

Monitoring of pesticide residues in some vegetable crops in Minia Governorate Markets with regard to their risk in human health.

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Abstract

Pesticide residue in vegetables (tomatoes, cucumbers, and potato) from various markets in three areas at Minia Governorate were determined. Using modified (QuEChERS) method vegetable samples are extracted and determination by Gas Chromatography Mass Spectrometry (GCMSMS). The results showed a strong correlation coefficient (≥ 0.992) within the detected residues that in a range of 10 to 1000 ng / g-1, along with a recovery rate between 64.4 to 92.16 percent. While, the limit of quantification ranged from 10 to 50 ng / g-1, respectively. After analyzing 54 vegetable samples, the pesticides residues were detected in 66.66 % percent of the samples. The detection limits lies between 0.0019 and 0.028 ng/gm-1. Residues of various pesticides were chlorofenpyer, and chloropyrifos (with frequency 18/54) followed by imidichlopride, azoxystrobin, (16/54) propagate (15/54), followed with lufenuron (11/54) and dimethemorph (12/54); carbendazim, thiophinate methyl, metalaxyl, and cyhalothrin (9/54) while as difenconzole, omethoate and methomyl were frequented (6/54) respectively. The least frequent pesticides were indoxicarb, cymoxanyl, cyfalothrin and acetampride in vegetables from various markets in three different locations at winter 2021 and summer 2022. Chlofenpyer, propargite, chloropyrifos, Carbendazim – lufenoron, and cypermethrin) were found in 44.67% of the vegetable samples hand were more than MRLs., while the other pesticides detected not exceeded the MRLs. Risk ratios were computed and the findings indicate that residues of chlorpyrifos, propargite, and methomyl from 48 pesticides tested are the most significant commodity contributing to the hazard index (HI) more than 100% and pose a severe public health risk.

1. Introduction

Monitoring pesticide residues in vegetables is crucial for evaluating the potential health hazards associated with their consumption. Several studies have been conducted to investigate the presence of pesticide residues vegetable. [1] developed a modified method called QuEChERS to efficiently extract and purify pesticide residues from fruits and vegetables. [2] measured the amounts of chlorpyrifos and methomyl residues in soil and vegetable samples. Their findings underscored the importance of implementing strict laws to minimize pesticide usage and mitigate their impact on soil quality and human health. [3] examined pesticide residues in fruits and vegetables obtained from local markets. Their study emphasized the urgent need for rigorous monitoring programs to address the potential risks associated with exposure to multiple pesticide residues. [4] developed a reliable method to simultaneously determine pesticide multi-residues in imported fruits and vegetables. Their work emphasized the necessity of

ongoing monitoring programs to ensure compliance with international agricultural and environmental policies. [5] devised an analytical multi-residue method for identifying various classes of pesticides in vegetables. Their research provided valuable insights into pesticide levels in different types of vegetable crops.

Pesticide usage cause environmental problems such as insect resistance and pollution specially in the developing countries that struggle with removing pesticide residues due to financial constraints and regulations, as well as monitoring them. [6, 7]. People are encouraged to eat more vegetables because they are nutritious and rich in vitamins and fiber. However, the media has highlighted the environmental and health concerns associated with the use of chemicals, particularly pesticides, in agriculture. It is important to note that these issues and risks have been somewhat exaggerated. Nevertheless, many vegetables still have small residues.[8-10]

Monitoring shown the potential dangers of pesticides to public health and are the key way for ensuring pesticides are used in accordance with Good Agricultural Practice (GAP). International organizations such as the Codex Alimentarius Commission of the United Nations Food and Agriculture Organization, the World Health Organization, and the European Commission have established maximum residue limits (MRLs) for various foods, and the surveillance system must monitor compliance with these MRLs. For several years, numerous Egyptian organizations have been monitoring food contamination levels. We haven't looked at how different methods of production may affect the number of pesticides left on vegetables until now. Although several studies examined the monitoring of pesticide residues in conventional and organic crops [7].

To protect consumer health, facilitate international trade, and ensure that vegetables comply with international maximum residue levels (MRLs), the study aimed to identify the levels of pesticide residues in Egyptian products and evaluate vegetables safety, and the legal limits of the use pesticides. Therefore, the pesticide residues in vegetable markets across different locations in Minia province during two seasons was monitored to establish a database on the vegetables residues levels by determining maximum residue limits (MRLs), the estimated daily intake (EDI) and comparing it with acceptable daily intake (ADI), as well as calculate the risk ratio for each pesticide.

