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Estimating the Multiple Pesticide Residues in Grapes and their Associated Health Risks for Egyptian Consumer

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Abstract

The research was conducted to apply a reliable analytical procedure for monitoring pesticides in fresh grapes by GC-MS/MS and LC-MS/MS systems. A total number of 466 pesticide residues in the 175 fresh grape samples gathered from different various markets across two Egyptian governorates (Cairo and Giza) through 2020 to 2021. In general, the average pesticide residue levels recorded in the targeted grape samples varied from 0.01 - 0.258 and 0.01 - 0.088 mg kg^{-1}, respectively. Data indicated that the detection of pesticide residues in Cairo and Giza samples is at higher levels than the Maximum Residue Levels (MRLs) and represents frequency percentages, ranging from 0.87 - 4.35% and 1.67 - 8.33%, respectively. The lowest percentage of acute risk (%ARfD) and chronic risk (%ADI) were recorded with all detected pesticides in grapes, ranged from 0.004 - 30 and 0.001 - 53.33 % in (Cairo) and from 0.006 - 7.5 and 0.011 - 16.67% in (Giza), respectively. Further data showed that all detected pesticides residues in/on grapes had no potential health risk individually, as their %ARfD and %ADI values were below (100%). Therefore, all identified pesticides were found to pose no potential health risk (HR) and/or hazard associated with human consumption of grapes from targeted markets in two governorates.

Keywords: Monitoring, Risk assessment, Pesticides residues, Grapes, Egypt.

1. Introduction

Grapes are a vital fruit crop with significant nutritional value, playing an important role in global trade, and are enjoyed in both fresh and processed forms [25]. It is regularly treated with large quantities of pesticides during the growing season to manage various pest species. Consequently, significant levels of harmful pesticide residues frequently persist on harvested grapes, which can eventually be consumed and gradually pose health risks.

Agricultural practices rely on pesticides to maintain abundant harvests by managing harmful insects, weeds, and plant pathogens. Since the mid-20th century, they have been extensively utilized across the globe due to their numerous advantages [26]. Various ailments and insect infestations affect fruits and vegetables, necessitating control measures since they serve as vital food sources for diverse populations [12]. A variety of pesticides are utilized to safeguard fruit and vegetable crops due to severe pest infestations [29]. Pesticides pose a threat to human health, as residual traces in vegetables and fruits may result in various illnesses [20].

Traces of pesticides can persist within fruits, vegetables, grains, and various other food products. The Environmental Protection Agency (EPA) establishes limits on allowable pesticide residues in food to safeguard the human food supply [4]. The presence of pesticide residues in the food we eat is strictly monitored. While some traces may still be present at harvest, they generally diminish over time as the pesticides degrade. Pesticide residues and its degradation or metabolites found in the food following application and their entry into the human diet is a significant concern today [1]. Hamed et al. in 2019 found the total of 55 pesticide specimens were obtained from local Egyptian markets, 31 (56.4%), of pesticide residues were identified in the grapes, and the 16.4% of detected pesticide residues were surpassed the MRL [19]

To safeguard public health, it is essential for regulators, producers, and consumers to have swift and dependable methods for identifying and measuring pesticide levels in both raw and processed foods [12]. Anastassiades et al. in 2003, were determined pesticides residues by QuEChERS method [3] and qualitative and quantitative analyzed with done by LC-MS and/or GC-MS [18,22]

The evaluation of pesticide-related health hazards relies on the overall concentration of pesticide residues observed in analyzed samples, measured against the standard acceptable daily intake (ADI) for specific pesticides. Residues exceeding maximum limit (MRL) in raw vegetables and fruits have been demonstrated to present possible health hazards to humans. Health risks were assessed in fruit and vegetable samples with pesticide residues, revealing that consumers may face health threats if the tolerable daily intake (%ADI) or acute reference dose (%ARfD) exceed 100% [13].

Therefore, the presence of pesticide residues on grape fruits poses significant health risks to consumers. Hence, monitoring residue levels should be regularly undertaken by relevant national authorities before the export or import of strawberries. In

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this research, this study sought to determine pesticide residues in grapes sourced from various markets in Cairo and Giza governorates, Egypt, during the period from 2020 to 2021.

2. Material and Methods

2.1 Pesticide Standards and Chemicals

Reference standards for pesticides were >98% purity and purchased from Augsburg, Germany (Dr. Ehrenstorfer GmbH). Standard solution Stocks were prepared in suitable solvents according to their polarity and solubility. A standard solution for each pesticide was created with a concentration of 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}, appropriate aliquots of 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 generated utilizing the Milli-Q water purification system, a product of Millipore.

2.2 Sampling

Altogether, 175 fresh grape samples, one kilogram each were gathered from commercial Egyptian markets at Cairo (115) and Giza (60) governorate during 2020-2021. The specimens were contained in sterile polyethylene bags and delivered to the laboratory using an ice chest. Following this, they were thoroughly blended and cut into small pieces utilizing a high-speed electrical blender [11]. 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, a total of 466 pesticide residues were successfully extracted and purified [3,21]. Qualitative and quantitative determination were done by gas chromatography-GC-MS/MS or high-performance liquid chromatography HPLC-MS/MS. Approximately 10 homogenized grams of grape samples were Transferred to a 50 mL polypropylene tube. After that, 0.1% acidified acetonitrile/MeCN (10 mL) was introduced, and the tube was vortexed for 3 min/4500 rpm. One gram of NaCl and four grams (anhydrous $MgSO_4$) were then introduced, and the tube was vortexed right away for one minute. After 30 seconds of mixing with 50 µL of Triphenyl Phosphate/TPP as internal standard solution, the extracts underwent 10-minute centrifugation at 4500 rpm. About 1 mL of the acetonitrile layer (MeCN) was placed in a 15 mL polypropylene tube that held 150 mg of anhydrous $MgSO_4$ and 25 mg of PSA (primary secondary amine) sorbent. After securing the tube's cap, it was manually shaken for five minutes. Five minutes were spent centrifuging the samples. A portion of the sample was passed through a (0.45 µm PTFE filter) and then placed into vials, ready for injection into (GC-MS/MS and/or HPLC-MS/MS) instruments directly.

