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Evaluation of Pesticide Residues in some Commonly Consumed Vegetables in Egypt and their Related Chronic Exposure

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ABSTRACT

A multi-residue quantitative method in combination with liquid and gas chromatography - tandem mass spectrometry, was employed to monitor 281 pesticide residus in the most consumed vegetables at the wholesale markets in Egypt during 2018. Among 506 samples analyzed, 66 different pesticide residues were detected in 405 samples (80%) whereas, 260 samples (51%) contaminated with levels lower than maximum residue limits and 145 samples (29%) were violated. The highest violation was observed at (60%, 58%, 46% and 33%) in parsley followed by pepper, beans and coriander, respectively. Chlorpyrifos, profenofos malathion, lambda-cyhalothrin and metalaxyl were the most frequently detected pesticides. Data Monitored was used for estimating the potential health risks associated with the exposures to the detected pesticides. The highest hazard index was found in tomato for emmactin benzoate (10%) against the acceptable daily intake value for adults. Tomato was the most contributing commodity to the chronic exposure representing 56% to the total risk. The values of cumulative exposure for carbamates, heterocyclic, organophosphorus, pyrethroids, and other groups were calculated and found to be < 1 (0.006-0.256), indicating no risk to consumers due to the exposure to pesticide residues in Egyptian-fresh vegetables. The results showed that despite the high presence of pesticide residues in some vegetables, they did not pose any health risks to consumers.

Keywords:
Chronic Exposure, Cumulative Risk Assessment, Pesticide Residues, Vegetables.

1. INTRODUCTION

Fresh daily consumed vegetables are considered a follow-essential source for a healthy food and balanced diet [1]. Furthermore they rich in carbohydrates, vitamins, fibers, lipids and many of a supplementary nutrients. On the other hand agriculture crops are subject to attack by many diseases

and pests that affect the yield and the quality of foodstuffs. Therefore, farmers worldwide use different groups of pesticides including organophosphorus, organochlrine, pyrethroids and carbamates in order to control diseases, protect crops, get high quality foodstuff to increase the agricultural production in line with population growth demands [2].

Pesticides are chemical compounds used during cultivation, post-harvest treatment, production and storage of agricultural products [3]. During their applications, pesticide residues have harmful, long-term and lethal effects on human health like heart diseases and Alzheimer's [4&5]. Also, contaminants resulting from pesticide residues have become one of the most critical hazards on humanity due to their chronic and acute impact as headaches, nausea, cancer, and endocrine disruption [6]. In 1990, the WHO announced 220 case death of three million cases representing the exposure values of chronic and acute poisoning in the world. However, misuse and application of pesticides are widely used in both the developed and developing countries [7].

In Egypt, different classes of pesticides (fungicides, insecticides, and herbicides) are used during the integrated pest management and/or pest control. However, many of farmers are spraying different pesticides against pests but ignoring pre-harvest intervals (PHI) due to their adequate un-awareness about the use of pesticides in pest control for various vegetable families [8]. Suc consume vegtable families eg. Cucurbitacea (cucumber), Solanaceae (tomato, pepper and eggplant) and leafy vegetables (lettuce, corinader and parsley) are daily consumed by many Egyptian. Leafy vegetables were reported to have violated pesticides exceeding the maximum residue limits (MRL) [9]. The most frequently detected pesticide in vegetables collected from Egyptian markets were the OP's and PY's residues [10].

In the developing countries, the main tools for the monitoring survey of pesticide residues in fruits and vegetables, from equipment, control programs and training of technical personnel are often lacking [11].Therefore, the monitoring of human exposure to pesticide residues is needed to conduct through comparing of residue levels with the international standards such as maximum residue limits (MRLs) that set by the Codex Alimentarius, European (EU) commissions and to acceptable daily intakes (ADIs) set by FAO/WHO. The acceptable daily intake is the permitted amount of chemicals in food expressed as (mg /kg body weight per day) that the human body can be exposed to it daily over a period of time life [12].The monitoring research are always interested in good agriculture practice of pesticides (GAP) such as the registration, authorization, application and compliance with MRL's [13]. Therfore, standard methods to assess the hazards due to pesticide residues and to evaluate the chronic and acute exposure are basde on the average estimated daily intakes per day [14].

The aim of the present study was to assess the concentration levels of residues detected in the most popular consumed vegetables of Egyptian wholesale markets during 2018. To evaluate the compliance of obtained results with MRL's set by Codex and/or EU [15-16]. The obtained monitoring results also evaluated to check the application of Good Agriculture Practice (GAP) and to estimate the dietary exposure and compared with safety limits such as the ADI and/or (ARfD) set by both FAO and WHO.

2. MATERIALS AND METHODS

2.1. Sampling

A total of 506 samples from 10 different vegetables of the most popular consumed and cultivated vegtables, four fruiting vegetables, i.e. cucumber, eggplant, peper and tomato; three leafy vegetables, i.e. coriander, parsley and lettuce; one root vegetable (carrot), one bulb onion and one legume bean were collected from two major wholesale markets (Obour & Six October) in Egypt during 2018. One to two kilograms of each plant crop were prepared for examination against 281 pesticide residues according to Codex Alimentarius Commission (CAC) guidelines, 1993 [17]. The samples were kept

in polythene bags and then transported on ice to the laboratory where they were analyzed immediately and / or grinded with high speed grinder 2 litter capacities jar with lid and stored at 0-5 ^{0}C for no longer than 2 days before analysis.

2.2. Selection of Targeted Pesticides and Analytical Multi-Residue Method

A total of 281 pesticides belong to four categories, insecticides (132), fungicides (76), herbicides (67) and acaricides (6) were monitored for detection of any trace levels of their residues in some commonly consumed market vegetables including beans, carrot, coriander, cucumber, eggplant, lettuce, onion, parsley, pepper and tomato. Pesticides were selected based on their either currently registered or banned and their commercial use in Egypt for controlling mites or ticks, fungi, unwanted weeds and insects with reference to Agricultural Pesticides Committee (APC).

A modified QuEChERS method EN 15662:2008, was used for extraction of samples and to minimize degradation of susceptible compounds (e.g. base and acid labile pesticides), expand the range of matrices amenable by this approach and increase sample throughput while reducing costs [18]. The procedures were carried out based on an initial single- phase extraction using a test homogeneous portion of 10 g sample (water content > 80%) with acetonitrile at 10 ml / 10 g of sample. A liquid –liquid partition is followed by adding one contents of QuEChERS extract kit, part no. 5982-5650. Centrifugation carried out at 10000 rpm for 10 minutes. An aliquot of upper layer, containing pesticide was transferred to 15 ml tube in which matrices were cleaned and the excess of water removed by mixing the acetonitrile (CAN) with magnesium sulfate anhydrous and PSA sorbents through Single d-SPE step, part no. 5982-5056. The final extract can be analyzed directly by either LC-MS/MS or GC-MS/MS technologies

2.3. Instrumentations and Conditions

2.3.1. Reagents and Reference Standards

All Pesticides active ingredients were obtained from Sigma Aldrich (Steinheim, Germany) with purity ≥ 95% and re-kept in refrigerator freezer at -20 ^{o}C. Stock standard solutions of 1000 µg/mL were prepared in 10 mL volumetric flask in acetonitrile and transferred to amber-screw-capped glass vial (12 mL). Pesticide Stock standard solutions were kept in the dark at -20 ± 2 ^{o}C [19]. Intermediate mixture standard solutions (100, 10 and 1) µg/mL was prepared in acetonitrile for LC-MS/MS and HA (9:1) in case of GC-MS/MS. A multi-level calibration mixture solution (5, 10, 25, 50 and 100) µg/L were prepared from of 1000 µg/L. Methanol, Acetonitrile (LC-MS grade), Hexane and Acetone (GC-MS grade). Ammonia solution 33% was obtained from Honeywell (Riedel-de-Haën). Formic acid 98–100% (Merck) was used as acid modifier of the LC mobile phase. De-ionized water was generated by Milli-Q unit (Millipore Corporate, USA) to get LC-grade water. Buffer salts were purchased from Agilent technologies: QuEChERS extract kit, part no. 5982-5650, containing magnesium sulphate 4 g; sodium chloride 1 g; trisodium citrate 1 g and disodium hydrogen sesquihydrate 0.5 g, with purity ≥ 99%. Dispersive SPE 15 ml, part no. 5982-5056, was containing 25 mg of the primary secondary amine bulk sorbent (PSA) and 150 mg magnesium sulphate with purity≥ 98%.