2. MATERIALS AND METHODS

2.1. Sample Collection and Preparation:

Six vegetable sample packages, each weighing approximately 3 kg, were collected from each store during each season (winter 2021, summer 2022) and mixed to create a composite sample. Each composite sample was divided into three one-kilogram replicates, mixed and ground using a blender, 100 grams of the composite sample of each replicate were extracted using multi-pesticide residue " QuEChERS method" developed by [10] and has become widely used in food safety analyses. Thus, 100g of a pure mixed vegetable was weighed with 100 ml acetonitrile in a 200-mL centrifuge tube from the homogenate vegetable sample. Afterward, 6 g MgSO₄ and 1.5 g of sodium acetate were added to the samples in a centrifuge tube. The centrifuge tube was mixed by vortexing for one min and centrifuged at 3700 rpm for 5 min. The aliquot of the acetonitrile phase was transferred into a primary secondary amine (PSA) tube containing 125 mg Primary Secondary amine (PSA) and 750 mg MgSO₄. This centrifuge tube was vortexed for 0.5 min and centrifuged at 3700 rpm for 5 min. All aliquot was then transferred to a clean 15-mL tube and evaporated to complete dryness under a gentle stream of nitrogen at room temperature. The dry residues were reconstituted in 1 mL acetonitrile for (GC- MS / MS) analysis [11, 12]

2.3. Reagents and chemicals

Active ingredient of pesticide used were obtained from Merck (Darmstadt, Germany), and anhydrous magnesium sulfate, sorbents (primary and secondary amine; PSA particle size 40 µm), from Sigma-Aldrich (St. Louis, MO, USA). All of the

organic solvents utilized were of the highest quality for high performance liquid chromatography (HPLC).

2.4. Preparation of standards

Individual stock solutions at 10 ng/ml for each pesticides were prepared in 10-mL volumetric flasks with acetonitrile and stored at -20 °C.

2.4.1. Working solutions:

According to the European Commission recommendations [13], calibration curves were created for each pesticide. To achieve concentrations from 0.01 to 10 mg/L, matrix-matched calibration standards were generated using multi-residue working solutions in vegetables blank acetonitrile extracts.[14].The standard is stored at -20 °C until needed. These standards were then used as standards (i.e., for the determination of limits of detection (LOD), limits of quantification (LOQ), the recovery experiment, and the linearity experiment. Peak area and concentration were plotted using an Excel program to draw a calibration curve. These standard curves were used throughout the study to maintain the accuracy and precision of the sample analysis. The standard deviation and slope of the curve were calculated for all samples using regression static in the Excel program.

LOD was calculated as follows:

$$\text{LOD} = 3.3 * \text{SE} / b \text{ and } \text{LOQ} = 10 * \text{SE} / b \text{ [15]}$$

Where SE= standard error of calibration curve

b= slope of calibration curve

Good sensitivity and repeatability were obtained with detection limits of 0.0017- 0.033 µg/g, The recovery rates for most pesticides in various vegetables were 66.5 - 91% with relative standard deviations 6.5 -21%.

2.5. Percentage of recovery

To avoid pesticide contamination, the samples were extracted with acetonitrile and used as blank samples for the spiking studies. The extracted samples were fortified with different pesticide concentrations, extracted using the same procedure, and evaluated by (GC- MS/MS). The percentages of recovery were computed as

[16]

$$\text{Recovery \%} = ((1 - (\text{CB} - \text{CA}) / \text{CB})) \times 100 \text{ where}$$

CA= concentration after treatment

CB= concentration before treatment

2.6. Mass spectrometer configuration

Thermo GC/MS (Thermo Scientific Trace GC with Single Quadrupole MS DSQ II, USA) was used that quipped with an HP-5 MS capillary column, Helium was employed as carrier

gas at 1 ml/ min. the injector, ion source, and transfer line were respectively set at 250, 250 and 280 °C. One microliter of sample was injected in splitless mode. Before analyzing each set of samples, the mass spectrometer was fully auto tuned. The interface heater was kept at 550 °C with an ion-spray (IS) voltage of 5500 ev. Using continuous infusion of each pesticide in the positive ionisation mode of ESI, a comprehensive scan of the mass spectra of all pesticides was acquired in order to pick the most abundant mass to charge ratio (m/z) ion (Q1). Because the product mass spectra were acquired by infusing each analyte continuously, Q1, which corresponded to the protonated precursor ion, remained constant. MRM analysis was then performed on the most abundant product ion for each chemical. At least two of the most intense product ions were isolated; one ion was used for quantification, whereas the other was used for confirmation, as per the three principle criteria given for mass spectrometry studies of pesticides [8-11, 17]. Analysis was performed in the SIM mode based on the use of one target and two qualifier ions. Pesticides were identified according to retention times, target and qualifier ions. The quantitation was based on the peak area ratio of the target ion divided by the internal standards.

