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Research Article
Pesticides Evaluation in Egyptian Fruits and Vegetables: A Safety Assessment Study

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Abstract

Background and Objective: Pesticides residues deem a great dilemma for food safety, these residues conjugated with health hazards and several diseases due to its accumulation in the tissues. The present study aimed to evaluate the contamination of residues in five selected horticulture crops. **Materials and Methods:** Forty five samples including apples, orange, potato, tomato and cucumber (9 samples per each) were purchased from different local markets at Giza Governorate during the spring season of 2017. Pesticides were extracted using QuEChERS technique and the determination was performed using GC-MS apparatus. **Results:** The results represented a wide contamination of five horticultures with moderate levels of pesticides. Endosulfan and fenpropathrin were significantly higher than permitted MRLs in apples. The pesticides that showed a significant violation to the MRLs values were propamocarb (in orange), profenophos and propargite (in tomato), Delta-hexachlorocyclohexane (δ-HCH), malathion, ortho-phenylphenol and profenophos (in potato). In cucumber, just 4 pesticides were detected in few samples. Moreover, the safety assessment study revealed that there were no risk in all samples except for heptachlor, heptachlor-epoxide and PP-DDT. **Conclusion:** Fruits and vegetables under investigation represented moderate levels of contamination by pesticide residues particularly for chlorpyriphos in apples, cucumber and tomato (260, 380 and 560 µg kg^{-1}, respectively). Application of integrated pest management programs represents the novel methods to solve the residues dilemma in the agriculture sector.

Key words: Fruits, vegetables, pesticide residues, determination, QuChERS technique, integrated pest management, safety assessment

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Food security is the condition in which adequate, safe and nutritious foods are available, all the time, for all people. While food safety refers to the procedures of food handling, preparing and storing that eliminate all kinds of contamination. Therefore, the safe food is defined as a food which is free from physical and chemical contaminants as well as biological contaminants such as viruses, bacteria, fungi and parasites. Chemical contamination of agricultural crops, as a result of the intensive use of pesticides in agro-systems, is one of the most important food contaminants that threaten the safety of food[1].

Globally, pesticides are intensively used in the pre- and/or post-harvest practices in order to control the pests that attack fruits and vegetables, consequently avoid the damages and reduction in the quantity and quality of the crops[2]. Pesticides have the stability and mobility properties that lead to their widespread in the environment[3].

Pesticides have the consequent long-term adverse impacts on the national income, ecological system and public health. Where, the presence of pesticides in foods, with levels over the permissible limits, may switch off the exports gate between countries leading to financial losses in the countries national income. Further, pesticides can cause environmental predicaments such as environmental contamination increase, disturbance of the natural balance and wildlife, harms to non-objectives organisms, pest resistance widespread and hazards to human health[3]. The risk of pesticides to human is related to its accumulation in the food chain which may consequently lead to the human exposure to elevated levels of pesticides in food.

The maximum residue limits (MRLs) and the recorded values of No-observed-adverse-effect level (NOAEL) for pesticides varied between fruit and vegetable samples according to the international regulations of pesticides residues cited in the EU Pesticide Database[4], the database of Codex Alimentarius international food standard[5], FDA US-Food and Drugs administration[6] and EPA US Environmental Protection Agency[7]. In the fruit samples, The MRLs values ranged in apple and orange from 10 to 5000 μg kg^{-1}. For vegetables, the MRLs were in the ranges of 10-10000, 10-7000 and 10-3000 μg kg^{-1} for tomato, potato and cucumber, respectively.

Concerning the previous researches on contamination with pesticides in Egypt, in fruits as same as vegetables, pesticide residues have shown their impact and are a problem in Egypt. For instance, the pesticide residues in tomato samples, from random markets of Egypt, showed a contamination by heptachlor-epoxide frequently more than 35%. Also, P, P-DDE and pirimiphos-methyl were presented in the same samples[8]. Otherwise, high concentrations of organophosphorus and organochlorine pesticides were reported in potato and cucumber samples[9-11].

Furthermore, most smallholders and stakeholders of horticultures in Egypt had a lack of knowledge and insufficient experience for pesticide handling, particularly the best ways of pesticide practices, pesticide chemical and physical properties and its human health effect.

