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Risk Assessment of Some Pesticide Residues in Freshly Home Food for Infants

Lamia M. Ryad, Maher El-Hashash, Ali A. Mahmoud and Hoda M. Alshimi

Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Center, Ministry of Agriculture, Dokki, Egypt.

ABSTRACT

Ready-to-eat baby foods should be free of pesticide residues according to the extremely low Maximum Residue Limits 0.01 mg/kg (MRLs) established by the European Community (2006). In the present work, a liquid chromatography tandem mass spectrometry (LC–MS/MS) and GC-MS/MS has been developed for the multiresidue of 420 pesticides in fruit and vegetables-based baby foods. The developed method is based on a simple sample treatment (QuEChERS), which consists of a liquid–liquid extraction using acetonitrile, followed by a clean-up step based on dispersive solid-phase extraction with primary secondary amine (PSA). Matrix effects were evaluated in LC–MS/MS mode experiments, obtaining a reduction of these effects when working in MS/MS mode for most of the analytes. Finally, the proposed method was applied to 73 fruits and vegetables based baby food samples obtained from local markets, 44% of samples were completely free from any pesticides. While the others 56% contained detectable residues and 34% (25 samples) had residues above the permissible limits. The most commonly detected pesticides were chloropyrifos then malathion and profenofos. The exposure to pesticide residues was calculated on a total of 16 residues. The estimated pesticides mean daily intake through the consumption of this kind of food has been calculated taking into account body weight and food consumption data for children aged 6–12 months. In order to assess the health risk derived from the exposure to these pollutants in children during the first year of life.

Key words: Pesticide Residues, Baby Food, LC-MSMS, Acceptable Daily Intake, Risk Assessment.

Introduction

Pesticides have played a very important role in the development of the agriculture and still irreplaceable until the present time (Kolberg *et al.,* 2011). In fact, pesticides present in fruits and vegetables may be transferred to the final product in any processing stage and this may constitute a risk for infant health. In this sense, post-harvest fungicides have to be specially controlled, due to its application after the harvesting stage (Lopez *et al.,* 2012).In recent years, regulatory agencies have emphasized more and more the need for the development and use of analytical methods able to determine, in food products, as many residues as possible from the many insecticides, fungicides and other compounds applied in agricultural practice (Sandra *et al.,* 2003).The choice of the mass analyser is determined not only by the required sensitivity and selectivity of the target analysis, but also by its affordability. Not all the food control laboratories worldwide may have access to state of the art LC–MS instrumentation (Lopez *et al.,* 2012).

MRLs in baby food are becoming more and more stringent and ultra-trace level analysis (mg/kg and sub-mg/kg) is required. Baby food is a more complex matrix because, besides vegetables or fruits, small quantities of fat are also present (Sandra *et al.,* 2003).

Ready-to-eat baby foods should be free of pesticide residues, according to the extremely low Maximum Residue Limits (MRLs) established by the European Community (2006) (Georgakopoulos *et al.,* 2011).

The more stringent regulations (Maximum Residue Levels (MRLs) established for pesticides in food are those applied in food intended for infant consumption. Children and infants represent a vulnerable risk group of the population in terms of pesticide toxicity and stringent regulations have been set to protect them from dietary exposure to these chemicals. The European Commission (EC) and on infant food, specified the general MRL of 10 µg kg-1 for any individual pesticide residue in baby food. Therefore, sensitive and reliable confirmatory methods are required to monitor pesticide residues in infant foods (Lopez *et al.,* 2012).

The results shown that the sensitivity obtained is appropriate for multi-residue analysis of pesticide residues in baby food samples at concentrations in the low µg kg-1 range, in compliance with the stringent 10 µg kg1 EU standard of the baby food directive (Lopez *et al.,* 2012).The method was given an acronymic name QuEChERS that reflected its major advantages (quick, easy, cheap, effective, rugged and safe). Sample preparation is always the major in the complete analytical procedure for the determination of pesticide residues

Corresponding Author: Lamia M. Ryad, Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Center, Ministry of Agriculture, Dokki, Egypt
E-mail: lamia.ryad@gmail.com

in food products (Kolberg *et al.,* 2011). It is also notable that these meals present the major risk of consuming large quantities of organophosphorus pesticide residues (OPs), such as chlorpyrifos and dimethoate, between the ages of 6 months to 1 year old; thus, the monitoring of pesticide residues in such high risk matrices should be accurate and reliable (Georgakopoulos *et al.,* 2011).

