

PESTICIDE RESIDUES IN HORTICULTURAL CROPS FROM DOMESTIC MARKETS OF GIZA, EGYPT: OCCURRENCE AND RISK ASSESSMENT

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Abstract

The occurrence of pesticide residues in commonly produced horticultural products in Egypt raises health concerns for consumers. Fresh horticultural crops at local markets are usually not analyzed for pesticide residues compared to export products. Thus, the objectives of this study were to determine pesticide residue levels in the most consumed and exported abroad fruits and vegetables like (orange, potato, pomegranate, tomato, green beans, strawberry and molokhia) in 4 local markets in Giza governorate, Egypt and to assess the potential human health risks as well. A total of 70 samples of frequently used vegetables and fruits were analyzed using QuEChERS method followed by Gas chromatography mass spectrometry and Liquid chromatography - mass spectrometry (GC-MS/MS and LC-MS/MS). Out of the total 70 analyzed samples, 8 (11.4%) samples were free from pesticide residues, 62 (88.6%) samples were contaminated and 30 (42.8%) samples from the contaminated samples exceeded the Maximum Residue Limits (MRL's). The most frequently pesticides detected were chlorpyrifos and chlorpropham. Risk assessment performed for only violated residues showed that no apparent potential human risk to consumers was observed based on Hazard Index calculated. Nonetheless, monitoring studies should be expanded to other fruits and vegetables consumed locally. Care also must be taken to apply pesticides correctly and safely to reduce pesticide levels; and farmers should comply with the estimated PHI.

Key words : Horticultural crops, Pesticide Residues, Estimated Daily Intake, Risk Assessment.

Introduction

In Egypt, horticultural crops are high value crops generating higher profits per unit of land and are an important source for farmers' income and the national economy. According to Food consumption patterns in the Eastern Mediterranean region 2011 the consumption rate of vegetables and fruits in Egypt is ranging from 174 to 420 g/person/day Musaiger, 2011. Orange, potato, pomegranate, tomato, green beans, strawberry and molokhia are among the most economically produced horticultural crops because of their great importance to the domestic consumption and to the European and global markets as well. However, the productivity and quality of such vegetables and fruits are affected by several pests (e.g. insects, fungi and mites) resulting in lower yield and value. In Egypt chemical pest control using pesticides is widely used by farmers and producers as proved to be the most effective pest control method. Organophosphates, Neonicotinoids, Carbamates, Spinosyns, insect growth regulators and a few new types of pesticides that were introduced recently to the market are representing the most important pesticides used According to Egyptian Agricultural Pesticides Committee, 2018. Potential contamination of the produce before sending them to the market is usually due to the application of pesticides close to harvest time of the crops, incorrect application technique and use of non-selective and toxic chemicals which are banned or restricted in other countries. Fresh fruits and vegetables designated for exportation are usually examined for pesticide residue limits to ensure agreement according to standards set by the destination country. Conversely, locally produced fresh

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fruits and vegetables sold and consumed at the national markets are not mostly subjected to surveillance for pesticide residues. The maximum residue limits (MRL's) expressed as acceptable daily intake (ADI) in mg.kg⁻¹ have been established worldwide for legally permitted pesticide residues in or on agricultural products to avoid the health hazard caused by pesticide residues Codex Alimentarius Commission, 2018.

Therefore, the objective of this study was to monitor the residues of used pesticides in certain fresh produce sold at four central domestic markets in Giza Governorate, Egypt as they reach the consumers. Assessing the risk of pesticide residues in the analyzed commodities intended for domestic human consumption will be also estimated based on the average consumption, average adult weight, and pesticide residue data. The results of the monitoring in combination with food consumption data based on GEMS/Food Consumption Cluster Diets 2006 would determine whether the estimated daily intake (EDI) of pesticides detected in fresh produce consumed locally may cause any adverse effects on consumers. Hence, data could be used when designing future control programs and taking preventive or mitigating action to minimize human health risk.

Materials and Methods

Chemical and Reagents

Solvent and chemicals described in the standard method CEN 275, 2007 were used. All HPLC grade chemicals such as (99.8%) toluene, (99.9%) acetonitrile, (99.9%) methanol, (97%) n hexane, (98-100%) formic acid, (30%) ammonia solution, and (99.8%) glacial acetic acid were purchased from Sigma-Aldrich (USA). QuEChERS Kits 5982-5650 reagent (1) and 5982-5056 reagent (2) were purchased from Agilent Technologies (USA). Deionized water was produced by a mille Q unit (Mille Pore). A total of 412 pesticide reference standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany) with purities >95% including 75 GC- pesticides, 199 LC- pesticides and 138 common pesticides analyzed by the both techniques. Injection standard solution of 0.1 Og/ml Aldrin in a mixture of n-hexane: acetone (9:1 v/v) was used for GC-MS/MS injection.