For these reasons, it is essential to regularly monitor and evaluate the levels of pesticides in the fruits and vegetables. Because the presence of pesticide residues in foods is considered a great reason for apprehension through the consumers. As well, the interim needs, with a vision of sustainable development in food production, request a better background to the current situation of pesticides. Therefore, the present investigation was designed (1) To study the incidence of pesticide residues in samples of fruits (apple and orange) and vegetables (potato, tomato and cucumber) collected from several regions of Giza Governorate, Egypt. (2) To assess the potential risk to public health, due to the multiple exposure to pesticides through fruits and vegetables, based on the Egyptian food habits and the recommended levels of both acceptable daily intake (ADI) and NOAELs (No-observed-adverse-effect levels) by the international legislations.

MATERIALS AND METHODS

Chemicals: All reagents and solvents were of analytical or HPLC grade. The pesticide standards and internal standard (tri-phenyl phosphate, TPP) were purchased from Sigma-Aldrich Corp, Chem Service (West Chester, PA, USA).

Sample collection and preparation: Forty Five samples of apples, orange, potato, tomato and cucumber (9 samples of each) were purchased from Giza local markets, Egypt, during 2017. Samples were collected from five great markets all over the governorate. Each sample was cut into small pieces and homogenized well using a laboratory blender. The homogenized sample was frozen for 24 h at -18°C before the extraction.

Samples extraction and clean-up following QuEChERS technique: Extraction of residual pesticides was performed according to the multi-residue method of Anastassiades *et al.*[12] and Fillion *et al.*[13]. Basically, the crashed samples were extracted with acetonitrile (ACN) and the ACN extract was cleaned-up by passing through the solid phase extraction (SPE) column (Supelclean™ PSA SPE Bulk Packing) containing 25 mg of the primary secondary amine (PSA), 12.5 mg of the graphitized carbon black (GCB) and 75 mg of $MgSO_4$. Following this clean-up procedure, the final dried extract was dissolved in 500 µL of ACN then subjected to the GC-MS for analysis.

GC-MS/MS system and analysis conditions: Analysis of pesticides was done on a model 6890 gas chromatograph with a model 5975 mass selective detector (Agilent Technologies, Little Falls, DE, USA) equipped with a Gerstel Dual rail MPS-2 Prepstation with DPX option (Linthicum, MD, USA). The Rtx-5 column (5% diphenyl/95% dimethyl polysiloxane, 30 m×0.25 mm i.d., 0.25 µm film thickness, Restek Corp., Bellefonte, PA, USA) was used for the separation of pesticides. Detailed conditions for detection and analysis were performed according to Anastassiades *et al.*[12].

Safety assessment of pesticides exposure: The following assumptions were made based on the U.S. Environmental Protection Agency's guidelines: (a) Hypothetical body weights of 70 kg for adults and (b) Maximum absorption rate of 100% and a bioavailability rate of 100%. Food consumption rates were based on the guidelines provided by the Egyptian Institute of Food Technology, which cited in the world bank data[14], including the following: (a) Cucumber 50 g day^{-1}, (b) Tomato 100 g day^{-1}, (c) potato 100 g day^{-1} and citrus fruit 12 g day^{-1}, apple 5 g day^{-1}. Hence, for each type of exposure, the estimated lifetime exposure dose (mg kg^{-1}/day) was obtained by multiplying the residual pesticide concentration (mg kg^{-1}) in the food of interest and the food consumption rate (kg day^{-1}) and dividing the product by the body weight (kg). The NOAELs (No-observed-adverse-effect level) were obtained from: the international regulations of pesticides residues cited in the EU Pesticide Database[4], the database of Codex Alimentarius international food standard[5], FDA US-Food and Drugs administration[6] and EPA US Environmental Protection Agency[7]. ADIs (Acceptable daily intake) were obtained from FDA US-Food and Drugs administration[6]. Value of NOAELs and ADIs were calculated for an adult person of 70 kg and were used in the comparison to the total exposure to every pesticide from the studied fruits and vegetables (Table 3). The hazard indices to adults was estimated as ratios between estimated pesticide exposure doses and the reference doses which are considered to be safe levels of exposure over the lifetime.

RESULTS

Sixty four pesticides that were commonly used in agriculture were determined in the present study using the QuECheRS technique coupled with GC-MS/MS. The applied method showed high sensitivity in the quantification limits (LOQ) for pesticides which varied between 0.5 and 1.0 ng (Table 1 and 2, Fig. 1 and 2).

