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Monitoring and Risk Assessment of Pesticide Residues in Some Egyptian Vegetables

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ABSTRACT

A total of 204 samples from 19 different vegetables most popular consumed and locally cultivated types were selected for monitoring of 215 pesticide residues. The standard method of European Committee for Standardization/(QuEChERS) was followed. The determination of pesticide residues carried out using GC-MS/MS and/or LC-MS/MS.Overall, 50 % of the analysed samples had no detectable pesticide residues. While the other 50% contained detectable residues which 32.5% of contaminated samples contain residues at levels lower than the MRL's and 17.5 % (36 samples) had residues above the permissible limits.The highest contamination percentages observed in leafy vegetables followed by fruiting vegetables and then root vegetables with percentages of 70.1%, 47.4% and 22.6%of which 29.8%, 16%, and 9.7% exceeded the permissible levels,respectively. The most commonly detected pesticide groups were organophosphorous (OP's) followed by pyrethroids then triazoles and carbamates, with frequencies percentages 41.5 %, 11.8% and 8.8% and 8.0%respectively. The most frequent(OP's) are chlorpyrifos, profenofos and Malathion. The exposure to pesticide residues was calculated on a total of 39 residues. The HQ's for the individual pesticide ranged from 0.00 to 0.66 with the values below 1 indicating no risk of adverse effects following exposure to the individual pesticides.Risk assessment of the cumulative exposure to the detected pesticides with common mechanism of action (organophosphorous, carbamate, and pyrethroids) has been also performed. The cumulative exposure valuesof organophosphorus pesticides was exceeded 1 (1.33for adults) indicates hazard to consumers due to presence of OP's residues in vegetables.

Key words: Pesticides Residues, Vegetables, ADI (acceptable daily intake), EDI (estimated daily intake), MRL (maximum residue limits), HI (Hazard index), Cumulative risk assessment.

Introduction

Vegetables are essential for a healthy and balanced diet, as well as adding variety, interest and flavour to the menu. But vegetables also attack with a wide range of pests and diseases, and require intensive pest management. In developing countries, most of the farmers who grow vegetables use pesticides. Many of them spray the same wide range of pesticides on all vegetables and ignore pre-harvest intervals (Ntow,et, al., 2006).Sometimes farmers spray pesticides one day before harvest to protect the vegetables from pests during sell period. This practice, in particular, exposes consumers to pesticides.Farmers around the world use different types of pesticides including organochlorines, organophosphorus, carbamate and pyrethroid insecticides, fungicides and herbicides against the possibility of a devastating crop loss from pests and diseases, as well as to increase agricultural productivity to provide adequate food supply for the increasing world population (Shakhaoat *et al*, 2013). However, pesticides use has also been associated with several concerns, including the potential risks to human health from both occupational and non-occupational exposures, the death of farm animals and alteration of the local environment (Mansour, *et al*., 2009).Many of these compounds can cause moderate to severe respiratory and neurological damage or act as genotoxic, carcinogenic and mutagenic agents, endocrine disruption, etc., through routes that include consumption of dietary residues (Hayat *et al* 2011, Choi, *et al* 2004 & Galloway and Handy, 2003).Very common effects of pesticide residues in human body include nausea, vomiting, blurred vision, coma, difficulty in breathing, deficit hyperactivity disorder, disorder in fetuses and children, etc.(Rauh, *et al* 2006, EPA, 1984 & 1999).

Many pesticides and their residues are also known to be contributory factors in several diseases such as cancer, heart diseases, Alzeheimer's and Parkinsonism(Khaniki, 2007).WHO in1990 estimates an annual three million cases of acute and severe pesticide poisoning worldwide with some 220,000 deaths. The majority of these cases of poisoning and deaths occur in developing countries, although far greater quantities of pesticides are used in the developed countries (Bhanti, M.; Shukla, G.; Taneja, A, 2004).

Analysis of pesticide residues in food is a key tool for monitoring the levels of human exposure to pesticide residues. Pesticide residues in food are usually monitored with reference to Maximum Residue Limits (MRLs) and acceptable Daily Intakes (ADIs). The MRL is an index that represents the highest concentration (expressed in mg kg^{-1}) of pesticide residue that is legally permitted or accepted in a food or animal feed after the use of pesticides. A consumer exposure is of concern if the estimated dietary exposure to a pesticide exceeds the ADI.

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The ADI is the estimate amount of a chemical in food (mg kg $^{-1}$body weight day^{-1}) that can be ingested daily over a life time without appreciable health risk to the consumer (FAO2002).

Exposure of the population to pesticides could be evaluated in Egypt where the vegetables are assumed to be potentially contaminated by pesticides. The proof of significant contamination of vegetables has been reported in many studies.Who have reported some levels of pesticides in common vegetables especially leafy vegetables (Dogheim *et al* 2004). However, in Egypt, there is no information on the health risk based on the exposure of the population to pesticides through different crops consumption.

The current study monitors the levels of pesticide residues in some vegetables crops collected from Egyptian local markets and compare the detected levels with the international established permissible limits MRL's. Although this gives a good indication,it lacks the information necessary for a proper interpretation andin terms of food safety.To evaluate the safety of consumers regarding pesticide residues, the exposure needs to beassessed and compared to health safety limits or toxicologicalendpoint values such as the ADI (acceptable daily intake) or theARfD (acute reference dose).This work also providesestimation of human health risk through estimated average daily intakes (EADIs)as compared with ADIs set by FAO/WHO (2010).

Materials and Methods

Sampling:

A total of 204 samples from 19 different vegetables, eight leafy vegetables i.e.grape leaf , green coriander, dill, parsley, lettuce, molokia, spinach and water cress, two root vegetables , i.e. carrot, potatoes, six fruiting vegetables i.e.cucumber, eggplant, okra, pepper, squash andtomato and two legume vegetables including green beans and Peas and one bulb vegetables,i.e. onion. The types selected from the most popular consumed and locally cultivated vegetables.The samples were collected from five Governorates, Cairo, Giza, Qualubiya, Ismailia and Fayium including retails and big markets from February to August 2011. The number of samples analyzed for each vegetable is shown in table (1).

Table 1: The number of analysed Egyptian vegetable samples and the frequencies of pesticide residues detected as well as the levels of residues and their violations.

Product Name	Sample No	Compound	freq	<LOQ	Min mg/kg	Max mg/kg	Mean mg/kg	EU MRL mg/kg	Codex MRL mg/kg	viol comp.
Grape leaf	2	Atrazine	1		0.01	0.01	0.01	0.01		
		Azoxystrobin	1		0.1	0.1	0.10	3	3	
		Boscalid	1		0.04	0.04	0.04	0.05	40	
		Carbendazim	1		1.27	1.27	1.27	0.1		1
		Chlorpyrifos	1	1	-	-	-	0.05		
		Cypermethrin	1		0.1	0.1	0.10	0.7	0.7	
		Diniconazole	1		0.01	0.01	0.01	0.01		
		Fenarimol	1	1	-	-	-			
		Flusilazole	1	1	-	-	-			
		L- Cyhalothrin	2		0.04	0.08	0.06	0.02		2
		Metalaxyl	1		0.11	0.11	0.11	0.05		1
		Penconazole	1		0.01	0.02	0.02	0.05		
		Propiconazol	1		0.02	0.02	0.02	0.05		
		Triadimenol	1		0.18	0.18	0.18	0.1		1
Green Coriander	5	Atrazine	4	2	0.01	0.33	0.17	0.05		1
		Carbendazim	1		5.18	5.18	5.18	0.1		1
		Chlorpyrifos	5	2	0.01	0.22	0.12	0.05		1
		Chlorpyrifos-Me	1	1	-	-	-			
		Cypermethrin	2		0.01	0.03	0.02	2	0.7	
		Diazinon	1	1	-	-	-	-		
		Ethion	1	1	-	-	-	0.01		
		Fenpropathrin	1		0.02	0.02	0.02	0.01		1
		L- Cyhalothrin	3		0.01	0.02	0.01	1		
		Malaoxon	1		0.01	0.01	0.01	-		
		Malathion	4	2	0.18	1.21	0.70	0.02		2
		Methomyl	1	1	-	-	-			
		Omethoate	2	1	0.01	0.01	0.01			
		Penconazole	2		0.13	0.13	0.13	0.05		1
		Pendimethalin	4		0.01	0.05	0.01	0.6		
		Profenofos	3	1	0.02	1.2	0.61	0.05		1
		Tecnazene	1	1	-	-	-			
		Thiobencarb	2	2	-	-	-			
		Trifluralin	1	1	-	-	-			