2.7. The temperature program used was as follows:

Initial temperature, 50° C held for 1 min, then at the rate of 20° C /min to 180° C, rate 10° C /min to 190° C, 3° C /min to 240° C and 10° C /min to 300° C and then maintaining this temperature 5 min. The temperature of the injection port was 220° C and a 1 ml volume was injected. The temperatures of ionization source were kept at 230° C. For identification, the major ions (m/z) and retention times both were considered.

2.7. Statistical analysis:

Data analysis was performed using Costat software. Pesticide data were analyzed in different vegetable samples via one-way ANOVA and LSD (least significant difference) test at $p < 0.05$ levels. Three-way analysis of variance of the pesticides was also conducted to compare the seasons, crops and localities.

3. Results and discussion

3.1. pesticide residues in vegetables collected from Minia Governorate markets.

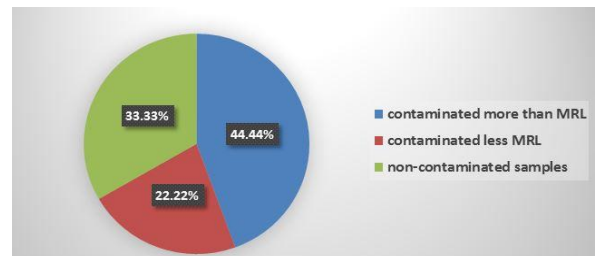
After analyzing 54 vegetable samples residues were detected in 66.67% percent of the samples. The detection limits lies between 0.0019 and 0.028 ng/gm-1. Residues of various pesticides that are more frequently in tested vegetables at Minia governorate, were chlorofenpyer, and chloropyrifos (18/54) followed by imidichlopride, azoxystrobin, propagate (15/54), followed with lufenuron and dimethemorph (12/54); carbendazim, thiophinate methyl, metalaxyl, and cyhalothrin (9/54) while as difenconzole, omethoate and methomyl were frequented (6/54). The least frequent pesticides were indoxicarb, cymoxanyl, cyfalthrin and acetampride in vegetables from various markets in three different locations, at (winter 2021 and summer 2022). Analysis revealed that 44.6% of the vegetable samples had values more than the Maximum Residue Limit (MRLs), while 22.3 % of the samples less than MRLs. Interestingly; no pesticides were detectable in 36.6% of the sample.

Analysis of pesticide residues in vegetable samples collected from 9 markets

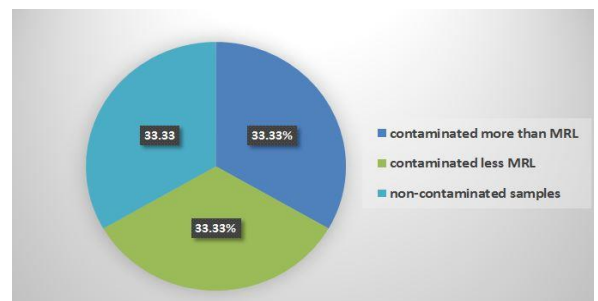
of Minia governorate, showed that samples contained higher residues in winter season than summer. The residues were in descending orders as follows: Minia, Abu Qurqas, Samalout, and pesticides (chlorfenpyer, propargite, chloropyrifos, carbendazim – lufenoron, and cypermethrin), were higher than MRLs while as the vegetable's crops were in descending order (tomatoes > cucumbers > potatoes), as shown in Table (1).

3.1.1. Residues of pesticides in vegetables collected from El-Miniacenter markets.

Data of winter season 2021, showed that samples of tomatoes were contaminated with chlorfenapyr, chlorpyrifos, cyhalothrin, cypermethrin, propargite, imidichlopride, azoxystrobin and leufenuron with concentrations ranged between 0.005 to 0.118 ug/g-1 pesticides. Clorfenapyr and propargite are exceeded MRLS in tomatoes at market Minia. While in cucumber samples only cypermethrin was detected with concentrations less than MRL. All potatoes samples were free from pesticide residues and not detected any of 48 tested pesticides Table 1. Results of summer 2022 showed that samples of tomatoes were contaminated with propargite and chlorfenapyr with concentrations more than MRLs. While cucumber samples from Minia center markets at the two seasons were contaminated with chloropyrifos, carbendazin, metalaxyl. Concentrations of metalaxyl, carbendasin and chlorpyrifos are exceeded MRLs values. While concentrations of cypermethrin, and lufenoron not exceeded MRLs values Table 1 and 2 and Fig 3 and 4.