Sampling

For monitoring of pesticide residues, a total of 70 samples (20 fruits sample of orange and pomegranate) and (50 vegetables sample of potato, tomato, green beans, strawberry and molokhia) were purchased during 2017-2018 from 4 different main local markets located in Giza Governorate, Egypt. Each representative vegetable or fruit sample was a composite of 10 subsamples of the

same commodity collected from each market at the same time through random sampling. All the samples (2 kg each) were placed in paper bags, labeled, and transported to the laboratory for analysis.

Each sample was chopped and grinded according to the generally recommended method Codex Alimentarius Commission, 1993 and stored at -200 °C until further analysis.

Sample Extraction and Clean-Up

Pesticides were extracted from samples using QuEChERS method as described by Anastassiades *et al.*, 2003. Ten grams of each sample were weighed in a 50 ml polypropylene (PP) tube, and 10 ml of acetonitrile was added and then shaken vigorously for one minute. After the addition of 4g of magnesium sulfate, 1g of sodium chloride and buffering citrate salts (pH 5 to 5.5), the mixture was shaken vigorously and centrifuged at 4000 rpm for 5 minutes for phase separation. An aliquot of the organic phase was injected into LC-MS/MS directly for analysis.

Another aliquot of the organic phase was cleanedup by dispersive solid phase extraction (DSPE) employing bulk sorbents as well as magnesium sulfate to remove water residue. Following cleanup with primary secondary amine sorbent (PSA), sample extracts were evaporated and redissolved in injection standard for GC-MS/MS analysis. Quantification was performed using aldrin as an internal standard, which was added directly before injection in GC-MS/MS system.

The method validated 412 compounds using LC-MS/ MS and GC-MS/MS. The detection and confirmation of pesticide residues in the samples were made using GC-MS/MS and LC-MS/MS.

Instrumentation

GC-MS/MS: Agilent Gas Chromatograph 7980A equipped with tandem mass spectrometer 7000B Quadrupole, EI source was used to perform analysis by using HP-5MS 5% phenyl methyl siloxane capillary column (30 m length x 0.25 mm id x 0.25 \bigcirc m film thickness). The GC oven temperature was programmed to initially held at 70°C for 2 min then increased to 150°C at 25°C/min (held for 0 min), and raised to 200°C at the rate of 3°C/min (held for 0 min), then went up from 200 to 280°C at 8°C/min (held for 10 min). This resulted in a total run time of 42 min and complete separation of all the analysts.

LC-MS/MS: Agilent 1200 series liquid chromatography system equipped with Applied Biosystems (API 5500 Q trape & API 4000 Q trape) tandem mass spectrometers with electrospray ionisation (ESI) interface. Separation was performed on a C18 column ZORBAX Eclipse XDB-C 18 4.6 x 150 mm, 5 Om particle size. The injection volume was 25 Ol. A mobile phase was at 0.3 ml/min flow rate, in which one reservoir contained 10 mM ammonium formate solution in MeOH:H2O (1:9 v/v). The ESI source was used in the positive ion mode, and Nitrogen was used as nebulizer gas, curtain gas, heater gas and collision gas according to manufacturer's settings; source temperature was 300°C, ion spray potential 5500 V, decluster potential and collision energy were optimized using a Harvard apparatus syringe pump. The Multiple Reaction Monitoring Mode (MRM) was used in which one MRM was used for quantification and the other was used for confirmation.

Quality Control

All analytical methods and instruments were carefully validated as a part of the laboratory quality assurance system and the validation was audited and accredited by the Center of Metrology and Accreditation Finnish Accreditation Service (FINAS) ISO/IEC Guide 17025.

The reproducibility expressed as relative standard deviation was less than 25%. The limit of quantification started at 0.01 mg kg⁻¹ and depended on the pesticide type and detection module. The measurement uncertainty expressed as expanded uncertainty in terms of relative standard deviation (at 95 % confidence level) was lower than the default value set by the EU (\pm 50 %).

Every analysis has a calibration curve to measure the concentration. The average recovery percentages of these pesticides at different commodities were recorded on control charts and they varied from 70 % to 120%.

The matrix effect is overridden by injecting standard matrix for each commodity before the samples analysis to test the matrix effect on instruments signal.

Repeated analysis of old samples was regularly carried out to control reproducibility. Analysis of certified reference material (CRM) was performed as internal quality control and proficiency test (PT) performed as external quality control.