Pesticides residues in apple: Concerning the pesticide residues estimation in apple samples, 8 out of more than 60 pesticides were detected in apple fruits. The most dominant pesticide in samples was recorded for chlorpyriphos, counterpart the lowest pesticide residue was recorded for diphenylamine (Table 1). Two pesticide residues, endosulfan and fenpropathrin, recorded higher concentrations than its regulated MRLs values. In case of endosulfan contamination, the detected amount (57 µg kg^{-1}) was not so far from its MRL (50 µg kg^{-1}). Otherwise the fenpropathrin residues showed a great problem because its concentration was more than 12 fold of its MRL value in apple and this means there is an urgent need for controlling its utilization.

Pesticides residues in orange: In Table 1, more than 50 pesticides were detected in orange samples. However, all the detected pesticides did not exceed their MRLs in orange except for propamocarb which showed a high concentration close to four times of its MRL value in orange. The overall vision represented low concentrations for pesticides in the positive samples but still there is a dilemma because of the large detected number of pesticide residues.

Pesticides residues in tomato: The results of tomato samples were summarized in Table 2. Eight pesticides were found in the studied samples with low magnitudes as compared to the MRLs levels. Even though profenophos and propargite had the highest detected concentrations in tomato but they still within the MRL levels. Otherwise, it was clear that the results recorded an absence of 46 out of the 64 pesticides under investigation.

Table 1: Pesticide residues in apples and orange represented the fruit samples

	Detected concentrations and MRLs ($\mu g\ kg^{-1}$)				
Pesticides	Apple	MRLs	Orange	MRLs	LOQ (ng)
Aldrin	ND	10	0.1	10	1.0
α- HCH	ND	10	0.3	10	1.0
γ- HCH	ND	10	6.8	10	1.0
δ- HCH	ND	10	0.1	10	1.0
Azoxystrbin	ND	NS	10.0	15000	0.5
Cadusafos	ND	10	0.001	10	1.0
Captan	110	NS	10.0	NS	1.0
Carbendazim	54	200	2.5	200	0.5
Chlorpyriphos	260	300	30.0	500	1.0
Chlorpyriphos-methyl	ND	1000	0.1	2000	1.0
Cypermethrin	ND	2000	5.0	1000	1.0
Cyprodinil	ND	2000	2.7	20	1.0
Deltamethrin	ND	200	1.0	20	1.0
Diazinon	ND	10	0.02	10	1.0
Dieldrin	ND	10	0.4	10	1.0
Dimethoate	ND	NS	0.1	5000	1.0
Dimethomorph	ND	NS	6.0	NS	1.0
Diphenylamine	10	100	7.5	50	1.0
Endosulfan	57	50	1.0	50	1.0
Endosulfan 11	ND	50	3.75	50	1.0
Endosulfan sulfate	ND	50	0.2	50	1.0
Endrin	ND	10	ND	10	1.0
Endrin aldehyde	ND	10	ND	10	1.0
Esfenvalerate	ND	20	7.5	100	1.0
Ethion	ND	10	0.1	10	1.0
Ethoprophos	ND	20	ND	20	1.0
Fenamiphos	ND	50	0.014	20	1.0
Fenamiphos-sulfate	ND	50	ND	10	1.0
Fenamiphos-sulfone	ND	20	0.014	10	1.0
Fenitrothion	ND	500	0.2	20	1.0
Fenpropathrin	121	10	ND	10	1.0
Fenpyroximate	ND	300	0.5	500	1.0
Flamprop	ND	NS	0.125	NS	1.0
Fludioxonil	ND	5000	3.1	10000	1.0
Heptachlor	ND	10	0.5	10	1.0
Heptachlor epoxide	ND	10	0.2	10	1.0
Imidacloprid	ND	500	ND	1000	1.0
Indoxacarb	ND	500	1.0	20	1.0
L-Cyhalothrin	10	100	0.5	200	1.0
Malathion	ND	20	1.03	2000	1.0
Deltamethrin	ND	200	ND	40	1.0
Metalaxyl	ND	700	3.0	5000	1.0
Methamidophos	ND	10	0.03	10	0.0
Methoxychlor	ND	10	0.7	10	1.0
Ortho-phenyl phenol	ND	10	39.0	1000	1.0
Oxamyl	ND	10	0.2	5000	1.0
Parathion	ND	50	0.001	50	1.0
Permethrin	ND	50	ND	50	1.0
Phenthoate	ND	NS	5.0	NS	1.0
Phorate	ND	10	0.05	10	1.0
Phosphamidon	ND	10	0.05	10	1.0
Pirimiphos-methyl	ND	10	0.25	10	1.0
PP-DDD	ND	50	ND	50	1.0
PP-DDE	ND	50	ND	50	1.0
PP-DDT	ND	50	ND	50	1.0