2.3.2. LC-MS/MS Determination

Acquity UPLC system equipped with binary pump, vacuum degasser, and auto sampler. gas generator designed to provide nitrogen gas at least 5 L/min at 60 psi, source gas (zero air) at least 22 L/min at 100 psi and exhaust gas (air) at least 8 L/min at 60 psi.LC–MS/MS was carried out using a Waters Xevo TQ-S (Waters systems) triple quadrupole mass spectrometer with mass range m/z 50 to 2000 and equipped with atmospheric pressure ion source (Turbo V). Separation was performed on ACQUITY BEF C18 2.1 x100 mm, 1.7 µm particle size. The injection volume was 2µL. A gradient elution program at 0.45 ml/min flow, in which one reservoir contained 10mM ammonium format solution in methanol-water (1:9) and the other contained methanol. The ESI source was used in the

positive mode, argon nebulizer and other gas setting were optimized according to recommendations made by the manufacturer; source temperature was 300°C, ion spray potential, 5500v, de-cluster potential and collision energy were optimizes using a Harvard apparatus syringe pump by introducing individual pesticide solutions into the MS instrument to allow optimization of the MS/MS conditions. The Multiple Reactions monitoring mode (MRM) was used in which one MRM was used for quantification and the other for confirmation.

2.3.3. GC-MS/MS Determination

Agilent gas chromatograph (7890A) equipped with triple quadrupole tandem mass spectrometer (7000B), EI source was introduced to perform analysis by using HP-5MS capillary column (30 m, 250 µm id, and 0.25 µm film thickness). Samples were injected with the following conditions: constant pressure, 36.73 psi; inlet temperature, 280 °C; injection volume, 3 µl (splitless); initial oven temperature, 70 °C, held for 2 min, then a 25 °C/min ramp to 150 °C and 3 °C/min ramp to 200 °C followed by a 8 °C/min ramp to 280 °C and held for 10 min.

2.3.4. Method Performance and Quality Assurance

To ensure the fitness of purpose for the method in accordance with European standard, the in-house method validation was carried out according to SANTE and Eurachem guideline's requirements and criteria. The method validation parameters including limit of detection (LOD), limit of quantification (LOQ), accuracy (precision and trueness), recovery method linearity and measurement uncertainty. LOQ's were 10 µg/L for all tested pesticides. The evaluation of linearity was performed in the range from (5-100) µg/L and the method linearity for most of pesticides was with correlation coefficient (R2) ≥ 0.995 and deviation of recalculations ≤ ±20%. Mean recoveries for all target pesticides were in the range from 70-120% expressed as trueness/accuracy [20]. The reproducibility expressed as a relative standard deviation (RSD) was ≤ 20%. The LOQ criteria should fulfil the requirements of precision and trueness/ accuracy regarding both recovery and RSD %. Furthermore, LOQ values were almost ≤ the lowest MRL. Expanded uncertainty expressed as RSD % and at confidence level 95% was found to be < ±50% (European default value) [21].

2.4. Estimated Daily Intake (EDI) Calculations

The exposure to the pesticide residues was evaluated via estimation of daily intake (EDI) and compared with toxicological criteria such as acceptable daily intakes (ADIs). EDI was calculated for each commodity/pesticide combinations using the following equation:

EDI (mg kg^{-1}bw day^{-1}) = [Mean Concentration (mgkg^{-1}) of pesticide residue X Amount of intake food (kgd^{-1}) per body weight (kg)] [22]. (1)

The evaluation of dietary exposure to pesticide residues was based on a total of detected residues and food consumption assumptions set by WHO/GEMS/Food Cluster diets, as showed in Table 1. Egypt was introduced in cluster G06 as countries clustered based on statistical similarities between dietary patterns. [23]. Hazard index (HI) was calculated by comparing the EDI value to its corresponding of ADI, taking in consideration of 60 kg as average adult's weight body [24&25]. The estimated daily intakes were used as an indication for health risks to consumers on long term. When HI >1; there is a risk to the consumer and the food is unacceptable and vice versa [26]. Cumulative risk (ΣHI's) equals the summation of HI for detectable pesticide belonging to the same chemical group.

3. RESULTS AND DISCUSSION

3.1. Monitoring surveys

The number of samples analyzed per each vegetable crop, detectable pesticides with their mean concentration range in mg/kg and violated compounds of each pesticide/commodity are illustrated in (Table 2).

In the current study, the results of the monitoring were evaluated versus to rules of Egyptian Agriculture Pesticides Committee (APC) which are applied in Egypt stated that " pesticide residue levels should be compared with Codex Alimentarius as it's available and to the EU-MRL's in case of codex MRL's lack" and EPA in case of EU lack. These rules would maintain the safety of agricultural products either consumed locally or exported abroad.

Overall, 20% (101 samples) of samples analyzed had no detectable residues. Whereas, 80% (405 samples) had detectable pesticide residues of which 29% contaminated at levels above the MRL's and 51% (260 samples) within limits.

The results of detectable residues (>LOQ) were included in calculation and therefore the results for values less than LOQ are considered zero.

Table 1. Scientific names and consumption rates of target vegetable crops according to WHO/GEMS/food, Cluster G06 (Egypt)

S.	Vegetable	Scientific name	Consumption (g/day)
1	Beans	*Phaseolus vulgaris*	0.49
2	Carrot	*Daucus carota*	6.1
3	Coriander	*Coriandrum sativum*	0.17
4	Cucumber	*Cucumis sativus*	34.92
5	Eggplant	*Solanum melongena*	20.12
6	Lettuce	*Lactuca sativa*	6.05
7	Onion	*Allium cepa*	43.38
8	Parsley	*Petroselinum crispum*	0.77
9	Pepper	*Capsicum annuum*	6.24
1	Tomato	*Solanum lycopersicum*	200.93

The obtained results for the contamination and violation rates were summarized for each group of plant crops. Whereas, the highest contamination percentages were recorded for fruiting vegetables of 32%, after that leafy vegetables (25%), bulb vegetables (11%) and then legume vegetables (10%) of which 10%, 11%, 3% and 5% were violated i.e. exceed the permissible limits, respectively. No violation was observed for root vegetables i.e. carrot while 6%, was observed for pepper and parsley, 5% for beans and 3% for coriander and onion (Table 3).

Table 2. The number of analyzed samples per each vegetable crop, frequency of residues levels, MRL's and their violated pesticides.