Risk Assessment

Based on monitoring results of the detected pesticide residues, an exposure evaluation was conducted to determine the degree of risk by the pesticide residues detected in various samples. The risk assessment is calculated by comparing the established acceptable daily intake (ADI) with the estimated acceptable daily intake (EDI) that depends on the concentration of pesticide residues and food consumption. The risk assessment was determined only for pesticide residues exceeding MRL. The EDI (mg kg⁻¹ bw⁻¹ day) for each violated pesticide residue was calculated by multiplying the mean concentration of pesticide residues (mg kg⁻¹), by food consumption and divided by body weight (kg day⁻¹) for each commodity, assuming an average adult's body weight is 60 kg. The estimated acceptable daily intake was based on WHO/Global Environment Monitoring System-food GEMS/FOODS, 2006.

$EADI= \Sigma \frac{Food \ chemical \ concentration \times Food \ consumption}{Body \ weight}$

All maximum residues limits (MRL's) and established acceptable daily intake (ADI) value were from EU Pesticides Database. The food consumption figures used were based on the data issued by The GEMS/Food Consumption Cluster Diets 2006. The long term risk assessment of pesticide residues was performed by calculating EDI as a % of ADI, by dividing the estimated daily intake with the relevant acceptable daily intake (ADI) according to the European Food Safety Authority EFSA, 2007 and El- Sawi *et al.*, 2012. When EDI as a % of ADI is < 100% ; this indicates that food is safe and considered accepted, while when EDI as a % of ADI is % (HI) is > 100% ; this indicates that food is considered as a risk to the consumers.

Results and Discussion

In this study, the level of pesticide residues in 70 vegetable and fruit samples was determined. Pesticide residues were not detected in 8 samples (11.4%), while 62 samples (88.6%) contained detectable amounts of pesticide residues. A total of 30 samples (42.9%) out of 62 contained pesticide residue above the MRLs, whereas 32 samples (45.7%) contained pesticide residue at or below the MRLs (Table 1).

The most contaminated commodities were oranges,

 Table 1: Samples number and there percentages of pesticide residue levels (%).

| | Samples Number | Without Residues | With Residue < MRL | With Residue > MRL |
|------------|-------------------|---------------------|-----------------------|-----------------------|
| No. | 70 | 8 | 32 | 30 |
| Percentage | 100 % | 11.4 % | 45.7 % | 42.9 % |
| MDI M. | р. [.] | 1 T · ·/ | | |

MRL= Maximum Residue Limits.

tomatoes, green beans, strawberries and molokhia with percentage of 100 %. While the highest concentration of pesticide residues that exceeded MRL was detected in tomato 60 % followed by molokhia 50 % then orange and green beans both 40 %. while the lowest contaminated commodity was potato as 60 % of the analyzed samples

 Table 2: Pesticide residues levels found in selected commodities, frequencies, there MRLs showed no detectable residues.

 and number of Violated samples.

