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Monitoring and risk exposure studies on some pesticide residues detected in some leafy vegetables in Egypt

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ABSTRACT

A monitoring study of pesticide residues was carried out in Egypt 2013. One hundred forty four samples of different types of leafy vegetables (Green Coriander, Green Dill, Green Parsley, Spinach and Water Cress) were collected from eight Egyptian local markets located in eight governorates. All samples were examined for residues of 450 pesticides. Overall, results showed that 10.4% of the samples had no detectable pesticide residues, however, 47.9% contained detectable residues without violation, of which 41.7% contained residues that exceeded maximum residue limits (MRLs). In contrary, data showed that the Green Dill recorded the highest violation % (i.e. 68.97%), followed by water cress (i.e. 57.89%), green parsley (i.e. 42.85%), green coriander (i.e. 36.11%), and spinach (i.e. 23.52%). The violated compounds were Acetamiprid, Atrazine, Carbendazim, Carbofuran, Chlorpyrifos, Chlorpyrifos-methyl, Cyfluthrin, Cypermethrin, Diclorvos, Dimethoate, Diniconazole, Emamectin, Ethion, Fenarimol, Fenitrothion, Flusilazole, hexaconazole, Lambda-Cyhalothrin, Malathion, Methamidophos, mehomyl, Myclobutanil, Omethoate, Penconazole, Profenofos, and Propiconazol. The highest frequently detected pesticide was Chlorpyrifos, followed by Profenofos, and Malathion. However, the lowest frequently detected pesticides, which detected only one time, were Aldicarb sulfoxide, Carbofuran, Cyfluthrin, Diclorovs, Diniconazole, Ethion, Ethoprophos, Fenhexamid, Fenitrothion, Hexaconazole, Imazalil, Imidacloprid, Iprobenfos, Kresoxim-methyl, Lufenuron, Methoxyfenozide, Phenthoate, Pirimiphos-methyl, Propamocarb, and Pyridaben. The dietary exposures of the most frequently detected pesticides were theoretically calculated to evaluate the risk for Egyptian consumer. As shown by the results, the intake of pesticide residues does not exceed the ADI (Acceptable Daily Intake) in any case. It is found to be below 2% of the ADI for all pesticides. The estimated exposure ranges from 0.0011% of the ADI for Pendimethalin and Biphenyl on Green Dill and Water Cress to 1.4372% of the ADI for the Profenofos on Green Dill.

Key words: Monitoring, Pesticide residues, leafy vegetables, Risk exposure

Introduction

Pesticides are the chemicals or any agent to kill or control pests (Environmental Protection Agency, 2007) or undesired organisms like insects, weeds, rodents, fungi and bacteria. The usage of pesticides in agriculture sector worldwide can enhance greater productivity to fulfill the increase needs in foodstuff. However, the slow degradation rate of pesticides and with the influenced of improper usage by farmers can affect the environmental quality by contaminating soil, water, air, other non-target plants and possibly humans (Rissoto *et al*., 2007).

A lot of studies had been conducted to determine the pesticides residues in plants worldwide include cabbage (Zhang *et al.,* 2007), spring tomato (Gambacorta et al., 2005), and orange, white cabbage and wheat (Kocourek *et al.,* 1998). Environmental Protection Agency, EPA, (2007) also conducted various studies to determine the maximum levels of pesticides that may introduced into food when harvesting, processing and marketing, and during preparing to be served. The values of pesticide residues are not similar in fruits and vegetables. This may be caused by the climatic condition and also the variation of the plants species (Tariq *et al.,* 2007). Norris (1969) indicates that

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the pesticide enters the plant when it makes a contact with the surface and compatibility with the cuticle and its behavior of pesticides on aerial portions of the plant, on the roots and pesticide residues in food have historically lagged far behind many comparable hazards as a cause for public health concern and action (Correia *et al.,* 2000). Pesticide residue contaminating food is the problem focused worldwide because of its direct implications on human health and international trade (Sanborn *et al.,* 2007). Reliable residue analysis data resulting from monitoring programs in foods, even if limited, may be of great value indicating the possible risks of pesticide exposure on human health and on international trade (DAF and FSAI, 2006).

Consumer protection is very highly considered by governments and authorities responsible for pesticides registration and use in each country and by the international organizations. Pesticide residue monitoring data in food serve in evaluating and clarifying the situation of potential human risk and trade problems. Such data could help decision makers in reviewing and reconsidering the registration and use of pesticides in the country.

Material and Methods

Sampling:

A total of One hundred forty four samples of leafy vegetables (Green Coriander, Green Dill, Green Parsley, Spinach and Water Cress) were collected from eight Egyptian local markets located in eight governorates (Great Cairo, Fayoum, Gharbia, Giza, Monufia, Ismailia, Sharkiya, and Qalyubia) during 2013. For residue analysis, 2 kg of each commodity was prepared according to Codex guidelines. The generally recommended method of sampling was used to obtain a representative part of the material to be analyzed. Samples were analyzed immediately upon their arrival at the laboratory, or they were stored at 0–5°C for 4 days before analysis. Samples were analyzed for detection of 450 pesticides.

Pesticide Residues Analysis:

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

The determination of residues carried out using GC-MS/MS and LC-MS/MS after acetonitrile extraction/partitioning and cleanup by dispersive SPE.

The homogeneous sample is extracted in frozen condition with the help of acetonitrile. 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 sorbent as well as magnesium sulfate for the removal of residual water. Following cleanup with amino-sorbents (e.g. primary secondary amine sorbent, PSA) extracts were 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 was performed using an internal standard, which was added directly before injection in GC-MSD system. The method validated 450 compounds using LC-MS/MS and GC-MS/MS. The detection and confirmation of pesticide residues in the samples was made using GC-MS/MS and LC-MS/MS.

Quality Assurance:

An analytical method and instruments were carefully validated as a part of the laboratory quality assurance system and were audited and accredited by the Center of Metrology and Accreditation Finnish Accreditation Service (FINAS) ISO/IEC Guide 17025. The criteria of quality assurance were followed to determine the performance of the standard method**.** The average recoveries tests on different types of 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 0.01 mg/kg and up depending on the pesticide type and detected 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 EU (± 50%).

