secondary amine) sorbent. After securing the cap of the tube, it was manually shaken for five minutes. The samples were then centrifuged for five minutes. A portion of the sample was filtered using a PTFE filter (0.45 µm) and subsequently placed into vials, ready for injection into the determination systems (GC-MS/MS and/or LC-MS/MS) directly.

2.4 Instrumentation

2.4.1 System of gas chromatography-MS/MS

At the QCAP laboratory, analyses were conducted using an Agilent 7890A gas chromatograph coupled with a 7010B triple quadrupole mass spectrometer operating in electron ionization mode. Agilent Technologies' DB-35MS ultra inert capillary column, composed of 65% dimethylpolysiloxane and 35% phenyl, with dimensions of 30 m length × 0.25 µm film thickness × 0.18 mm i.d., was employed to achieve chromatographic separation of pesticides. After 1.3 minutes at 70°C, the oven temperature program ramped up to 150°C at a rate of 70°C per minute, then to 270°C at 12°C per minute, and lastly to 310°C at 18°C per minute, a temperature maintained for 6.3 minutes. The entire process lasted 21 minutes. The injection volume was one microliter, injected using splitless mode, with an inlet temperature of 250°C. More than 99.999 percent pure helium gas was used at a steady flow rate of 0.7 ml per minute, with nitrogen as the colliding gas. The ion source was maintained at 320°C, while the quadrupole temperature was held at 180°C. The GC-MS/MS interface was also held at 320°C, with an ionization energy of 70 eV. The electron impact mode was employed. Data collection, analysis, and instrument control were performed using MassHunter software. Standard curves were prepared for each pesticide, typically at 0.006 and 0.5 µg ml-1 for chlorothalonil analyzed by GC-MS/MS.

2.4.2 System of liquid chromatography-MS/MS

An Agilent 1200 Series HPLC connected to a 4500 tandem mass spectrometer (LC-MS/MS SCIEX Triple Quadrupole 4500) was utilized (QCAP Lab). Separation was conducted using a column (C18) with a length of 150 mm, an internal diameter of 4.6 mm, and 5.0 µm particle size (ZORBAX Eclipse XDB). The injection volume was five µL, while the column temperature was set at 40°C. The two solvent components, solvent B (a mixture of MeOH: DIW (9:1, v/v)) and solvent A (a mixture of DIW: MeOH (9:1, v/v) and ammonium formate at pH 3.78). The initial flow rate was 0.5 mL/min while component A was 100%. Over 6 min, it progressively changed to 5% A (95% B), and it remained constant at 0.3 ml/min for 17 min. Following these 23 minutes, a 2-minute post-run was conducted utilizing the original 100% of A at a 0.5 milliliters per minute flow rate. Electrospray ionization (ESI) with multiple reaction monitoring (MRM) mode was used for MS/MS analysis. An ion spray voltage of 5000 V, ion source gas pressures of 1.40 psi and 2.40 psi, and a curtain gas pressure of 25 psi were used. A source temperature of 450°C and a medium collision gas were applied. Data collection and processing, as well as instrument control, were done using Analyst Software 1.6. MRM in positive mode (ESI) was used for all LC-MS/MS analyses. Standard curves with five concentrations (e.g., 0.001-0.1 µg mL^{-1} of emamectin) were prepared for quantitative analysis.

2.5 Validation of Methods

The analytical technique QuEChERS was validated to determine the limit of quantification (LOQ) and rates of recoveries for pesticide residues according to the European Commission (2009, 2013). LOQ is used to measure the level of sensitivity and accuracy. It was established as the minimum detectable concentration of analyte generating signal-to-noise ratios (S/N) of 10:1. To evaluate recovery rates, homogenized blank potato samples (2.0 g) were spiked by adding the proper amounts of the pesticide standard mixture solutions at different concentrations located in the range of 0.01 and 0.25 mg kg^{-1} (relying upon the value of the pesticide MRL). After spiking the samples for one hour (equilibration time), the analysis method was carried out. According to SANTE/2020/12830 (European Commission, 2021), acceptable recoveries should range between 70% and 120%.

The developed analytical method and instruments were validated for pesticide analysis in potatoes, as studied based on SANTE/11813/2017 (European Commission, 2017). The control and fortified samples were analyzed using the analytical technique described earlier to assess the extraction efficiency.