2.4 Instrumentation

2.4.1 Gas Chromatography Tandem Mass Spectrometry System

At central laboratory of residue analysis of pesticides and heavy metals in food (QCAP), 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) (65% dimethylpolysiloxane-35% Phenyl) with a 30 m length × 0.25 µm film thickness × 0.18 mm i.d. was employed to achieve pesticide chromatographic separation. After 1.3 minutes at 70°C, the oven temperature program ramped up to 150 at 70°C per minute, then up to 270 at 12°C per minute, and lastly up to 310 at 18°C per minute, which was maintained for 6.3 minutes. The entire process lasted 21 minutes. The injection volume attained 1 µL, injected through splitless mode, and the temperature of inlet was 250°C. More than 99.999 percent pure helium gas was used at a steady flow rate of 0.7 ml per minute and the colliding gas was nitrogen. The ion source was maintained at 320°C, while the temperature of quadrupole was kept at 180°C. Additionally, the GC-MS/MS interface was also held at 320°C, and the ionization energy used was 70 eV. The electron impact mode was employed. Data collection and analysis, as well as instrument control, were done using MassHunter software.

2.4.2 Liquid Chromatography Tandem Mass Spectrometry System

At the QCAP lab, an Agilent 1200 Series HPLC connected to an API (4500 tandem mass spectrometer) (SCIEX Triple Quad 4500 LC-MS/MS) was utilized. Separation was conducted using an Agilent column (C18) (ZORBAX Eclipse XDB) with a length of 150 mm in, an internal diameter of 4.6 mm, and 5.0 µm particle size. The column temperature was set at 40°C, while the injection volume was 5 µL. Gradient elution was used to separate the two components, solvent B: a mixture of MeOH: DIW (9:1, v/v) and solvent A: a mixture of DIW: MeOH (9:1, v/v) of (pH 3.78), utilizing ammonium formate. Starting with 100% of component A, the initial flow rate was 0.5 ml/min. Over the course of 6 min, it progressively changed to 5% A (95% B), and it remained constant at 0.3 ml/min for 17 min. Following this 23-minute period, a 2-minute post-run was conducted utilizing the original 100% of A at 0.5 milliliters per minute flow rate. The multiple reaction monitoring mode (MRM) with the positive ion mode Electrospray ionization (ESI) was utilized to perform the MS/MS analysis. Ion spray voltage of (5000 V), ion source gas of 2.40 psi, and ion source gas of 1.40 psi were utilized, along with curtain gas pressure of 25 psi, temperature of source 450°C, and collision gas/medium. Data collection and processing, as well as instrument control, were done using analyst software 1.6. MRM in positive (ESI) mode was used for all LC-MS/MS analyses.

2.5 Methods Validation

According to EC-European 2009 & 2013, the analytical technique (QuEChERS) was verified to determine the limits of quantity (LOQ) and rates of pesticide residues recovery [10,9]. The lowest analyte concentration that could be measured with a reasonable level of precision and accuracy was known as the (LOQ) and employed in assessing the method's sensitivity &

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 samples of potatoes (2.0 g) were spiked by adding the proper amounts of the pesticide standard mixture solutions at different concentrations spanning 0.01 to 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 EC-European 2020 recoveries that are acceptable should be ranging between 70 - 120 percent [7].

The developed analytical method and instruments were validated for the pesticides analysis in grapes according to EC-European 2017 [8]. To assess the extraction effectiveness, both the control and fortified samples were analyzed employing the analytical technique described earlier. The chosen pesticides' average recoveries in potato samples varied between 70 - 120 percent. RSD (Relative standard deviation) for repeatability was less than 20%, and LOQ spanning 0.01 to 0.05 mg kg^{-1}.

2.6 Estimation of Consumer Daily Intake of Grapes and Health Risk Assessment

Acute reference dose percentage, which was utilized to determine the potato acute risks [6,12] in grapes, tolerable or intolerable risks depend on the computed %ARfD. The acute risk is deemed tolerable if the %ARfD is <100%, but inappropriate when %ARfD is ≥100%. Therefore, lower risk corresponds to smaller %ARfD values, as determined by equations (1) and (2):

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

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

where ESTI is the estimated short-term intake (mg kg^{-1} day), HFC is the highest amount of food consumption by youth individuals in a day (kg), HRC is the highest residual concentration measured for a pesticide (mg kg^{-1}) and b.wt. is the body wight.

To determine the risk linked to chronic dietary intake for each pesticide residue in grape samples, the acceptable daily intake percentage (%ADI) [4,10] was utilized. Equations (3) and (4) were used to calculate acceptable daily intake (%ADI):

$$EDI = (AFC \times APR)/b.wt. \quad (3)$$

$$\%ADI = (EDI \times 100)/ADI \quad (4)$$

where EDI is the estimated daily intake (mg kg^{-1} day), AFC is the average daily food consumption (kg), APR is average pesticide residue (mg kg^{-1}), b.wt. is the body wight and ADI is the acceptable daily intake (mg kg^{-1} day).

The Estimated Daily Intake (EDI) of each violated pesticide residue (mg/kg body weight/day) was calculated by multiplying the mean pesticide residue concentration (mg/kg) in consumed food by the daily intake and then dividing the result by the standard adult body weight of 70 kg, as specified in equation 3. According to GEMS/FOODS from the WHO's Global Environment Monitoring System [28] and Food and Agriculture Organization [17], acceptable daily intake was determined.

The consumer health risk associated with pesticide-contaminated samples was assessed employing %ADI. The chronic risk was deemed tolerable or inappropriate by utilizing the health risk index. It is determined by dividing the EDI by the corresponding ADI values (mg/kg body weight) determined by WHO/FAO, as demonstrated in Equation 4. As stated by the European Food Safety Authority [14,15], a food item is deemed safe for consumption if the ADI% remains below 100%. However, if it exceeds this threshold, it poses a potential health hazard (HR) to consumers [16].

The evaluation of acute and chronic risks from pesticide residues in grapes was conducted based on two consumption rates: 0.1 kg per day for chronic risk and 0.2 kg per day for acute risk, applicable to all analyzed samples [12]. In addition, the daily consumption rate of strawberries was appreciated by adult consumers of average weight 70 kg [27,4].

3. Results and Discussion

3.1 Pesticide Residues in Grapes Surveyed at Different Local Markets of Cairo and Giza governorates, Egypt during 2020 to 2021

To enhance crop yield and quality, pesticides are applied to fruits and vegetables. However, if these chemicals do not break down naturally, traces may remain in the produce. This research focused on assessing pesticide residues present in commercially available grapes and evaluating the potential dietary risks associated with their consumption.

Market monitoring program was planned to detect the presence or absence of pesticide residues in different samples of grapes gathered from multiple markets across Cairo and Giza governorates, Egypt during 2020 to 2021.