Cont table (1).,

Product Name	Sample No	Compound	freq	<LOQ	Min mg/kg	Max mg/kg	Mean mg/kg	EU MRL mg/kg	Codex MRL mg/kg	viol comp.
G. Dill	6	Atrazine	1	1				0.05		
		Carbendazim	1		5.58	5.58	5.58	0.1		1
		Chlorpyrifos	5		0.01	0.11	0.01	0.05		2
		Chlorpyrifos-Me	1	1	-	-	-			
		Cypermethrin	1		0.01	0.01	0.01	2	0.7	
		Diazinon	2	1	0.02	0.02	0.02	0.01		1
		Diniconazole	1		0.31	0.31	0.31	0.02		1
		Ethion	1		0.05	0.05	0.05	0.01		1
		Fenpropathrin	1		0.01	0.01	0.01	0.01		
		L- Cyhalothrin	1		0.94	0.94	0.94	1		
		Malaoxon	1		0.01	0.01	0.01			
		Malathion	5	1	0.01	11.2	0.02	0.02		1
		Methomyl	1		0.01	0.01	0.01	0.3		
		Omethoate	1		0.05	0.05	0.05			
		Penconazole	2		0.8	1.03	1.03	0.05		2
		Pendimethalin	4		0.02	0.07	0.03	0.6		
		Phenthoate	1	1	-	-	-			
		Profenofos	5		0.01	0.05	0.01	0.05		
		Thiobencarb	2		0.01	0.01	0.01	0.1		
G.Parsley	7	Atrazine	3	1	0.01	0.01	0.01	0.05		
		Carbendazim	1		0.09	0.09	0.09	0.1		
		Chlorpyrifos	5		0.01	0.06	0.01	0.05		1
		Diazinon	1	1	-	-	-			
		Fenpropathrin	1		0.02	0.02	0.02	0.01		1
		L- Cyhalothrin	1		0.01	0.01	0.01	1		
		Malathion	3	2	0.01	0.01	0.01	0.02		
		Methomyl	1		0.02	0.02	0.02	0.3		
		Penconazole	3		0.01	0.55	0.03	0.05		1
		Pendimethalin	2	1	0.01	0.01	0.01	2		
		Profenofos	4		0.01	0.03	0.02	0.05		
		Thiobencarb	2	2	-	-	-			
Lettuce	4	Carbendazim	1		0.02	0.02	0.02	0.1	5	
		Pendimethalin	1	1				-		
		Triadimenol	1		0.1	0.1	0.1	0.1		
Molokia	18	Chlorpyrifos	4	1	0.01	0.01	0.01	0.05		
		Cypermethrin	1		0.04	0.04	0.04	0.7	0.7	
		Dicofol	1	1	-	-	-	-		
		Malathion	1		0.01	0.01	0.01	0.02		
		Methomyl	3		0.01	0.28	0.01	0.05		1
		Pendimethalin	1	1	-	-	-	-		
		Profenofos	1	1	-	-	-	-		
Spinach	9	Chlorpyrifos	3	1	0.01	0.02	0.02	0.05		
		Cypermethrin	1		0.07	0.07	0.07	0.7	0.7	
		L- Cyhalothrin	1		0.01	0.01	0.01	0.5		
		Malathion	1		0.02	0.02	0.02	0.02	3	
Water Cress	6	Atrazine	1	1	-	-	-	0.01		
		Bromuconazole	1		0.01	0.01	0.01	0.05		
		Carbendazim	1		0.12	0.12	0.12	0.1		1
		Chlorpyrifos	4	3	0.01	0.01	0.01	0.05		
		Chlorpyrifos-Me	1		-	-	-			
		L-Cyhalothrin	3		0.21	1	1.00	0.02		3
		Malathion	2		0.01	0.01	0.01	0.02		
		Methomyl	1		0.01	0.01	0.01	0.02		
		Omethoate	1		0.01	0.01	0.01			
		Profenofos	1		0.01	0.01	0.01	0.05		
Root vegetables										
Carrot	11	Chlorpyrifos	1	1	-	-	-	-		
Potatoes	20	Chlorfenapyr	1	1	-	-	-			
		Chlorpropham	1		0.13	0.13	0.13	10	30	
		Chlorpyrifos	3	1	0.01	0.34	0.18	0.05	2	1
		Methomyl	1		1.82	1.82	1.82	0.02	0.02	1
		Phenthoate	2		0.27	0.79	0.53	0.01		2

Cont table (1)