Pesticides residues detected	Freq	< LOQ	Min	Max	Mean	Codex MRL	EU MRL	Viol Compounds
			mg/kg					
Commodity No. 1. Beans, Total analyzed sample: (60)								
Acetamiprid	8	1	0.010	0.080	0.036	0.40	0.30	
Azoxystrobin	7	1	0.010	0.060	0.032	0.06	3.00	
Buprofezin	1		0.020	0.020	0.020	0.70	0.01	1
Carbendazim	11	1	0.010	0.250	0.088		0.20	
Chlorpyrifos	13		0.010	0.260	0.100		0.01	9
Cypermethrin	14		0.010	0.290	0.080	0.07	0.70	
Cyprodinil	5		0.020	0.240	0.130	2.00	2.00	
Difenoconazole	15		0.010	0.140	0.056	0.70	1.00	

Dimethoate	4		0.020	0.210	0.078		0.01	4
Dimethomorph	2		0.010	0.140	0.075	0.70	0.01	1
Diniconazole	4		0.010	0.060	0.033	0.01	0.01	3
Fenpropathrin	2	1	0.020	0.020	0.020		0.01	1
Fenpyroximate	1		0.030	0.030	0.030	0.20	0.70	
Flusilazole	4		0.010	0.030	0.020		0.01	3
Hexythiazox	1		0.010	0.010	0.010		0.50	
Imidacloprid	8		0.020	0.240	0.090	2.00	2.00	
Indoxacarb	2		0.030	0.030	0.030		0.50	
Iprodione	7		0.010	1.000	0.298		0.01	5
Lambda-Cyhalothrin	9	1	0.010	0.020	0.015	0.30	0.40	
Malathion	2		0.030	0.090	0.060	1.00	0.02	2
Metalaxyl	4	1	0.010	0.040	0.025		0.20	
Myclobutanil	3		0.010	0.010	0.010	0.80	0.80	
Omethoate	3		0.010	0.020	0.015		0.01	2
Penconazole	1		0.020	0.020	0.020		0.01	1
Profenofos	3		0.010	0.020	0.015		0.01	1
Propamocarb	5		0.010	0.080	0.037		0.10	
Propiconazol	1		0.010	0.010	0.010		0.01	
Pyridaben	1		0.010	0.010	0.010		0.20	
Pyrimethanil	1		0.110	0.110	0.110		3.00	
Spinosad	2		0.030	0.080	0.055		0.30	
Tebuconazole	1		0.070	0.070	0.070	3.00	2.00	
Thiacloprid	1		0.580	0.580	0.580		0.40	
Thiobencarb	1		0.010	0.010	0.010		0.01	
Thiophanate-methyl	5		0.020	0.420	0.184		0.10	2
Triadimenol	1		0.010	0.010	0.010	1.00	0.01	
Commodity No. 2. Carrot, Total analyzed sample: (37)								
Chlorpyrifos	3	1	0.010	0.160	0.085	0.10	0.10	
Difenoconazole	1		0.010	0.010	0.010	0.20	0.40	
Dimethomorph	1		0.010	0.010	0.010		0.01	
Flutolanil	1		0.160	0.160	0.160		0.01	1
Malathion	1		0.010	0.010	0.010		0.02	
Myclobutanil	1		0.010	0.010	0.010		0.20	
Omethoate	1		0.010	0.010	0.010		0.02	
Penconazole	1		0.010	0.010	0.010		0.01	
Propamocarb	1		0.010	0.010	0.010		0.01	
Pyridaben	1		0.010	0.010	0.010		0.01	
Commodity No. 3. Coriander, Total analyzed sample: (60)								
Acetamiprid	3		0.010	0.010	0.010		0.05	
Atrazine	2		0.010	0.560	0.285		0.10	
Carbendazim	16	1	0.010	0.350	0.133		0.10	3
Chlorpyrifos	39	9	0.010	1.700	0.376		5.00	
Cypermethrin	3	1	0.010	0.020	0.015		0.10	
Diazinon	2		0.010	0.010	0.010		5.00	
Difenoconazole	1		0.040	0.040	0.040		0.30	

Fenarimol	1		0.010	0.010	0.010		0.05	
Flusilazole	5	2	0.010	0.010	0.010		0.05	
Hexaconazole	1		0.020	0.020	0.020		0.05	
Imidacloprid	1		0.070	0.070	0.070		0.05	
Iprodione	1		0.050	0.050	0.050		0.05	
Lambda-Cyhalothrin	4		0.010	0.050	0.030		0.01	1
Malathion	22	4	0.010	0.380	0.108		0.02	6
Metalaxyl	12	3	0.010	0.080	0.036		0.05	
Myclobutanil	2		0.010	0.010	0.010		0.05	
Oxyfluorfen	1		0.010	0.010	0.010		0.05	
Penconazole	9		0.010	0.110	0.050		0.05	
Pendimethalin	20	3	0.010	0.550	0.185		0.05	8
Profenofos	27	4	0.010	1.000	0.238		0.05	9
Propamocarb	1		0.050	0.050	0.050		0.05	
Propiconazol	2		0.140	0.560	0.350		0.05	2
Tebuconazole	3		0.010	0.030	0.020		1.50	
Thiophanate-methyl	1		0.080	0.080	0.080		0.10	
Triadimenol	1		0.010	0.010	0.010		0.05	
Commodity No. 4. Cucumber, Total analyzed sample: (43)								
Acetamiprid	2		0.020	0.090	0.055	0.30	0.30	
Azoxystrobin	3		0.050	1.800	0.925	1.00	1.00	1
Benalaxyl	1		0.020	0.020	0.020		0.05	
Carbendazim	1		0.020	0.020	0.020	0.50	0.10	
Carbofuran	1		0.030	0.030	0.030		0.02	1
Chlorpropham	1		0.010	0.010	0.010		0.01	
Chlorpyrifos	2		0.020	0.060	0.040		0.01	2
Cypermethrin	1		0.100	0.100	0.100	0.07	0.20	
Dimethomorph	2		0.010	0.070	0.040	0.50	0.50	
Ethion	1		0.060	0.060	0.060		0.01	1
Flutolanil	1		0.010	0.010	0.010		0.01	
Hexythiazox	2		0.020	0.240	0.130	0.05	0.50	1
Imidacloprid	1		0.020	0.020	0.020	1.00	1.00	
Indoxacarb	1		0.010	0.010	0.010	0.50	0.50	
Iprodione	1		0.190	0.190	0.190	2.00	0.01	1
Malathion	1		0.010	0.010	0.010	0.20	0.02	
Mandipropamid	2		0.020	0.040	0.030	0.20	0.20	
Metalaxyl	7	1	0.010	0.260	0.082	0.50	0.50	
Myclobutanil	1		0.020	0.020	0.020	0.20	0.20	
Profenofos	1		1.060	1.060	1.060		0.01	1
Propamocarb	9		0.030	0.530	0.213	5.00	5.00	
Propiconazol	2		0.010	0.020	0.015		0.01	1
Tetraconazole	1		0.010	0.010	0.010		0.20	
Thiamethoxam	3		0.010	0.070	0.033	0.50	0.50	
Thiophanate-methyl	1		0.120	0.120	0.120		0.10	
Trifloxystrobin	1		0.040	0.040	0.040		0.30	