Pesticides residues were determined by QuEChERS method and qualitative and quantitative analyzed with done by GC-MS and/or LC-MS. This method was first published in 2003 and later amended to the present procedure to broaden the analyte and matrix spectrum. The outcomes demonstrated that the mean recoveries of the pesticide residues obtained from experiments (spiking levels 0.01 mg kg^{-1} to 0.25 mg kg^{-1}) were usually between 70 % and 110 %. The limits of quantification (LOQ) of pesticide residues for the approach spanned from 0.01 to 0.05 mg kg^{-1}.

Examination of the obtained data revealed that contamination surveyed grape samples at different levels of various pesticide residues depending on pesticide type and market location. To facilitate the presentation of data, each governorate will be dealt with separately as follows:

3.1.1 Residues of Pesticides in Grapes at Cairo Governorate

The one hundred and fifteen grape samples were selected for pesticide residue monitoring and the findings are tabulated in Table (1). The results indicated the residue levels of the identified pesticides, which belong to various chemical and functional groups in grape samples that were collected from different markets of Cairo, Egypt. These results indicated the detection of 36 pesticide residues namely, acetamiprid, boscalid, carbendazim, carbosulfan, chlorpropham, chlorpyrifos, cyflufenamide, cyfluthrin, cypermethrin, cyprodinil, deltamethrin, difenoconazole, dimethoate, fenhexamid, fenpyroximate, fludioxonil, imidacloprid, indoxacarb, kresoxim-methyl, lambada-cyhalothrin, lufenuron, methomyl, myclobutanil, omethoate, oxamyl, penconazole, profenofos, propiconazole, proquinazid, prothioconazole, pyraclostrobin, pyriproxyfen, spirotetramate, thiacloprid, thiamethoxam and thiophanate-methyl. These pesticides were detected in grape samples from different Cairo markets at various average values that ranged from 0.01 - 0.258 mg kg^{-1}.

Table 1: Pesticide residues (mg kg^{-1}) in grape samples at Cairo governorate

Pesticides Detected / Statues of Registration	Residues (Average)	Frequency of (+) Samples %	Frequency of (-) Samples%	Frequency of (+) Samples Exceeded MRL %	MRLs (mg/kg) Codex / EC
Acetamiprid / U	0.049 (0.012-0.152)	5.22	94.78		0.5/0.5
Boscalid / R	0.059 (0.01-0.137)	6.96	93.04	0.00	5/ 5
Carbendazim / U	0.078 (0.012-0.592)	6.09	93.91		3 /0.3
Carbosulfan / U	0.02*	0.87	99.13	0.87	- /0.002
Chlorpropham / U	0.01	0.87	99.13	0.00	- /0.01
Chlorpyrifos / U	0.013* (0.012-0.026)	4.35	95.65	4.35	- /0.01
Cyflufenamid / R	0.01	0.87	99.13	0.00	- /0.2
Cyfluthrin / U	0.043* (0.019-0.078)	3.48	96.52	4.35	- /0.01
Cypermethrin / U	0.048 (0.01-0.102)	4.35	95.65		0.2/0.5
Cyprodinil / R	0.258 (0.073-0.444)	1.74	98.26	0.00	3 /3
Deltamethrin / U	0.035	0.87	99.13		0.2/0.2
Difenoconazole / R	0.01	0.87	99.13		3/3
Dimethoate / U	0.255* (0.01-0.85)	3.48	96.52	2.61	- /0.01
Fenhexamid / R	0.067 (0.042-0.092)	1.74	98.26		15/ 15
Fenpyroximate / R	0.01	0.87	99.13		0.3 /0.3
Fludioxonil / R	0.017 (0.034-0.18)	1.74	98.26	0.00	2 / 5
Imidacloprid / U	0.164 (0.029-0.82)	9.57	90.43		1 /0.7
Indoxacarb / R	0.028* (0.01-0.047)	1.74	98.26	1.74	2 /0.01
Kresoxim-methyl / R	0.01	0.87	99.13	0.00	1.5 /1.5
Lambada-Cyhalothrin / U	0.032 (0.01-0.089)	5.22	94.78		0.3 /0.08
Lufenuron / R	0.023*	0.87	99.13	0.87	- /0.01
Methomyl / U	0.214 (0.02-0.347)	2.61	97.39	2.61	0.3 /0.01
Myclobutanil / R	0.065 (0.014-0.12)	4.35	95.65	0.00	0.9/1.5
Omethoate / U	0.112* (0.027-0.2)	3.48	96.52	3.48	- /0.01
Oxamyl / R	0.01	1.74	98.26	0.00	- /0. 01
Penconazole / R	0.079 (0.021-0.194)	2.61	97.39		0.4 /0.5
Profenofos / U	0.023* (0.013-0.036)	2.61	97.39	2.61	- /0.01
Propiconazole / R	0.102* (0.034-0.17)	1.74	98.26	1.739	- /0.01
Proquinazid / R	0.015	0.87	99.13	0.00	- /0.5

Prothioconazole / U	0.16	0.87	99.13		- /0.01
Pyraclostrobin / R	0.015 (0.01-0.024)	5.22	94.78		2/0.3
Pyriproxyfen / U	0.03 (0.025-0.035)	1.74	98.26		- /0.05
Spirotetramate / R	0.014	0.87	99.13		2/-
Thiacloprid / U	0.065* (0.019-0.136)	2.61	97.39	2.608	- /0.01
Thiamethoxam / U	0.014	0.87	99.13	0.00	- /0.4
Thiophanate-methyl/R	0.23* (0.014-0.756)	5.22	94.78	0.88	- /0.1

R: Registered, **U**: Un Registered**, -**: Not allocated, Values between brackets represent minimum and maximum residues. *: Limits above MRL recorded by European Commission (EC-MRLs) [9].

In addition, data showed frequency of positive samples percent ranged from 0.87 - 6.96%, and corresponding frequencies of negative samples percent ranged from 93.04 - 99.13% in grape samples gathered from different regional markets of Cairo governorate, Egypt.

On the other hand, the results in the same table indicated the detection of nine pesticide residues namely, carbosulfan, chlorpyrifos, cyfluthrin, dimethoate, omethoate, profenofos, propiconazole, thiacloprid and Thiophanate-methyl were found at levels higher than the MRL established by European Commission (EC) [9], and not allocated by Codex Alimentarius Committee (FAO-WHO) and representing the frequencies samples exceeded MRL,s percentages, ranged from 0.87 - 4.35%.