Product Name	Sample No	Compound	freq	<LOQ	Min mg/kg	Max mg/kg	Mean mg/kg	EU MRL mg/kg	Codex MRL mg/kg	viol comp.
Fruiting veg.-others										
Cucumber	13	Acetamiprid	3		0.01	0.09	0.09	0.05	0.2	
		Carbendazim	1		0.64	0.64	0.64	0.1	0.05	1
		Chlorpyrifos	4	2	0.02	0.02	0.02	0.05		
		Fenpropathrin	1		0.03	0.03	0.03	0.01		1
		Hexythiazox	1		0.01	0.01	0.01	0.5		
		Indoxacarb	1	1	-	-	-			
		L- Cyhalothrin	2		0.01	0.03	0.02	0.1	0.05	
		Metalaxyl	3		0.01	0.07	0.07	0.5	0.5	
		Methomyl	3		0.04	0.08	0.08	0.02	0.1	2
		Oxamyl	1		0.55	0.55	0.55	0.02	2	
		Propamocarb	4	1	0.01	0.03	0.03	10	5	
		Triadimenol	1		0.01	0.01	0.01	0.2	0.2	
Eggplant	9	Carbendazim	1		0.01	0.01	0.01			
		L-Cyhalothrin	1	1	-	-	-	0.5	0.3	
		Methomyl	1	1	-	-	-	0.02	0.1	
		Triadimenol	2		0.01	0.03	0.01	1	1	
Okra	17	Chlorpyrifos	8	3	0.01	0.03	0.01	0.5		
		Cypermethrin	1	1	-	-	-			
		Ethion	1	1	-	-	-			
		Profenofos	6	5	0.02	0.02	0.02	0.01		1
Pepper	13	Acetamiprid	3		0.04	0.2	0.20	0.3	0.2	
		Boscalid	1		0.02	0.02	0.02	3	10	
		Bromuconazole	1		0.02	0.02	0.02	0.05		
		Buprofezin	1	1	-	-	-			
		Carbendazim	3		0.02	0.2	0.02	0.1	2	1
		Ethion	1		0.06	0.06	0.06	0.01		1
		Fenpyroximate	1		0.04	0.04	0.04	0.2	0.2	
		Flusilazole	1		0.24	0.24	0.24	0.02		1
		Hexythiozox	1	1	-	-	-			
		Imidacloprid	1	1	-	-	-			
		Methomyl	2		0.03	0.08	0.08	0.02	0.7	
		Methoxyfenozide	1		0.02	0.02	0.02	1	2	
		Myclobutanil	2		0.01	0.05	0.05	0.5		
		Penconazole	2	2	-	-	-			
		Profenofos	1	1	-	-	-			
		Triadimenol	2	1	0.04	0.04	0.04	1	1	
Squach	10	Carbendazim	1	1	-	-	-	0.1	0.5	
		Chlorfenapyr	1		0.01	0.01	0.01	0.01		
		Chlorpyrifos	1		0.04	0.04	0.04	0.05		
		Fenpropathrin	1		0.01	0.01	0.01	0.01		
		L-Cyhalothrin	2		0.01	0.01	0.01	0.1	0.3	
		Methomyl	1	1	-	-	-		0.1	
		Methoxyfenozide	1		0.05	0.05	0.05	0.02		1
		Phenthoate	1		0.01	0.01	0.01	0.01		
		Profenofos	1	1	-	-	-			
Tomato	21	Azoxystrobin	1		0.1	0.1	0.1	0.3		
		Carbendazim	3		0.01	0.08	0.01	0.3	0.5	
		Carbofuran	1		0.08	0.08	0.08	0.01		1
		Chlorfenapyr	3		0.02	0.02	0.02	0.05		
		Chlorpyrifos	7	3	0.01	0.08	0.03	0.5	0.5	
		Chromafenozide	1	1	-	-	-			
		Dimethoate	1		0.34	0.34	0.34	0.02		1
		Ethion	1		0.02	0.02	0.02	0.01		1
		Famoxadone	2		0.02	0.03	0.02	1	2	
		Imidacloprid	2		0.04	0.05	0.04	0.5	0.5	
		Indoxacarb	1							
		L-Cyhalothrin	3	2	0.01	0.01	0.01	0.1	0.3	
		Malathion	1		0.02	0.02	0.02	0.02	0.5	
		Metalaxyl	1	1				0.2	0.5	
		Methamidophos	1		0.17	0.17	0.17	0.01		1
		Methomyl	1	1				0.02	1	
		Methoxyfenozide	1		0.02	0.02	0.02	2	2	
		Omethoate	1		0.1	0.1	0.1			
		Phenthoate	2		0.01	0.02	0.02	0.01		2
		Profenofos	9	1	0.02	0.28	0.03	0.01	10	
		Propamocarb	1		0.56	0.56	0.56	10	2	
		Spinosad	2	1	0.08	0.08	0.08	1	0.3	
		Thiabendazole	1	1						

Cont table (1).,

Product Name	Sample No	Compound	freq	<LOQ	Min mg/kg	Max mg/kg	Mean mg/kg	EU MRL mg/kg	codex MRL mg/kg	viol comp.
legume veg										
G beans	13	Boscalid	1		0.01	0.01	0.01	3	3	
		Carbendazim	1		0.05	0.05	0.05	0.2	2	
		Chlorpyrifos	2		0.01	0.17	0.17	0.05	0.01	1
		Cypermethrin	1	1	-	-	-			
		Fenpropathrin	1		0.23	0.23	0.23	0.01		1
		Iprodione	1		0.04	0.04	0.04	5	2	
		Metalaxyl	1		0.01	0.01	0.01	0.05		
		Methomyl	1	1	-	-	-			
G Peas	14	Bifenthrin	2	2	-	-	-			
		Carbendazim	2		0.01	0.1	0.01	0.2	0.02	
		Deltamethrin	1		0.03	0.03	0.03	0.2	0.2	
		L-Cyhalothrin	1	1	-	-	-	0.2	0.2	
		Spinosad	1		0.07	0.07	0.07	0.5	0.3	
Bulb veg										
onion	6	Phenthoate	1	1	-	-	-			
Total samples	204									

From one to two kilograms of each sample were collected and prepared for residue analysis according to Codex Alimentariuos Commission, CAC (1993).Two hundred and fifteen (215) pesticides either currently registered or banned in Egypt were subjected to analysis. Samples preparation was performed according to the generally recommended method of sampling to achieve a representative part of the material to be analysed (Codex Alimentariuos Commission 1993). Samples analyses were carried out either immediately upon their arrival to the laboratory or the samples were stored at 0-5 ^{o}C for no longer 2 days before analysis.

Pesticide Residues Analysis:

The standard methodof European Committee for Standardization/Technical Committee 275 (2007) for foods of plant origin: prEN 15662 (QuEChERS) was followed.

The method allowed the determination of 215 compounds of different pesticide chemical groups.The determination of residues carried out usingGC-MS/MS and LC-MS /MSafter acetonitrile extraction/partitioning and cleanup by dispersive SPE.

The homogeneous sample is extracted in frozen condition with the help of acetonitrile. Samples with low water content (< 80 %) require the addition of water before the initial extraction to get a total of approximately 10g of water. After addition of magnesium sulfate, sodium chloride and buffering citrate salts (pH 5 to 5.5);the mixture is shaken intensively and centrifuged for phase separation. An aliquot of the organic phase is cleaned-up by dispersive solid phase extraction (D-SPE) employing bulk sorbents as well as magnesium sulfate for the removal of residual water. Following cleanup with amino-sorbents (e.g. primary secondary amine sorbent, PSA) extracts are acidified by adding a small amount of formic acid, to improve the storage stability of certain base-sensitive pesticides. The final extract can be directly employed for GC- and LC-based determinative analysis. Quantification is performed using an internal standard, which is added directly before injection in GC-MSD system. The method validated for 151 compounds using LC-MS/MS and 64 compounds using GC-MS/MS.The detection and confirmation of pesticides residues in the samples was made usingGC- MS/MS and LC-MS/MS.

Quality Assurance:

The analytical method and instruments were fully validated as part of a laboratory quality assurance system and were accredited according to ISO/IEC 17025:2005 by FINAS (Center for Metrology and Accreditation) Finland. Codex quality assurance criteria were followed to determine the performance of the standard method.

The method is applicable for determination of pesticide residues in fresh food samples with fat content lower than 20%. The standard method performance was tested using recovery tests on different types of pesticides such asorganophosphorous, organonitrogen, organochlorine, carbamates, benzimidazoles, urea derivatives. The average recoveries of these pesticides at different concentration levels varied between 70-120 %. The reproducibility expressed as relative standard deviation was less than 25%. The limit of quantification started at 0.01mg/kg and up depending on the pesticide type and detection module. The measurement uncertainty expressed as expanded uncertainty and in terms of relative standard deviation (at 95 % confidence level) is lower than the default value set by the EU (± 50 %).

Blank samples were fortified with the pesticides mixture and analyzed as a normal sample with each set of samples. The results were recorded on control charts. Repeated analysis of old samples was regularly carried out to control reproducibility.

Apparatus:

(a) LC-MS/MS System:

Agilent 1200 series liquid chromatography system equipped with Applied Biosystems (API 4000 Qtrape) tandem mass spectrometers with electrospray ionisation (ESI) interface.Separation was performed on a C18 column ZORBAX Eclipse XDBC18 4.6 mm x 150 mm, 5 µm particle sizes. The injection volume was 25 µl. A gradient elution program 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) and the other contained methanol. The ESI source was used in the positive mode, and Nitrogen was used as nebulizer gas, curtain gas, heater gas and collision gas according to manufacturer's settings; source temperature was 300^{o}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 other was used for confirmation.

(b) 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 µm film thickness). Samples were injected in a splitless mode and helium was used as carrier gas (1 ml/min). Injector temperature was 250°C, transfer line temperature was 285°C, ion source temperature was 280°C and quadrupole temperature was 150°C. 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 analytes.