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) 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. The ADI is the estimate amount of a chemical in food (mg/kg body weight/day) that can be ingested daily over a life time without appreciable health risk to the consumer (FAO, 2002)

The higher the ADI, the "safer" a compound is for regular ingestion. The ADI concept can be understood as a measure to indicate the toxicity from long-term exposure to repeated ingestion of chemical compounds in foods (present and/or added), as opposed to acute toxicity (WHO, 1997) and also help in deciding pesticides strategy in the country.

Sampling

In this study 73 fresh samples (14 G. beans, 12 Squash, 9 Carrot, 7 Potato, 2 Sweet Potato, 8 Guava, 10 Orange and 11 Banana) were collected from five Governorates (Cairo, Giza, Qualubiya, Ismailia and Fayium), and analyzed for detecting pesticide residues using LCMS-MS.

From one or two kilograms of each sample were collected and prepared for residue analysis according to Codex Alimentarious Comission, CAC (1993). Samples analysis were carried out either immediately upon their arrival to the laboratory or the samples were stored at 0-5ºC for no longer 2 days before analysis.

Material and methods

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.

LC Mobile Phase Stock Solution (50mM ammonium formate solution in methanol-water (1:9): add 1.73ml formic acid to 900ml water, adjust the pH to about 3.78±0.02 with ammonia solution and then add 100 ml methanol.

HPLC analysis

HPLC analyses were performed on a C18 reversed-phase column (100mm × 2.1mm, 4_m from Jones Chromatography) and were operated at room temperature. The LC Mobile phase was composed of (5 mM ammonium formate solution in methanol/buffer (1:9): dilute 50 ml of stock buffer with 450 ml methanol/buffer (1:9), the PH should be 2.78 ± 0.1, adjust if necessary, stable for one week in refrigerator.

(b) GC-MS/MS: Agilent Gas Chromatography 7980A equipped with tandom 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 (1ml/min). Injector temperature was 250ºC, transfer line temperature was 285ºC, ion source temperature was 280ºC and Quadrapole temperature was 150ºC. The GC oven temperature was programmed to initially held at 70ºC for 2 min then increased to 150ºC at 25ºC/min (held for 0 min), and raised to 200ºC at the rate of 3ºC/min (held for 0 min), then went up from 200 to 280ºC at 8ºC/min (held for 10 min). This resulted in a total run time of 42 min and complete separation of all the analytes.

Reagents

De-ionized water was Generated by Millipore water-purification system, acetonitrile, 99.9% was obtained from HPLC grade (LabScan) or similar quality. Methanol 99.9% was obtained from HPLC grade (Merck) or similar quality. Formic acid 98-100% was obtained from (Riedel–de Haen). Ammonia solution, 33% was obtained from Riedel–de Haen. Tetradecane, 99% was obtained from HPLC grade (Aldrich). Ethyl acetate, 99.8 % was obtained from Lab Scan or similar quality, n-hexane, 97% was obtained from Sigma Aldrich or similar quality and anhydrous magnesium sulphate fine powder and magnesium sulphate grit were obtained from (Fluka). Sodium chloride and sodium hydroxide 99% were obtained from Reidel de Haen. Disodium Hydrogencitrate Sesquihydrate and trisodium citrate dehydrate were obtained Fluka, Florisil, 60-100 mesh, pesticide residue analysis grade was obtained from (Fluka), and silica gel 60 was obtained from (Fluka) also.

Method of Analysis:

The employed QuEChERS procedure comprised the following steps: a representative 10g portion of previously homogenised sample was weighed in a 50 mL PTFE centrifuge tube. Then 10 mL of acetonitrile was added and the tube was vigorously shaken for 1 minute. After this time, 4.0 g anhydrous magnesium sulphate grit, 1g sodium chloride, 0.5g disodium citrate and 1g trisodium citrate were added and was shaked for five minutes vigorously.