Blank samples were fortified with the pesticides mixture and analyzed as a normal sample with 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 mobile phase was at 0.3 ml/min flow rate, in which one reservoir contained 10 mM ammonium formate solution in MeOH:H2O (1:9, v/v). The ESI source was used in the positive mode, and Nitrogen was used as nebulizer gas, curtain gas, heater gas and collision gas according to manufacturer's settings; source temperature was 300°C, ion spray potential 5500 V,decluster potential and collision energy were optimized using a Harvard apparatus syringe pump. The Multiple Reaction Monitoring Mode (MRM) was used in which one MRM was used for quantification and 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 analysts.

Reagents:

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

Pesticides reference standards:

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

Results and Discussion

Pesticide residues are substances that remain in or on air, water, soil, or food following its use. Even food grown without direct pesticide use can still contain residues due to spray drift from nearby farms, long range air transport, or existing groundwater or soil contamination (Magkos *et al.,* 2003).

A total of One hundred forty four samples of leafy vegetables (Green Coriander, Green Dill, Green Parsley, Spinach and Water Cress). All samples were examined for residues of 450 pesticides. The detected pesticides, minimum, maximum, mean detected levels, numbers and percentages of violated samples are shown in Tables 1, 2, 3, 4 and 5. The MRLs of Codex Alimentarius were used for comparison when those limits were available. In the absence of Codex MRLs, European limits were used.

In the present study, a total number of 62 different pesticides were detected in the leafy vegetable samples. . Frequencies, concentration range and identity of pesticides found in the analyzed

Table 1: Total analyzed samples, contamination %, frequency, minimum, maximum and mean of pesticide residues monitored in Green Coriander in Egypt during 2013

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
36	36	100%	Acetamiprid	2	0.02	0.09	0.055	3	0	0.0%	13	36.11%
			Aldicarb sulfoxide	1	0.005	0.005	0.005	0.02	0	0.0%		
			Atrazine	14	0.01	0.71	0.133	0.05	4	11.1%		
			Azoxystrobin	2	0.01	0.07	0.04	70	0	0.0%		
			Biphenyl	4	0.005	0.01	0.009	0.1	0	0.0%		
			Boscalid	5	0.01	0.09	0.04	40	0	0.0%		
			Butralin	5	0.005	0.02	0.013	0.02	0	0.0%		
			Carbendazim	4	0.01	0.64	0.185	0.1	1	2.8%		
			Chlorfenapyr	1	0.01	0.01	0.01	0.02	0	0.0%		
			Chlorfluazuron	2	0.02	0.06	0.04	-	-	-		
			Chlorpropham	3	0.005	0.01	0.008	0.02	0	0.0%		
			Chlorpyrifos	36	0.005	0.6	0.031	0.05	2	5.6%		
			Chlorpyrifos-methyl	2	0.01	0.02	0.015	0.05	0	0.0%		
			Cypermethrin	7	0.01	0.35	0.106	0.7	0	0.0%		
			delta-HCH	1	0.01	0.01	0.01	-	-	-		
			Diazinon	2	0.005	0.005	0.005	0.02	0	0.0%		
			Dimethoate	2	0.04	0.05	0.045	0.02	2	5.6%		
			Dimethomorph	1	0.005	0.005	0.005	10	0	0.0%		
			Emamectin	1	0.02	0.02	0.02	1	0	0.0%		
			Fludioxonil	1	0.005	0.005	0.005	15	0	0.0%		
			Flusilazole	2	0.005	0.01	0.008	0.02	0	0.0%		

Table 1: ***Continued***

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
36	36	100%	Imidacloprid	1	0.02	0.02	0.02	2	0	0.0%	13	36.11%
			Iprodione	4	0.03	0.28	0.13	20	0	0.0%		
			Lambda-Cyhalothrin	8	0.005	0.21	0.054	1	0	0.0%		
			Malathion	13	0.005	0.11	0.029	0.02	4	11.1%		
			Metalaxyl	3	0.005	0.05	0.025	2	0	0.0%		
			Methomyl	1	0.03	0.03	0.03	0.3	0	0.0%		
			Omethoate	3	0.01	0.34	0.173	0.02	2	5.6%		
			Penconazole	6	0.01	0.49	0.14	0.05	2	5.6%		
			Pendimethalin	20	0.005	0.26	0.044	0.6	0	0.0%		
			Piperonyl butoxide	6	0.005	0.19	0.043	-	-	-		
			Pirimicarb	2	0.005	0.01	0.008	5	0	0.0%		
			Profenofos	14	0.005	6.53	0.654	0.05	6	16.7%		
			Propiconazol	1	0.01	0.01	0.01	0.05	0	0.0%		
			Pyraclostrobin	4	0.005	0.04	0.015	2	0	0.0%		
			Pyridaben	1	0.03	0.03	0.03	0.05	0	0.0%		
			Pyrimethanil	1	0.005	0.005	0.005	20	0	0.0%		

MRL: Maximum Residue limit according to codex

Table 2: Total analyzed samples, contamination %, frequency, minimum, maximum and mean of pesticide residues monitored in Green Dill in Egypt during 2013