Table 1: Continue

Pesticides	Detected concentrations and MRLs (µg kg^{-1}) Apple	MRLs	Orange	MRLs	LOQ (ng)
Profenophos	ND	10	ND	10	1.0
Propamocarb	ND	10	39.0	10	1.0
Propargite	130	3000	2.0	3000	1.0
Prothiophos	ND	10	0.01	10	1.0
Pyriproxyfen	ND	200	7.0	600	1.0
Quinalphos	ND	10	0.2	10	1.0
Thiophanate-methyl	ND	500	8.0	6000	1.0
Triazophos	ND	10	0.5	10	1.0

ND: Not detected according to the limit of quantification, LOQ: Limit of quantification, HCH: Hexa-chloro cyclohexane, NS: Not assigned

Table 2: Pesticide residues in tomato, potato, and cucumbers represented the vegetable samples

Pesticides	Detected concentrations and MRLs (µg kg^{-1}) Tomato	MRL	Potato	MRL	Cucumber	MRL	LOQ (ng)
Aldrin	ND	10	0.1	10	6	20	1.0
α-HCH	ND	10	10	10	ND	100	1.0
γ- HCH	ND	10	2.7	10	ND	10	1.0
δ- HCH	ND	10	30	10	ND	10	1.0
Azoxystrbin	ND	10000	10	7000	ND	1000	0.5
Cadusafos	ND	10	0.001	10	ND	10	1.0
Captan	ND	5000	50	50	ND	3000	1.0
Carbendazim	18	500	2.5	100	ND	50	0.5
Chlorpyriphos	28	500	0.03	200	ND	50	1.0
Chlorpyriphos-methyl	ND	1000	0.1	10	ND	50	1.0
Cypermethrin	14	200	0.014	NS	ND	70	1.0
Cyprodinil	ND	2000	2.7	2000	ND	500	1.0
Dazinon	ND	500	0.02	10	54	100	1.0
Deltamethrin	ND	300	1	10	ND	200	1.0
Deldrin	ND	10	ND	10	ND	10	1.0
Dimethoate	ND	NS	0.1	50	ND	500	1.0
Dimethomorph	ND	1500	6	50	ND	500	1.0
Diphenylamine	ND	NS	7.5	NS	ND	NS	1.0
Endosulfan	ND	500	1	50	ND	1000	1.0
Endosulfan 11	ND	500	3.75	50	ND	NS	1.0
Endosulfan sulfate	ND	100	0.2	20	ND	50	1.0
Endrin	ND	10	ND	10	ND	50	1.0
Endrin aldehyde	ND	10	ND	20	ND	100	1.0
Esfenvalerate	ND	100	7.5	20	ND	20	1.0
Ethion	ND	10	0.1	10	ND	10	1.0
Ethoprophos	ND	10	3.8	50	ND	10	1.0
Fenamiphos	ND	1000	0.014	20	ND	200	1.0
Fenamiphos-sulfide	ND	70	0.125	1	ND	10	1.0
Fenamiphos-sulfone	ND	50	0.1	1	ND	10	1.0
Fenitrothion	ND	10	0.2	10	ND	10	1.0
Fenpropathrin	ND	1000	0.7	10	ND	10	1.0
Fenpyroximate	ND	200	0.5	10	ND	80	1.0
Fenthion	ND	NS	0.3	NS	ND	NS	1.0
Flamprop	ND	NS	7	NS	ND	NS	1.0
Fludioxonil	ND	3000	3.1	5000	ND	400	1.0
Heptachlor	ND	NS	0.5	NS	ND	NS	1.0
Heptachlor epoxide	ND	NS	0.2	NS	8	NS	1.0
Imidacloprid	19	500	15	500	ND	1000	1.0
Indoxacarb	16	500	0.03	20	ND	500	1.0
L-Cyhalothrin	ND	100	0.5	20	ND	100	1.0
Malathion	ND	20	23	20	ND	20	1.0
Deltamethrin	18	70	13	300	ND	200	0
Metalaxyl	ND	500	0.5	50	ND	500	1.0
Methamidophos	ND	10	5	50	ND	10	1.0
Methoxychlor	ND	10	0.3	10	ND	10	1.0