| Commodity | Residue | Freq | Min | Max | MRL's ppm | Above MRL |
|-------------|---------------------|------|--|--|-----------|--------------|
| Orange | Chlorpyrifos | 6 | 0.01 | 0.05 | 0.3 | - |
| 8 | Cyfluthrin | 1 | 0.01 | 0.01 | 0.02 | - |
| | Dimethoate | 3 | <loq< th=""><th>0.07</th><th>0.01</th><th>2</th></loq<> | 0.07 | 0.01 | 2 |
| | Ortho-Phenyl Phenol | 3 | 0.01 | 0.94 | 10 | - |
| | Carbendazim | 2 | 0.02 | 0.03 | 0.2 | - |
| | Omethoate | 2 | 0.04 | 0.04 | 0.01 | 2 |
| | Thiabendazole | 2 | 0.01 | 0.15 | 7 | - |
| | Malathion | 1 | 0.01 | 0.01 | 2 | - |
| | Lambda-Cyhalothrin | 8 | <loq< th=""><th>0.08</th><th>0.2</th><th>-</th></loq<> | 0.08 | 0.2 | - |
| | Diazinon | 1 | 0.04 | 0.04 | 0.01 | 1 |
| | Cypermethrin | 2 | 0.01 | 0.01 | 2 | - |
| | Imazalil | 6 | 0.01 | 1.18 | 5 | - |
| Potato | Gamma-HCH | 1 | 0.22 | 0.22 | 0.01 | 1 |
| | Total DDT's | 1 | 0.1 | 0.1 | 0.05 | 1 |
| | alpha-HCH | 1 | 0.39 | 0.39 | 0.01 | 1 |
| | beta-HCH | 1 | 0.14 | 0.14 | 0.01 | 1 |
| | delta-HCH | 1 | 0.3 | 0.3 | 0.01 | 1 |
| | Chlorpropham | 4 | 0.01 | 9 | 10 | - |
| | Chlorpyrifos | 3 | <loq< td=""><td>0.02</td><td>0.01</td><td>2</td></loq<> | 0.02 | 0.01 | 2 |
| | Diazinon | 1 | <loq< td=""><td><loq< td=""><td>0.01</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.01</td><td>-</td></loq<> | 0.01 | - |
| | Thiobencarb | 1 | <loq< th=""><th><loq< th=""><th>0.01</th><th>-</th></loq<></th></loq<> | <loq< th=""><th>0.01</th><th>-</th></loq<> | 0.01 | - |
| Pomegranate | Imidacloprid | 3 | 0.04 | 0.04 | 1 | - |
| | Chlorpyrifos | 3 | 0.04 | 0.03 | 1 | - |
| | Lambda-Cyhalothrin | 5 | 0.01 | 0.02 | 0.02 | 3 |
| | Chlorpropham | 2 | 0.01 | 0.01 | 0.01 | 2 |
| | Piperonylbutoxide | 1 | 0.01 | 0.01 | 0.05 | - |
| | Thiamethoxam | 1 | 0.01 | 0.01 | 0.01 | 1 |
| | Cyfluthrin | 1 | 0.02 | 0.02 | 0.02 | 1 |
| | Cypermethrin | 2 | 0.01 | 0.1 | 0.05 | 1 |
| | Fenpyroximate | 1 | 0.01 | 0.01 | 0.01 | 1 |
| | Diazinon | 1 | <loq< th=""><th><loq< th=""><th>0.01</th><th>-</th></loq<></th></loq<> | <loq< th=""><th>0.01</th><th>-</th></loq<> | 0.01 | - |
| | Spirodiclofen | 1 | <loq< th=""><th><loq< th=""><th>0.02</th><th>-</th></loq<></th></loq<> | <loq< th=""><th>0.02</th><th>-</th></loq<> | 0.02 | - |
| Tomato | Chlorpyrifos | 5 | 0.01 | 0.22 | 0.01 | 5 |
| | Lambda-Cyhalothrin | 5 | <loq< th=""><th>0.05</th><th>0.1</th><th>1</th></loq<> | 0.05 | 0.1 | 1 |
| | Cypermethrin | 5 | <loq< th=""><th>0.06</th><th>0.5</th><th>-</th></loq<> | 0.06 | 0.5 | - |
| | Propargite | 3 | <loq< th=""><th>0.54</th><th>0.01</th><th>2</th></loq<> | 0.54 | 0.01 | 2 |
| | Imidacloprid | 3 | <loq< th=""><th>0.01</th><th>0.5</th><th>-</th></loq<> | 0.01 | 0.5 | - |
| | Chlorpropham | 2 | 0.01 | 0.06 | 0.01 | 2 |
| | Difenoconazole | 1 | 0.01 | 0.01 | 2 | - |
| | Chlorfenapyr | 8 | <loq< th=""><th>0.12</th><th>0.01</th><th>6</th></loq<> | 0.12 | 0.01 | 6 |
| | Buprofezin | 2 | <loq< th=""><th>0.01</th><th>1</th><th>-</th></loq<> | 0.01 | 1 | - |
| | Myclobutanil | 1 | 0.02 | 0.02 | 0.3 | - |
| | Dimethoate | 1 | 0.01 | 0.01 | 0.01 | 1 |
| | Omethoate | 2 | 0.01 | 0.02 | 0.01 | 2 |

The most frequent pesticide residues detected in commodities were as follows: chlorpyrifos as repeated 25 times, lambda-cyhalothrin as repeated 23 times, cypermethrin repeated 15 times and finally chlorpropham as repeated 13 times.

The number of pesticides exceeded the limit of MRL's were 26 and the most violated compounds was chlorpyrifos with the concentration of (0.32 ppm) followed by chlorpropham with level of (9 ppm) and lambda-cyhalothrin (0.08 ppm).

Data shown in (Table 2). in case of analysed violated orange samples, the highest concentrations of dimethoate and omethoate were found with levels of 0.07 and 0.04 ppm, respectively, followed by chlorpyrifos in potato with concentration of 0.02 ppm followed by lambda-cyhalothrin in pomegranate with concentration of 0.02 ppm which is considered acceptable limit.

The data also indicated that the level of chlorfenapyr and chlorpyrifos residues in tomato were found to exceed MRL in 6 and 5 samples with the highest concentration of 0.12 and 0.22 ppm, respectively, followed by chlorpropham in 3 analysed samples of green beans with concentration of 0.02 ppm, then methomyl, dimethoate and iprodione in strawberry with concentration of 0.08, 0.11 and 0.26 ppm, respectively, and finally residues of chlorpyrifos and carbendazim in molokhia

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Table 2 contd....