Commodity No. 5. Eggplant, Total analyzed sample: (44)								
Acetamiprid	5		0.010	0.380	0.176	0.20	0.20	1
Azoxystrobin	3	2	0.020	0.020	0.020	3.00	3.00	
Carbendazim	1		0.010	0.010	0.010		0.50	
Chlorpyrifos	3		0.090	1.500	0.610		0.01	3
Clothianidin	1	1		< LOQ			0.04	
Diazinon	1	1		< LOQ			0.01	
Dimethomorph	1		0.020	0.020	0.020	1.50	1.00	
Famoxadone	2		0.030	0.120	0.075		1.50	
Fenpropathrin	3		0.070	0.340	0.247		0.01	3
Imidacloprid	2	1	0.750	0.750	0.750	0.20	0.50	1
Metalaxyl	2	1	0.010	0.010	0.010		0.01	
Myclobutanil	1		0.010	0.010	0.010		0.30	
Profenofos	1		0.010	0.010	0.010		0.01	
Thiamethoxam	5	1	0.010	0.050	0.030	0.70	0.20	
Commodity No. 6. Lettuce, Total analyzed sample: (22)								
Atrazine	2		0.140	0.240	0.190		0.05	2
Carbendazim	3		0.260	1.200	0.700	5.00	0.10	2
Chlorpyrifos	3	1	0.010	0.010	0.010		0.01	
Imidacloprid	7	1	0.020	0.080	0.054	2.00	2.00	
Iprodione	3	1	0.010	0.020	0.015	10.00	0.01	
Lambda-Cyhalothrin	1		0.050	0.050	0.050		0.15	
Malathion	1	1		< LOQ			0.50	
Metalaxyl	3		0.020	0.040	0.030	2.00	3.00	
Omethoate	1		0.010	0.010	0.010		0.01	
Propamocarb	1		0.020	0.020	0.020	100.00	40.00	
Commodity No. 7. Onion, Total analyzed sample: (60)								
Acetamiprid	1		0.100	0.100	0.100	0.02	0.01	1
Azoxystrobin	15	1	0.020	1.510	0.261		10.00	
Carbendazim	5	1	0.010	0.040	0.025		0.10	
Chlorpyrifos	9	1	0.010	0.020	0.015	0.20	0.20	
Cypermethrin	4		0.090	0.130	0.110		0.05	4
Cyprodinil	2	2		< LOQ		0.30	0.30	
Diazinon	2		0.110	0.170	0.140	0.05	0.05	2
Difenoconazole	1		0.170	0.170	0.170	0.10	0.50	1
Dimethomorph	12	2	0.010	0.130	0.046	0.60	0.60	
Emamectin benzoate	1		0.010	0.010	0.010		0.01	
Flutolanil	2		0.020	0.030	0.025		0.01	2
Imidacloprid	2		0.050	0.050	0.050	0.10	0.10	
Indoxacarb	4		0.020	0.080	0.043		0.02	
Iprodione	3		0.030	0.160	0.093	0.20	0.01	3
Lambda-Cyhalothrin	18		0.010	0.250	0.090		0.20	
Lufenuron	1		0.020	0.020	0.020		0.01	1
Malathion	3		0.010	0.010	0.010	1.00	0.02	
Metalaxyl	10	2	0.010	0.260	0.103	2.00	0.50	
Metribuzin	1	1		< LOQ			0.10	

Penconazole	1	1		< LOQ			0.01	
Pendimethalin	6	2	0.010	0.020	0.015	0.05	0.05	
Profenofos	7		0.010	1.300	0.484		0.02	4
Propamocarb	7		0.010	0.540	0.144	2.00	2.00	
Spinosad	1		0.150	0.150	0.150	0.10	0.07	
Thiacloprid	2		0.010	0.020	0.015		0.01	1
Thiophanate-methyl	1		0.040	0.040	0.040		0.10	
Trifloxystrobin	1		0.020	0.020	0.020		0.01	1
Commodity No. 8. Parsley, Total analyzed sample: (60)								
Acetamiprid	3		0.020	0.190	0.083		3.00	
Carbendazim	4	1	0.010	0.020	0.015		0.10	
Chlorpyrifos	33	4	0.020	1.000	0.206		0.02	28
Cypermethrin	3		0.010	0.010	0.010	0.70	2.00	
Diazinon	1	1		< LOQ			0.02	
Dimethoate	1		0.320	0.320	0.320		0.02	1
Ethion	1	1		< LOQ			0.01	
Ethoprophos	1		0.010	0.010	0.010		0.02	
Flusilazole	1		0.010	0.010	0.010		0.02	
Lambda-Cyhalothrin	13	1	0.010	0.430	0.135		0.70	
Malathion	38	7	0.010	3.650	0.647		0.02	15
Metalaxyl	5	3	0.020	0.030	0.025		3.00	
Penconazole	2	1	0.020	0.020	0.020		0.02	
Pendimethalin	8		0.030	0.580	0.173			
Profenofos	36	5	0.010	2.550	0.396			4
Propiconazol	1		0.010	0.010	0.010		0.02	
Thiophanate-methyl	5		0.010	0.100	0.054		0.10	
Commodity No. 9. Pepper, Total analyzed sample: (60)								
Acetamiprid	22	1	0.010	0.490	0.155	0.20	0.30	2
Azoxystrobin	3		0.020	0.110	0.053	3.00	3.00	
Bifenthrin	2		0.010	0.040	0.025		0.50	
Buprofezin	3	1	0.030	0.540	0.285		0.01	2
Carbendazim	3		0.010	0.050	0.030		0.10	
Carbofuran	1		0.010	0.010	0.010		0.002	1
Carbosulfan	1	1		< LOQ			0.002	
Chlorpropham	1		0.030	0.030	0.030		0.01	1
Chlorpyrifos	32	8	0.010	7.400	0.705	2.00	0.01	19
Cypermethrin	16	4	0.010	0.200	0.080	0.10	0.50	1
Difenoconazole	3		0.040	0.280	0.137	0.60	0.90	
Dimethoate	2	1	0.010	0.010	0.010	0.50	0.01	
Diniconazole	1		0.050	0.050	0.050		0.01	1
Ethion	1		0.450	0.450	0.450		0.01	1
Fenpropathrin	2		0.010	0.030	0.020		0.01	1
Hexythiazox	2	1	0.020	0.020	0.020		0.50	
Imidacloprid	13	2	0.010	0.820	0.204		1.00	
Indoxacarb	2	1	0.020	0.020	0.020		0.30	
Iprodione	1		0.270	0.270	0.270		0.01	1

Lambda-Cyhalothrin	25	3	0.010	0.210	0.072			2
Malathion	4	1	0.030	0.030	0.030		0.02	1
Metalaxyl	1	1		< LOQ			0.50	
Methamidophos	2		0.230	0.430	0.330		0.01	2
Myclobutanil	1		0.030	0.030	0.030		0.50	
Omethoate	3	1	0.010	0.050	0.030		0.01	1
Permethrin	1		0.030	0.030	0.030		0.05	
Phosalone	1		0.370	0.370	0.370		0.01	1
Profenofos	13	3	0.010	0.780	0.223		0.01	8
Propamocarb	2	1	0.640	0.640	0.640	3.00	3.00	
Pyridaben	7	4	0.010	0.020	0.015		0.01	2
Pyrimethanil	1		0.890	0.890	0.890		2.00	
Pyriproxyfen	1		0.020	0.020	0.020		1.00	
Spirodiclofen	1		0.080	0.080	0.080	0.20	0.20	
Tebuconazole	1		0.350	0.350	0.350	1.00	0.60	
Thiacloprid	3		0.010	0.020	0.015	1.00	1.00	
Thiamethoxam	5		0.030	0.240	0.125	0.70	0.70	
Thiophanate-methyl	8		0.040	0.860	0.346		0.10	5
Triadimenol	1		0.290	0.290	0.290	1.00	0.50	
Trifloxystrobin	2		0.100	0.180	0.140	0.30	0.40	
Commodity No. 10. Tomato, Total analyzed sample: (60)								
Acetamiprid	2		0.010	0.030	0.020	0.20	0.50	
Azoxystrobin	2	1	0.130	0.130	0.130	3.00	3.00	
Bromuconazole	1		0.020	0.020	0.020		0.01	1
Carbendazim	4	1	0.010	0.020	0.015	0.50	0.30	
Chlorpyrifos	8		0.010	0.230	0.100		0.10	1
Cymoxanil	1		0.010	0.010	0.010		0.40	
Cypermethrin	4	1	0.010	0.050	0.033	0.20	0.50	
Cyprodinil	1	1		< LOQ		2.00	1.50	
Diazinon	7		0.010	0.110	0.056	0.50	0.01	10
Difenoconazole	2		0.010	0.020	0.015	0.80	2.00	
Dimethoate	1		0.010	0.010	0.010		0.01	
Dimethomorph	5		0.010	0.130	0.058	1.50	1.00	
Emamectin benzoate	2		0.010	0.020	0.015		0.02	
Famoxadone	3		0.010	0.180	0.070	2.00	2.00	
Fluopicolide	1	1		< LOQ		1.00	1.00	
Imidacloprid	3		0.020	0.050	0.035	0.50	0.50	
Lambda-Cyhalothrin	2		0.010	0.010	0.010	0.30	0.70	
Metalaxyl	5		0.010	0.250	0.070	0.50	0.30	
Profenofos	5		0.030	0.270	0.093	10.00	10.00	
Propamocarb	5		0.060	26.400	7.420	2.00	4.00	2
Spinosad	1	1		< LOQ		0.30	0.70	
Tebuconazole	1		0.010	0.010	0.010	0.70	0.90	
Thiacloprid	4		0.010	0.040	0.023	0.50	0.50	
Thiamethoxam	2	1	0.040	0.040	0.040	0.70	0.20	
Thiophanate-methyl	3	1	0.050	0.130	0.090		1.00	