Reagents:

Solvents and chemicals described in the standard method CEN 275, 2007.

Pesticides reference standards:

All reference materials are certified provided by Dr. EhrenstorferGmbh, Gogginger Str. 78 D- 8900 Augoburg.

Estimated daily intake (EDI) calculation:

From a potential health perspective, it is certainly important to compare exposure estimates to established toxicological criteria such as ADI. Actually EDI is a realistic estimation of pesticide residues exposure that was calculated in the agreement with the international guidelines. EDI of pesticide residues for each combination of pesticide and commodity was calculated by multiplying the mean residual pesticide concentration (mg kg $^{-1}$) in the food of interest and the food consumption rate (kg d $^{-1}$) and divided by body weight (Darko and Akoto, 2008)as shown in the equation:

Exposure = (Concentration of pesticide residue x Food consumed)/ body weight

The food consumption figures used were based on the consumption data issued by WHO/Global Environment Monitoring System–Food Contamination, Monitoring and Assessment Program average consumption cluster C diets (WHO/GEMS/FOODS, 2006) (table 4) .If data from food balance sheets are not available for a commodity, the consumption level for a similar food is used (WHO 1997). No consumption rate available for coriander, dill, grape leaf and molokhia, consumption level for a similar food is used.

The health risk indices were obtained by dividing the EDI by their corresponding values of ADI (FAO/WHO, 2010); assuming average adult's body weight of 60 kg.Estimated daily intakes (EDIs) of a pesticide residue and food consumption assumption were used to determine long term health risks to consumers.

When the health risk index >1; the food involved is considered a risk to the consumers. When the index <1, the food involved is considered acceptable (Hamilton and Crossley, 2004 and Darko and Akoto, 2008).Then HRI of the residues was computed using theequation,HRI = EDI/ADI,(EFSA2013).

Cumulative risk obtained for the detected pesticides belonging to the same chemical group organophosphates, organochoride, carbamate and pyrethroids by summing up HRIfor the individual pesticides (ΣHRI's).

Results and Discussion

Monitoring results:

Table (1) showed the number of samples of each commodity, the detected pesticide, and the range of detected pesticides, minimum, maximum and mean in mg/kg and the maximum residue limits MRL's for each detected pesticide residues /commodity combination.

The Codex Alimentarious Maximum Residue Limits MRLs were followed to compare the current monitoring data where the Egyptian MRLs were mainly those of the Codex Committee. However, in many cases (pesticide/commodity) combination have no MRLs available neither from the codex nor from Egypt. In such case the European MRLs was followed.

The aim of pesticide monitoring studies is to ensure that crops comply with maximum residues levels (MRLs) allowed by Egypt, and no misuse of pesticides that could result in unexpected residues in food and that good agricultural practices (GAP) are maintained.

A total of 204 samples of commonly consumed vegetables were collected from five Egyptian locationsfrom Feb to August 2011 monitored for pesticide residues analysis. Nineteentypes of commonly consumed vegetablesand locally cultivated types were identified.

All samples were subjected to multi-residue analysis for 215 pesticide residues using the standard methodCEN 275, 2007.The new techniques using LC-MS/MS with GC-MS/MSallowed the detection of wide range of residues with low quantification levels to achieve the international requirements. By this method it could precisely identify the small quantity (< LOQ)for each compound andthe number of pesticidessought in the analytical scope have beenincreased. Theanalysedwide range include many group of pesticides such as, organophosphorus and nitrogen compounds, organochlorine, pyrethroid, and other groups of pesticide that are widely used or banned in Egypt.

Overall, 50 % of the samples had no detectable pesticide residues and the other 50% contained detectable residues which 32.5% of contaminated samples contain resides at levels lower than the MRL's and 17.5 % (36 samples)had residues above the permissible limits, table (2). The obtained results lower than the rates found in study conducted by (Khaled *et al*., 2010) in Saudi Arabia who indicated that, residues were foundin 55.6% and 33.7% of samples were found above the maximum residue levels (MRLs) . Farag etal., 2011inspected the residues in some Egyptian vegetables at 2011 indicated 27 % contamination and 13% violation. They also found (17 pesticide residues) belong to different chemical groups and classified the detected residues to compounds that are sharing a common mechanism of action are those belonging to the organophosphorus and the carbamate groups, endocrine disruption and others are potential human carcinogen.

Table 2: The number of analysed samples, free, contaminated as well as violated and their percentages.

Commodities	Total	Free	Contaminated not violated	Violated
Leaf veg and freash herbs				
Grape leaf	2	-	-	2
Green Coriander	5	-	1	4
Green Dill	6	1	-	5
Green Parsley	7	1	4	2
Lettuce	4	2	2	-
Molokia	18	8	9	1
Spinach	9	4	5	-
Water Cress	6	1	2	3
Total	57	17	23	17
%		29.8	40.3	29.8
Root veg.				
Carrot	11	10	1	-
Potatoes	20	14	3	3
Total	31	24	4	3
%		77.4	12.9	9.7
Fruiting veg.-others				
Cucumber	13	4	5	4
Eggplant	9	6	3	-
Green beans	13	10	2	1
Green Peas	14	11	3	-
Okra	17	9	7	1
Onion	6	5	1	-
Pepper	13	3	6	4
Squash	10	5	4	1
Tomato	21	8	8	5
Total	116	61	39	16
%		52.6	33.6	13.8
Total analysed veg	204	102	66	36
%		50	32.5	17.5

Also in India, 51% of foods commodities are contaminated with pesticide residues and out of these, 20% have pesticides residues above the maximum residue level values on a worldwide basis, (Gupta,2004).

MRLs may be exceeded because of pesticide misuse, false positives due to naturally occurring substances, differences in national MRLs, lack of registered pesticides and incorrect pesticide application (EFSA, 2010). However, the violations rates could be varied depending on the MRL sources. Whereas,the MRL's setting is based on the national registered good agriculture practice (GAP) data combined with the estimated likely residue from the supervised trials, mean residue (STMR), ADI and ARfD.For example, the MRL of profenofos on tomato is 10 mg/kg in codex and 0.01 mg/kg in European standards accordingly the violation percentages will completely different. For this reasons it is important to compare the results with more rigidness toxicological end point such as ADI or ARfD to evaluate the real risk of exposure. The Egyptian authorization should be consider establishing national MRLs based on local GAP and local supervised trails.

Table (2) showed the percentages of free, contaminated and violated samples of different vegetables categories, however the highest contamination percentages observed in leafy vegetables followed by fruiting vegetables and then root vegetables with percentages of 70.1%, 47.4% and 22.6%of which 29.8% , 16% , 9.7% exceeded the permissible levels,respectively.

Comparing the current results with the previous monitoring data carried out by Dogheim *et al*.,at 1999, 2001,2002 and 2004 at Egyptian markets in the following table showed that, current data had higher contamination and violation percentages than all previous resultswith the sametrend of pesticides detected groups. However, organophos phorouspesticide residues were the most detectedgroupin allvegetables samples.leafy vegetable were the most contaminated group, 60% of contamination was with OP's observed in leafy vegetables that might be attributed to cultivation of such crops besides other crops such as cotton that may have been subjected to extensive spraying with pesticides.