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| Commodity | Residue | Freq | Min | Max | MRL's ppm | Above |
|-------------|--------------------|------|--|--|-----------|-------|
| | | | | | | MRL |
| | Lufenuron | 2 | <loq< td=""><td>0.01</td><td>0.4</td><td>-</td></loq<> | 0.01 | 0.4 | - |
| | Boscalid | 2 | 0.01 | 0.03 | 3 | - |
| | Methomyl | 2 | 0.02 | 0.08 | 0.01 | 2 |
| | Thiacloprid | 1 | 0.04 | 0.04 | 0.5 | - |
| | Indoxacarb | 2 | 0.01 | 0.04 | 0.5 | - |
| | Fenpyroximate | 1 | 0.1 | 0.1 | 0.2 | - |
| | Benalaxyl | 1 | 0.03 | 0.03 | 0.5 | - |
| | Cyfluthrin | 1 | <loq< td=""><td><loq< td=""><td>0.05</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.05</td><td>-</td></loq<> | 0.05 | - |
| | Tebuconazole | 2 | 0.01 | 0.01 | 0.9 | - |
| | Fenpropathrin | 1 | 0.03 | 0.03 | 0.01 | 1 |
| | Dimethomorph | 1 | 0.06 | 0.06 | 1 | - |
| | Carbendazim | 1 | 0.01 | 0.01 | 0.3 | - |
| | Thiophanate-methyl | 1 | 0.07 | 0.07 | 1 | - |
| | Flutolanil | 1 | 0.01 | 0.01 | 0.01 | 1 |
| | Azoxystrobin | 2 | 0.01 | 0.01 | 3 | - |
| | Famoxadone | 1 | <loq< td=""><td><loq< td=""><td>2</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>2</td><td>-</td></loq<> | 2 | - |
| | Triadimenol | 1 | 0.01 | 0.01 | 0.3 | - |
| | Fenvalerate | 1 | 0.01 | 0.01 | 0.1 | - |
| | Deltamethrin | 1 | <loq< td=""><td><loq< td=""><td>0.07</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.07</td><td>-</td></loq<> | 0.07 | - |
| | Fenitrothion | 1 | 0.01 | 0.01 | 0.01 | 1 |
| | Acetamiprid | 1 | 0.01 | 0.01 | 0.5 | - |
| | Azinophos-methyl | 1 | 0.02 | 0.02 | 0.05 | - |
| | Phosmet | 1 | 0.03 | 0.03 | 0.05 | - |
| | Zoxamide | 1 | 0.04 | 0.04 | 0.5 | - |
| Green beans | Cypermethrin | 3 | 0.01 | 0.07 | 0.7 | - |
| | Chlorpropham | 3 | 0.01 | 0.02 | 0.01 | 3 |
| | Difenoconazole | 4 | <loq< td=""><td>0.01</td><td>1</td><td>-</td></loq<> | 0.01 | 1 | - |
| | Carbendazim | 1 | 0.01 | 0.01 | 0.2 | - |
| | Iprodione | 1 | 0.03 | 0.03 | 2 | - |
| | Propiconazole | 1 | <loq< td=""><td><loq< td=""><td>0.01</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.01</td><td>-</td></loq<> | 0.01 | - |
| | Fenpyroximate | 1 | 0.02 | 0.02 | 0.7 | - |
| | Cyhalothrin | 1 | 0.01 | 0.01 | 0.2 | - |
| | Diniconazole | 1 | <loq< td=""><td><loq< td=""><td>0.01</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.01</td><td>-</td></loq<> | 0.01 | - |
| | Azoxystrobin | 2 | 0.01 | 0.01 | 3 | - |
| | Chlorpyrifos | 1 | 0.01 | 0.01 | 0.05 | - |
| | Methamidophos | 1 | 0.13 | 0.13 | 0.01 | 1 |
| | Cyprodinil | 1 | 0.07 | 0.07 | 2 | - |
| | Fludioxonil | 1 | 0.02 | 0.02 | 1 | - |
| Strawberry | Methomyl | 3 | 0.01 | 0.08 | 0.05 | 1 |
| | Dimethoate | 2 | <loq< td=""><td>0.11</td><td>0.05</td><td>1</td></loq<> | 0.11 | 0.05 | 1 |
| | Omethoate | 1 | 0.04 | 0.04 | 0.05 | - |
| | Difenoconazole | 3 | 0.02 | 0.11 | 20 | - |
| | Acetamiprid | 2 | 0.01 | 0.01 | 0.05 | - |
| | Azoxystrobin | 4 | 0.02 | 0.1 | 60 | - |
| | Spinosad | 1 | 0.02 | 0.02 | 0.1 | - |
| | = | 1 | 1 | 1 | | |

exhibited the highest detected concentration of 0.32 and 1.42 ppm, respectively. This study provides significant data on pesticide residues on fruits and vegetables sold on the major fresh produce markets in Giza, Egypt.