Figure(1): percentage of contaminated and non-contaminated samples that exceeded MRL values in vegetable samples collected from Governorate Market Minia Winter 2021.



Figure(2): percentage of contaminated and non-contaminated samples that exceeded MRL values in vegetable samples collected from Governorate market Minia Summer 2022.

3.1.2. Residues of pesticides in vegetables from Samalout-

Data of winter season 2021, showed that samples of tomatoes were contaminated with chlorfenapyr, chlorpyrifos, propargite, with concentrations more than MRLS values. While cypermethrin, imidachlopride, lufenuron, difenconzole, omethoate and cyfluthrin with concentrations ranged between 0.005 to 0.145 ug/g-1 pesticides. While in cucumber samples cypermethrin, imidachlopride, azoxystrobin, metalaxyl and dimethomorph were detected with concentrations less than MRL. All potatoes samples were free from pesticide residues and not detected any of 48 tested pesticides Table 1. Results of summer 2022 showed that samples of tomatoes were contaminated with propargite with concentrations more than MRLs. While these samples were contaminated with chlorfenapyr, cyhalothrin, cypermethrin, imidachlopride and azoxystrobin. While cucumber samples from Samalot center markets at the two seasons were contaminated with metalaxyl and exceeded MRLs values. While concentrations of cypermethrin, imidachlopride, azoxystrobin, and dimethomorph with concentrations not exceeded MRLs values Table 1 and 2. Results of winter 2021 and summer 2022 indicated that no one of the tested pesticides was detected within limit of detection in potatoes samples within limit of detection (LOD).

Table (1) :Residues of different pesticides (PPM) in different vegetables crops in Minia Governorate during winter 2021 season with MRL

Detected pesticides	Frequency From 27 Samples	Minia			Samalot			Abuqorkas			MRLs values		
		Tomato	Cucu-cmber	Potatos	Tomato	Cucu-cmber	Potatos	Tomato	Cucu-cmber	Potatos	Tomato	Cucu-cmber	Potatos
		PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Chlorfenapyr	9	0.020	ND	ND	0.038	ND	ND	0.01	ND	ND	0.01	0.01	0.01
Chlorpyrifos	9	0.005	ND	ND	0.145	ND	ND	0.01	ND	ND	0.01	0.01	0.01
Cyhalothrin	6	0.020	ND	ND	ND	ND	ND	0.010	ND	ND	0.50	0.50	0.50
Cypermethrin	9	0.005	0.005	ND	0.019	0.003	ND	ND	ND	ND	0.01	0.01	0.01
Propargite	9	0.118	ND	ND	0.067	ND	ND	0.263	ND	ND	0.01	0.01	0.01
Imidacloprid	12	0.014	ND	ND	0.005	0.023	ND	0.010	ND	ND	0.3	0.3	0.3
Azoxystrobin	9	0.010	ND	ND	ND	0.005	ND	0.017	ND	ND	0.3	0.3	0.3
lufenuron	6	0.050	ND	ND	0.005	ND	ND	ND	ND	ND	0.4	0.4	0.4
Difenconzole	3	ND	ND	ND	0.005	ND	ND	ND	ND	ND	0.1	0.1	0.1
Omethoate	3	ND	ND	ND	0.010	ND	ND	ND	ND	ND	0.01	0.01	0.01
Cyfluthrin	3	ND	ND	ND	0.023	ND	ND	ND	ND	ND	0.05	0.05	0.05
Dimethomorph	3	ND	ND	ND	0.018	ND	ND	ND	ND	ND	0.5	0.5	0.5
Metaxyl	3	ND	ND	ND	0.053	ND	ND	ND	ND	ND	0.05	0.053	0.05
Acetamprid	3	ND	ND	ND	ND	ND	ND	0.010	ND	ND	0.03	0.2	0.3

Table (2): Residues of different pesticides (PPM) in different vegetables crops in Minia Governorate during summer 2022 season with MRL.