Monitoring year	Leafy veg		Vegetables		Root veg		All veg		Ref.
	cont%	viol%	cont%	viol%	cont%	viol%	cont%	viol%	
1995							40.6%	1.6%	Dogheim *et al* 1999
1996	10.1%	3.5%	21.8%	2.2%	2.34%	-	17.4%	2.2%	Dogheim *et al* 2001
1997	4.7%	0.42	17.5%	2.3%	1.9%	-	14.3%	1.8%	Dogheim *et al* 2002
1999	16.9%	6.3%	no result		no result		NS		Dogheim *et al* 2004
2011	70.1%	29.8%	47.4%	13.8%	22.6%	9.7%	50%	17.6%	current work

The same trend also obtained by Mi-Ra Jang *et al* 2011 who conducted monitoring study for vegetables in Korea and illustrated that the detection rate of pesticide and the exceeding of MRL's are shown in the leafy vegetables.

Evaluation by pesticides:

In total, 311 detections of 53 different pesticides were stated. Of which (27.7%) of the residues detected were lower than the limit of quantification (LOQ).Leafy vegetables are the most contaminated group with multiple residues 25 out of 40 samples (62.5%) contaminated with more than 2 pesticides per sample.

Table (3) and figure (1) showed the detected pesticides could be classified in many groups, the most commonly groups were, organophosphorous OPs followed by pyrethroids the ntriazoles and carbamates, with frequencies percentages 41.5 %, 11.8% ,8.8% and 8.0% respectively.

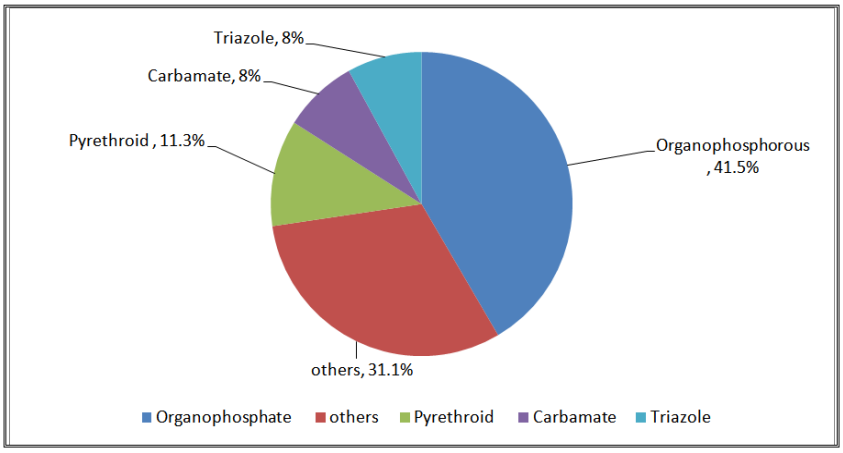

Fig. 1: The most detected pesticides groups in vegetables samples analysed during 2011.

Table 3: The detected pesticide residues and their frequencies in analyzed Egyptian vegetable samples.

Substance group	Pesticides	Total No. of frequencies	% of frequencies
Organophosphorous	Chlorpyrifos	53	17.0
	Chlorpyrifos-methyl	3	1.0
	Diazinon	4	1.3
	Dimethoate	1	0.3
	Ethion	5	1.6
	Malathion	17	5.5
	Malaoxone	2	0.6
	Methamidophos	1	0.3
	Omethoate	5	1.6
	Phenthoate	7	2.3
	Profenofos	31	10.0
		129	41.5
Pyrethroid	Bifenthrin	2	0.6
	Cypermethrin	8	2.6
	Deltamethrin	1	0.3
	Fenpropathrin	6	1.9
	Lambda-Cyhalothrin	20	6.4
		37	11.8
Carbamate	Carbofuran	1	0.3
	Chlorpropham	1	0.3
	Methomyl	17	5.5
	Oxamyl	1	0.3
	Propamocarb	5	1.6
		25	8.0
Triazole	Bromuconazole	2	0.6
	Diniconazole	2	0.6
	Flusilazole	2	0.6
	Myclobutanil	2	0.6
	Penconazole	11	3.5
	Propiconazol	1	0.3
	Triadimenol	7	2.3
		27	8.8
Benzimidazole	Carbendazim	18	5.8
	Thiabendazole	1	0.3
		19	6.1

The detection number includes the pesticide with results at level of <LOQ and >LOQ

Cont table (3),

Substance group	Pesticides	Total No. of frequencies	% of frequencies
Other groups			
Carboxamide	Hexythiazox	2	0.6
Carboxamide	Boscalid	3	1.0
Chlorophenyl	Tecnazene	1	0.3
Diacylhydrazine	Chromafenozide	1	0.3
Dicarboximide	Iprodione	1	0.3
Dinitroaniline	Pendimethalin	12	3.9
Dinitroaniline	Trifluralin	1	0.3
Neonicotinoid	Acetamiprid	6	1.9
Neonicotinoid	Imidacloprid	3	1.0
Organochlorine	Dicofol	1	0.3
Oxadiazine	Indoxacarb	2	0.6
Oxazole	Famoxadone	2	0.6
Phenylamide	Metalaxyl	6	1.9
Pyrazole	Fenpyroximate	1	0.3
Pyrimidine	Fenarimol	1	0.3
Pyrrole	Chlorfenapyr	5	1.6
Strobilurin	Azoxystrobin	2	0.6
Diacylhydrazine	Methoxyfenozide	3	1.0
Thiocarbamate	Thiobencarb	6	1.9
Triazine	Atrazine	10	3.2
Unclassified	Buprofezin	1	0.3
Synergist	Piperonylbutoxide	1	0.3
Macrocyclic Lactone	Spinosad	3	1.0
		74	23.7
Total detection	53 pesticide residues	311	

The detection number includes the pesticide with results at level of <LOQ and >LOQ

Overall contaminated samples, organophosphorous OPs including chlorpyrifos found in 17%, followed byprofenofos 10% and then Malathion 5.5%. However, the second most frequent detecting group in descending

order was pyrethroidsit includes, lambda-cyhalothrinfound infound in (6.4%),cypermethrin(2.6%), and fenpropathrin, (1.9%), in analysedvegetables samples. Organochlorinecompounds did not detected in any ofanalysed samples indicated disappearance of such persistencepesticides from Egyptian environment.

Fig (2)identifies the ten mostfrequently detected pesticides in order of frequency percentages in analysed Egyptian vegetables during 2011, and they were in descending order, chlorpyrifos (17%), profenofos (10%), lambda-cyhalothrin (6.4%), carbendazim(5.8%),malathion and methomyl(5.5%), pendimethalin (3.9%), penconazole (3.5%), atrazine (3.2%) and cypermethrin (2.6%). OP's are the most of highly detected residues and it have been used in agriculture applications since many years. However, OP's, carbamates, pyrethriods and atrazines replaced the Organochlorine compounds since 1980's and registered by the Egyptian Agriculture Pesticides Committee (APC). Thecheep price and efficacy might be the reason of long period use in Egyptian markets and the farmers can't change easily their usage pattern. Roshini *et al*., (2008) carried out review raises concerns that exposure to OP's pesticides at levels currently regarded as safe have adversely affect human reproductive function and survival.

Processing techniques may lead to reduction of residues; however, general processing factors have been derived by many researchers, for washing (0.76), peeling (0.44) and canning (0.74) for fruits and vegetables but they could not find the general processing factor for a group such as organophosphorus,Keikotlhaile, and Spanoghe(2010).

Frequent occurrence of pesticide residues in vegetables may be due to the lack of awareness of the growers about the dosage, right ways of application and the suitable interval between harvesting and pesticide treatment. The carelessness or non-availability of correct guidance concerning the pesticide application may be another reason for pesticide residues in the vegetables samples. These contaminated vegetables are potential health risks to the consumers. The misuse or overuse of pesticides and casual combinations of pesticides of different groups without any prior guidance and knowledge are become serious problems.

It was concluded fromthe previous described results, establishment of new legislations for handling of pesticides at cultivation stage should be considered in Egypt.