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
29	29	100%	Acetamiprid	3	0.01	0.38	0.137	3	0	0.0%	20	68.97%
			alpha-HCH	1	0.005	0.005	0.005	-	-	-		
			Atrazine	7	0.005	0.03	0.012	0.05	0	0.0%		
			Azoxystrobin	4	0.01	0.07	0.028	70	0	0.0%		
			Biphenyl	8	0.005	0.01	0.008	0.1	0	0.0%		
			Boscalid	6	0.005	0.02	0.013	40	0	0.0%		
			Butralin	1	0.005	0.005	0.005	0.02	0	0.0%		
			Carbendazim	5	0.005	0.52	0.181	0.1	2	6.9%		
			Carbofuran	1	0.12	0.12	0.12	0.02	1	3.4%		
			Chlorfenapyr	1	0.01	0.01	0.01	0.02	0	0.0%		
			Chlorfluazuron	1	0.05	0.05	0.05	-	-	-		
			Chlorpropham	3	0.005	0.02	0.012	0.02	0	0.0%		
			Chlorpyrifos	29	0.005	6.6	0.531	0.05	7	24.1%		
			Chlorpyrifos-methyl	7	0.005	0.32	0.058	0.05	1	3.4%		
			Cypermethrin	10	0.005	0.57	0.099	0.7	0	0.0%		
			Cyprodinil	2	0.005	0.03	0.018	50	0	0.0%		
			Diazinon	6	0.005	0.01	0.007	0.02	0	0.0%		
			Diclorovs	1	0.02	0.02	0.02	0.01	1	3.4%		
			Difenoconazole	1	0.03	0.03	0.03	2	0	0.0%		
			Dimethoate	1	0.01	0.01	0.01	0.02	0	0.0%		
			Dimethomorph	1	0.01	0.01	0.01	10	0	0.0%		

Table 2: *Continued*

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
29	29	100%	Diniconazole	1	0.13	0.13	0.13	0.02	1	3.4%	20	68.97%
			Ethion	1	0.06	0.06	0.06	0.01	1	3.4%		
			Ethoprophos	1	0.005	0.005	0.005	0.02	0	0.0%		
			Fenarimol	2	0.02	0.21	0.115	0.02	1	3.4%		
			Fenhexamid	1	0.02	0.02	0.02	50	0	0.0%		
			Fenitrothion	1	0.04	0.04	0.04	0.02	1	3.4%		
			Fludioxonil	1	0.005	0.005	0.005	15	0	0.0%		
			Flusilazole	2	0.01	1.02	0.515	0.02	1	3.4%		
			Hexaconazole	1	0.18	0.18	0.18	0.02	1	3.4%		
			Iprobenfos	1	0.02	0.02	0.02	-	-	-		
			Iprodione	7	0.01	2.2	0.333	20	0	0.0%		
			Lambda-Cyhalothrin	13	0.005	1.7	0.175	1	1	3.4%		
			Malathion	20	0.005	0.47	0.089	0.02	6	20.7%		
			Metalaxyl	1	0.26	0.26	0.26	2	0	0.0%		
			Methamidophos	2	0.19	0.46	0.325	0.02	2	6.9%		
			Methomyl	3	0.02	0.34	0.14	0.3	1	3.4%		
			Myclobutanil	3	0.005	0.17	0.062	0.02	1	3.4%		
			Omethoate	1	0.005	0.005	0.005	0.02	0	0.0%		
			p,p-DDE	2	0.005	0.005	0.005	-	-	-		
			Penconazole	11	0.005	1.47	0.42	0.05	7	24.1%		
			Pendimethalin	19	0.005	0.12	0.039	0.6	0	0.0%		
			Piperonyl butoxide	8	0.005	0.53	0.115	-	-	-		
			Pirimiphos-methyl	1	0.005	0.005	0.005	0.05	0	0.0%		
			Profenofos	20	0.005	21.9	2.663	0.05	13	44.8%		
			Propiconazol	3	0.01	1.9	1.037	0.05	2	6.9%		
			Pyraclostrobin	2	0.005	0.01	0.008	2	0	0.0%		

samples are portrayed in Table 1, 2, 3, 4 and 5 and Figures 1, 2, 3, 4 and 5. Overall, 10.4% of the samples were free from any detectable pesticide residues, however, 47.9% contained detectable residues, of which 41.7% contained residues that exceeded maximum residue limits (MRLs). In contrary, data showed that the Green Dill recorded the highest violation % (i.e. 68.97%), followed by water cress (i.e. 57.89%), green parsley (i.e. 42.85%), green coriander (i.e. 36.11%), and spinach (i.e. 23.52%).

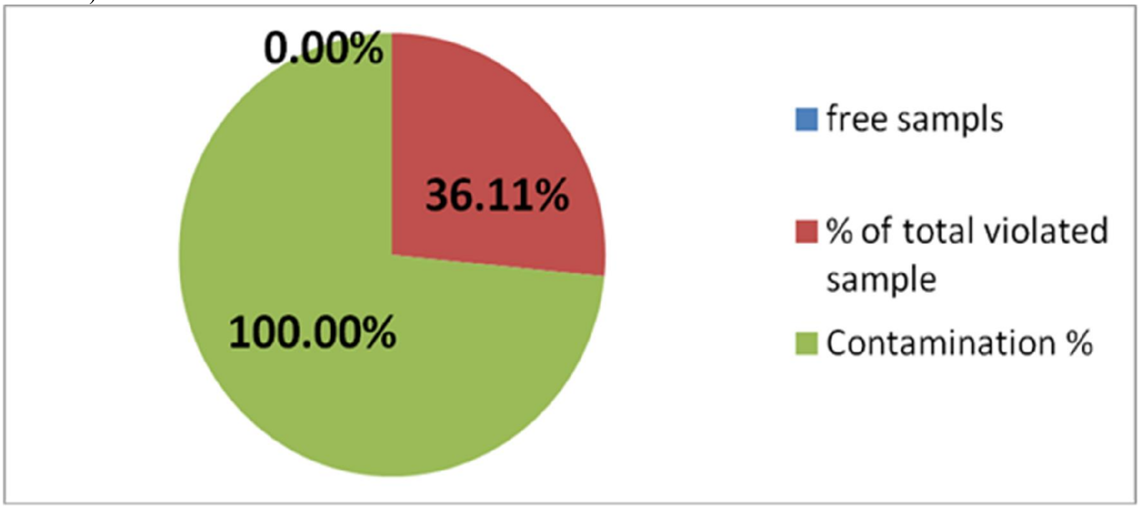

Fig. 1: The contamination and the violation percentages in Green Coriander in Egypt during 2013