Table 2: Continue

	Detected concentrations and MRLs (µg kg^{-1})						
Pesticides	Tomato	MRL	Potato	MRL	Cucumber	MRL	LOQ (ng)
Ortho-phenyl phenol	ND	10	39	10	ND	10	1.0
Oxamyl	ND	2000	0.2	100	ND	2000	1.0
Parathion	ND	50	0.01	50	17	50	1.0
Permethrin	ND	1000	21	50	ND	500	1.0
Phenthoate	ND	NS	1	NS	ND	NS	1.0
Phorate	ND	10	0.05	300	ND	10	1.0
Phosphamidon	ND	10	0.05	10	ND	10	1.0
Pirimiphos-methyl	ND	10	0.25	10	ND	10	1.0
PP-DDD	ND	50	0.3	50	ND	50	1.0
PP-DDE	ND	50	0.5	50	ND	50	1.0
PP-DDT	ND	50	0.5	50	ND	50	1.0
Profenophos	560	1000	12	10	280	10	1.0
Propamocarb	ND	400	39	500	ND	3000	1.0
Propargite	183	200	2	30	ND	NS	1.0
Prothiophos	ND	10	0.01	10	ND	10	1.0
Pyriproxyfen	ND	1000	3	50	ND	100	1.0
Quinalphos	ND	10	0.2	10	ND	10	1.0
Thiophanate-methyl	ND	1000	8	100	ND	100	1.0
Triazophos	ND	10	0.5	10	ND	10	1.0

ND: Not detected according to the limit of quantification, LOQ: Limit of quantification, HCH: Hexa-chloro cyclohexane, NS: Not assigned

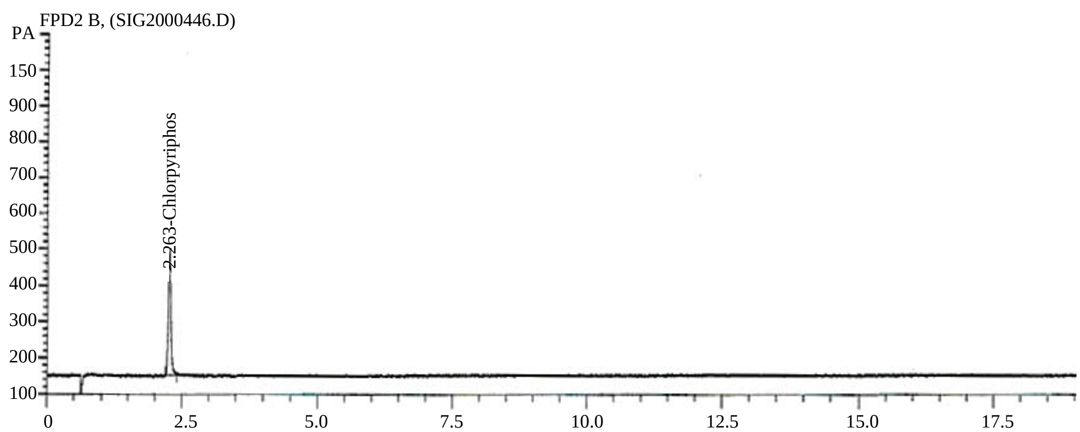

Fig. 1: GC-MS/MS chromatogram for a positive orange sample to chlorpyriphos

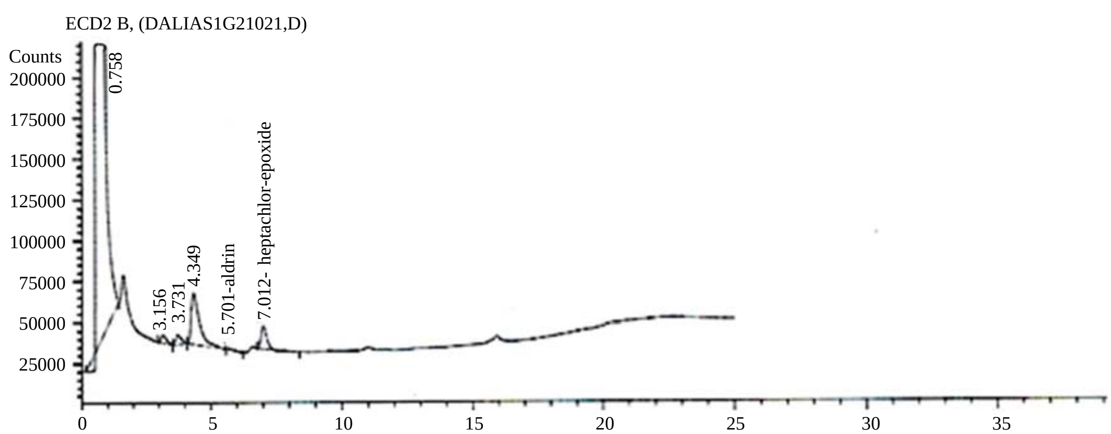

Fig. 2: GC-MS/MS chromatogram for a positive potato sample to aldrin and heptachlor-epoxide