Risk assessment:

When assessing chronic exposure, the level of pesticide exposure over a lifetime and the likely effects onhealth of such exposure is considered. This assessment method is well developed and considers the meanlevels of exposure in relation to the Acceptable Daily Intake (ADI) values established for individualpesticides. In the case of consumers exposed to residues of chronically toxic pesticides, their healthwould only be at risk if their dietary intake exceeded the ADI every day for an extended period of time.The calculation of the chronic exposure assessment in Table (5) is based on the assumption that foodwith levels of pesticides found is consumed on a daily basis over a lifetime. Therefore, it is regardedas an overestimate of the real exposure to pesticides.

The exposure to pesticide residues was calculated on a total of 39 residues. The detected residues higher than LOQ are involved in calculation of exposure to avoid overestimation of EDI. The total exposure to a given pesticide residue, was obtained by summing exposures from all residue pesticide/food combinations.

Table (5) showed the estimated average daily intake (EDI ug kg $^{-1}$bw $^{-1}$) and the hazard index (HI) for each pesticide residues (the ratio of EDI to ADI) in samples of vegetables analysed.The data showed that, the highest intake of pesticides group through the vegetables in descending order were, carbamates followed by OP's then pyrethroidswith values of, 3.332, 2.223, and 0.145 (ug kg $^{-1}$bw $^{-1}$ day^{-1}) respectively. However, the intake of other misalliancepesticides was 12.663 (ug kg $^{-1}$bw $^{-1}$ day^{-1}).

The data in table (5) also showed that, none of individual HI of pesticides detected in vegetables samples exceeded one indicates norisk associated with consumption of such vegetables.

However comparing the estimated daily intake of OP"s and carbamateswith Threshold of Toxicological Concern (TTC) used in EFSA as a tool for providing scientific advice about possible human health risks from low level exposures, it was found that the estimated intake of OP's and carbamates highly exceeded the established TTC values which is (0.3 µg/kg body weight per day) for organophosphate and carbamate substances with anti-cholinesterase activity, (EFSA 2012).

Organophosphaots ,carbamates and pyrethroidswerethe major pesticides groups used in Egypt since1980'swhichindicatesexposureof the Egyptian populations forthose groupsofpesticidesfor long periods, thatmight be cause chronic health impact, even throughsmall amounts it was usedover a long periodof more than25 years.

It has been observed that long-term, low-dose exposure are increasingly linked to human health effects such as immune-suppression, hormone disruption, diminished intelligence, reproductive abnormalities, and cancer, Gupta (2004). In this light, problems of pesticide safety, regulation of pesticide use, use of biotechnology, and biopesticides, and use of pesticides obtained from natural plant sources such as neem extracts are some of the future strategies for minimizing human exposure to pesticides.

Table 4: Scientific names and consumption rate of analysed commodities in g/day based on GEMS/food total diet food balance sheet.

Type	Scientific name	Consumption g/day
Carrot	*Daucuscarota*	8.1
Coriander	*coriandrumsativum*	0.9
Cucumber	*Cucumissativus*	5.9
Dill	*anethumgraveolens*	0.9
Egg plant	*Solanummelongena*	12.3
Grape leaf (*grape vine)*	*VitisVinifera*	8.3
Green beans	*Phaseolus vulgaris*	4.1
Green Peas	*Pisumsativum*	6
Lettuce	*Lactuca sativa*	1
Molokai (Jews mallow)	*Corchorusolitorius*	5.3
Okra	*Abelmoschusesculentus*	5.3
Onion	*Allium cepa*	33
Parsley	*Petroselinumcrispum*	1.5
Pepper	Pipernigrum	13
Potato	*Solanumtuberosum*	61.2
Spinach	*Spinaciaoleracea*	1.1
Squash	Cucurbitapepo	11.4
Tomato	*Solanumlycopersicum*	118
Water Cress	*Nasturtium officinale*	3.3

- Consumption rate issued by GEMS/ Food regional diet, WHO (2006).

Table 5: The Estimated intake (EDI) and the hazard index (HI) of pesticide residues detected in Egyptian vegetables samples.

Substance group	Pesticides	ADI ug kg^{-1}bw day^{-1}	Source	EDI ug/kg.bw	HI
Organophosphate	Chlorpyrifos	10	JMPR 1999	0.263	0.03
	Diazinon	2	JMPR 2001	0.000	0.00
	Dimethoate	2	JMPR 2003	0.669	0.33
	Ethion	2	JMPR 1990	0.053	0.03
	Malathion	300	JMPR 1997	0.052	0.00
	Methamidophos	4	JMPR 2002	0.334	0.08
	Omethoate	0.3	EFSA 2006	0.198	0.66
	Phenthoate	3	JMPR 1984	0.582	0.19
	Profenofos	10	JMPR 1990	0.071	0.01
				2.223	HI=∑HI's= 1.33
Pyrethroid	Cypermethrin	50	JECFA 1996	0.019	0.00
	Deltamethrin	10	JMPR 2000	0.003	0.00
	Fenpropathrin	30	JMPR 2006	0.022	0.00
	Lambda-Cyhalothrin	5	EU 2000	0.102	0.02
				0.145	HI=∑HI's= 0.02
Carbamate	Carbofuran	1	JMPR 1996	0.157	0.16
	Chlorpropham	50	JMPR 2005	0.133	0.00
	Methomyl	20	JMPR 2001	1.884	0.09
	Oxamyl	9	JMPR 2002	0.054	0.01
	Propamocarb	400	JMPR 2005	1.104	0.00
				3.332	HI=∑HI's= 0.26
Triazole	Bromuconazole	No ADI	-	0.005	-
	Diniconazole	not authorized	-	0.006	-
	Flusilazole	7	JMPR 2007	0.052	0.01
	Myclobutanil	30	JMPR 1992	0.011	0.00
	Penconazole	30	JMPR 1992	0.020	0.00
	Triadimenol	30	JMPR 1985	0.038	0.00
Benzimidazole	Carbendazim	30	JMPR 1995	0.440	0.01
Carboxamide	Hexythiozox	30	JMPR 2011	0.001	0.00
	Boscalid	40	EU 2008	0.011	0.00
Dicarboximide	Iprodione	60	JMPR 2001	0.003	0.00
Dinitroaniline	Pendimethaline	125	EU Dir 03/31	0.001	0.00
Neonicotinoid	Acetamiprid	70	JMPR 2011	0.052	0.00
	Imidacloprid	60	JMPR 2006	0.079	0.00
Oxazole	Famoxadone	6	JMPR 2003	0.039	0.01
Phenylamide	Metalaxyl	80	JMPR 2002	0.023	0.00
Pyrazole	Fenpyroximate	10	JMPR 1995	0.009	0.00
Pyrrole	Chlorfenapyr	15	EU 1999	0.041	0.00
Strobilurin	Azoxystrobin	200	JMPR 2011	0.211	0.00
Synthetic	Methoxyfenozide	100	JMPR 2006	0.053	0.00
Triazine	Atrazine	20	JMPR 2007	0.004	0.00
Unclassified	Spinosad	20	JMPR 2011	0.164	0.01
				12.663	

Only the results higher than LOQ are involved in calculation to avoid overestimation of EDI.