It is worth noting that 18 of the detected pesticide residues (boscalid, cyflufenamide, cyprodinil, difenoconazole, fenhexamid, fenpyroximate, fludioxonil, indoxacarb, kresoxim-methyl, lufenuron, myclobutanil, oxamyl, penconazole, propiconazol, proquinazid, pyraclostrobin, spirotetramate and thiophanate-methyl) on grape fruits collected from Cairo Governorate were registered by European Commission (EC) and recommended by Approved Recommendations for Control Agricultural Pests - Ministry of Agriculture and Land Reclamation, Egypt, 2023, representing 50%, while 50% of the other detected pesticides (acetamiprid, carbendazim, carbosulfan, chlorpropham, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, dimethoate, imidacloprid, lambada-cyhalothrin, methomyl, omethoate, profenofos, prothioconazole, pyriproxyfen, thiacloprid and thiamethoxam) were not registered and/or recommended in grape crop in Egypt.

3.1.2 Residues of Pesticides in Grapes at Giza Governorate

The sixty grape samples were selected for pesticide residue monitoring and the findings are tabulated in **Table (2)**. From the results it can report that, the existence of pesticide residues which belong to different chemical and functional groups in grape samples, which collected from different markets of Giza, Egypt at various levels. These results indicated the detection of 29 pesticide residues namely, acetamiprid, boscalid, carbendazim, chlorpyrifos, cyfluthrin, cypermethrin, cyprodinil, dimethoate, diniconazole, fenhexamid, fludioxonil, imidacloprid, lambda-cyhalothrin, metalaxyl, methoxyfenozide, metrafenon, myclobutanil, omethoate, profenofos, propamocarb, propiconazole, prothioconazole, pyraclostrobin, pyridaben, spirotetramate, sulfoxaflor tetraconazole, thiacloprid and triadimenol in grape samples from different Cairo markets at various average values, spanned from 0.01 to 0.088 mg Kg^{-1}.

Table 2: Pesticide residues (mg kg^{-1}) in grape samples at Giza governorate

Pesticides Detected / Statues of Registration	Residues (Average)	Frequency of (+) Samples %	Frequency of (-) Samples %	Frequency of (+) Samples Exceeded MRL %	MRLs (mg/kg) Codex / EC
Acetamiprid / U	0.088 (0.015-0.161)	3.33	96.67		0.5/0.5
Boscalid / R	0.023 (0.01-0.04)	6.67	93.33	0.00	5/ 5
Carbendazim / U	0.067 (0.01-0.141)	5	95		3 /0.3
Chlorpyrifos / U	0.0125* (0.012-0.013)	3.33	96.67	3.33	- /0.01
Cyfluthrin / U	0.012* (0.01-0.014)	5	95	3.33	- /0.01
Cypermethrin / U	0.051 (0.029-0.073)	3.33	96.67	0.00	0.2/0.5
Cyprodinil / R	0.039	1.666	98.33		3 /3
Dimethoate / U	0.033* (0.01-0.055)	3.333	96.67	1.67	- /0.01
Diniconazole / U	0.01	1.67	98.33	0.00	- / 0.01
Fenhexamid / R	0.11	1.67	98.33		15/ 15

Fludioxonil / R	0.025	1.67	98.33		2 / 5
Imidacloprid / U	0.0396 (0.01-0.19)	13.33	86.67		1 /0.7
Lambda-Cyhalothrin / U	0.032 (0.01-0.06)	6.67	93.33		0.3 /0.08
Metalaxyl / R	0.01	1.67	98.33		1.5/2
Methoxyfenozide / R	0.03 (0.01-0.49)	3.33	96.67		1/1
Metrafenone / R	0.02	1.67	98.33		5/7
Myclobutanil / R	0.028 (0.014-0.044)	5	95		0.9/1.5
Omethoate / U	0.0359* (0.021-0.051)	3.33	96.67	3.33	- /0.01
Profenofos / U	0.024*	1.67	98.33	1.67	- /0.01
Propamocarb / R	0.071*	1.67	98.33	1.67	- /0.01
Propiconazole / R	0.057* (0.021-0.1)	8.33	91.67	8.33	- /0.01
Prothioconazole / U	0.017*	1.67	98.33	1.67	- /0.01
Pyraclostrobin / R	0.01	3.33	96.67	0.00	2/0.3
Pyridaben / R	0.011	1.67	98.33	0.00	-/0.01
Spirotetramate / R	0.03	1.67	98.33		2/-
Sulfoxaflor / R	0.016	1.67	98.33		2/2
Tetraconazole / R	0.01	1.67	98.33		- /0.07
Thiacloprid / U	0.088*	1.67	98.33	1.67	- /0.01
Triadimenol / R	0.015 (0.013-0.016)	3.33	96.67	3.33	0.3/0.01

R: Registered, **U**: Un Registered**, -**: Not allocated, Values between brackets represent minimum and maximum residues. *: Limits above MRL recorded by European Commission (EC-MRLs).

In addition, data showed frequency of positive samples percent ranged from 1.67 - 13.33%, and corresponding frequencies of negative samples percent ranged from 86.67 - 98.33% in grape samples gathered from different regional markets of Giza governorate, Egypt.

On the other hand, the results in the same table indicated the detection of nine pesticide residues namely, chlorpyrifos, cyfluthrin, dimethoate, omethoate, profenofos, propamocarb, propiconazole, prothioconazole and triadimenol were found at levels higher than the MRL,s established by European Commission (EC), and not allocated by Codex Alimentarius Committee (FAO-WHO) and representing the frequencies samples exceeded MRL percentages, ranged from 1.67 - 8.33%.

It is worth noting that 14 of the detected pesticide residues (boscalid, cyprodinil, fenhexamid, fludioxonil, metalaxyl, methoxyfenozide, metrafenon, myclobutanil, propamocarb, propiconazole, pyraclostrobin, spirotetramate, sulfoxaflor and triadimenol) on grape fruits collected from Cairo governorate were registered by European Commission (EC) and recommended by Approved Recommendations for Control Agricultural Pests - Ministry of Agriculture and Land Reclamation, Egypt, 2023, representing 48.28%, while 51.72% of the other detected pesticides (acetamiprid, carbendazim, chlorpyrifos, cyfluthrin, cypermethrin, dimethoate, diniconazole, imidacloprid, lambda-cyhalothrin, omethoate, profenofos, prothioconazole, pyridaben, tetraconazole and thiacloprid) were not registered and/or recommended in grape crop in Egypt.