The contaminated vegetables and fruits are representing potential health risks to the consumers. Occurrence of pesticide residues may be due to the lack of awareness of the growers/ farmers about complying with the right recommended rate of pesticide use, correct method of application and neglecting of the estimated pre-harvest intervals. The justification for certain commodities (e.g. tomato and strawberry) that have greater amount of pesticides could be attributed to that these crops are cultivated under greenhouse conditions making them more prone to pests and diseases which in turn requires successive applications of pesticide treatments, leaving higher levels of residues that are tolerated and protected from rapid degradation by direct sunlight Latif et al., 2011.

Furthermore, the frequency of pesticides application particularly in some vegetable farms reached from twice a month to once a week, depending on the crop. In addition, pesticides are usually applied directly to the edible part of fruit or vegetable close to the time of harvest to ensure better plant protection. To avoid detrimental effects of

Table 2 contd....

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|-----|------|-----|-----|---|-------|
| | | | | | |

| Commodity | Residue | Freq | Min | Max | MRL's ppm | Above MRL |
|-----------|--------------------|------|--|--|-----------|--------------|
| | Carbendazim | 3 | ⊲LOQ | 0.01 | 0.1 | - |
| | Chlorpyrifos | 3 | <loq< td=""><td>0.01</td><td>0.5</td><td>-</td></loq<> | 0.01 | 0.5 | - |
| | Penconazole | 2 | 0.01 | 0.01 | 0.1 | - |
| | buprofezin | 1 | 0.36 | 0.36 | 0.5 | - |
| | Boscalid | 2 | 0.08 | 0.11 | 0.9 | - |
| | Pyraclostrobin | 3 | 0.01 | 0.05 | 0.1 | - |
| | Fenhexamid | 1 | 0.01 | 0.01 | 0.05 | - |
| | Novaluron | 1 | 0.04 | 0.04 | 0.01 | 1 |
| | Propiconazole | 2 | 0.01 | 0.01 | 0.05 | - |
| | Iprodione | 1 | 0.26 | 0.26 | 0.05 | 1 |
| | Metalaxyl | 1 | <loq< td=""><td><loq< td=""><td>0.05</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.05</td><td>-</td></loq<> | 0.05 | - |
| | Pyrimethanil | 1 | 0.1 | 0.1 | 0.05 | 1 |
| | Lambda-Cyhalothrin | 1 | 0.04 | 0.04 | 1 | - |
| | Propargite | 1 | 0.05 | 0.05 | 0.05 | 1 |
| | Cyfluthrin | 1 | 0.01 | 0.01 | 0.1 | - |
| Molokhia | Chlorpyrifos | 4 | 0.02 | 0.32 | 0.05 | 2 |
| | Carbendazim | 4 | 0.03 | 1.42 | 0.1 | 2 |
| | Difenoconazole | 2 | 0.03 | 0.06 | 3 | - |
| | Azoxystrobin | 2 | 0.06 | 0.26 | 15 | - |
| | Lambda-Cyhalothrin | 4 | ⊲LOQ | 0.03 | 0.5 | - |
| | Penconazole | 1 | 0.01 | 0.01 | 0.05 | - |
| | Atrazine | 2 | <loq< td=""><td>0.01</td><td>0.05</td><td>-</td></loq<> | 0.01 | 0.05 | - |
| | Cyfluthrin | 1 | <loq< td=""><td><loq< td=""><td>0.02</td><td>-</td></loq<></td></loq<> | <loq< td=""><td>0.02</td><td>-</td></loq<> | 0.02 | - |
| | Cypermethrin | 3 | <loq< td=""><td>0.03</td><td>0.7</td><td>-</td></loq<> | 0.03 | 0.7 | - |
| | Chlorfenapyr | 1 | 0.05 | 0.05 | 0.01 | 1 |
| | Chlorpropham | 2 | 0.02 | 0.05 | 0.05 | 1 |

example, out of 1,579 samples from eight fresh produce markets in Egypt, 23.9% contained detectable pesticide residues Dogheim et al., 2001. Also in other countries, Lee et al., 1998 indicated that 36.2% of 126 samples from seven markets in Mauritius were contaminated. Moreover. Knejzevi'c and Serdar, 2009 reported that 25.8% of 240 samples in Croatia had detectable pesticides. Besides, about two times of these values (43.5%) were found in Ghana. based on 350 samples analysed from six fresh produce markets Bempah et al., 2011. Out of total 131 analyzed samples, 53 were (40%)found contaminated with pesticide residues while only 3 (2%) samples were exceeded the MRLs of some pesticides Latif et al., 2011.