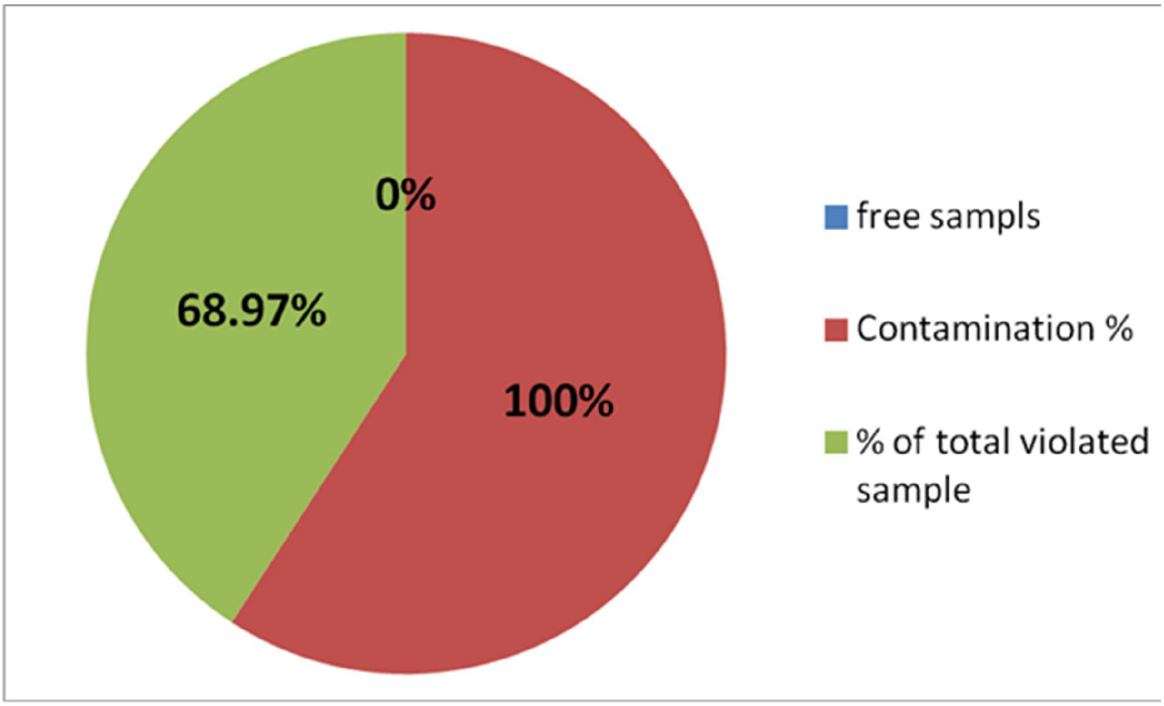

Fig. 2: The contamination and the violation percentages in Green Dill in Egypt during 2013

Table 3: Total analyzed samples, contamination %, frequency, minimum, maximum and mean of pesticide residues monitored in Green Parsley in Egypt during 2013

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
29	28	96.55%	Acetamiprid	1	0.03	0.03	0.03	3	0	0.0%	12	42.86%
			alpha-HCH	1	0.01	0.01	0.01	-	-	-		
			Atrazine	12	0.005	0.03	0.015	0.05	0	0.0%		
			Azoxystrobin	3	0.22	3	1.38	70	0	0.0%		
			beta-HCH	1	0.005	0.005	0.005	-	-	-		
			Biphenyl	5	0.01	0.03	0.016	0.1	0	0.0%		
			Boscalid	5	0.005	0.03	0.014	40	0	0.0%		
			Carbendazim	3	0.06	1.1	0.413	0.1	1	3.6%		
			Chlorfenapyr	1	0.01	0.01	0.01	0.02	0	0.0%		
			Chlorfluazuron	1	0.01	0.01	0.01	-	-	-		
			Chlorpropham	3	0.01	0.02	0.017	0.02	0	0.0%		
			Chlorpyrifos	28	0.005	11.8	0.864	0.05	9	32.1%		
			Chlorpyrifos-methyl	4	0.005	0.01	0.006	0.05	0	0.0%		
			Cypermethrin	4	0.005	0.05	0.019	0.7	0	0.0%		
			Cyprodinil	3	0.005	0.01	0.008	50	0	0.0%		
			delta-HCH	1	0.01	0.01	0.01	-	-	-		
			Diazinon	5	0.005	0.01	0.006	0.02	0	0.0%		
			Difenoconazole	1	0.18	0.18	0.18	10	0	0.0%		
			Fenhexamid	1	0.01	0.01	0.01	50	0	0.0%		
			Flusilazole	2	0.01	0.1	0.055	0.02	1	3.6%		
			Kresoxim-methyl	1	0.005	0.005	0.005	0.02	0	0.0%		

Table 3: *Continued*

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
29	28	96.55%	Lambda-Cyhalothrin	2	0.005	0.01	0.008	1	0	0.0%	12	42.86%
			Lufenuron	1	0.02	0.02	0.02	0.05	0	0.0%		
			Malathion	15	0.005	0.35	0.033	0.02	3	10.7%		
			Metalaxyl	2	0.01	0.02	0.015	2	0	0.0%		
			Myclobutanil	1	0.005	0.005	0.005	0.02	0	0.0%		
			Penconazole	6	0.005	1.24	0.301	0.05	3	10.7%		
			Pendimethalin	4	0.005	0.01	0.008	2	0	0.0%		
			Phenthoate	1	0.005	0.005	0.005	-	-	-		
			Piperonyl butoxide	5	0.005	0.09	0.023	-	-	-		
			Profenofos	11	0.005	4.47	0.783	0.05	2	7.1%		
			Propiconazol	2	0.01	0.02	0.015	0.05	0	0.0%		
			Pyraclostrobin	2	0.005	0.005	0.005	2	0	0.0%		

Table 4: Total analyzed samples, contamination %, frequency, minimum, maximum and mean of pesticide residues monitored in Spinach in Egypt during 2013