Our findings may be attributed to the misuse of pesticides (types and quantities) without any consideration of the pre-harvest interval (PHI) established for vegetables and fruits. Thus, violating all known official recommendations creates a very critical situation. The overuse of pesticides in Egypt suggests a departure from Good Agricultural Practice (GAP), indicating that the pre-harvest interval (PHI) is not adhered to, or the pesticide application rate and concentration do not align with GAP guidelines [2]. The data highlights an urgent necessity to implement the GAP and official guidelines for authorized pesticides. This can be accomplished by training and certifying farmers and applicators, particularly for the use of high-risk pesticides [2].

Such finding is an agreement with that obtained by several investigators, i.e., El-Sheikh et al. 2022 reported that, grape samples gathered from the Governorate of Sharkia (farmer markets), Egypt were recorded 18 pesticide residues, namely, acetamprid, boscalid, carbendazim, chlorfenapyr, chlorpyrifos, cypermethrin, deltamethrin, dimethoate, imidacloprid, lambda-cyhalothrin, myclobutanil, omethoate, permethrin, pyraclostrobin, pyriproxyfen, thiacloprid, thiamethoxam and thiophanate methyl, and represents mean concentrations of 0.016, 0.037, 0.277, 0.1, 0.021, 0.03, 0.014, 0.073, 0.094, 0.01, 0.02, 0.028, 0.014, 0.019, 0.01, 0.167, 0.054 and 0.368 mg kg^{-1}, respectively [12].

3.2 Consumer Health Risk Assessment of Grapes Based on Dietary Intake

As for estimated daily intake (EDI) of pesticides residues (acetamiprid, boscalid, carbendazim, carbosulfan, chlorpropham, chlorpyrifos, cyflufenamide, cyfluthrin, cypermethrin, cyprodinil, deltamethrin, difenoconazole, dimethoate, fenhexamid, fenpyroximate, fludioxonil, imidacloprid, indoxacarb, kresoxim-methyl, lambada-cyhalothrin, lufenuron, methomyl, myclobutanil, omethoate, oxamyl, penconazole, profenofos, propiconazol, proquinazid, prothioconazole, pyraclostrobin, pyriproxyfen, spirotetramate, thiacloprid, thiamethoxam and thiophanate-methyl), data indicated that, the EDI spanned from 1×10^{-5} - 3.7×10^{-4} mg kg^{-1}/Person at Cairo governorate. On the other hand, the EDI for detected pesticides residues (acetamiprid, boscalid, carbendazim, chlorpyrifos, cyfluthrin, cypermethrin, cyprodinil, dimethoate, diniconazole, fenhexamid, fludioxonil, imidacloprid, lambda-cyhalothrin, metalaxyl, methoxyfenozide, metrafenon, myclobutanil, omethoate, profenofos, propamocarb, propiconazole, prothioconazole, pyraclostrobin, pyridaben, spirotetramate, sulfoxaflor, tetraconazole, thiacloprid and Triadimenol) at Giza governorate spanned from 1 x 10^{-5} - 2 x 10^{-4} mg Kg^{-1}/Person, Table (3). Therefore, the intake of grape samples by an average adult consumer (70 kg average weight) is expected to be permissible levels of acceptable daily intake (ADI) for detected pesticide residues at two targeted governorates.

Table 3: ESTI and EDI (mg kg^{-1} day) for pesticide residues identified in grape samples at Cairo and Giza governorate

Pesticides	Cairo		Giza	
	ESTI	EDI	ESTI	EDI
Acetamiprid	4.3×10^{-4}	7×10^{-5}	4.6×10^{-4}	1.3×10^{-4}
Boscalid	4×10^{-4}	8×10^{-5}	1.1×10^{-4}	3×10^{-5}
Carbendazim	1.7×10^{-3}	1.1×10^{-4}	4×10^{-4}	1×10^{-4}
Carbosulfan	6×10^{-5}	3×10^{-5}	ND	
Chlorpropham	3×10^{-5}	1×10^{-5}		
Chlorpyrifos	7×10^{-5}	2×10^{-5}	4×10^{-5}	2×10^{-5}
Cyflufenamide	3×10^{-5}	1×10^{-5}	ND	
Cyfluthrin	2.2×10^{-4}	6×10^{-5}	4×10^{-5}	2×10^{-5}
Cypermethrin	3×10^{-4}	7×10^{-5}	2.1×10^{-4}	7×10^{-5}
Cyprodinil	1.27×10^{-3}	3.7×10^{-4}	1.1×10^{-4}	6×10^{-5}
Deltamethrin	1×10^{-4}	5×10^{-5}	ND	
Difenoconazole	3×10^{-5}	1×10^{-5}		
Dimethoate	2.43×10^{-3}	3.6×10^{-4}	1.6×10^{-4}	5×10^{-5}
Diniconazole	ND		3×10^{-5}	1×10^{-5}
Fenhexamid	2.6×10^{-4}	1×10^{-4}	3.1×10^{-4}	2×10^{-4}
Fenpyroximate	3×10^{-5}	1×10^{-5}	ND	
Fludioxonil	5×10^{-4}	2×10^{-5}	7×10^{-5}	4×10^{-5}
Imidacloprid	2.3×10^{-3}	2.3×10^{-4}	5.4×10^{-4}	6×10^{-5}
Indoxacarb	1.3×10^{-4}	4×10^{-5}	ND	
Kresoxim-methyl	3×10^{-5}	1×10^{-5}		
Lambada-Cyhalothrin	2.5×10^{-4}	5×10^{-5}	1.4×10^{-4}	5×10^{-5}
Lufenuron	7×10^{-5}	3×10^{-5}	ND	
Metalaxyl	ND		3×10^{-5}	1×10^{-5}
Methomyl	1×10^{-3}	3.1×10^{-4}	ND	
Methoxyfenozide	ND		1.4×10^{-3}	4×10^{-5}
Metrafenon			6×10^{-5}	3×10^{-5}
Myclobutanil	3.4×10^{-4}	9×10^{-5}	1.3×10^{-4}	4×10^{-5}
Omethoate	5.7×10^{-4}	1.6×10^{-4}	1.5×10^{-4}	5×10^{-5}
Oxamyl	3×10^{-5}	1×10^{-5}	ND	
Penconazole	5.5×10^{-4}	1×10^{-4}		
Profenofos	1×10^{-4}	3×10^{-5}	7×10^{-5}	3×10^{-5}
Propamocarb	ND		2×10^{-4}	1×10^{-4}
Propiconazol	4.9×10^{-4}	1.5×10^{-4}	3×10^{-4}	8×10^{-5}
Prothioconazole	4.6×10^{-4}	2.3×10^{-4}	5×10^{-5}	2×10^{-5}
Proquinazid	4×10^{-5}	2×10^{-5}	ND	
Pyraclostrobin	7×10^{-5}	2×10^{-5}	3×10^{-5}	1×10^{-5}
Pyridaben	ND		3×10^{-5}	2×10^{-5}
Pyriproxyfen	1×10^{-4}	4×10^{-5}	ND	
Spirotetramate	4×10^{-5}	2×10^{-5}	9×10^{-5}	4×10^{-5}
Sulfoxaflor	ND		5×10^{-5}	2×10^{-5}
Tetraconazole			3×10^{-5}	1×10^{-5}
Thiacloprid	3.9×10^{-4}	9×10^{-5}	2.5×10^{-4}	1.3×10^{-4}
Thiamethoxam	4×10^{-5}	2×10^{-5}	ND	
Thiophanate-methyl	2.2×10^{-3}	3.3×10^{-4}		
Triadimenol	ND		5×10^{-5}	2×10^{-5}