Pesticides residues in potato: Concerning the obtained results of potato samples as the second kind of the studied vegetables, the data in Table 2 declared that the majority of the studied pesticides (61 out of 64) were presented in potato samples. Only 4 out of the detected 61 pesticides had concentrations higher than the MRLs reported for potatoes, these pesticides were delta-hexachloro cyclohexane (δ-HCH), malathion, ortho-phenyl phenol and profenophos. While two pesticides (α-HCH and captan) recorded residual amounts comparable to the MRLs for them in potato according to the global regulations.

Pesticides residues in cucumber: Recorded results of cucumber (Table 2) showed the same scenario of tomato samples, where few pesticide residues were detected in the positive samples. The estimated pesticides were aldrin, diazinon, heptachlor epoxide, parathion and profenophos. All these pesticides had concentrations lower than the MRLs levels recommended by the Europe Union (EU) except for profinophos which recorded a much higher value than its assigned MRL in cucumber.

Risk assessments of pesticides exposure: Since numerous Egyptian experiments reported the pesticides residuals of food crops to have hazardous concentrations in fruits, vegetables and milk[15-19]. As well, more than 75% of the Egyptian population rely on the agricultural crops for their main food, therefore it is highly recommended to periodically evaluate the safety of these food crops for human consumption.

In the present study, the total exposure to pesticides through the consumed amounts of fruits plus vegetables were summarized in Table 3. As well, the NOAELs and ADIs levels calculated for an adult person of 70 kg for the safety assessment study were shown in the same Table. The results showed that values of the total exposure were in the range of 0.1 μg day^{-1} (phenthoate) and 318.03 μg day^{-1} (chlorpyriphos). Also, the limits of ADIs$_{70}$ ranged between 7 and 22262.1 (μg day^{-1}) for phenthoate and chlorpyriphos, respectively. These results mean that although the pesticide residues varied from a food commodity to another one, however the levels of exposure to the 64 pesticides were all in the safe limits as compared to the ADIs$_{70}$, taking into consideration the other sources of the daily exposure to pesticides.

Regarding the comparison between the total values of exposure and the NOAELs$_{70}$ limits, it was also found that the total daily exposure to heptachlor, heptachlor-epoxide and PP-DDT (8.2, 35 and 891 μg day^{-1}) exceeded the NOAELs$_{70}$ limits (7, 7 and 700 μg day^{-1}), respectively. These findings revealed that the total values of all detected pesticides fallen within the safe limits of NOAELs$_{70}$ except for heptachlor, heptachlor-epoxide and PP-DDT. The risk is recorded, when the levels of exposure exceeded the NOAEL limits as these high levels will affect the body tissues safety reflecting harmful changes in tissues.

DISCUSSION

Concerning pesticide residues in fruits (Table 1), orange and apple samples shared the contamination by residuals of captan, carbendazim, chlorpyriphos, di-phenyl amine, propargite, endosulfan and L-cyhalothrin. Except for fenpropathrin, which was presented in apple samples and not observed in orange samples, 52 pesticides out of 61 were detected in orange samples. The presence of chlorpyrifos

Table 3: Assessment characteristics for the potential risk of exposure to pesticides

	μg day^{-1}				
Pesticides	Exposure from 3 vegetables	Exposure from 2 fruits	Total exposure	NOAEL* (70 kg person)	ADI** (70 kg person)
Aldrin	6.1	0.0	6.1	7	427
α-HCH	10.0	0.3	10.3	56000	721
γ-HCH	2.7	6.8	9.5	35000	665
δ-HCH	30.0	0.1	30.1	1400	2107
Azoxystrbin	10.0	10.0	20.0	14000	1400
Cadusafos	0.001	0.001	0.002	35	0.14
Captan	50.0	120.0	170.0	7000	11900
Carbendazim	20.5	56.5	77.0	2100	5390
Chlorpyriphos	28.03	290.0	318.03	7000	22262.1
Chlorpyriphos-methyl	0.1	0.1	0.2	7000	14
Cypermethrin	14.014	5.0	19.014	1400	1330.98
Cyprodinil	2.7	2.7	5.4	2100	378
Deltamethrin	54.02	1.0	55.02	350	3851.4