2.6 Evaluation of consumer daily intake of potatoes and health risks

The ARfD percentage represents the acute dietary consumption and is utilized to determine the acute potato risks (El-Sheikh et al 2022). %ARfD less than 100%, the acute risk is considered acceptable, but if it exceeds 100%, it is deemed unacceptable. Consequently, a lower %ARfD value expresses decreased risk; it is determined using equations (1) and (2):

$$ESTI = (HFC \times HRC)/b.wt. \quad (1)$$

$$\%ARfD = (ESTI \times 100)/ARfD \quad (2)$$

The HFC represents the highest quantity of food consumed by young people in a day (kg), HRC denotes the maximum residual concentration of a pesticide found (mg kg^{-1}) and ESTI is the estimated short-term intake (mg kg^{-1}/day). The (%ADI) was used to determine the risk associated with chronic dietary intake. (El-Sheikh et al 2022) for each pesticide residue in potato samples. ADI percentage was computed using equations (3) and (4):

$$EDI = (AFC \times APR)/b.wt. \quad (3)$$
$$\%ADI = (EDI \times 100)/ADI \quad (4)$$

EDI indicates the estimated daily intake (mg kg^{-1}/day), APR refers to the average pesticide residue (mg kg^{-1}), AFC represents the average daily food consumption (kg), ADI denotes the acceptable daily intake (mg kg^{-1}/day), and b.wt stands for body weight.

According to Equation 3, the Estimated Daily Intake (EDI) of pesticide residues that exceed the permissible limit was calculated by multiplying the mean concentrations of pesticide residues (mg kg^{-1}) found in food by the average body weight (b.wt) of an adult (70 kg) for each product. This calculation adheres to the WHO's Global Environment Monitoring System's World Health Organization - GEMS/FOODS (2006) and Food and Agriculture Organization - FAO (2016) guidelines to determine the acceptable daily intake.

The health risk was utilized to assess the acceptability of the chronic risk. Consumers' health risks from ingesting pesticide-polluted samples were evaluated using the ADI percentage. It is calculated by dividing the EDI by the ADI (mg/kg body weight), as stated by WHO/FAO (equation 4). According to EFSA (2012, 2013), when the ADI percentage is lower than 100%, it is considered safe for consumption. However, if the (%ADI) exceeds 100%, it is regarded as a health risk of food (HR) to the consumers (Sarkar et al 2021).

Two distinct consumption rates were applied to assess both acute and chronic risks associated with pesticide residues: 0.2 kg/day for acute risk evaluation and 0.1 kg/day for chronic risk analysis across all studied samples (El-Sheikh et al 2022). Additionally, the daily consumption rate of potatoes was appreciated by adult consumers with an average weight of 70 kg (Walpole et al 2012, Arabameri et al 2020).

3 Results and Discussion

3.1 Potato pesticide residues

Pesticides are usually applied to fruit and vegetable crops to control insect pests and plant diseases, enhancing their yield and quality. If agricultural pesticides do not break down naturally, their residues remain in the crops. Our research aimed to evaluate pesticide residues in potatoes sold for human consumption and assess the dietary risks associated with these residues. We designed a market monitoring program to detect the presence or absence of pesticide residues in different potato samples collected from various markets in the Cairo and Giza governorates.

Pesticide residues were extracted using the QuEChERS method while identified and quantified using GC-MS and/or LC-MS. This technique was first published in 2003 and later amended to the present procedure to broaden the analyte and matrix spectrum.

Examination of the acquired data revealed that contamination surveyed potato tubers at different levels of various pesticide residues depending on pesticide type. For validation, each governorate is presented separately as follows:

Table 1 presents the detected pesticide residue levels in potato tubers collected in Cairo. Seven pesticide residues have been identified: chlorothalonil, chlorpropham, chlorpyrifos, difenoconazole, emamectin, imidacloprid, and pencycuron. These pesticides were found in potato samples from various markets in Cairo, with average values ranging from 0.01 to 5.63 mg kg^{-1}. The data indicated that the percentage of positive samples ranged from 5.5% to 33.3%, while the corresponding percentage of negative samples ranged from 66.7% to 94.5% in potatoes. Overall, the average quantities of pesticide residues found in potato tuber samples ranged from 0.01 to 5.634 mg kg^{-1}. Most detected pesticides were found at levels below the MRL based on the Codex Alimentarius Committee (FAO-WHO) and European Commission (EC), except for chlorothalonil and imidacloprid (**Table 1**). These findings are consistent with Reis et al (2020), who concluded that the analyzed potatoes pose no significant risk to human health, as the detected insecticide residues were below the MRLs established by the Codex Alimentarius, EU, and other regulatory bodies. However, exceptions were noted for chlorothalonil, emamectin and imidacloprid, where their levels exceeded their MRLs.