ND: Not Detected under Limit of Detection (0.001 ppm).

The results presented in **Tables (4 and 5)** demonstrate the evaluation of the acute and chronic risks of pesticide residues identified in grapes at various levels, and by utilizing two rates of consumption (0.2 kg day^{-1} for acute risk and 0.1 kg day^{-1} for chronic risk) for all the targeted samples. The lowest percentage of acute risk (%ARfD) and chronic risk (%ADI) were recorded with all detected pesticides in grape samples, ranged from 0.004 - 30 and 0.001 - 53.33% (Cairo) and from 0.006 - 7.5 and 0.011 - 16.67% (Giza), respectively. Therefore, all the data gathered of acute and/or chronic risks were much less than 100%, which displayed no health risks (HR) when ingesting the grape samples.

Table 4: Acute (%ARfD), chronic (%ADI) and health risk (HR) connected to the consumption of grapes contaminated with pesticides (Cairo markets)

Pesticides	ARfD *	%ARfD	ADI *	%ADI	HR
Acetamiprid	0.025	1.72	0.07	0.1	N
Boscalid	Unnecessary	-	0.04	0.2	N
Carbendazim	0.02	8.5	0.03	0.37	N
Carbosulfan	0.02	0.3	0.01	0.3	N
Chlorpropham	0.5	0.006	0.05	0.02	N
Chlorpyrifos	0.05	0.14	0.01	0.2	N
Cyflufenamide	0.05	0.06	0.04	0.03	N
Cyfluthrin	0.04	0.55	0.04	0.15	N
Cypermethrin	0.001	30	0.02	0.35	N
Cyprodinil	Unnecessary	-	0.03	1.23	N
Deltamethrin	0.01	1	0.01	0.5	N
Difenoconazole	0.16	0.02	0.01	0.1	N
Dimethoate	0.02	12.15	0.001	36	N
Fenhexamid	Unnecessary	-	0.2	0.001	N
Fenpyroximate	0.02	0.15	0.005	0.2	N
Fludioxonil	Unnecessary	-	0.37	0.01	N
Imidacloprid	0.08	2.88	0.06	0.38	N
Indoxacarb	0.1	0.13	0.01	0.4	N
Kresoxim-methyl	Unnecessary	-	0.4	0.003	N
Lambada-Cyhalothrin	0.02	1.25	0.02	0.25	N
Lufenuron	Unnecessary	-	0.02	0.15	N
Methomyl	0.0025	40	0.02	1.55	N
Myclobutanil	0.31	0.11	0.025	0.36	N
Omethoate	0.002	28.5	0.0003	53.33	N
Oxamyl	0.0001	30	0.0001	10	N
Penconazole	0.5	0.11	0.03	0.33	N
Profenofos	1	0.01	0.03	0.1	N
Propiconazole	0.1	0.49	0.04	0.38	N
Proquinazid	0.2	0.02	0.01	0.2	N
Prothioconazole	0.01	4.6	0.01	2.3	N
Pyraclostrobin	0.03	0.23	0.03	0.07	N
Pyriproxyfen	Unnecessary	-	0.1	0.04	N
Spirotetramate	1	0.004	0.05	0.04	N
Thiacloprid	0.02	1.95	0.01	0.9	N
Thiamethoxam	0.5	0.008	0.026	0.08	N
Thiophanate-methyl	0.2	1.1	0.08	0.41	N

* ARfD and ADI standard values (mg kg^{-1} bw) were obtained from the European Commission (EC) database and/or relevant international organization. ARfD is deemed unnecessary because of its minimal oral toxicity and the absence of developmental toxicity subsequent a single dose [23,24]. HR: Health Risk (Positive or Negative).

Table 5: Acute (%ARfD), chronic (%ADI) and health risk (HR) connected to the consumption of grape contaminated with pesticides (Giza markets)

Pesticides	ARfD *	%ARfD	ADI *	%ADI	HR
Acetamiprid	0.025	1.84	0.07	0.186	N
Boscalid	Unnecessary	-	0.04	0.075	N
Carbendazim	0.02	2	0.03	0.333	N
Chlorpyrifos	0.02	0.2	0.01	0.2	N
Cyfluthrin	0.04	0.1	0.04	0.05	N
Cypermethrin	0.001	21	0.02	0.35	N
Cyprodinil	Unnecessary	-	0.03	0.2	N
Dimethoate	0.02	0.8	0.001	5	N
Diniconazole	0.3	0.01	0.02	0.05	N
Fenhexamid	Unnecessary	-	0.2	0.1	N
Fludioxonil	Unnecessary	-	0.37	0.011	N
Imidacloprid	0.08	0.68	0.06	0.1	N
Lambda-Cyhalothrin	0.02	0.85	0.02	0.25	N
Metalaxyl	0.5	0.006	0.08	0.013	N
Methoxyfenozide	0.1	1.4	0.1	0.04	N
Metrafenon	Unnecessary	-	0.025	0.12	N
Myclobutanil	0.31	0.042	0.025	0.16	N
Omethoate	0.002	7.5	0.0003	16.67	N

Profenofos	1	0.007	0.03	0.1	N
Propamocarb	1	0.02	0.29	0.034	N
Propiconazole	0.1	0.3	0.04	0.2	N
Prothioconazole	0.01	0.5	0.01	0.2	N
Pyraclostrobin	0.03	0.1	0.03	0.033	N
Pyridaben	0.05	0.06	0.01	0.2	N
Spirotetramate	1	0.009	0.05	0.08	N
Sulfoxaflor	0.25	0.02	0.04	0.05	N
Tetraconazole	0.05	0.06	0.004	0.25	N
Thiacloprid	0.02	1.25	0.01	1.3	N
Triadimenol	0.05	0.1	0.05	0.04	N

* ARfD and ADI standard values (mg kg^{-1} bw) were gathered from the European Commission (EC) database and/or relevant international organization. ARfD is deemed unnecessary because of its minimal oral toxicity and the absence of developmental toxicity subsequent a single dose. HR: Health Risk (Positive or Negative).