Table 3: Continue

	µg day^{-1}				
Pesticides	Exposure from 3 vegetables	Exposure from 2 fruits	Total exposure	NOAEL* (70 kg person)	ADI** (70 kg person)
Diazinon	1.0	0.02	1.02	700	71.4
Dieldrin	0.0	0.4	0.4	7350	28
Dimethoate	0.1	0.1	0.2	9800	14
Dimethomorph	6.0	6.0	12.0	14000	840
Diphenylamine	7.5	17.5	25.0	5600	1750
Endosulfan	1.0	58.0	59.0	420	4130
Endosulfan 11	3.75	3.75	7.5	70	525
Endosulfan sulfate	0.2	0.2	0.4	7	28
Endrin	0.0	0.0	0.0	1.4	130
Endrin aldehyde	0.0	0.0	0.0	1.4	130
Esfenvalerate	7.5	7.5	15.0	1400	1050
Ethion	0.1	0.1	0.2	3500	14
Ethoprophos	3.8	0.0	3.8	2800	266
Fenamiphos	0.014	0.014	0.028	560	1.96
Fenamiphos-sulfide	0.125	0.0	0.125	560	8.75
Fenamiphos-sulfone	0.1	0.014	0.114	140	7.98
Fenitrothion	0.2	0.2	0.4	420	28
Fenpropathrin	0.7	121.0	121.7	210	8519
Fenpyroximate	0.5	0.5	1.0	2100	70
Fenthion	7.0	3.1	10.1	490	707
Flamprop	3.1	0.5	3.6	8750	252
Fludioxonil	0.5	0.2	0.7	28000	49
Heptachlor	8.2	0.0	8.2	7	574
Heptachlor epoxide	34.0	1.0	35.0	7	2450
Imidacloprid	16.03	10.5	26.53	630000	1857.1
Indoxacarb	0.5	1.03	1.53	700	107.1
L-Cyhalothrin	23.0	0.0	23.0	1400	1610
Malathion	31.0	3.0	34.0	21000	2380
Meothrin	0.5	0.03036	0.53036	77000	37.1252
Metalaxyl	5.0	0.7	5.7	5600	399
Methamidophos	0.3	39.0	39.3	280	2751
Methoxychlor	39.0	0.2	39.2	7000	2744
Ortho-phenyl phenol	0.2	0.001	0.201	7000	14.07
Oxamyl	17.01	0.0	17.01	630	1190.7
Parathion	21.0	5.0	26.0	280	1820
Permethrin	1.0	0.05	1.05	3500	73.5
Phenthoate	0.05	0.05	0.1	210	7
Phorate	0.05	0.25	0.3	49	21
Phosphamidon	0.25	0.0	0.25	210000	17.5
Pirimiphos-methyl	0.3	0.0	0.3	70000	21
PP-DDD	0.5	0.0	0.5	700	35
PP-DDE	0.5	0.0	0.5	700	35
PP-DDT	852.0	39.0	891.0	700	62370
Profenophos	39.0	132.0	171.0	21000	11970
Propamocarb	185.0	0.01	185.01	28000	12950.7
Propargite	0.01	7.0	7.01	700	490.7
prothiophos	3.0	0.2	3.2	700	224
Pyriproxyfen	0.2	8.0	8.2	7000	574
Quinalphos	8.0	0.5	8.5	70000	595
Thiophanate-methyl	6.1	0.0	6.1	5600	427
Triazophos	10.0	0.3	10.3	105000	721

NOAEL: No-observed-adverse-effect level, *NOAEL*70 was calculated for an average person with 70 kg b.wt., **ADI: Acceptable daily intake

either in the apple samples or in the orange samples reflected the frequent contamination by organophosphorus pesticides during the season of 2017. According to the 6th report of pesticide hazard, organophosphates are not only toxicants to the insects but also they have a toxic effect for the mammalian including human. These compounds have the ability to affect the central nervous system through the inhibition of some important enzymes like acetyl-choline as confirmed in many cases of exposed animal experiments[20].

In a study of pesticides evaluation in Egyptian fruit samples by Gad Alla *et al.*[21], it was found that 52% of the 177 tested fruit samples were contaminated by pesticides, however more than 70% of the positive samples had concentrations over the MRLs of the European regulations. These findings were in contrary to our study which recorded low levels of pesticides in apple. Moreover, although a large number of pesticides was recorded in orange samples of our investigation, meanwhile propamocarb was the only pesticide which exceeded the MRLs.