According to our results, it is recommended that regular determination of pesticide residues should be made on each fresh vegetable and fruit.

LOQ = limit of quantification.

MRL= Maximum Residue limit according to EU data base.



Fig. 1: The contamination and the violation percentages per each commodity.

pesticide residues on public health, it is important to establish pest control means that ensure each pesticide should be below MRLs in the fruits and vegetables to be marketed. Similar studies in local markets from Egypt have showed also higher levels of pesticides Gad Alla *et al.*, 2015, Ibrahim *et al.*, 2018 and Badr *et al.*, 2019. For Data also suggested that these detected pesticides have been used indiscriminately as main pest control agents. Thus effects should be made to develop strategies for pesticide reduction through wise and safe use of pesticides, and promote alternatives to chemical pest control Jallow *et al*, 2017. Based on our monitoring results, the violated detected pesticides in the samples analyzed, were selected for the dietary risk assessment and exposure evaluation.

As shown in table 3 the estimated daily intake of pesticide residues did not exceed the established ADI in any case. The EDI as a % of ADI is ranges from 0.0020% of the ADI for fungicide pyrimethanil in strawberry to 8.56 % of the ADI for insecticide omethoate in tomato.

The results pointed out that as the EDI as a % of ADI is less than 100%, the detected pesticides are not harmful to humans and the commodities analysed are considered safe for domestic consumption. Although organochlorine insecticides have long been banned in Egypt, a few were detected in this study including DDT.