Reviewing the above-mentioned results, it can conclude that the lowest to moderate values of acute reference dose percentages (%ARfD) and acceptable daily intake percentages (%ADI) values were obtained with the most detected individual pesticides in grapes collected from different markets of Cairo and Giza governorates, ranged from 0.004 -30 and 0.001 - 53.33, respectively. Thus, the %ARfD and % ADI values of the most detected pesticides were below 100, suggesting no hazard of adverse impacts on consumers after intake to individual pesticides. In this respect, the lower to moderate %ARfD values were noticed of some detected pesticides like cypermethrin (30), methomyl (40), omethoate (28.5) and oxamyl (30) / Cairo markets and cypermethrin (21) / Giza markets. On the other hand, the lowest to moderate acceptable daily intake percentages (%ADI) were recorded of some detected pesticides like dimethoate (36), omethoate (53.33) and oxamyl (10) / Cairo markets and dimethoate (5) and omethoate (16.67) / Giza markets. Therefore, strict regulations and regular monitoring of pesticide residues in food are essential to ensure the protection of consumers' health. Thus, the levels of detected pesticides and the daily intake should be less than the MRL and ADI values for grapes in Egypt. Also, pre harvest intervals PHI values for pesticides utilized and recommended on grapes in Egypt, particularly those identified in this research, should be continually reviewed. The exported grapes to European nations should not present any health hazards (HR) to consumers due to the lower projected regional food intake levels.

In agreement with our results, [6] assessed the potential hazards of food contamination from 26 insecticides on strawberries. They discovered that, although there were elevated detection frequencies for these residues, the risks associated with both acute and chronic exposure remained below 100%. In this context, a study by [12] assessed the acute (%ARfD) and chronic (%ADI) risk of pesticide residues detected in grape samples gathered from Sharkia Governorate (farmer markets), Egypt. The research concentrated on samples surpassing the maximum residue limits, employing two consumption rates: 0.2 kg for acute risk and 0.1 kg for chronic risk. In this respect, risk assessment residues of carbendazim, chlorfenapyr, chlorpyrifos, dimethoate, omethoate, thiacloprid and thiophanate methyl pesticides were detected to have acute and chronic risks in consumers (60 Kg) of grapes, and represents (9.48 and 2031), (3.82 and 1.11), (0.8 and 0.34), (18 and 6.11), (7.33 and 2.33), (5 and 2.79) and (1.06 and 0.77) for %ARfD and %ADI respectively. The chronic risk is deemed acceptable if the ADI% is below 100%, indicating that the food is safe for consumption. However, if the ADI% exceeds 100%, the food is deemed a potential risk to the consumer [16]. In addition, [13] demonstrated that the risk assessment of omethoate, dimethoate, fipronil, and lambda-cyhalothrin residues in strawberry, kaki, zucchini, and spinach, correspondingly, can lead to both acute and chronic risks when ingested at daily rates of 0.1 and 0.2 kg. Hence, continuous surveillance of pesticide residues in vegetables and fruits in markets is essential for ensuring food safety and security. A study in India [25] found that the overuse of pesticides on grapes leads to negative health impacts in developing nations. Apples and grapes are contaminated with various types of pesticides, like organophosphates, which pose significant health hazards to consumers.

4. Conclusion

Various amounts and types of pesticide residues were identified in all grape samples gathered from different markets of Cairo and Giza governorates, Egypt and varied according to sampling location. In general, all pesticides detected were found at levels lower than the permissible maximum residue limit (MRL) except some samples from Cairo and Giza which contained a higher level of pesticide residue than the MRL and representing the frequencies samples exceeded MRL percentages, ranged from 0.87 - 4.35% and 1.67 - 8.33%, respectively. In addition, the lowest percentage (lower than 100%) of acute risk (%ARfD) and chronic risk (%ADI) were recorded with all detected pesticides in grapes. Furthermore, and as for EDI of pesticides residues by adult consumers, the intake of some pesticide residues in grape samples from the surveyed areas are within the permissible levels. Therefore, all identified pesticides had no potential health risk (HR) and/or hazards related to human consumption of grapes from targeted markets at two governorates.

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References

[1] Abdulhamid, Z.; Agbaji, B.E.; Gimba, C.E. and Agbaji, A.S. (2015). Determinatiom of organochlorine and pyrethroid pesticide residues in some vegetables by QuECHRS method and gas chromatography triple quadrupole mass spectrometry. J. of Environmental science, Toxicology and Food Technology, 9,14-20. DOI: 10.9790/2402-09631420.

[2] Agricultural Pesticide Committee, 2024. The approved recommendations for agricultural pest control - Egyptian Agricultural Pesticides Commit_tee. [WWW Document]. https://doi.org/http://www.apc.gov.eg/en/default.aspx.

[3] Anastassiades, M.; Lehotay, S. J. 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. J AOAC Int, 86:412–431. https://doi.org/10.1093/jaoac/86.2.412.

[4] Arabameri M.; Mohammadi M. M.; Monjazeb, M. L.; Mehdinia, S. M.; Abdolshahi, A. and Dezianian, A. (2020) Pesticide residues in pistachio nut: a human risk assessment study. Int J Environ Anal Chem 7:1-4. https://doi.org/10.1080/03067319.2020.1777289.

[5] Beyuo, J.; Sackey, L. N. A.; Yeboah, C.; Kayoung, P. Y. and Koudadje, D. (2024) The implications of pesticide residue in food crops on human health: a critical review. Discov Agric 2, 123. https://doi.org/10.1007/s44279-024-00141-z

[6] Chu, Y.; Tong, Z.; Dong, X.; Sun, M.; Gao, T.; Duan, J. and Wang, M. (2020). Simultaneous determination of 98 pesticide residues in strawberries using UPLC-MS/MS and GC-MS/MS. Microchem. J.; 156:104975. https://doi.org/10.1016/j.microc.2020.104975.