Table 1. Detected Pesticide residues (mg kg^{-1}) in potatoes collected from Egyptian markets

Pesticides Detected / Statutes of Registration	Pesticides Chemical Groups	Residues Average (mg kg^{-1})	Frequency of (+) Samples %	Frequency of (-) Samples (%)	Frequency of (+) Samples Exceeded MRL (%)	MRLs (mg kg^{-1}) Codex / EU	Analysis System	LOQ (mg kg^{-1})
Chlorothalonil[1] / R	Chloronitrile	2.8	5.5	94.5	11.11	-/0.01	G	0.05
Chlorpropham[1] / U	Carbamate	5.634 (0.038-9.54)	33.3	66.7		30/0.35	G	0.05
Chlorpyrifos[1] / U	Organophosphate	0.01	5.5	94.5		-/0.01	G & L	0.01
Difenoconazole[1] / R	Conazole	0.01	5.5	94.5		4/0.1	G & L	0.01
Emamectin[1] / R	Micro-organism derived substance	0.011	5.5	94.5		-/0.002	L	0.01
Imidacloprid[1] / R	Neonicotinoid	0.014	5.5	94.5		-/0.01	L	0.01
Pencycuron[1] / R	Phenylurea	0.029	5.5	94.5		-/0.1	L	0.01
Chlorpropham[2] / U	Carbamate	3.282 (0.038-9.78)	66.66	33.34	0	30 /0.35	G	0.05
Chlorpyrifos[2] / U	Organophosphate	0.01	6.66	93.34		No/0.01	G & L	0.01
Metalaxyl[2]/ R	Acylamino acid	0.01	6.66	93.34		0.02/0.02	G & L	0.01

[1] and [2] Pesticides detected in Cairo and Giza governorates, respectively, **R** Registered, **U** Unregistered**, G** GC–MS/MS, **L** LC–MS/MS, (+) allocated**, (-)** Not allocated, Values between brackets represent minimum and maximum residues.

It is worth noting that five of the detected potato pesticide residues (Chlorothalonil, difenoconazole, emamectin, imidacloprid and pencycuron) representing 71.43%, were registered by European Commission (EC) and Pesticides Committee, Egyptian Ministry of Agriculture and Land Reclamation, while 28.57% of the other detected pesticides (chlorpropham and chlorpyrifos) were not registered and/or recommended for use on potato crop.

For the second site, Giza, **Table 1** presents the detected pesticide residue levels from various chemical groups in potato samples. These results showed the presence of three pesticide residues in potato tubers: chloropropham, chloropyrifos, and metalaxyl, with different average levels of 3.28, 0.01, and 0.01 mg kg-1, respectively. Additionally, the frequency of positive samples ranged from 6.66% to 66.66%. The average values for detected pesticide residues in the potato tubers varied from 0.01 to 3.28 mg kg−1, and all detected pesticides were found at levels lower than the MRL established by the Codex Alimentarius Committee and the European Commission (EC).

It is evident that the same trend observed in the Cairo governorate also appeared in the Giza governorate concerning the detection of unregistered pesticides. Only one pesticide residue (metalaxyl) was detected and registered by the European Commission (EC) and approved by the Pesticide Committee of the Egyptian Ministry of Agriculture and Land Reclamation. Registered pesticides account for 33.33%, while unregistered pesticides make up 66.67% of the detected pesticides (chloropropham and chlorpyrifos).

Typical standard GC-MS/MS chromatograms of the five chlorothalonil concentrations are given in **Fig 1,** while the resulting standard curve is presented in **Fig 2.** Chromatograms of a blank sample and a sample spiked with chlorothalonil are found in **Fig 3.**

Typical LC-MS/MS of emamectin chromatograms are given in **Fig 4**. A standard calibration curve of emamectin pesticide at five different concentrations is shown in **Fig. 5**. The recovery of emamectin pesticide at concentrations 0.05 and 0.1 reached at 86.8 and 103 %, respectively (**Fig 6**).