Trifloxystrobin	1		0.090	0.090	0.090	0.70	0.70	

Table 3. The number of analyzed samples, not detected, contaminated and percentages violation

Crops Groups	Commodities	Total	Free (ND)	Contaminated not violated	Violated
Fruiting vegetables	Cucumber	43	14	22	7
	Eggplant	44	16	23	5
	Pepper	60	5	23	32
	Tomato	60	8	44	8
Total		207	43	112	52
%		41%	8.5%	22%	10%
Leafy vegetables	Coriander	60	6	36	18
	Parsley	60	5	22	33
	Lettuce	22	7	12	3
Total		142	18	70	54
%		28%	3.5%	14%	11%
Root vegetables	Carrot	37	27	9	1
%		7%	5.5%	2%	0%
Bulb vegetables	Onion	60	5	41	14
%		12%	1%	8%	3%
Legume vegetables	Beans	60	8	28	24
%		12%	1.5%	5%	5%
Total analyzed Vegetables		506	101	260	145
%		**100%**	**20%**	**51%**	**29%**

3.2. Evaluation of detected pesticide

About 66 pesticide residues were detected in the analyzed vegetable samples. The highest detected pesticide residue was emmactin benzoate with contribution percentage of 18.26%, while bromuconazole recoded the lowest contribution percentage of 1.06% (Figure 1). The contribution percentage of other detected pesticide residues ranged from 1.18% (imidacloprid) to 14.62% (chlorpyrifos) (Figure1). The contribution percentage was calculated by dividing of the hazard index of each pesticides/Sum of total hazard indices.

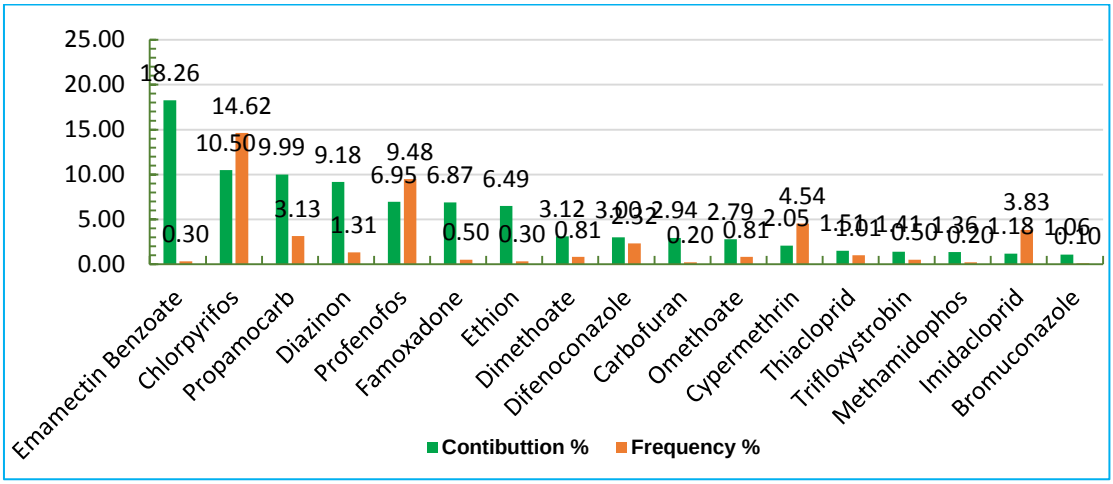

Figure1. The contribution % of pesticides in total hazard indices of detected pesticides residues and their frequencies %, >1%

Organophosphorous was the most detected group followed by heterocyclic, carbamates and pyrethoids. Chlorpyrifos is an organophosphorous insecticide with a broad-spectrum activity. However, its mode of action (Cholinesterase inhibition) can cause a potential toxicity in humans [27]. Chlorpyrifos was recorded as the highest detected residue with highest violation rates in 28 vegetable samples collected from Polish farmers' fields [28]. Moreover, both of chlorpyrifos and cypermethrin were commonly used as effective insecticides which affect the nervous system of insects through disrupting both axon and synaptic transmission of the nerve impulses [29].

In the current study, the detected pesticides are classified according to chemical groups and the mode of applications classes with their percentages of detections and were found as follow; four chemical groups of organophosphorous (15%), organochlorine (9%), pyrethoids (8%), carbamates (11%), heterocyclic (35%) and (23%) other groups (Figure 2). The major classes were insecticides (28 compounds) with percentage of 42%, fungicides (27) 41%, herbicides (9) 14% and acaricides (2) with percentage 3%. These obtained results are in line with other previous published studies, whereas most detected pesticides collected from Riyadh, KSA were organophosphorous, organochlorine, pyrethoids and carbamates [30].

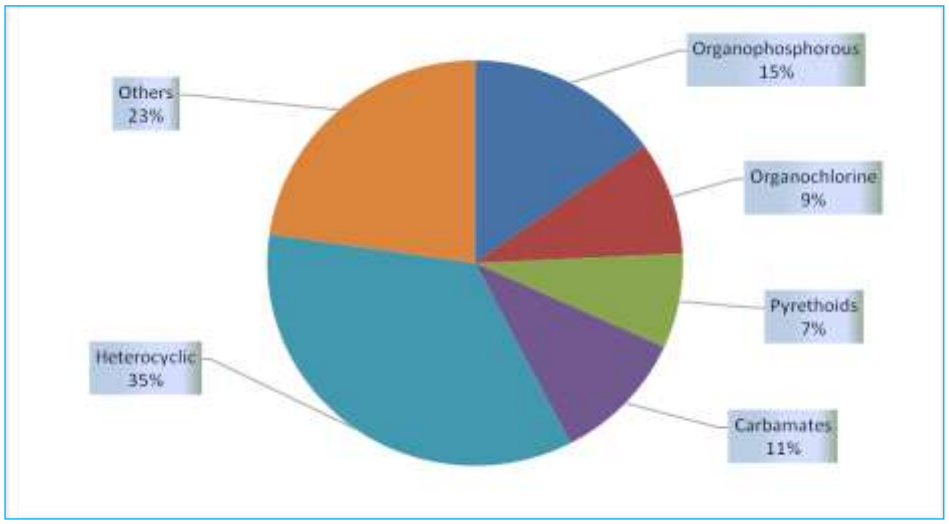

Figure 2. The contribution percentage of chemical groups of pesticide residues in the surveyed Egyptian vegetable crops

The results also, showed that the highest contamination and violation rates were observed for leafy vegetables i.e. coriander, parsley, and lettuce. This might be due to the extensive and misuse of the applied pesticides especially on broad leaves.