| Commodity | Pesticide residues | Mean Conc | Food | FDI | FDI | ADI | FDI as a |
|-------------|--------------------|-----------|-------------|-----------|--------------------------|----------|----------|
| commonly | | mg/kg | Consumption | mg/kg/day | mg/kg. | mg/kg bw | % of ADI |
| | | 55 | gm/day | 555 | bw/day | | |
| Orange | Dimethoate | 0.03 | 38 | 0.0011 | 1.90 x 10 ⁻⁵ | 0.0010 | 1.9000 |
| | Omethoate | 0.04 | 38 | 0.0015 | 2.53 x 10 ⁻⁵ | 0.0003 | 8.4444 |
| | Diazinon | 0.04 | 38 | 0.0015 | 2.53 x 10 ⁻⁵ | 0.0002 | 12.6667 |
| Potato | Gamma-HCH | 0.22 | 61.2 | 0.0135 | 22.44 x 10 ⁻⁵ | Banned | Banned |
| | Total DDT's | 0.10 | 61.2 | 0.0061 | 10.20 x 10 ⁻⁵ | 0.0100 | 1.0200 |
| | alpha-HCH | 0.39 | 61.2 | 0.0239 | 39.78 x 10 ⁻⁵ | Banned | Banned |
| | beta-HCH | 0.14 | 61.2 | 0.0086 | 14.28 x 10 ⁻⁵ | Banned | Banned |
| | delta-HCH | 0.30 | 61.2 | 0.0184 | 30.60 x 10 ⁻⁵ | Banned | Banned |
| | Chlorpyrifos | 0.01 | 61.2 | 0.0008 | 1.36 x 10 ⁻⁵ | 0.0010 | 1.3566 |
| Pomegranate | Lambda-Cyhalothrin | 0.02 | 113.4 | 0.0018 | $3.02 x 10^{-5}$ | 0.0025 | 1.2096 |
| | Chlorpropham | 0.01 | 113.4 | 0.0011 | 1.89 x 10 ⁻⁵ | 0.0500 | 0.0378 |
| | Thiamethoxam | 0.01 | 113.4 | 0.0011 | 1.89 x 10 ⁻⁵ | 0.0260 | 0.0727 |
| | Cyfluthrin | 0.02 | 113.4 | 0.0023 | 3.78 x 10 ⁻⁵ | 0.0030 | 1.2600 |
| | Cypermethrin | 0.06 | 113.4 | 0.0062 | 10.40 x 10 ⁻⁵ | 0.0500 | 0.2079 |
| | Fenpyroximate | 0.01 | 113.4 | 0.0011 | 1.89 x 10 ⁻⁵ | 0.0100 | 0.1890 |
| Tomato | Chlorpyrifos | 0.06 | 102.8 | 0.0060 | 9.94 x 10 ⁻⁵ | 0.0010 | 9.9373 |
| | Lambda-Cyhalothrin | 0.03 | 102.8 | 0.0027 | 4.45 x 10 ⁻⁵ | 0.0025 | 1.7819 |
| | Propargite | 0.19 | 102.8 | 0.0198 | 33.07 x 10 ⁻⁵ | 0.0300 | 1.1022 |
| | Chlorpropham | 0.04 | 102.8 | 0.0036 | 6.00 x 10 ⁻⁵ | 0.0500 | 0.1199 |
| | Chlorfenapyr | 0.04 | 102.8 | 0.0044 | 7.28 x 10 ⁻⁵ | 0.0150 | 0.4854 |
| | Dimethoate | 0.01 | 102.8 | 0.0010 | 1.71 x 10 ⁻⁵ | 0.0010 | 1.7133 |
| | Omethoate | 0.02 | 102.8 | 0.0015 | 2.57 x 10 ⁻⁵ | 0.0003 | 8.5667 |
| | Methomyl | 0.05 | 102.8 | 0.0051 | 8.57 x 10 ⁻⁵ | 0.0025 | 3.4267 |
| | Fenpropathrin | 0.03 | 102.8 | 0.0031 | 5.14 x 10 ⁻⁵ | 0.0300 | 0.1713 |
| | Flutolanil | 0.01 | 102.8 | 0.0010 | 1.71 x 10 ⁻⁵ | 0.0900 | 0.0190 |
| | Fenitrothion | 0.01 | 102.8 | 0.0010 | 1.71 x 10 ⁻⁵ | 0.0050 | 0.3427 |
| Green beans | Chlorpropham | 0.02 | 7.5 | 0.0001 | 0.21 x 10 ⁻⁵ | 0.0500 | 0.0043 |
| | Methamidophos | 0.13 | 7.5 | 0.0010 | 1.63 x 10 ⁻⁵ | 0.0010 | 1.6250 |
| Strawberry | Methomyl | 0.04 | 2 | 0.0001 | 0.13 x 10 ⁻⁵ | 0.0025 | 0.0533 |
| | Dimethoate | 0.06 | 2 | 0.0001 | 0.20 x 10 ⁻⁵ | 0.0010 | 0.2000 |
| | Novaluron | 0.04 | 2 | 0.0001 | 0.13 x 10 ⁻⁵ | 0.0100 | 0.0133 |
| | Iprodione | 0.26 | 2 | 0.0005 | 0.87 x 10 ⁻⁵ | 0.0200 | 0.0433 |
| | Pyrimethanil | 0.10 | 2 | 0.0002 | 0.33 x 10 ⁻⁵ | 0.1700 | 0.0020 |
| | Propargite | 0.05 | 2 | 0.0001 | 0.17 x 10 ⁻⁵ | 0.0300 | 0.0056 |
| Molokhia | Chlorpyrifos | 0.11 | 9.7 | 0.0010 | 1.74 x 10 ⁻⁵ | 0.0010 | 1.7379 |
| | Carbendazim | 0.45 | 9.7 | 0.0043 | 7.19 x 10 ⁻⁵ | 0.0200 | 0.3597 |
| | Chlorfenapyr | 0.05 | 9.7 | 0.0005 | 0.81 x 10 ⁻⁵ | 0.0150 | 0.0539 |
| | Chlorpropham | 0.04 | 9.7 | 0.0003 | 0.57 x 10 ⁻⁵ | 0.0500 | 0.0113 |

Table 3: Estimated Acceptable daily intake (EADI) of violated pesticide residues in different commodities.

Hence, their persistence in the environment, particularly soils Weaver *et al.*, 2012 and the likelihood to contaminate food Florence *et al.*, 2015 require continuous monitoring and frequent follow-up screening.

Results on risk assessment are in agreement with Gad Alla *et al.*, 2015. However, the current study is limited to a relatively small group of vegetables and fruits.

Moreover, the estimated risk assessment via long-term exposure is based on toxicological evaluation of the single compounds and not based on an evaluation of cumulative exposure to multiple pesticide residues in crops. Consequently, advanced research to quantify Egyptian dietary risk pesticide exposure data among Egyptian consumers is needed.

Conclusion

This study showed that observed levels of pesticide residues were not apparently associated with a potential health risk to consumers. Nevertheless, investigation into continuous surveillance in other agricultural produce which are consumed raw is highly recommended to ensure food safety for consumers. Awareness must be raised to develop strategies for pesticide reduction in agriculture by training and education farmers on judicious and better pesticide use, stick to pesticide label instructions, and comply with estimated safety periods. Farmers and growers should be also encouraged to apply alternatives to chemical pest control. Consumers should be careful about used processing and preparatory steps such as washing, boiling and peeling to reduce the level of pesticides in the fresh commodities.

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