Several investigators have reported the presence of unregistered or unapproved pesticide residues in potatoes. In the Fayoum governorate, among 50 potato tubers analyzed, pesticide residues were not detected in 20 samples (40%), while 30 samples (60%) showed detectable pesticide levels; only three of them contained profenofos that surpassed the Maximum Residue Limit (MRL) as per Codex Alimentarius standards. Other detected pesticides included chlorpropham, imidacloprid and thiophanate methyl (Ibrahim et al 2022). In Turkey, out of 104 potato samples, pesticide residues were detected in eleven samples, nine of them above the MRLs. Detected pesticides were clothianidin (banned in Turkey since 31 July 2019), thiamethoxam and acetamiprid (Balkan and Yılmaz 2023). In addition, testing fifteen potato samples collected from various local markets across Poland revealed that eight samples contained at least one pesticide with concentrations surpassing the European Union's MRLs, while ten samples showed traces of at least one pesticide degradation product. Detected pesticides were rimsulfuron, deltamethrin, lambda-cyhalothrin, thiamethoxam, and metalaxyl (Danek et al 2021).

Residue analysis of the commonly used insecticides in potato cultivations (deltamethrin, λ-cyhalothrin, chlorpyrifos and acrinathrin) was determined utilizing an ultra-HPLC-photodiode array detector (UHPLC-PDA) according to Reis et al (2020).

These studies underscore the importance of using reliable and accurate methods to maintain ongoing surveillance of pesticide residues within the food supply system.

3.2 Evaluation of potatoes' risk to consumer health based on dietary consumption

Data indicated that the EDI of chlorothalonil, chlorpropham, chlorpyrifos, difenoconazole, emamectin, imidacloprid and pencycuron pesticide residues ranged from 0.14×10^{-4} to 78.88×10^{-4} mg Kg^{-1}/Person in Cairo governorate. Nevertheless, the EDI for detected pesticide residues of chlorpropham, chlorpyrifos and metalaxyl in Giza governorate ranged from 0.14×10^{-4} to 45.95×10^{-4} mg kg^{-1}/Person (**Table 2**). Therefore, the intake of potatoes by an average adult consumer (with an average weight of 70 kg) is expected to be within the permissible levels of the acceptable daily intake (ADI) for detected pesticide residues in the two targeted governorates. These results are consistent with those reported by Ibrahim and Shalaby (2023).

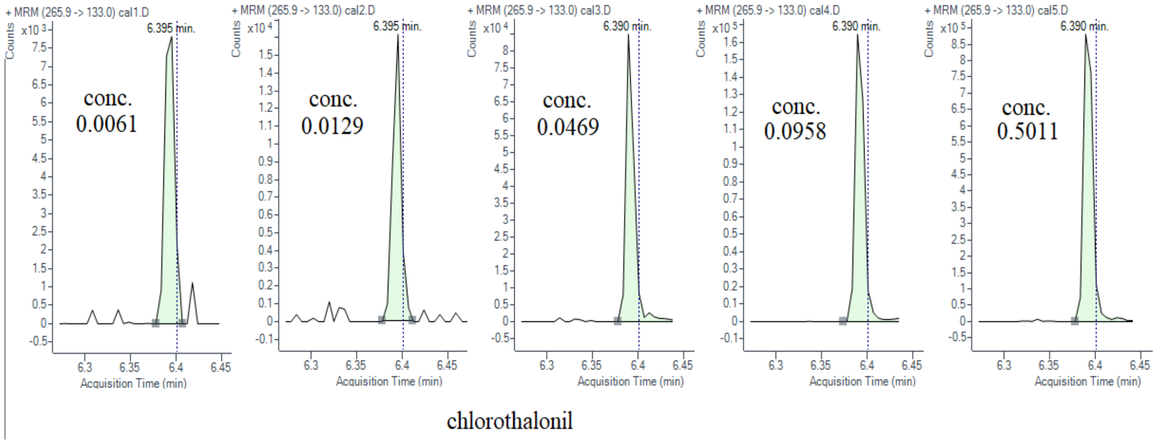

Fig 1. Chromatograms of different standard concentrations of chlorothalonil pesticide analyzed by GC- MS/MS