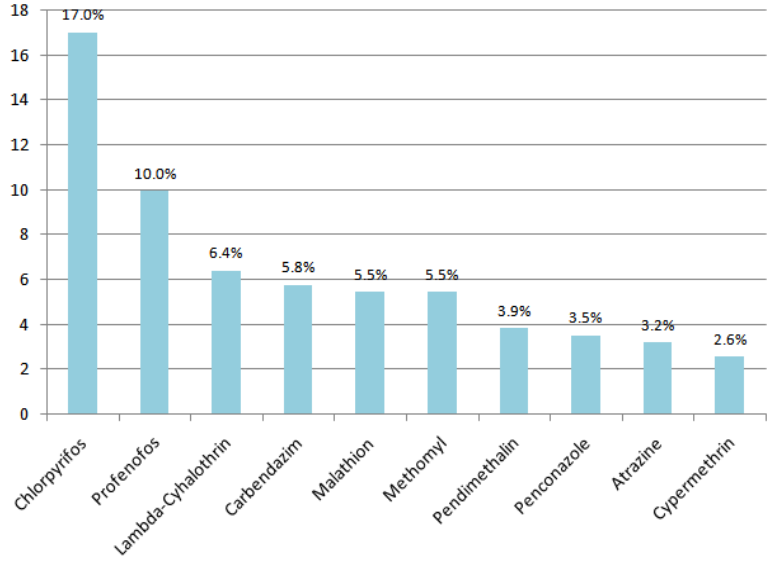

Fig. 2: The top ten detected pesticide percentages in analysed Egyptian vegetables during 2011.

Cumulative risk assessment:

Cumulative risk assessment one of important approach to access hazards due to multiple residues. EFSA has used for the first time a methodology for cumulative risk assessment at 2010. This is a technique that considers the potential effects from combined exposure to pesticides that share similar toxicological properties. Cumulative effects will only occur when pesticides that share similar toxicological characteristics are present together on food. A number of methods are available for cumulating toxicity. The most useful methods, in increasing levels of complexity and refinement, are the hazard index, the reference point index, the Relative Potency Factor method and physiologically based toxicokineticmodeling, although this last method would only be considered should a highly refined assessment be necessary. For the assessment of multiple residues in regulatory practice, the Federal institute for risk assessment(BfR) recommends that the cumulative risk be evaluated by means of the determination and addition of hazard indices (HI) for the individual active substances. It is a simple and fast method which provides consumers with adequate protection at the same time and which can be refined step-by-step if necessary by including additional toxicological information (BfR 2013). The hazard index is a measure of the extent to which the residue of an active substance ingested via food reaches its toxicological limit values (ADI, ARfD). In the current study, the hazard risk index (HI) is applied to assess the potential health risk from consumption of pesticide residues containing foodstuff.

The calculated HI for 39 detected pesticides were shown in table (5). The residues groups as their chemical classes and the HI's summed for the group of similar mechanism i.eorganophosphorous, carbamates, pyrethroids to obtain the cumulative risk of such group, the details of these values found in table (5).

The HI's for the individual pesticides ranged from 0.00 to 0.66 with the values below 1 indicating no risk of adverse effects following exposure to the individual pesticides.

Risk assessment of the cumulative exposure to the detected pesticides with common mechanism of action (organophosphorous, carbamates, and pyrethroids) has been performed by summing up the HI's for the individual pesticides of such group to provide a so-called Hazard Index (HI). The cumulative exposure values (hazard index) of organophosphorus pesticides was exceeded 1 (1.33for adults)indicates hazard to consumers due to presence of OP's in vegetables. However, The (HI) values of carbamates (cumulative risk) estimated for the adults (60kg) did not exceeded the value of 1 and it was (0.26) and for pyrethroids(0.02). Results indicate that there is a negligible risk associated with the exposure via the consumption of selected agricultural products for carbamates and pyrethroids. Even with lower individual HI than 1 but when cumulate the exposure of different individual's pesticides of the same group; it exceeded 1 that ensures the important of estimating the cumulative risk as a new approach.

It was also determined which pesticides and commodities contributed in total Hazard Index (HI)and it illustrated in fig (3). The contribution percentage of each pesticide HQ (HI) to the total HI is calculated by summing the HQ for all detected pesticide and the percentage for each pesticide was calculated. The pesticides that contributed most to the HI are shown together with the contribution from the rest of the pesticides called 'others'. Omethoate, dimethoat and phenthoate are the pesticides among the most important contributors in hazards.

The contributions of each commodity to the HI;s have been calculated and the most commodities that contribute most to the HI are illustrated.As are shown in Fig 3. The most commodities contributed to hazard

(HI) were tomato and potato. Therefore, they had exposures above acceptable levels and represented certain hazards to consumers but in general the levels of residues in vegetables could be reduced due to the home processing such as washing, cooking, frying ect.

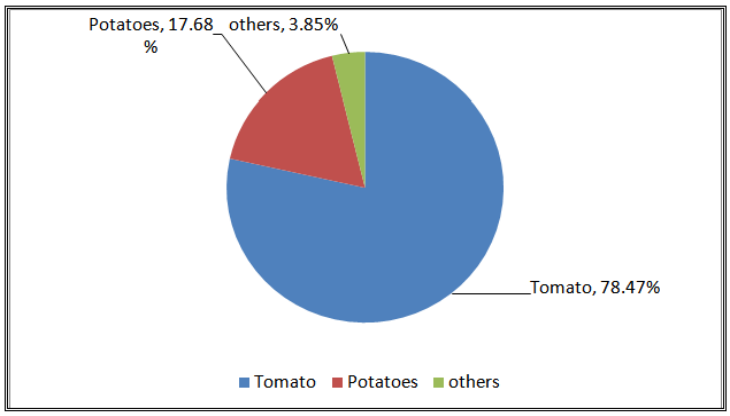

Fig. 3a): The most contributed commodities in total hazard index (HI%).

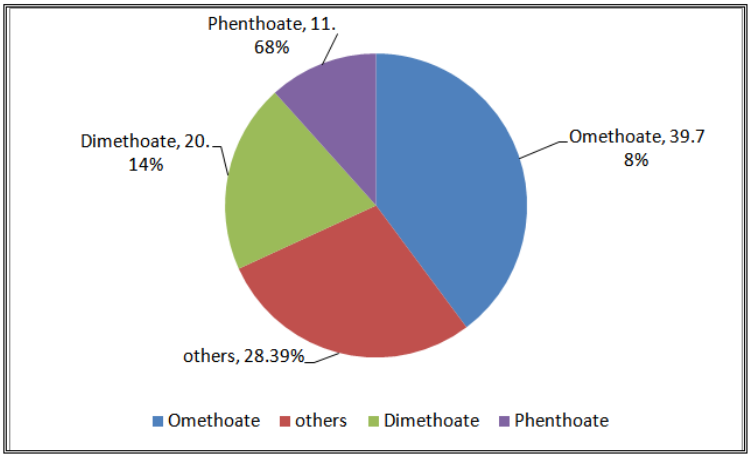

Fig. 3b): The most contributed pesticides in total hazard index (HI%).

Fig. 3: The most contributed commodities and pesticides in total Hazard Index (HI).

Conclusion:

The monitoring of pesticide residues in food items is required to prevent, control and reduce the pollution and to minimize health risks. The Egyptian authorization should do effort for establishing national MRLs based on local GAP and local supervised trials and also to establish control system of pesticide residues at all production stages, from cultivation stage until the products reach the markets.

The output of a pesticide surveillance program (detection frequency and number of exceeding measures) consider preliminary tool for screening of residues levels and can lead to unnecessary concern among consumers since they lack information concerning the actual exposure.Cumulative risk assessment becomes important approach to access hazards due to multiple residues. The estimation of dietary exposure study becomes more essential requirement. The lack of consumption data for different group of population considered one of the barriers to conduct this study.

References

Bhanti, M., G. Shukla, A. Taneja, 2004**.** Contamination levels of organochlorine pesticides andfarmers' knowledge, perception, practices in rural India-A case study. *Bull. Environ. Conta. Toxicol.*, 73: 787-793.