Detected Pesticides	Frequency From 27 Samples	Minia			Samalot			Abuqorkas			MRLs values		
		Tomato	Cucu-cmber	Potatoes	Tomato	Cucu-cmber	Potatoes	Tomato	Cucu-cmber	potatoes	Tomato	Cucu-cmber	potato's
		PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Chlorfenapyr	9	0.005	ND	ND	0.01	ND	ND	0.02	ND	ND	0.01	0.01	0.01
Chlorpyrifos	8	ND	0.043	ND	ND	ND	ND	0.01	ND	ND	0.01	0.01	0.01
Cyhalothrin	3	ND	ND	ND	0.02	ND	ND	ND	ND	ND	0.50	0.50	0.50
Cypermethrin	4	ND	ND	ND	0.004	ND	ND	0.014	ND	ND	0.01	0.01	0.01
Propargite	6	0.81	ND	ND	0.104	ND	ND	ND	ND	ND	0.01	0.01	0.01
Imidacloprid	3	ND	ND	ND	0.01	ND	ND	ND	ND	ND	0.3	0.3	0.3
Azoxystrobin	7	ND	ND	ND	0.01	0.005	ND	ND	0.041	ND	0.3	0.3	0.3
Lufenuron	5	ND	ND	ND	ND	ND	0.005	ND	ND	ND	0.4	0.4	0.4
Carbendazim	9	0.01	0.03	ND	ND	ND	ND	0.014	ND	ND	0.3	0.1	0.1
Difenconzole	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.01	0.1
Omethoate	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01	0.01	0.01
Cyfluthrin	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05	0.05	0.05
Dimethomorph	9	ND	ND	ND	0.018	ND	0.014	0.013	ND	0.5	0.5	0.5	
Metaxyl	6	ND	0.05	ND	ND	0.053	ND	ND	ND	ND	0.05	0.053	0.05
thiophanate-methyl	9	0.014	0.085	ND	ND	ND	ND	0.019	ND	ND	0.1	0.1	0.1
Cymoxanil	3	ND	ND	ND	ND	ND	ND	0.014	ND	ND	0.4	0.08	0.4
Methomyl	6	ND	0.25	ND	ND	ND	ND	0.032	0.12	ND	0.25	0.01	0.01
Indoxcarb	3	ND	ND	ND	ND	ND	ND	0.005	ND	ND	0.5	0.5	0.5

3.1.3. Residues of pesticides in vegetables from Abu Qurqas:

Results of samples collected during winter 2021 indicated that tomato samples from markets of Abu Qurqas are highly contaminated with Propargite with concentration more than MRLs (0.263Ug/g) and with cypermethrin, chlorpyrifos, cyhalothrin, azoxystrobin and imidachlopride with concentrations less than MRLs values (0.01 – 0.017 ug/g).

While tomatoes of summer 2022 results showed that clorafenpyr and thiophinate methyl with concentrations more than MRLs values (0.02 and 0,019 µg/g). Also, samples of tomatoes of Abu Qurqas were contaminated with clorafenpyr, lufenuron, carbendazin, cymoxanil, methomyl, and indoxicarb with concentrations ranged between (0.005 – 0.014 µg/g). Cucumber samples were contaminated with acetamprid and was less than MRL. (0.01ug/g-1). cucumber samples collected during Summer 2022 from markets of Abu Qurqas were also more contaminated where chlorafinpyr, was detected with concentrations equal MRLs value and dimethomorph, methomyl and Azoxystrobin were detected with concentrations less than MRL. Analysis of variance indicated that Minia markets are the most markets contaminated followed by Abu Qurqas and Samalut. Tomatoes are the most crop contaminated.

Several studies have been conducted in Egypt to determine pesticide residues in vegetables and fruits. For tomato samples, the detected analytes were chlorpyrifos, chlorfenpyr, and propargite, which were similar to those reported by [8] However, our results were inconsistent with theirs in the case of chlorpyrifos, and propargite, as they didn't report the other analytes in their survey while we did. In the case of potato samples, the results were inconsistent with [8] for clorafenpyr and methomyl, as they didn't report it in their survey, whereas we found them. For tomatoes samples our results were similar to those reported by [8]. Similarly, the violated analytes detected in the tomato samples (dimethoate and profenofos) were also reported by [4] although our results were inconsistent with their findings for other pesticides such as Carbendazim, chlorpyrifos, lufenuron, omethoate, and thiophanate methyl. These pesticides were not reported by [18, 19].

The detected pesticide residues were applied on a wide range of different agricultural crops in Egypt according to the approved recommendations of the Egyptian Agricultural Pesticides Committee (APC). It is possible that the occurrence of pesticide residues in our study may be due to the lack of awareness among growers/farmers about the importance of following the recommended rate of pesticide use, correct application methods, and the need to adhere to the guidelines set by the APC.

The occurrence of pesticide residues in crops may be caused by growers/farmers not following the correct recommended rate, method of application, or pre-harvest intervals. Some commodities, such as tomatoes and cucumber, may have higher levels of pesticide residues due to the severity of pest and disease attacks, which require multiple applications. Pesticides are often applied directly to the edible part of the crop near harvest time to ensure plant protection. Additionally, some vegetable farms apply pesticides as frequently as twice a month to once a week. To ensure public health is not negatively impacted by pesticide residues, it is important to establish pest control methods that ensure pesticide levels in marketed vegetables are below the MRLs.