Besides, Gad Alla *et al.*[21] compared their results with their other results obtained from previous studies covering the period from 1995 to 1977[22,23]. The comparison declared a decrease in the percentages of pesticides free samples. Furthermore, Dasika *et al.*[24] documented the presence of chlorpyrifos in two types of apples and added that either before or after washing apples using warm or salted warm water, the level of chlorpyrifos still higher.

In the light of these results, a variation in the type of pesticide residue was recorded on the Egyptian apple and orange samples between the present and the previous investigations. Not only the pesticide was changed but also the dominant pesticide group was altered. Therefore, a periodical mentoring survey for pesticide should be suggested, as it has a relationship with the safety assessment of fruits used in human food.

Detected pesticides levels in tomato and cucumber did not exceed the MRLs except for profinophos which was higher than the EU-MRLs in cucumber. In contrary, potato samples represented the great contaminated horticulture with the presence of most investigated pesticides. Concentrations of delta-hexachloro cyclohexane (δ-HCH), malathion, ortho-phenyl phenol and profenophos exceeded the MRLs in potato.

Comparing to the previous study, the pattern of pesticides in tomato reported the presence of HCB, lindane, dieldrin, heptachlor epoxide and DDT at 0.009, 0.003, 0.006, 0.008 and 0.083 mg kg^{-1}, respectively. However, the detection levels of dimethoate, pirimiphos-methyl and profenofos were 0.461, 0.114 and 0.206 mg kg^{-1}, respectively[25]. Otherwise, a study of Ahmed *et al.*[8] elucidated that, more than 13 pesticides were found in tomato and the majority of detected pesticides was recorded for heptachlor-epoxide and profenofos pesticides. In a monitoring study for organochlorine and organo-phosphorus pesticide residues in Egyptian samples of potato, fruits and fish[26], the MRLs for residual gamma-hexachlorocyclohexane (γ-HCH) and DDT were overrun in potato samples. In another study by Mansour *et al.*[17], for pesticides and heavy metals monitoring in cucumber, the organophosphorus pesticides (thiometon, phorate and chlorpyrifos-methyl) were detected at concentrations greater than the MRLs.

Generally, the high incidence for the majority of tested pesticides in orange and potato samples of the current investigation may be due to the different control programs followed by the Ministry of Agriculture in the different stages of plant growth and these programs are varying from one province to another depending on the type of injury and the different environmental conditions.

The results of current investigation proved that a potential risk to public health was expected, when a human exposed to the total detected levels of heptachlor, heptachlor-epoxide and PP-DDT as compared to the limits of $NOAELs_{70}$. These high levels of the highlighted pesticides can affect the body tissues safety reflecting harmful changes in tissues as confirmed by the clinical studies. Wherein, it was found that high levels of heptachlor seemed to increase type 2 diabetes risk[27,28] to about 7%. Additionally, animals, exposed to heptachlor-epoxide during gestation and infancy, were found to have changes in the nervous system and immune function[27,28]. As a result, recommended corrective actions are requested to turn the light on reaching the safe levels for heptachlor, heptachlor-epoxide and PP-DDT in fruits and vegetables.

One of the best techniques to avoid the hazard of pesticide residues is the modern application of integrated pest management programs (IPMPs). In this type of programs, several types of solutions are available such as using the bio-pesticide application using the natural chelators and increment the awareness of smallholders and stakeholder by the optimum pesticides practice in the horticulture sector. The IPMPs offer the monitoring with prevention and control actions to pesticides which is an occasion for the reduction of residual pesticides in agricultural products. Indeed, application of cultural, biological and structural strategies is highly needed for the control of multitude pest problems. This consequently can eliminate the risk of exposure to toxic levels of pesticides in foods.

CONCLUSION

The present study declared that although the positive samples contained a wide number of pesticides (specifically in orange and potato), however the contamination level was moderate with some exceeding to MRLs for several pesticides. The risk assessment study showed no potential risk to public health due to the total exposure to pesticides from fruits and vegetables according to the ADIs. Meanwhile, in case of the calculated NOAELs, there was a potential risk for the exposure to heptachlor, heptachlor-epoxide and PP-DDT. Therefore, risk management and risk prevention programs are needed to decrease the implementation of heptachlor, heptachlor-epoxide and PP-DDT pesticides in fruits and vegetables as much as possible.

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