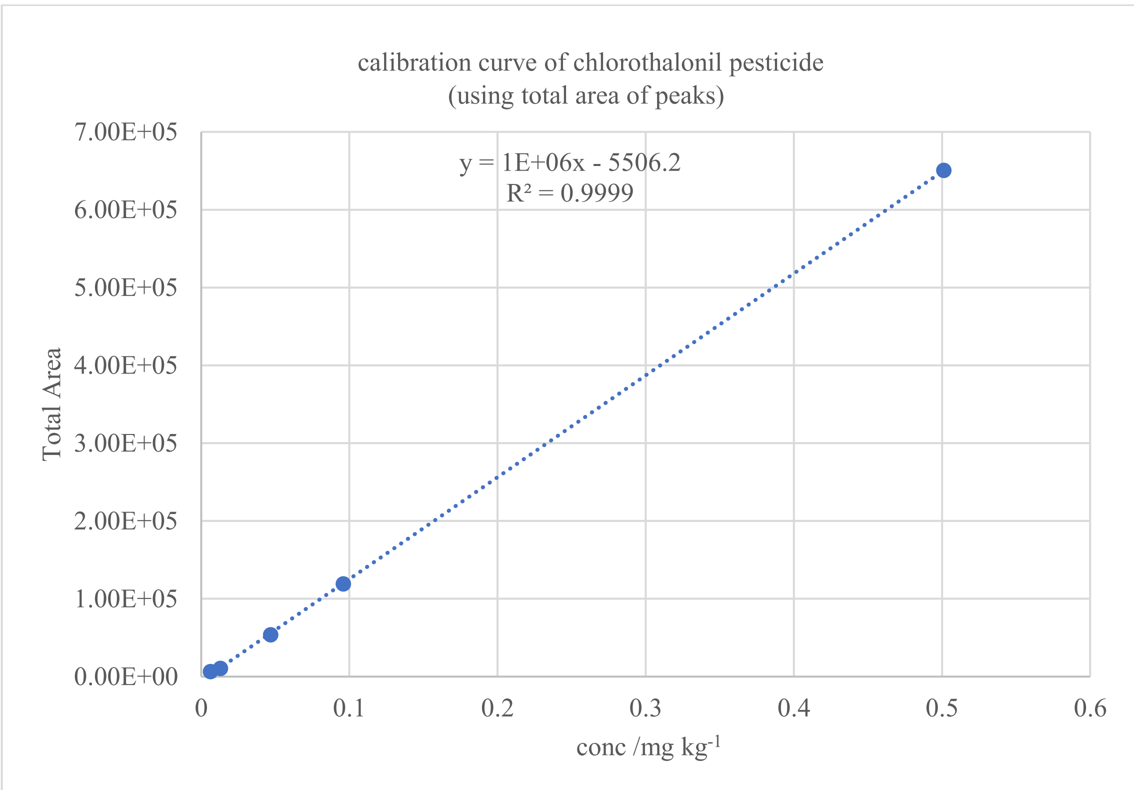

Fig 2. Standard calibration curve of chlorothalonil pesticide determined by GC- MS/MS.

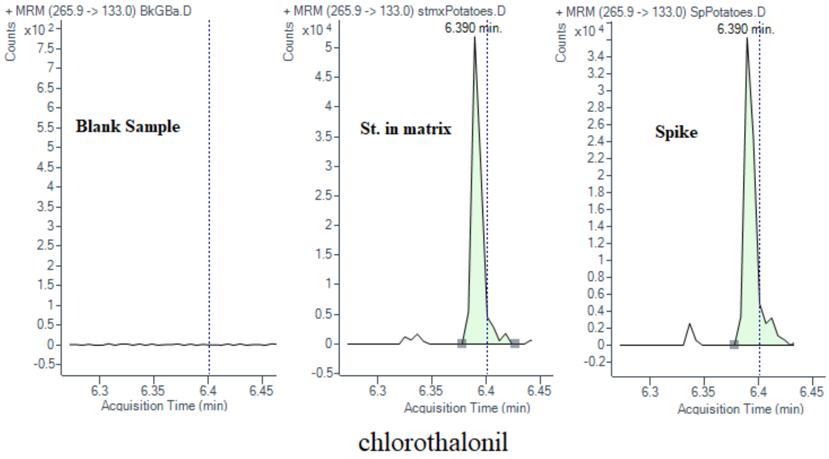

Fig 3. Chromatograms of blank sample and chlorothalonil (standard solution and spiked sample) determined by GC-MS/MS