[7] EC-European Commission (2020). Guidance document on pesticide analytical methods for risk assessment and post-approval control and monitoring purposes, Document No. SANTE/2020/12830, 1-36. https://www.fao.org/faolex/results/details/en/c/LEX-FAOC034557/.

[8] EC- European Commission (2017). SANTE, Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed, Document no. SANTE/11813/2017 European Commission, 2017.

[9] EC-European Commission (2013). Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. Document SANCO/12571/2013.

[10] EC-European Commission (2009). Method validation and quality control procedures for pesticide residues analysis in food and feed. Document SANCO/10684/2009.

[11] EC-European Commission (2002). Directive (2002/63/EC). Establishing Community methods of sampling for the official control of pesticide residues in and on products of plant and animal origin. Official Journal of the European Communities, 187, 30-45.

[12] El-Sheikh, E.S.A.; Ramadan, M.M.; El-Sobki, A.E.; Shalaby, A.A.; McCoy, M.R.; Hamed, I.A.; Ashour, M.B. and Hammock, B.D. (2022). Pesticide residues in vegetables and fruits from farmer markets and associated dietary risks. Molecules.; 27:8072. https://doi.org/10.3390/molecules27228072.

[13] El-Sheikh, E.S.A.; Li, D.; Hamed, I. A.; Ashour, M. B. and Hammock, B.D. (2023). Residue Analysis and Risk Exposure Assessment of Multiple Pesticides in Tomato and Strawberry and Their Products from Markets. Foods. May; 12(10): 1936. https://doi.org/10.3390/foods12101936.

[14] EFSA (2012). Panel on Plant Protection Products and their Residues (PPR). Scientific Opinion on the science behind the development of a risk assessment of Plant Protection Products on bees (Apis mellifera, Bombus spp. and solitary bees). EFSA Journal. 10(5):2668. https://doi.org/10.2903/j.efsa.2012.2668.

[15] EFSA (2013). Panel on Genetically Modified Organisms (GMO). Scientific Opinion on application EFSA-GMO-NL2007-45 for the placing on the market of herbicide tolerant, high-oleic acid, genetically modified soybean 305423 for food and feed uses, import and processing under Regulation (EC) No 1829/2003 from Pioneer. EFSA Journal. 11(12):3499. https://doi.org/10.2903/j.efsa.2013.3499.

[16] EU-European Union Directorate-General for External Policies (2021). The Use of Pesticides in Developing Countries and Their Impact on Health and the Right to Food. https://data.europa.eu/doi/10.2861/28995.

[17] FAO (2009). Manual on the Submission and Evaluation of Pesticide Residues Data. Rome: Food and Agriculture Organization. http://www.fao.org/3/a-i5452e.pdf.

[18] Frenich, A. G.; Vidal, J. M.; Pastor-Montoro, E. and Romero-González, R. (2008). High-throughput determination of pesticide residues in food commodities by use of ultra-performance liquid chromatography-tandem mass spectrometry. Anal Bioanal Chem., 390: 947– 959. https://doi.org/10.1007/s00216-007-1746-5.

[19] Hamed, S. A.; EL-Ghanam, A. A. A. and Dalia E. E. (2019). Fast and Easy Method of 55 Pesticide Residues Determination in Commonly Fruits and Vegetables Collected from Egyptian Local Markets. J. of Plant Protection and Pathology, Mansoura Univ., Vol. 10 (12):587-595. DOI:10.21608/jppp.2019.77998.

[20] Hassain, Z. and Siddiqe, S. (2010). Determination of pesticides in fruits and vegetables using acetonitrile extraction and GC/MS technique. Jouranal of Scientific Research. 2, 19-29.

[21] ILNAS-EN 15662. (2018). Foods and plant origin - Multimethod for the determination of pesticide residues using GC and LC- based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE-Modular QuEChERS method. European Committee for Standardization, Brussels. https://www.scribd.com/document/584321778/EN-15662-2018-E.

[22] Lehotay, S. J. (2011). QuEChERS Sample Preparation Approach for Mass Spectrometric Analysis of Pesticide Residues in Foods. In: Zweigenbaum J (ed) Mass Spectrometry in Food Safety: Methods and Protocols, Methods in Molecular Biology. Springer Science & Business Media, LLC 2011, pp 65– 91. https://link.springer.com/protocol/10.1007/978-1-61779-136-9_4.

[23] Malhat, F.; Abdel-Megeed, M.; El-Sayed S.; Shokr A. S. S. and Saber, A. N. (2025a). Monitoring and risk assessment of pesticide residues in bananas: Insights from Egypt. Journal of Food Composition and Analysis. 143, 107610. https://doi.org/10.1016/j.jfca.2025.107610.

[24] Malhat, F.; Abdel-Megeed, M.; El-Sayed S.; Shokr A. S. S. and Saber, A. N. (2025b). Comprehensive analysis of pesticide residues in Egyptian cucumbers (2021–2023): Unveiling acute and chronic dietary risks and regulatory insights. Journal of Food Composition and Analysis 143, 107584. https://doi.org/10.1016/j.jfca.2025.107584.

[25] Sinha, S.N.; Rao, M.V.; Vasudev, K. and Odetokun, M. (2012). A liquid chromatography mass spectrometrybased method to measure organophosphorous insecticide, herbicide and non-organophosphorous pesticide in grape and apple samples. Food Control, 25: 636-646. https://doi.org/10.1016/j.foodcont.2011.11.031.

[26] Tudi, M.; Ruan, H.D.; Wang, L.; Lyu, J.; Sadler, R.; Connell, D.; Chu, C. and Phung, D.T. (2021). Agriculture development, pesticide application and its impact on the environment. Int. J. Environ. Res. Public Health.; 18:1112. https://doi.org/10.3390/ijerph18031112.

[27] Walpole, S.C.; Prieto-Merino, D.; Edwards, P.; Cleland, J.; Stevens, G. and Roberts, I. (2012). The weight of nations: an estimation of adult human biomass. BMC Public Health 12: 439. https://doi.org/10.1186/1471-2458-12-439.

[28] World Health Organization. (2006). GEMS/Food regional diets: regional per capita consumption of raw and semi-processed agricultural commodities. World Health Organization; Available from: http://www.who.int/foodsafety/publications/chem/regional_diets/en/.

[29] Yu, R.; Liu, Q.; Liu, J.; Wang, Q. and Wang, Y. (2016). Concentration of organophosphorus pesticides in fresh vegetables and related human health risk assessment in Changchun, Northeast China. Food.Control.60: 353-360.