In Egypt, leafy vegetables like molokhia and lettuce are cultivated in the field beside other crops which lead to high contamination due to the extensive use of pesticides [31 & 32]. The current study is matched with compare to the presented study from Lucknow city, India, whereas, 23 pesticide residue with concentration range from (0.005-12.35 mg/kg). Moreover, some organochlorine pesticide residues which were banned in worldwide [33].

The monitoring survey of 180 samples collected from wholesale market in Korean, showed the presence of contamination rate of 6.7% was recorded for in 15 leafy vegetables [34].

3.3. Chronic exposure assessment

The long-term risk (chronic exposure) assessment requires a comparison between the exposure calculated with the mean pesticide residue levels consumed and the ADI.

Human health is subject to be at risk if the chronic exposure to toxic residues exceeded the acceptable daily intake on long term. However, in other reported there was health risk due to the residues of OP's i.e. chlorpyrifos, dicrovofos, monocrotophos and omethoate in some Ghanaian vegetables [35].

Dietary exposure was estimated for 66 pesticide residues with a detectable figure (not less than limit of quantification) to avoid overdose intake of contaminated food. The total exposure was evaluated by calculating all exposure cases of pesticide residues/food combinations. The estimated average daily intake (EDI ug kg $^{-1}$bw $^{-1}$) and the ratio of EDI to ADI for each pesticide residues i.e. hazard index (HI) were calculated. If the hazard index exceeds 1, means the pesticide has exceeded the maximum acceptable level (e.g. ADI or ARfD) and there might thus be a risk. The obtains results illustrated in (Table 4).

Overall, the long-term exposure of the Egyptian consumers to pesticide residues through the consumption of vegetables appears to be relatively low. In most cases the HI's for detected pesticides were in the range of (0.00028- 11%). The highest HI was observed for emmactin benzoate (18% of total HI's).

3.4. Cumulative exposure

Cumulative risk is one of the important approaches to evaluate hazard resulting from multiple residues. The methodology for cumulative risk assessment was used for the first time in 2010 by EFSA [36]. The presence of similar toxicological characteristics on food is the only case for the occurrence of cumulative effects.

Federal institute recommends evaluating the cumulative risk of pesticide residues via calculating the hazard indices for each pesticide belongs to the same chemical group. That is would provide us with adequate information about toxicity data to save the safety for the consumers [37]. The hazard index is a significant approach to evaluate the toxicological extent in food through comparing the ADL values with ADI and ARfD. Accordingly, determine the probability of any of risk through consumption of pesticide residues containing foodstuff.

In the current study, the values of Cumulative risk (ΣHR's) were obtained by calculating all HI for each pesticide belonging to the same chemical group.

The cumulative exposure values (hazard index) were found to be for, organophosphorous, pyrethoids, carbamates and heterocyclic <1 (0.006-0.256) for adults, indicates no hazard to the consumers through the consumption of such vegetables (Table 4).

The obtained data showed that, the highest intakes were observed for organophosphates group followed by heterocyclic, carbamates and pyrethoids. However, the calculated intake indicated that, there was no risk associated to the consumption of vegetable samples whereas, all calculated HI for individual pesticides have values less than one indicated negligible risk.

The contributions percentages were calculated to the total HI, tomato was the most contributed commodity to HI with percentage of 56%, followed by onion, cucumber, pepper and eggplant with contribution percentages of 13%, 12%, 11% and 5%, respectively. Hence, there were relatively some levels of dietary exposure, lead to certain health risk to consumers. But reduced for leafy vegetables due to home washing and cooking process (Figure 3)

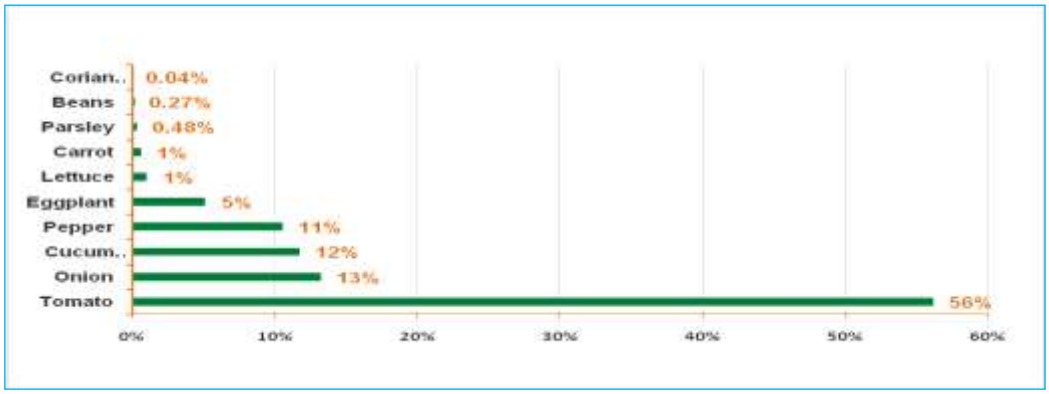

Figure 3. The % contribution of target commodity for the total hazard index%

Organophosphate and pyrethroid pesticides were the major groups used in Egypt for more than 25 years (1980's), which refers to the exposure of consumers to these groups of pesticides for long periods that may be needed continuous evaluation of exposure via all sources such as food, environment, and water.

However, the exposure to lower levels of pesticides residues for a long periods were associated with harmful effects on human health such as cancer diseases and reproductive abnormalities [38].That is emphasized the need for new strategies to reduce dietary exposure to OP's PY's, carbamates, and other heterocyclic pesticides. Furthermore, introduce the bio pesticides in a farm work of integrated pest management (IPM)

Table 4. Total intake values and HI % of pesticide residues in some Egyptian Vegetables during 2108

SN	Substance Group	Pesticides Detected	ADI	ARfD	Source	Total EDI	HI Total
			ug/kg.bw	ug/kg.bw		ug/ kg. bw	%
1	**Organophosphorus**	Chlorpyrifos	10	100	JMPR_2004	0.661	6.61053
		Diazinon	5	30	JMPR_2006	0.289	5.77566
		Dimethoate	2	20	JMPR_2003	0.039	1.96340
		Ethion	2	2000	JMPR_1990	0.082	4.08600
		Ethoprophos	0	50	JMPR_1999	0.000	0.03208
		Malathion	300	2000	JMPR_2003	0.026	0.00876
		Methamidophos	4	10	JMPR_2002	0.034	0.85800
		Omethoate	0	0	JMPR_1985	0.005	1.75583
		Phosalone	20	300	JMPR_2001	0.038	0.19240
		Profenofos	30	1000	JMPR_2007	1.312	4.37274
HI=ΣHI's							**25.65541**