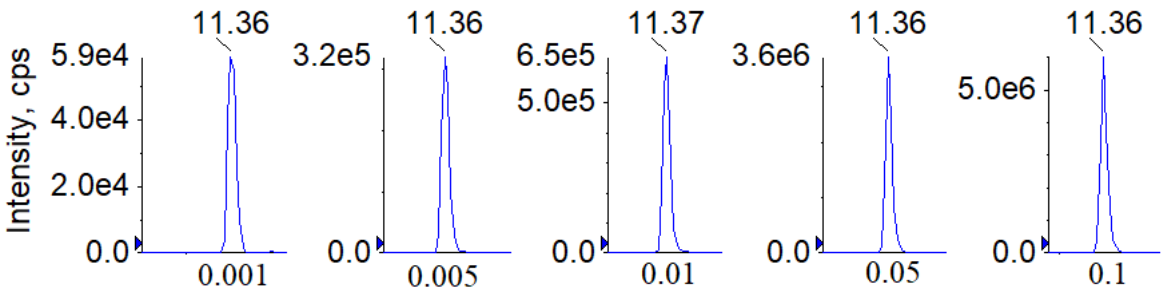

Fig 4. Chromatograms of different standard concentrations of emamectin pesticide analyzed by LC-MS/MS

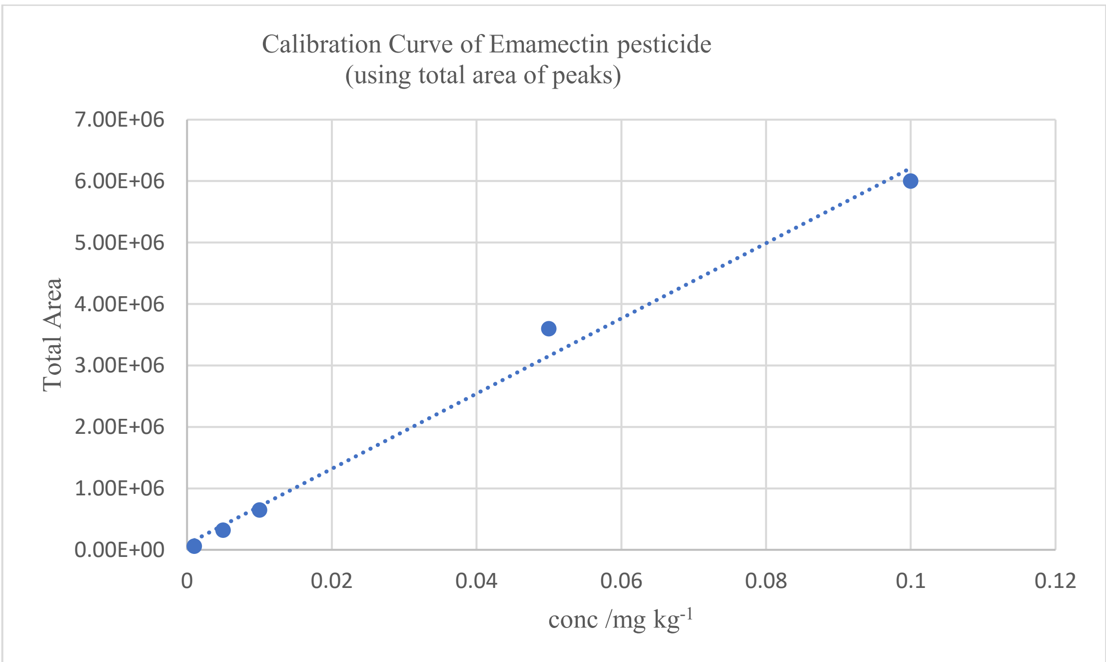

Fig 5. Standard calibration curve of emamectin pesticide determined by LC-MS/MS

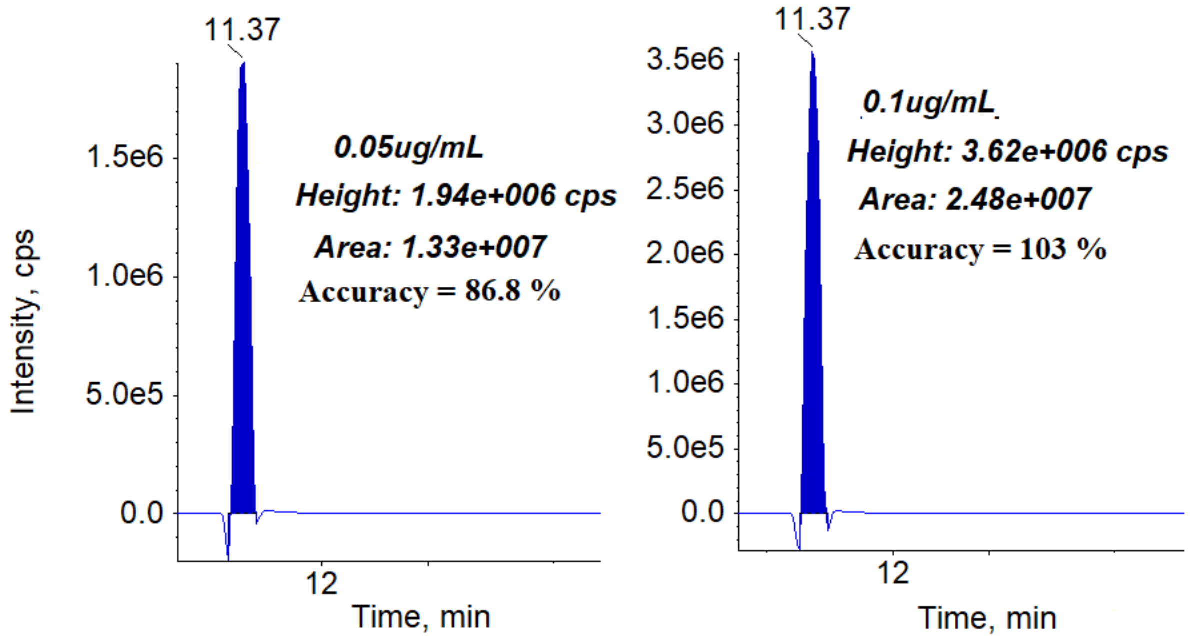

Fig 6. The accuracy of emamectin pesticide (0.05 and 0.1 ug ml^{-1}) determined by LC-MSLMS

Table 2. ESTI and EDI (mg kg^{-1}/day) for pesticide residues detected in potato tubers

Pesticides	ESTI	EDI
Chlorothalonil[1]	0.008000	0.003920
Chlorpropham[1]	0.027257	0.007888
Chlorpyrifos[1]	0.000029	0.000014
Difenoconazole[1]	0.000029	0.000014
Emamectin[1]	0.000031	0.000015
Imidacloprid[1]	0.000040	0.000020
Pencycuron[1]	0.000083	0.000041
Chlorpropham[2]	0.027943	0.004595
Chlorpyrifos[2]	0.000029	0.000014
Metalaxyl[2]	0.000029	0.000014

[1] and [2] Pesticides detected in Cairo and Giza governorates, respectively

Table 3 presents the evaluation of acute and chronic risks associated with pesticide residues found in potatoes at varying concentrations, using consumption rates of 0.2 kg/day and 0.1 kg/day for acute and chronic exposure, respectively, across all analyzed samples. The lowest recorded percentages of