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	Frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
30	17	56.67%	Acetamiprid	1	<LOQ	<LOQ	<LOQ	5	0	0.0%	4	23.53%
			alpha-HCH	1	0.02	0.02	0.02	-	-	-		
			Atrazine	1	<LOQ	<LOQ	<LOQ	0.05	0	0.0%		
			Carbendazim	5	<LOQ	0.02	0.01	0.1	0	0.0%		
			Chlorpropham	1	<LOQ	<LOQ	<LOQ	0.05	0	0.0%		
			Chlorpyrifos	5	<LOQ	1.16	0.236	0.05	1	5.9%		
			Chlorpyrifos-methyl	1	0.01	0.01	0.01	0.05	0	0.0%		
			Cyfluthrin	1	0.04	0.04	0.04	0.02	1	5.9%		
			Cypermethrin	3	0.01	0.22	0.083	0.7	0	0.0%		
			Emamectin	2	0.01	0.02	0.015	0.01	1	5.9%		
			Fenhexamid	1	<LOQ	<LOQ	<LOQ	0.01	0	0.0%		
			Lambda-Cyhalothrin	5	<LOQ	0.24	0.055	0.5	0	0.0%		
			Malathion	1	<LOQ	<LOQ	<LOQ	3	0	0.0%		
			Metalaxyl	1	<LOQ	<LOQ	<LOQ	2	0	0.0%		
			Methomyl	2	<LOQ	0.13	0.068	0.05	1	5.9%		
			Methoxyfenozide	1	0.06	0.06	0.06	4	0	0.0%		
			Pendimethalin	1	<LOQ	<LOQ	<LOQ	0.05	0	0.0%		
			Profenofos	1	0.01	0.01	0.01	0.01	0	0.0%		
			Propamocarb	1	0.01	0.01	0.01	40	0	0.0%		
			Pyrimethanil	1	<LOQ	<LOQ	<LOQ	0.01	0	0.0%		

Table 5: Total analyzed samples, contamination %, frequency, minimum, maximum and mean of pesticide residues monitored in Water Cress in Egypt during 2013

Total analyzed samples	Number of Contaminated samples	Contamination %	The detected pesticide	frequency	Min mg/kg	Max mg/kg	Mean mg/kg	MRL mg/kg	No. of violated	violated %	Total violated samples	Total violated samples %
20	19	95%	Acetamiprid	2	0.44	1.6	1.02	0.01	2	10.5%	11	57.89%
			alpha-HCH	1	0.05	0.05	0.05	-	-	-		
			Atrazine	6	0.005	0.02	0.013	0.05	0	0.0%		
			Azoxystrobin	1	0.03	0.03	0.03	0.01	0	0.0%		
			beta-HCH	1	0.01	0.01	0.01	-	-	-		
			Carbendazim	4	0.005	0.03	0.014	0.1	0	0.0%		
			Chlorfluazuron	1	0.01	0.01	0.01	-	-	-		
			Chlorpropham	3	0.005	0.005	0.005	0.01	0	0.0%		
			Chlorpyrifos	9	0.005	1.1	0.195	0.05	3	15.8%		
			Chlorpyrifos-methyl	1	0.01	0.01	0.01	0.05	0	0.0%		
			Cypermethrin	5	0.005	0.75	0.251	0.7	1	5.3%		
			delta-HCH	1	0.01	0.01	0.01	-	-	-		
			Diazinon	1	0.01	0.01	0.01	0.01	0	0.0%		
			Difenoconazole	1	0.01	0.01	0.01	0.5	0	0.0%		
			Dimethoate	3	0.005	0.01	0.007	0.02	0	0.0%		
			Imazalil	1	0.02	0.02	0.02	0.05	0	0.0%		
			Lambda-Cyhalothrin	6	0.005	0.73	0.244	0.02	5	26.3%		
			Malathion	1	0.005	0.005	0.005	0.02	0	0.0%		
			Metalaxyl	1	0.03	0.03	0.03	0.05	0	0.0%		
			Omethoate	4	0.005	0.15	0.045	0.02	1	5.3%		
			Pendimethalin	4	0.005	0.01	0.009	0.05	0	0.0%		
			Piperonyl butoxide	1	0.01	0.01	0.01	-	-	-		
			Profenofos	7	0.005	6.16	1.261	0.01	3	15.8%		

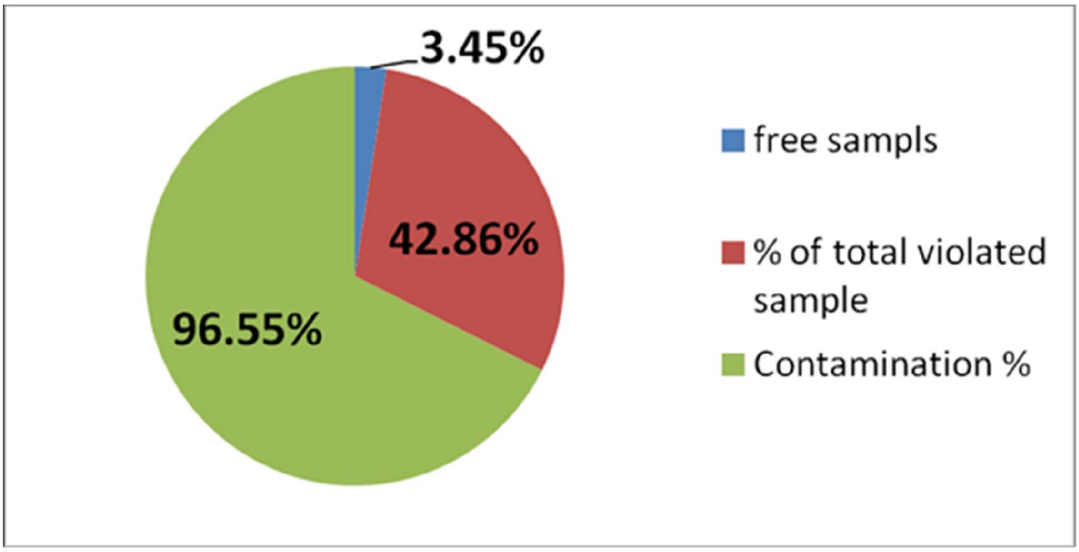

Fig. 3: The contamination and the violation percentages in Green Parsley in Egypt during 2013