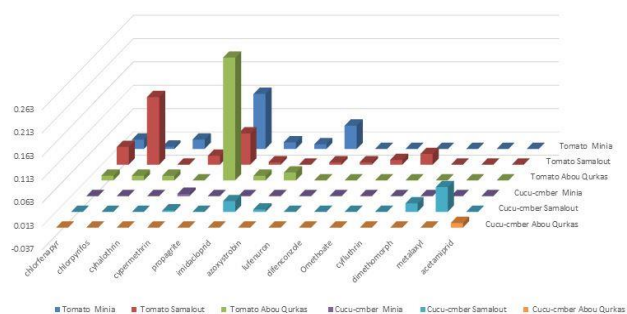
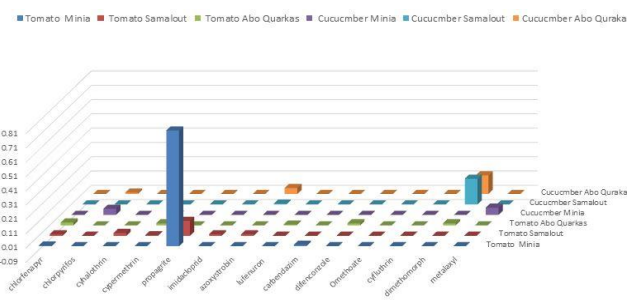


Figure (3): Residues of different pesticides (PPM) in different vegetables crops in Minia Governorate during winter 2021 season



Figure(4): Residues of different pesticides (PPM) in different vegetables crops in Minia Governorate during Summer 2022 season.

3.2. Dietary intake of tested pesticide residues through vegetables from area of Minia.

Data obtained was used for estimating the potential health risk associated with the exposure to these pesticide residues. Results obtained were used to calculate expected daily intake (EDI) expressed as mg pesticide residues per kilogram body weight per day (mg/kg b.w/day). The EDI is a realistic estimation of pesticide exposure that was calculated in agreement with the international guidelines [20], using the following equation:

$$EDI = (\sum C \times F) / (D \times W) \quad (1) \quad (\text{Osman et al. 2010}).$$

Where $\sum C$ is the sum of concentration of pesticide residues in each commodity (mg/kg),

F = is mean annual intake of food per person,

D = is number of days in a year (365) and

W = is the mean body weight (60 kg).

Health risk indices of the residues were computed using the data obtained and food consumption. The food consumption rate in Minia Governorate was determined by making a quachinera to 600 persons in (Minia - Samalout - Abu Qurqas) region and calculated the average of consumption from each vegetable were 71.47, 52.32, 60.21 Kg/ year for tomatoes respectively, and (55.40, 45.60 and 48.55 Kg/ year for cucumber respectively. And 68.65, 49.44, 53.54 Kg/ year for potatoes respectively. Estimated the hazard indices were obtained by dividing the EDI (mg /kg/day) by their corresponding values of WHO/FAO acceptable daily intakes, ADI (WHO, 2004).

$$\text{Risk indices} = ((EDI \times 1000) / ADI) \times 100$$

The results underline that some pesticides are present in vegetables on Minia Governorate markets and that routine monitoring of these pollutants in food items is required to prevent, control and reduce the pollution and to minimize health risks.

- In some cases, pesticide concentrations were above the ADI set by Codex Alimentarius Commission (WHO, 2004) chlorpyrifos and propagrite in Minia and Samalout at samples of tomato. Methomyl was high risk in cucumber at Minia markets. The hazard indices (EDI/ADI) ranged from (0 to 620 %) for the tested compounds. Thus, lifetime consumption of these vegetables could not pose health risk for Minia Governorate population as the indices for some the residues were less than 100%. However, the present study shows a high incidence of pesticide residues (mostly insecticides) in vegetables grown under greenhouse conditions, attention should be considered because most of the tested vegetables are used without cooking treatment and are used fresh in preparing salad dishes. Moreover, vegetable consumers could be exposed to more than one pesticide at the same time. Finally, the above discussion suggests that the consumer of Minia Governorate is exposed only to the lower concentrations of pesticides that may cause chronic diseases. The concentration of the various pesticides were variables from below and over (MRL) thus continuous consumption of such vegetables with moderate contamination level can accumulate in the receptor's body and may prove fatal for human population in the long term.

Table (3): Analysis of variance of different sources Regions, pesticides and different crops during two seasons.