ARfD and ADI for all detected pesticides in potatoes were 0.01-90.86 and 0.03-20.76 in Cairo, and 0.06-93.14 and 0.02-9.19% in Giza. Therefore, the information gathered about acute and/or chronic risks was significantly below 100%, indicating that consuming potatoes did not pose a health risk.

Table 3. Acute (%ARfD), chronic (%ADI) and health risk (HR) associated with the consumption of potatoes

Pesticides	ARfD	% ARfD	ADI	% ADI	HR
Chlorothalonil[1]	0.6	1.33	2.8	0.14	N
Chlorpropham[1]	0.03	90.86	0.038	20.76	N
Chlorpyrifos[1]	0.05	0.06	0.01	0.14	N
Difenoconazole[1]	0.3	0.01	0.01	0.14	N
Emamectin[1]	0.01	0.31	0.011	0.14	N
Imidacloprid[1]	0.8	0.01	0.06	0.03	N
Pencycuron[1]	Unnecessary	-	0.2	0.02	N
Chlorpropham[2]	0.03	93.14	0.05	9.19	N
Chlorpyrifos[2]	0.05	0.06	0.01	0.14	N
Metalaxyl[2]	0.5	0.06	0.08	0.02	N

[1] and [2] Pesticides detected in Cairo and Giza governorates, respectively, ARfD and ADI standard values (mg kg^{-1} bw) were obtained from the European Commission (EC) database and/or relevant international organization. An acute reference dose ARfD is considered unnecessary due to its low oral toxicity and the absence of any developmental toxicity after a single dose.
HR: Health Risk (Positive or Negative).