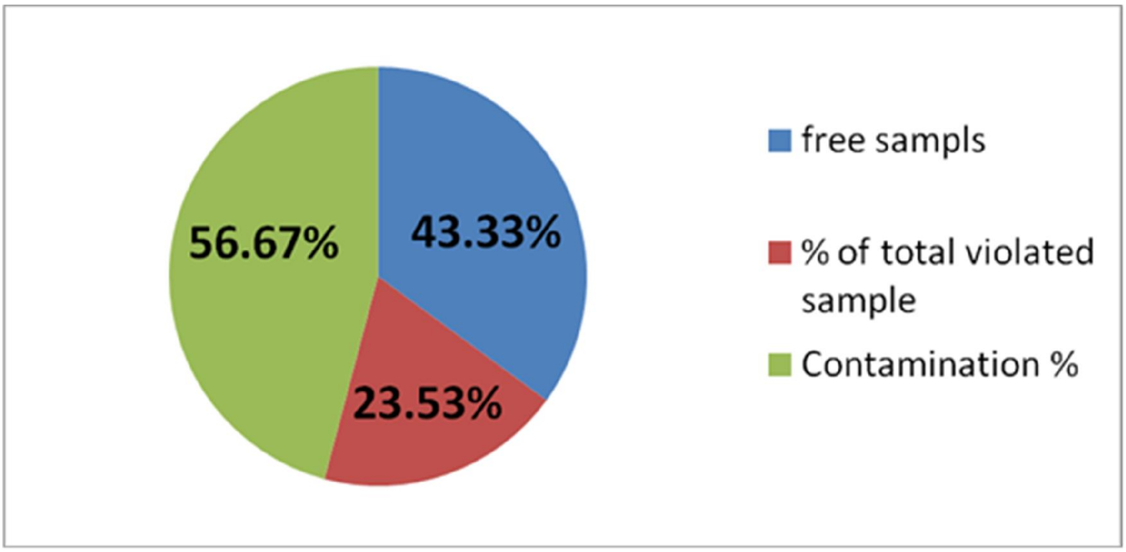

Fig. 4: The contamination and the violation percentages in Spinach in Egypt during 2013

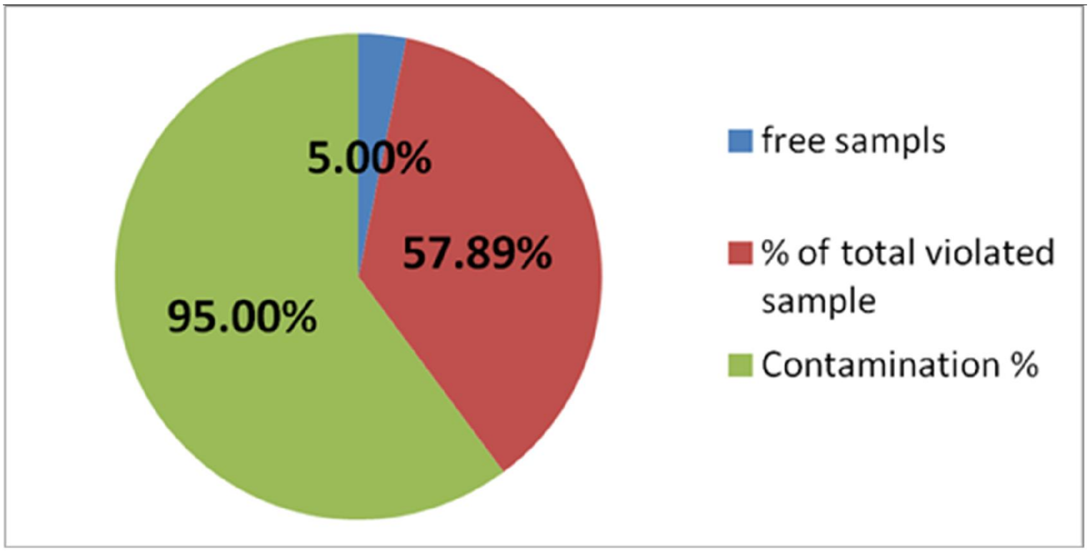

Fig. 5: The contamination and the violation percentages in Water Cress in Egypt during 2013

The violated compounds were Acetamiprid, Atrazine, Carbendazim, Carbofuran, Chlorpyrifos, Chlorpyrifos-methyl, Cyfluthrin, Cypermethrin, Diclorvos, Dimethoate, Diniconazole, Emamectin, Ethion, Fenarimol, Fenitrothion, Flusilazole, hexaconazole, Lambda-Cyhalothrin, Malathion, Methamidophos, mehomyl, Myclobutanil, Omethoate, Penconazole, Profenofos, and Propiconazol. The highest frequently detected pesticide was Chlorpyrifos, followed by Profenofos, and Malathion. However, the lowest frequently detected pesticides, which detected only one time, were Aldicarb sulfoxide, Carbofuran, Cyfluthrin, Diclorovs, Diniconazole, Ethion, Ethoprophos, Fenhexamid, Fenitrothion, Hexaconazole, Imazalil, Imidacloprid, Iprobenfos, Kresoxim-methyl, Lufenuron, Methoxyfenozide, Phenthoate, Pirimiphos-methyl, Propamocarb, and Pyridaben.

The previous data showed that monitored leafy vegetables in 2013 recorded low contamination with different pesticides in contrary with data represented by Gad Alla *et al.,* (2015) who found that leafy vegetables showed high residue level of pesticides residues in comparison to other crops. Similar trend of results was also reported by Mi-Ra *et al.* (2011) who conducted a monitoring study for vegetables in Korea and indicated that exceeding of MRL's is rather common in the leafy vegetables.