Source of variance	Avg. of residual	F value	LSD05
Chlorfenapyr	0.0007 ^{ad}	6.75	0.0546
Chlorpyrifos	0.4 ^{ab}		
Cyhalothrin	0.0033 ^{abc}		
Cypermethrin	0.0035 ^{abc}		
Propagrite	0.0497 ^{ab}		
Imidacloprid	0.005 ^{abc}		
Azoxystrobin	0.521 ^{ab}		
Lufenuron	0.011 ^{abc}		
Carbendazim	0.034 ^{ab}		
Difencenzole	0.0004 ^{bc}		
Cyfluthrin	0.0004 ^{bc}		
Metalaxyl	0.0099 ^{6abc}		
Acetamiprid	0.000011 ^{1b}		
Dimethomorph	0.0789 ^a		
Regions		7.23	0.0026
Minia	0.03 ^a		
Samalout	0.00003 ^b		
	Abo Qurakas	0.009 ^a	
Vegetables		16.07	0.0262
Tomato	0.05 ^a		
cucumber	0.0099 ^b		
Potatoes	0.0009 ^b		

Table (4): Three-way Anova completely randomized two seasons of data.

Source						
Main Effects	SS	DF	MS	F	P	-
Crop	0.007717805	2	0.0038589025	7.8280412369	0006	***
Cent	0.0028238174	2	0.0014119087	2.8641509769	0599	ns
Inse	0.0401597065	8	0.0050199633	10.183330549	0000	***
Interaction						
Crop*cent	0.0403	4	0.010097897	20.484257779	0000	***
Crop*inse	0.1156415365	16	0.007227596	14.661660823	0000	***
Cent*inse	0.0796166797	16	0.0049760425	10.094234208	0000	***
Crop*cent*inse	0.1974174285	32	0.0061692946	12.514825838	0000	***
Error	0.07985934	162	4.929589E-04			
Total	0.5636279013	242				

Conclusion:

Our research provides important information about the contamination of pesticides residues in some fresh vegetables collected from some markets in Minia governorate. Whereas, samples were exceeded the permissible limits (MRL) and not associated with health risks to consumers. Therefore, we recommended constantly monitored pesticide residues and randomly for analysis. Moreover, an extension program should

be put in place for the farmers to increase their awareness of the safe use and application of pesticides and the importance of adhering

Table (5): Risk assessment of pesticide residues in vegetables crops at Minia governorate during summer 2021 and winter 2022 with their Hazard index.

Pesticide	PPM	Crops	Season	Centers	ADI (mg/kg body/weight/day (Average consumption	EDI (mg/kg body/weight/day(RIZK)EDI / ADI(Results
Chlorfenpyr	0.02	Tomato	summer	Minia	0.01	71.47	0.056	56%	safe
chlorpyrifos	0.005	Tomato	summer	Minia	0.01	71.47	0.014	14%	safe
Cyhalothrin	0.02	Tomato	summer	Minia	0.07	71.47	0.056	8%	safe
Cypermethrin	0.005	Tomato	summer	Minia	0.5	71.47	0.014	0%	safe
Propagrite	0.118	Tomato	summer	Minia	0.01	71.47	0.330	330%	danger
Imidacloprid	0.014	Tomato	summer	Minia	0.3	71.47	0.039	1%	safe
Azoxystrobin	0.01	Tomato	summer	Minia	3	71.47	0.028	0%	safe
Lufenuron	0.05	Tomato	summer	Minia	0.4	71.47	0.140	3%	safe
Cypermethrin	0.005	Cucumber	summer	Minia	0.2	55.40	0.011	1%	safe
Chlorpyrifos	0.145	Tomato	summer	Samalout	0.01	52.32	0.297	297%	danger
Cypermethrin	0.019	Tomato	summer	Samalout	0.5	52.32	0.039	1%	safe
Omethoate	0.01	Tomato	summer	Samalout	0.01	52.32	0.020	20%	safe
Imidacloprid	0.005	Tomato	summer	Samalout	0.3	52.32	0.010	0%	safe
Propargite	0.067	Tomato	summer	Samalout	0.01	52.32	0.137	137%	danger
Chlorfenapyr	0.038	Tomato	summer	Samalout	0.01	52.32	0.078	78%	safe
Cyflthurin	0.023	Tomato	summer	Samalout	0.05	52.32	0.047	9%	safe
Difenconzole	0.005	Tomato	summer	Samalout	0.01	52.32	0.010	10%	safe
Lufenuron	0.005	Tomato	summer	Samalout	0.4	52.32	0.010	0%	safe
Dimethomorph	0.018	Cucumber	summer	Samalout	0.5	45.60	0.032	1%	safe
Metalaxyl	0.053	Cucumber	summer	Samalout	0.5	45.60	0.095	2%	safe
Azoxystrobin	0.005	Cucumber	summer	Samalout	3	45.60	0.009	0%	safe
Chlorfenpyr	0.01	Tomato	summer	Abo Quarkas	0.05	60.21	0.024	5%	safe
Cypermethrin	0.01	Tomato	summer	Abo Quarkas	0.5	60.21	0.024	0%	safe
Propagrite	0.263	Tomato	summer	Abo Quarkas	0.01	60.21	0.620	620%	danger
Acetamiprid	0.01	Cucumber	summer	Abo Quarkas	0.4	48.55	0.019	0%	safe
Imidacloprid	0.01	Tomato	summer	Abo Quarkas	0.5	60.21	0.024	0%	safe
Azoxystrobin	0.017	Tomato	summer	Abo Quarkas	3	60.21	0.040	0%	safe
Carbendazim	0.01	Tomato	winter	Minia	0.3	71.47	0.028	1%	safe
Thiophanate-methyl	0.014	Tomato	winter	Minia	1	71.47	0.039	0%	safe
Propargite	0.081	Tomato	winter	Minia	0.01	71.47	0.227	227%	danger
Chlorfenapyr	0.005	Tomato	winter	Minia	0.01	71.47	0.014	14%	safe