Numerous investigations have focused on pesticide residues in potatoes and the associated risks. For instance, Ibrahim and Shalaby (2023) examined the surveillance and cumulative risk of residues in commonly cultivated vegetables in the Eastern Nile Delta. The health risk values were below 100%, suggesting that the safety risk associated with exposure to individual pesticides was within acceptable limits. However, the cumulative risk index revealed an unacceptable risk to individuals, exceeding the individual health index due to pesticide toxicity index values surpassing 1.0 in some vegetables. Enhanced monitoring and regulation of vegetable pesticide residues are crucial for standardizing application and minimizing misuse. According to Ibrahim et al. (2022), carbendazim, cypermethrin, and chlorpyrifos were the most commonly identified pesticides in samples collected from various markets. Based on the estimated Health Index (HI), the risk evaluations for the samples that exceeded limits seemed to pose no significant health risks to consumers. However, pesticide residues should be routinely and widely monitored in other fresh produce and across different governorates.

Minuț et al (2020) found that the carbendazim residues in potatoes exceed their MRL (0.1 mg kg^{-1}), posing acute health risks, with ARfD percentages reaching 954.1% for children and 185.2% for adults. They also detected thiophanate methyl (1.377 mg kg^{-1}) exceeding the MRL of (0.1 mg kg^{-1}), posing significant acute health risks to children, with ARfD 105.9%. However, the study found that other pesticides present in the potatoes had ARfD values well below 100%, indicating no immediate threat to human health from these substances.

Reviewing the results mentioned above, we can conclude that the lowest values of (ARfD%) and (ADI%) were obtained from the most frequently detected individual pesticides in potatoes collected from Cairo and Giza governorates, ranging from 0.01-93.14% and 0.02-20.76%, respectively. Consequently, all the most commonly found pesticides had ARfD and ADI percentage values below 100%, indicating that exposure to individual pesticide residues is unlikely to lead to adverse health effects for consumers. Nonetheless, rigorous regulatory measures and systematic surveying of pesticide residues in food items must be prioritized to keep the detected pesticide levels and daily intake under the MRL and ADI values, thus ensuring the protection of public health. Additionally, pre-harvest interval values (PHI) for pesticides used and recommended on potatoes, especially those identified in this research, must be continually reviewed. To ensure consumer safety, potatoes exported to European markets should meet health risk (HR) standards, particularly given the relatively low regional food consumption estimates. It should be noted that the information available regarding chlorpropham on potatoes is limited since it is not registered for potato crops. However, EFSA (2017) estimated the ARfD and acute risk assessment for chlorpropham on potatoes, as it is used as a sprout growth inhibitor during the storage period.

4 Conclusion

The analytical methods used were effective for extraction and recovery (QuEChERS), as well as for identification and quantification (GC-MS/MS and LC-MS/MS) of various pesticide residues (organophosphates, neonicotinoids, conazoles, chloronitriles, carbamates, acylamino acids, and phenylureas) from potato tubers in two governorates. The amounts and types of pesticide residues detected in potato tubers varied based on the pesticide type and sampling location. Generally, most pesticides were found below the Maximum Residue Limit (MRL). Acute reference dose (ARfD) and Acceptable Daily Intake (ADI) were recorded for all detected pesticides. Furthermore, the Estimated Daily Intake (EDI) of pesticide residues for adult consumers indicated that the consumption of certain pesticide residues in potato tubers from the surveyed areas remains within permissible levels. Consequently, consuming potato tubers from the markets in these two governorates poses no significant health risks. The methods can be periodically and confidentially employed to ensure that different pesticide residues are within acceptable limits.

Acknowledgement

The authors thank the Central Laboratory of Residue Analysis of Pesticides & Heavy Metals in Food (QCAP), Ministry of Agriculture, for running the GC-MS/MS and LC-MS/MS analyses.

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