2	**Pyrethroids**	Bifenthrin	10	10	JMPR_ 2009	0.003	0.02600
		Cypermethrin	20	40	JMPR_2006	0.259	1.29251
		Fenpropathrin	30	30	JMPR_2012	0.085	0.28320
		Lambda-Cyhalothrin	20	20	JMPR_2007	0.113	0.56526
		Permethrin	50	50	JMPR_1999	0.003	0.00624
		HI=ΣHI's					**2.17320**
3	**Organochlorine**	Atrazine	20	100	JMPR_ 2007	0.020	0.09983
		Fenarimol	10	0	JMPR_1995	0.000	0.00028
		Indoxacarb	10	100	JMPR_2005	0.039	0.39475
		Pyridaben	10	50	EFSA 10	0.003	0.02658
		Spirodiclofen	10	10	JMPR_2009	0.008	0.08320
		HI=ΣHI's					**0.60465**
4	**Carbamates**	Carbendazim	30	100	JMPR_2005	0.158	0.52762
		Carbofuran	1	1	JMPR_ 2008	0.019	1.85000
		Carbosulfan	10	20	JMPR_2003	0.000	0.00000
		Chlorpropham	50	500	JMPR_ 2005	0.009	0.01788
		Propamocarb	400	2000	JMPR_2005	25.146	6.28654
		Thiophanate-methyl	80	80	JMPR_2006	0.439	0.54823
		HI=ΣHI's					**9.23028**
5	**Heterocyclic**	Acetamiprid	70	100	JMPR_2011	0.248	0.35402
		Bromuconazole	10	100	10/92/EU	0.067	0.66977
		Buprofezin	8	500	JMPR_ 2009	0.030	0.37254
		Clothianidin	100	600	JMPR_ 2010	0.000	0.00000
		Cyprodinil	30	30	JMPR_2003	0.001	0.00354
		Difenoconazole	10	300	JMPR_2007	0.189	1.88941
		Famoxadone	6	600	JMPR_2003	0.260	4.32614
		Fenpyroximate	10	20	JMPR_2007	0.000	0.00245
		Flusilazole	7	20	JMPR_2007	0.000	0.00457
		Hexaconazole	5	0	JMPR_1990	0.000	0.00113
		Hexythiazox	30	30	JMPR-2008	0.078	0.25941
		Imidacloprid	60	400	JMPR_2001	0.444	0.74011
		Iprodione	60	0	JMPR_1995	0.210	0.35038
		Myclobutanil	30	300	JMPR_2014	0.019	0.06413
		Penconazole	30	0	JMPR_1992	0.002	0.00526
		Propiconazol	70	300	JMPR_2004	0.010	0.01419
		Pyrimethanil	200	0	JMPR_2007	0.093	0.04673
		Tebuconazole	30	300	MPR_2010	0.071	0.23506
		Tetraconazole	4	50	EFSA 08	0.006	0.14550
		Thiacloprid	10	30	JMPR_2006	0.095	0.95281
		Thiamethoxam	80	1000	JMPR_2010	0.176	0.22052
		Triadimenol	30	80	JMPR_2004	0.030	0.10090
		HI=ΣHI's					**10.7585**

							7
6	**Other**						
	Antihelmintics	Emamectin Benzoate	1	20	JMPR_2014	0.057	**11.49250**
	Benzoylurea	Lufenuron	20	20	JMPR_2015	0.014	0.07230
	Bezamide	Flutolanil	90	90	JMPR_2002	0.040	0.04462
	Dimethylaniline	Metalaxyl	80	500	2010/28/EU	0.363	0.45383
	Dinitrophenol	Pendimethalin	100	1000	JMPR_2016	0.014	0.01359
	Ethylurea	Cymoxanil	13	80	EFSA 08	0.033	0.25760
	Hydroxymethylamine	Spinosad	20	20	JMPR_2004	0.109	0.54450
	Methoxyacrylateate	Azoxystrobin	200	200	JMPR_2008	1.175	0.58743
	Morpholine	Dimethomorph	200	600	JMPR_2007	0.259	0.12955
	Methoxylimine	Trifloxystrobin	40	40	JMPR_2004	0.354	0.88424
	Phenylacetamide	Benalaxyl	70	100	JMPR_ 2005	0.012	0.01663
	Ynoxyacetamide	Mandipropamid	200	200	JMPR_2008	0.017	0.00873
	Trifluoromethylbenzene	Oxyfluorfen	3	300	(EU) 2017/359	0.000	0.00094
	Yloxypyridine	Pyriproxyfen	100	100	JMPR_2001	0.002	0.00208
		HI=ΣHI's					**14.50854**

4. CONCLUSION

The monitoring survey studies of pesticide residues in Egyptian vegetable markets still poses special concern since of their use for some types of pesticides such as OP's and carbamates for long years. However, possible accumulation of these hazards in plant crops and environment components could cause considerable health problems for both famers and the consumers. Accordingly, the Egyptian authorization should strengthen their efforts on establish official control plan as well as a regular monitoring studies, to ensure following of local GAP and promote education on the potential risks and the safe use of pesticides. Moreover, cumulative risk assessment is considered as an indicator for the lethal effects that related to the human health because of the exposure to pesticide residues over a long period to multiple pesticide groups i.e. organophosphorus, organochlrine, pyrethroids and carbamates.

Compliance with Ethical Standards

Conflicts of interest: None

Ethics approval: This article does not involve any human or animal participants by any of the given authors

REFERENCES

[1] DIET, nutrition and the prevention of chronic diseases "report of a Joint WHO/FAO Expert Consultation, WHO Technical Report Series" No. 916. Geneva: World Health Organization, 2003. https://www.who.int/dietphysicalactivity/publications/trs916/en/

[2] Shakhaoat, H.,Alamgir, H., Abdur, R., Mainul, I., Atiqur, R., Tanveer, M.A. "Health risk assessment of pesticide residues via dietary intake of market vegetables from Dhaka, Bangladesh" Foods,Vol. 2, Issue 1, pp. 64–75, 2013. https://doi.org/10.3390/foods2010064

[3] FAO/WHO, Retrieved January 2013. http://www.codexalimentarius.net

[4] Khaniki, G.R. "Chemical contaminants in milk and public health concerns" A review. International Journalof Dairy Science, Vol. 2, Issue 2, pp. 104-115, 2007. https://scialert.net/abstract/?doi=ijds.2007.104.115

[5] Bhanti, M., Taneja, A. "Contamination of vegetables of different seasons with organophosphorus pesticides and related health risk assessment in northern India" Chemosphere, Vol. 69, Issue 1, pp. 63–68, 2007. https://doi.org/10.1016/j.chemosphere.2007.04.071

[6] Berrada, H., Fernandez, M., Ruiz, M. J., Molto, J. C., Manes, J., Font, G. "Surveillance of pesticide residues in fruits from Valencia during twenty months (2004/2005)" Food Control, Vol. 21, Issue 1, pp. 36–44, 2010. https://doi.org/10.1016/j.foodcont.2009.03.011

[7] Bhanti, M., ShuklaG., Taneja A., "Contamination levels of organochlorine pesticides andfarmers' knowledge, perception, practices in rural India-A case study"Bulletin of Environmental Contamination and Toxicology, Vol. 73, Issue 5, pp. 787-793, 2004. https://doi.org/10.1007/s00128-004-0496-8

[8] Ntow, W.J.,Gijzen,H.J., Kelderman,P.,Drechsel,P., "Farmer perceptions and pesticide use practices in vegetable production in Ghana" Pest Management Science, Vol. 62, Issue 4, pp. 356-365, 2006. https://doi.org/10.1002/ps.1178

[9] Duck, W. P., Kwang, G. K., Eun, A. C., Gyeong, R. K., Tae, S. K.,Yong, S. Y., Bae, S. C. "Pesticide residues in leafy vegetables, stalk and stem vegetables from South Korea: A long-term study on safety and health risk assessment" Food Additives and Contaminants Part A, Vol. 33, Issue 1, pp. 105-118, 2016. https://doi.org/10.1080/19440049.2015.1108524

[10] Sohair, A. G. A., Almaz, M. M., Thabet, W. M., Nabil, M. M. "Evaluation of pesticide residues in some Egyptian fruits" International Journal of Environment, Vol. 4, Issue 1, pp. 87–97, 2015. http://www.curresweb.com/ije/ije/2015/87-97.pdf

[11] Hjorth, K. B. Johansen, A. Holen, Andersson,H.B., Christensen,K., Siivinen,M., Toome,"Pesticide residues in fruits and vegetables from South America e A Nordic project" Food Control, Vol. 22, Issue 11, pp. 1701-1706, 2011.https://doi.org/10.1016/j.foodcont.2010.05.017

[12] FAO 2002a "Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed, 1st ed. Rome" Food and Agriculture Organization of the United Nations, FAO Plant Production and Protection Paper, No. 170, 2002. http://www.fao.org/ag/agp/agpp/pesticid/JMPR/ Download/FAOM2002.pdf