Carbendazim	0.3	Cucumber	winter	Minia	0.1	55.4	0.650	65%	safe
Chlorpyrifos	0.043	Cucumber	winter	Minia	0.01	55.4	0.093	93%	safe
Thiophanate-methyl	0.085	Cucumber	winter	Minia	0.1	55.4	0.184	18%	safe
Methomyl	0.25	Cucumber	winter	Minia	0.01	55.4	0.542	542%	danger
Metalaxyl	0.05	Cucumber	winter	Minia	0.5	55.4	0.108	2%	safe
Chlorpyrifos	0.145	Tomato	winter	Samalout	0.01	52.32	0.297	297%	danger
Cypermethrin	0.019	Tomato	winter	Samalout	0.5	52.32	0.039	1%	safe
Omethoate	0.01	Tomato	winter	Samalout	0.01	52.32	0.020	20%	safe
Imidacloprid	0.005	Tomato	winter	Samalout	0.3	52.32	0.010	0%	safe
Propargite	0.067	Tomato	winter	Samalout	0.01	52.32	0.137	137%	danger
Chlorfenapyr	0.038	Tomato	winter	Samalout	0.01	52.32	0.078	78%	safe
Cyflthurin	0.023	Tomato	winter	Samalout	0.05	52.32	0.047	9%	safe
Difenconzole	0.005	Tomato	winter	Samalout	0.01	52.32	0.010	10%	safe
Lufenuron	0.005	Tomato	winter	Samalout	0.4	52.32	0.010	0%	safe
Dimethomorph	0.018	Cucumber	winter	Samalout	0.5	45.60	0.032	1%	safe
Metalaxyl	0.053	Cucumber	winter	Samalout	0.5	45.60	0.095	2%	safe
Azoxystrobin	0.005	Cucumber	winter	Samalout	3	45.60	0.009	0%	safe
Carbendazim	0.014	Tomato	winter	Abo Quarkas	0.3	60.21	0.033	1%	safe
Chlorpyrifos	0.01	Cucumber	winter	Abo Quarkas	0.01	48.55	0.019	19%	safe
Thiophanate-methyl	0.019	Tomato	winter	Abo Quarkas	1	60.21	0.045	0%	safe
Cypermethrin	0.014	Tomato	winter	Abo Quarkas	1	60.21	0.033	0%	safe
Chlorfenapyr	0.02	Tomato	winter	Abo Quarkas	0.01	60.21	0.047	47%	safe
Lufenuron	0.005	Tomato	winter	Abo Quarkas	0.4	60.21	0.012	0%	safe
Indoxacarb	0.005	Tomato	winter	Abo Quarkas	0.5	60.21	0.012	0%	safe
Dimethomorph	0.014	Tomato	winter	Abo Quarkas	1	60.21	0.033	0%	safe
Metalaxyl	0.032	Cucumber	winter	Abo Quarkas	0.5	48.55	0.061	1%	safe
Azoxystrobin	0.041	Cucumber	winter	Abo Quarkas	1	48.55	0.078	1%	safe
Cymoxanil	0.014	Tomato	winter	Abo Quarkas	0.4	60.21	0.033	1%	safe
Dimethomorph	0.013	Cucumber	winter	Abo Quarkas	0.5	48.55	0.025	0%	safe
Cymoxanil	0.012	Cucumber	winter	Abo Quarkas	0.08	48.55	0.023	3%	safe

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