Dietary exposure and dietary risk assessment:

Dietary exposure assessment is defined by Codex Alimentarius as "the qualitative and/or quantitative evaluation of the likely intake of chemical agents via food as well as exposure from other sources, if relevant". Exposure is basically a function of the amount of consumed food and the concentration of the chemical (e.g. pesticide residue concentration) and can be expressed by the following equation:

$$\text{Dietary exposure} = \frac{\Sigma\ (\text{residue concentration} \times \text{food consumption})}{\text{Body weight}}$$

In the chronic (long-term) risk assessment, the estimated dietary exposure is compared to the relevant toxicological reference values, i.e. the acceptable daily intake (ADI) which was derived after a full hazard characterization of the compound. The consumer is considered to be adequately protected if the estimated dietary intake of a pesticide residue does not exceed the ADI.

The estimation of the exposure to pesticide residues in the Egyptian population was performed, using recent residue data generated by the monitoring program (2010) and food consumption data obtained from GEMS food consumption (cluster, 2012) data, C, in kg/day/ body weight, based on a 60 kg person (WHO, 1997). The calculated Theoretical Acceptable Daily Intake TADI's were compared with the acceptable daily intake for the compounds, ADI (Codex, 2010), and expressed as % ADI.

% ADI = (TMDI / ADI) X 100

Tables 6, 7, 8, 9, and 10 showed the pesticides, which were the most frequently detected in the samples, were chosen for the dietary intake assessment; the chronic risk assessment is performed for all commodities. The average pesticides residue levels were calculated by using residue data from the monitoring data. The results of the TMDI calculation are reported separately for each pesticide in an exposure assessment. If the ADI was not exceeded in any commodity, a chronic consumer risk can be excluded.

Table 6: Estimated dietary intake for chronic risk for most frequently pesticides, which were detected in the Green Coriander 2013.

The detected pesticide	Mean mg/kg	food consumption g/day	EADI mg/kg/day	EADI mg/kg.bw /day	ADI mg/kg bw	as a % of ADI
Atrazine	0.133	9.71	0.001291	0.0000215102	0.02	0.1076%
Boscalid	0.04	9.71	0.000389	0.0000064762	0.04	0.0162%
Chlorpyrifos	0.031	9.71	0.000301	0.0000050146	0.01	0.0501%
Cypermethrin	0.106	9.71	0.001027	0.0000171157	0.02	0.0856%
Lambda-Cyhalothrin	0.054	9.71	0.000522	0.0000087024	0.02	0.0435%
Malathion	0.029	9.71	0.000280	0.0000046703	0.3	0.0016%
Penconazole	0.14	9.71	0.001360	0.0000226667	0.03	0.0756%
Pendimethalin	0.044	9.71	0.000423	0.0000070429	0.125	0.0056%
Piperonyl butoxide	0.043	9.71	0.000413	0.0000068810	0.2	0.0034%
Profenofos	0.654	9.71	0.006356	0.0001059322	0.03	0.3531%

Note: Body weight 60Kg

As shown by the results in table (7), the intake of pesticide residues does not exceed the ADI in any case. The estimated exposure ranges from 0.0016% of the ADI for the Malathion to 0.3531% of the ADI for the Profenofos.

Table 7: Estimated dietary intake for chronic risk for most frequently pesticides, which were detected in the Green Dill 2013.

The detected pesticide	Mean mg/kg	food consumption g/day	EADI mg/kg/day	EADI mg/kg.bw /day	ADI mg/kg bw	as a % of ADI
Atrazine	0.012	9.71	0.000118	0.0000019660	0.02	0.0098%
Biphenyl	0.008	9.71	0.000079	0.0000013155	0.125	0.0011%
Boscalid	0.013	9.71	0.000121	0.0000020238	0.04	0.0051%
Carbendazim	0.181	9.71	0.001758	0.0000293048	0.03	0.0977%
Chlorpyrifos	0.531	9.71	0.005162	0.0000860330	0.01	0.8603%
Chlorpyrifos-methyl	0.058	9.71	0.000562	0.0000093674	0.01	0.0937%
Cypermethrin	0.099	9.71	0.000962	0.0000160286	0.02	0.0801%
Diazinon	0.007	9.71	0.000065	0.0000010794	0.005	0.0216%
Iprodione	0.333	9.71	0.003233	0.0000538913	0.06	0.0898%
Lambda-Cyhalothrin	0.175	9.71	0.001696	0.0000282711	0.02	0.1414%
Malathion	0.089	9.71	0.000862	0.0000143691	0.3	0.0048%
Penconazole	0.420	9.71	0.004076	0.0000679265	0.03	0.2264%
Pendimethalin	0.039	9.71	0.000383	0.0000063910	0.125	0.0051%
Piperonyl butoxide	0.115	9.71	0.001117	0.0000186191	0.2	0.0093%
Profenofos	2.663	9.71	0.025869	0.0004311533	0.03	1.4372%

As shown by the results in table (8), the intake of pesticide residues does not exceed the ADI in any case. The estimated exposure ranges from 0.0011% of the ADI for the Biphenyl to 1.4372% of the ADI for the Profenofos.

Table 8: Estimated dietary intake for chronic risk for most frequently pesticides, which were detected in the Green Parsley 2013.

The detected pesticide	Mean mg/kg	food consumption g/day	EADI mg/kg/day	EADI mg/kg.bw /day	ADI mg/kg bw	as a % of ADI
Atrazine	0.015	9.71	0.000142	0.0000023611	0.02	0.0118%
Biphenyl	0.016	9.71	0.000155	0.0000025905	0.125	0.0021%
Boscalid	0.014	9.71	0.000136	0.0000022667	0.04	0.0057%
Chlorpyrifos	0.864	9.71	0.008391	0.0001398455	0.01	1.3985%
Diazinon	0.006	9.71	0.000058	0.0000009714	0.005	0.0194%
Malathion	0.033	9.71	0.000324	0.0000053968	0.3	0.0018%
Penconazole	0.301	9.71	0.002922	0.0000487064	0.03	0.1624%
Piperonyl butoxide	0.023	9.71	0.000223	0.0000037238	0.2	0.0019%
Profenofos	0.783	9.71	0.007608	0.0001268011	0.03	0.4227%

As shown by the results in table (9), the intake of pesticide residues does not exceed the ADI in any case. The estimated exposure ranges from 0.0018% of the ADI for the Malathion to 1.3985% of the ADI for the Chlorpyrifos.