[13] Claeys, W.L., Jean-Francois,S., Bragard, C., Maghuin- Rogister, G., Luc,P. "Schiffers,B., Exposure of several Belgian consumer groups to pesticide residues through fresh fruit and vegetable consumption: Food Contaminants , Vol. 22, Issue 3, pp. 508-516, 2011. http://hdl.handle.net/2268/175292

[14] FAO/WHO "Codex Alimentarius Commission. Committee on Pesticide Residues, Guidelines for predicting dietary intake of pesticide residues, Global Environment Monitoring System-Food Contamination Monitoring and Assessment Programme (GEMS/Food)'' WHO, 1997. https://apps.who.int/iris/handle/10665/63787

[15] Codex Alimentarius International Food standards. Codex Maximum Residue Limits (MRLs). http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/

[16] European Commission. EU Pesticides database. Maximum Residue Limits (MRLs). https://ec.europa.eu/food/plant/pesticides/eu-pesticides database/public/?event=homepage&language=EN

[17] Commission Codex Alimentarius. "Portion of commodities to which maximum residue limits apply and which is analyzed CAC/GL 41-1993" Joint FAO/WHO food standards program, Vol. 2, p. 391, 1993.file:///C:/Users/TALA/Downloads/CXA_004_1993e.pdf

[18] European Union, Foods of Plant Origin "Determination of pesticide residues using GC–MS and/or LC–MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE QuEChERS method" BS EN, 15662, 2008. http://www.chromnet.net/Taiwan/QuEChERS_Dispersive_SPE/QuEChERS_%E6%AD%90%E7%9B%9F%E6%96%B9%E6%B3%95_EN156622008_E.pdf

[19] Banerjee, K., Dasharath, P., Dasgupta, O. S., Patil, S. B., Patil S. H., Savant, R.,Adsule, P. G."Validation and uncertainty analysis of a multi-residue method for pesticides in grapes using ethyl acetate extraction and liquid chromatography–tandem mass spectrometry" Journal of Chromatography A, Vol. 1173, Issue 1-2, pp. 98-109, 2007. https://doi.org/10.1016/j.chroma.2007.10.013

[20] Eurachem guide "The fitness for purpose of analytical methods – A laboratory guide to method validation and related topics" Eurachem 2nd ed., ISBN 978-91-87461-59-0, 2014. https://www.eurachem.org/images/stories/Guides/pdf/MV_guide_2nd_ed_EN.pdf

[21] Eurachem guide "Quantifying uncertainty in analytical measurement" Eurachem 3d edition, ISBN978-0-948926-30-3, 2012. File:///C:/Users/amohammed/Documents/QUAM2012_P1.pdf

[22] Darko, G., Akoto, O. "Dietary intake of organophosphorous pesticide residues through vegetables from Kumasi, Ghana" Food Chemical Toxicology, Vol. 46, Issue 12, pp. 3703-3706, 2008.https://doi.org/10.1016/j.fct.2008.09.049

[23] WHO/GEMS/Food Cluster diets, 2012. https://extranet.who.int/sree/Reports?op=vs&path=/WHO_HQ_Reports/G7/PROD/EXT/GEMS_cluster_diets_2012&userid=G7_ro&password=inetsoft123

[24] FAO/WHO "Pesticide residues in food and feed. Acceptable Daily Intake" Codex Alimentarius Commission, FAO/WHO Food standards, 2010. http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/en/

[25] EFSA, Scientific Colloquium Summary Report "Cumulative Risk Assessment of Pesticides to Human Health" 2013.http://www.efsa.europa.eu/en/supporting /doc/colloquiapesticides.pdf

[26] Hamilton, D. & Crossley, S. "Pesticide Residues in Food and Drinking Water: Human Exposure and Risks" John Wiley and Sons Ltd. Chichester, England, ISBN: 978-0-470-09160-9, pp.378, 2004.https://www.wiley.com/enus/Pesticide+Residues+in+Food+and+Drinking+Water%3A+Human+Exposure+and+Risks-p-9780470091609

[27] Oliver, G. R., Bolles, H. G., Shurdut, B. A. "Chlorpyrifos: Probabilistic assessment of exposure and risk" Neurotoxicology, Vol. 21, Issue 1-2, pp. 203–208, 2000. https://pubmed.ncbi.nlm.nih.gov/10794401

[28] Qozowicka, B., Jankowska, M., &Kaczy, N. P. "Pesticide residues in Brassica vegetables and exposure assessment of consumers" Food Control, Vol. 25, Issue2, pp. 561–575, 2012. http://dx.doi.org/10.1016/j.foodcont.2011.11.017

[29] Rosa, M. G., Raquel, R. O., Beatriz, C. G. J., Simal, G. N. "Occurrence of fungicide and insecticide residues in trade samples of leafy vegetables" Food Chemistry, Vol.107, Issue 3, pp. 1342–1347, 2008.https://doi.org/10.1016/j.foodchem.2007.09.045

[30] Selim, M. T., El-Saeid, M. H., Al-Dossari, L. M. "Multiresidues analysis of pesticides using gas chromatography mass spectrometry: I-leafy vegetables. Research Journal of Environmental Sciences, Vol. 5, Issue 3, pp. 248–258, 2011. DOI: 10.3923/rjes.2011.248.258

[31] Dogheim, S. M., El-Marsafy, A. M., Gad Alla, S. A., Khorshid, M.A., Fahmy, S. M. "Pesticides and heavy metals levels in Egyptian leafy vegetables and some aromaticmedicinal plants" Food Additives and Contaminants, Vol. 21, Issue 4, pp. 323–330, 2004.

http://dx.doi.org/10.1080/02652030310001656361

[32] Sohair, A. G. A., Wasfi, M. T., Emil, Y. S. "Monitoring and risk assessment of pesticide residues in some Egyptian vegetables"Middle East Journal of Applied Sciences, Vol. 3, Issue 4, pp. 216-230, 2013. http://www.curresweb.com/mejas/mejas/2013/216-230.pdf

[33] Ashutosh, K. S., Purushottam, T., Srivastava, M. K., Lohani, M., Laxman, P. S. " Monitoring of pesticide residues in market basket samples of vegetable from Lucknow City, India: QuEChERS method" Environmental Monitoring and Assessment, Vol. 176, Issue 1-4, pp. 465–472, 2011. DOI: 10.1007/s10661-010-1597-y

[34] Hyum, H. N., Young, S. P., Kyung, W. K. P., Kwang, H. L., Jae, Y.L., Kyung, W. Y. Kee, S. K. "Monitoring of pesticide residues in leafy vegetables collected from wholesale and traditional markets in Cheongju" The Korean Journal ofPesticide Science, Vol. 14, Issue 2, pp. 381–393, 2010.http://www.koreascience.or.kr/article/JAKO201015537949207.pdf

[35] Godfred, D., & Osei, A. "Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana" Food and Chemical Toxicology, Vol. 469, Issue 12, pp.3703–3706, 2008.https://doi.org/10.1016/j.fct.2008.09.049

[36] EFSA "Annual report on pesticide residues according to article 32 of regulation (EC) No 396/2005" EFSA Journal, Vol. 8, Issue 6, pp. 1646, 2010. https://efsa.onlinelibrary.wiley.com/doi/pdf/10.2903/j.efsa.2010.1646

[37] The Federal Institute for Risk Assessment (BfR), 2013. https://www.bfr.bund.de/en/press_information/2013/10/risk_at_a_glance-186393.html

[38] Gupta P.K."Pesticide exposure-Indian scene" Toxicology, Vol. 198, Issue 1-3, pp. 83-90, 2004. https://doi.org/10.1016/j.tox.2004.01.021