BfR, Federal institute for risk assessment(2013), http://mobile.foodqualitynews.com/Public-Concerns/Pesticide-residue-assessment-must-be-simple-and-transparent-says-BfR.

Choi, S.M., S.D. Yoo, B.M. Lee, 2004. Toxicological characteristics of endocrine disrupting chemicals: Developmental toxicity, carcinogenicity, and mutagenicity. *J. Toxicol. Environ. Health B Crit. Rev.*, 7: 1-24.

CodexAlimentarius Commission, CAC, 1993. Joint FAO/WHO Food Standards Program, 2: 391.

Darko and Akoto, G. Darko O. Akoto, 2008. Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana Food Chem. Toxicol., 46: 3703-3706.

Dogheim, S.M., A.M. El-Marsafy, S.A. Gad Alla, M.A. Khorshid and S.M. Fahmy, 2004. Pesticides and heavy metals levels in Egyptian leafy vegetables and some aromatic medicinal plants, Food Additives and Contaminants, 4: 323-330.

Dogheim, S.M., A.M. El-Marsafy, E.Y. Salama, S.A. Gad Alla and Y.M. Nabil, 2002. Monitoring of pesticide residues in Egyptian fruits and vegetables during 1997. Food Additives and Contaminants, 84: 519-531.

Dogheim, S.M., S.A. Gad Alla and A.M. El-Marsafy, 2001. Monitoring of pesticide residues in Egyptian fruits and vegetables in 1996. Journal of the Association of official Analytical Chemists, 84: 519-531.

Dogheim, S.M., S.A. Gad Alla, A.M. El-Marsafy, 1999. Monitoring of pesticide residues in Egyptian fruits and vegetables in 1995. Journal of the Association of Official Analytical Chemists, 82: 948-955.

EFSA, 2010. 2008 Annual report on pesticide residues according to article 32 of regulation (EC) No 396/2005. *EFSA Journal 2010*, 8(6): 1646.

EFSA Journal, 2012. Scientific Opinion on Exploring options for providing advice about possible human health risks based on the concept of Threshold of Toxicological Concern (TTC), 10(7): 2750, http://www.efsa.europa.eu/en/efsajournal/pub/2750.htm.

EFSA, 2013**.** Scientific Colloquium Summary Report. Cumulative Risk Assessment of Pesticides to Human Health: The Way Forward. Available online: http://www.efsa.europa.eu/en/supporting /doc/colloquiapesticides.pdf (access on 05 February 2013).

EPA (US Environmental Protection Agency)., 1984. Health and Environmental Effects Profile for Carbaryl; Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development: Cincinnati, OH, USA.

EPA (US Environmental Protection Agency)., 1999. *Integrated Risk Information System (IRIS) on Carbaryl*; National Center for Environmental Assessment, Office of Research and Development: Washington, DC, USA.

European Committee for Standardization/Technical Committee 275 (2007), Foods of plant origin: prEN 15662: Determination of pesticide residues using GC-MS and/or LC-MS(/MS) following acetonitrile extraction/partitioning and cleanup by dispersive SPE- QuEChERS method. European Committee for Standardization, Brussels.

FAO, 2002a. (Food and Agriculture Organization). *Submission and Evaluation of Pesticide Residues Data for the Estimation of Maximum Residue Levels in Food and Feed*; FAO: Rome, Italy, pp: 1-279.

FAO/WHO, 2010. Pesticide residues in food and feed. Acceptable Daily Intake; Codex Alimentarius Commission, FAO/WHO Food standards.

Farag, R.S., M.S. Abdel Latif, A.E. Abd El-Gawad and S.M. Dogheim, 2011. Monitoring of pesticide residues in some Egyptian herbs, fruits and Vegetables. International Food Research Journal, 18: 659-665.

Galloway, T., R. Handy, 2003. Immunotoxicity of organophosphorous pesticides. *Ecotoxicology*, *12*, 345–363.

Gupta P.K**(**2004**)**. Pesticide exposure-Indian scene, Toxicology, 198(1-3): 83-90.

Hamilton and Crossley, D. Hamilton S. Crossley, 2004. Pesticide Residues in Food and Drinking Water: Human Exposure and Risks, John Wiley and Sons Ltd. Chichester, England, pp: 28-59.

Hayat, K., M. Ashfaq, U. Ashfaq, M.A. Saleem, 2011. Determination of pesticide residues in blood samples of villagers involved in pesticide application at District Vehari (Punjab), Pakistan. *African J. Environ. Sci. Tech.*, 4: 666-684.

Keikotlhaile, B.M. and P. Spanoghe, 2010. Ghent University, 2010. Pesticide Residues in Fruits and Vegetables, Belgium, www.intechopen.com, Pesticides - Formulations, Effects, Fate, 243-152.

Khaled A. Osman, A.I. Al-Humaid, S.M. Al-Rehiayani, K.N. Al-Redhaiman, 2010. Estimated daily intake of pesticide residues exposure by vegetables grown in greenhouses in Al-Qassim region, Saudi Arabia, Food Control, 1-7.

Khaniki, G.R., 2007. Chemical contaminants in milk and public health concerns: 2007. A review. *Int. J. Dairy Sci.*, 2: 104-115.

Mansour, S.A., M.H. Belal, A.A. Abou-Arab, M.F. Gad, 2009**.** Monitoring of pesticide and heavy metals in cucumber fruits produced from different farming system. *Chemosphere*, 75: 601-609.

Mi-Ra Jang, Hyun-Kyung Moon, Tae-Rang Kim, In-Sook Hwang, Moo-Sang Kim, Jung-Hun Kim, andYoung-Zoo Chae, 2011. Dietary Exposure to Pesticide Residues of Vegetables for Seoulites by Ages in Korea. International Conference on Chemical, Biological and Environment Sciences (ICCEBS'2011) Bangkok Dec., 337-341.

Ntow, W.J., H.J. Gijzen, P. Kelderman and P. Drechsel, 2006. Farmer perceptions and pesticide use practices in vegetable production in Ghana. *Pest Management Science*, 62(4): 356-365.

Rauh, V.A., R. Garfinkel, F.P. Perera, H.F. Andrews, L. Hoepner, D.B. Barr, R. Whitehead, D. Tang, R.W. Whyatt, 2006. Impact of prenatal chlorpyrifos exposure on neurodevelopment in the first 3 years of life among inner-city children. *Pediatrics*, 118: 1845-1859.

Roshini J. Peiris-John, Rajitha Wickremasinghe, 2008. Impact of low-level exposure to organophosphates on human reproduction and survival. Transactions of the Royal Society of Tropical Medicine and Hygiene, 102(3): 239-245.

Shakhaoat, H., H. Alamgir, R. Abdur, I. Mainul, R. Atiqur and M.A. Tanveer, 2013. Health Risk Assessment of Pesticide Residues via Dietary Intake of Market Vegetables from Dhaka, Bangladesh, *Foods*, 2: 64-75.

WHO, 1997. Guidelines for predicting dietary intake of pesticide residues (revised) global environment monitoring system - food contamination monitoring and assessment programme (GEMS/Food) in collaboration with Codex Committee on pesticide residues. Programme of Food Safety and Food Aid, pp: 1-44.

WHO (World Health Organization in collaboration with UNEP), 1990. *Public Health Impact of Pesticides Used in Agriculture*; WHO: Geneva, Switzerland, pp: 1-129.

WHO/GEMS/FOODS, 2006. GEMS/food regional diets (regional per capita consumption of raw and semi-processed agricultural commodities). http://www.who.int/foodsafety/publications/chem/regional_diets/en/.