Table 9: Estimated dietary intake for chronic risk for most frequently pesticides, which were detected in the Spinach 2013.

The detected pesticide	Mean mg/kg	food consumption g/day	EADI mg/kg/day	EADI mg/kg.bw /day	ADI mg/kg bw	as a % of ADI
Carbendazim	0.01	9.71	0.000097	0.0000016191	0.03	0.0054%
Chlorpyrifos	0.236	9.71	0.002293	0.0000382096	0.01	0.3821%
Cypermethrin	0.083	9.71	0.000810	0.0000134921	0.02	0.0675%
Emamectin	0.015	9.71	0.000146	0.0000024286	0.0005	0.4857%
Lambda-Cyhalothrin	0.055	9.71	0.000534	0.0000089048	0.02	0.0445%
Methomyl	0.068	9.71	0.000656	0.0000109286	0.02	0.0546%

As shown by the results in table (10), the intake of pesticide residues does not exceed the ADI in any case. The estimated exposure ranges from 0.0054% of the ADI for the Carbendazim to 0.4857% of the ADI for the Emamectin.

As shown by the results in table (10), the intake of pesticide residues does not exceed the ADI in any case. The estimated exposure ranges from 0.0011% of the ADI for the Pendimethalin to 0.6804% of the ADI for the Profenofos.

It is clear from the previous data of risk assessment of pesticide residues in studied leafy vegetables (green coriander, green dill, green parsley, spinach and water cress) that no risk will be found from consuming these types of leafy vegetables. These results are in compatable with **Gad Alla *et al.,* (2015).**

Pesticides can have a cumulative "toxic loading" effect both in the immediate and long term, and each person accumulates and responds to chemicals in a way that is biochemically and biographically unique. From birth, we build up a chemical "body burden" that reflects a combination of childhood and workplace exposures, pesticide residues on food, chemicals in home and personal care products and the quality of air and water in our communities.

The process of dietary pesticide risk assessment has been presented and three major components of the process estimation of pesticide residue levels, estimation of food consumption patterns, and characterization of risk based on a comparison of exposure estimates with toxicological criteria have been identified. Each component of the process is subjected to considerable uncertainty that may compromise the accuracy of the final risk assessment. In estimating pesticide residue levels, common practices range from highly theoretical models assuming that all residues are present at a predetermined level (typically at the tolerance level) to the use of market basket survey data obtained at the time the food is ready for consumption.

Table 10: Estimated dietary intake for chronic risk for most frequently pesticides, which were detected in the Water Cress 2013.

The detected pesticide	Mean mg/kg	food consumption g/day	EADI mg/kg/day	EADI mg/kg.bw /day	ADI mg/kg bw	as a % of ADI
Atrazine	0.013	9.71	0.000130	0.0000021587	0.02	0.0108%
Carbendazim	0.014	9.71	0.000134	0.0000022262	0.03	0.0074%
Chlorpyrifos	0.195	9.71	0.001894	0.0000315715	0.01	0.3157%
Cypermethrin	0.251	9.71	0.002438	0.0000406382	0.02	0.2032%
Lambda-Cyhalothrin	0.244	9.71	0.002372	0.0000395318	0.02	0.1977%
Omethoate	0.045	9.71	0.000437	0.0000072857	0.002	0.3643%
Pendimethalin	0.009	9.71	0.000085	0.0000014167	0.125	0.0011%
Profenofos	1.261	9.71	0.012247	0.0002041161	0.03	0.6804%

Risk of adverse health effects is a function of pesticide toxicity and exposure. Exposure to a pesticide determines the dose and the pesticide's toxicity determines the potency of the dose. For pesticides that do not cause cancer, there is a dose below which there will be no effect. For pesticides that do not cause cancer, a no effect threshold has been determined for each pesticide, which is inversely related to its potency.

For pesticides that may cause cancer the probability that exposure will result in cancer is related to dose, the greater of exposure the greater of cancer probability. In each case risk is directly related to exposure, as exposure determines dose. If exposure is low enough the risk of adverse health effects is nil.

The Egyptian Organizations of Standardization should sets and revise the Egyptian maximum residue levels according risk exposure data and Egyptian food habit consumption, what it calls an "approved usage" level of a pesticide - essentially a safety limit on how much can make its way into the food chain. However, the approved usage level is set down for adults, potentially putting children at risk.

Currently, there is very limited data on Egyptian dietary pesticide exposure levels, and no data on the relative health risks and benefits of consuming organically- versus conventionally-grown food. Available data suggest that organic food contains fewer synthetic pesticide residues than conventional food, and eating an organic diet can result in lower exposures to some pesticides. However, given the current weight-of-evidence, it cannot be concluded based on its potential for reduction of exposure to pesticides that an organic diet provides greater health benefits than a conventional diet, although organically-grown food may provide other perceived benefits to consumers.

Egypt really need more research to quantify Egyptian dietary risk exposure data and other sources of pesticide exposures among different segments of the Egyptian population, also potential health effects from low-level dietary pesticide exposures, and the relative risks and benefits of an organic versus conventional diet. In particular, there remain significant gaps in scientific knowledge with respect to differences in pesticide residue (synthetic and natural), microbial pathogen, mycotoxin, and natural toxin levels in organically-grown versus conventionally-grown food.

Conclusion:

From the calculated data of risk exposure according to monitoring of pesticide residues in Egyptian leafy vegetables all the contaminated samples including that exceeded MRL was about 2%

of the Acceptable Daily Intake (ADI) which insure that no risk will be found from consuming these types of leafy vegetables.

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