The extract was then centrifuged (3000 rpm) for 5 min. 2 mL of the supernatant (acetonitrile phase) was then taken with a pipette, transferred into 50 ml glass flask and the solvent was evaporated using rotary evaporator at 40°C. The residue was dissolved in 2 ml of injection standard and then was injected into 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 multi-residue method. The average percentage recoveries for the tested pesticides from different commodities ranged from 70- 120. The reproducibility expressed as relative standard deviation was less than 20%. The limit of quantification started at 0.01 mg/kg. The measurement uncertainty expressed as expanded uncertainty and in term 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.

Estimated daily intake (EDI) calculation:

From a potential health perpective, 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) in the food consumption rate (kg/d) 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 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 intake (EDIs)) of the pesticide residues 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 the equation, HRI = EDI/ADI, (EFSA 2013).

Results and Discussion

The monitoring program for pesticide residues should be established routinely to provide a check on compliance with Good Agriculture Practice (GAP) on the use of pesticides.
Pesticide residues in food and the environment are monitored regularly in developed countries. In Egypt, monitoring of pesticide residues in food and in environment began as limited program in 1985, 1999, 2001, 2002 and 2004 (Dogheim *et al*., 1988, 1996, 1999, 2001, 2002).
Our study done within the national residues monitoring program started in the Ministry of Agriculture of Egypt during 2013-2014.

Monitoring of pesticide residues in vegetables and fruits estimated the potential health risks associated with the exposure to violated pesticides:

In this study 73 of fresh vegetable and fruit samples were analyzed, 14 green beans, 12 squash, 9 carrot, 7 potato, 2 sweet potato, 8 guava, 10 orange and 11 banana. 44% of samples were completely free from any pesticides. In the contaminated samples chloropyrifos was the most pesticide appeared then malathion and profenofos.

On the other side, Mansour *et al.* (2009 – a), who analyzed 144 kg of potato samples representing two different types of farming production, conventional and organic farming, found that in both types organochlorine pesticides OCPs (e.g., HCB, lindane, heptachlor and DDT metabolites) as well as organophosphorous pesticides OPPs (methamidophos, thiometon, chloropyrifos- methyl, pirimiphos-methyl and profenofos) were frequently found at concentrations exceeding the MRLs for most of them. As comparison with previous studies, our results are in contrast with those reported by Dogheim *et al.* (2001) in which the author found only one pesticide residue chlorothalonil in 36 banana samples and the percentage of

contaminated samples was 2.8% without any violated samples. Another study, in Brazil was conducted by Jardim and Caldas, (2012) revealed that out of 122 potato samples analyzed for the presence of 92 pesticide, 25.9% of potato samples were contaminated with pesticide residues.

Each table showed the number of analyzed samples of each commodity, the detected pesticide, the rang of detected pesticides, minimum, maximum and mean in mg/kg and the maximum residue limits MRL's for each detected pesticide residues/commodity combination, violation of each pesticides, and number of violated samples.

Fourteen green bean samples were analyzed, all samples were contaminated but only 57% exceeded the MRL as shown in Table (1). Acetaimirid, ethion and azoxystrobin not exceeded the MRLs and the most violated were carbendazim, primicarb, profenofos, dimethoate and omethoate while the malathion violated in two samples only. Our results are in agreement with those obtained by Dogheim *et al*. (2001) who examined 161 green beans samples, which was found 53 pesticides and reported that the percentage of contamination and violation were 25.5 and 2.48%, respectively. Similarly, Dogheim *et al*. (2002) analyzed 54 pesticides in 161 green bean samples and found that the percentage of contamination and violation was 21.4 and 2.1%, respectively.

Table 1: Monitoring of pesticide residues in green beans.

Analyzing samples n=(14)		Detected pesticides	Pesticides level		Mean mg/kg	Frequency.	MRL mg/kg	No. of violated. compound		No. of violated. samples	
Contaminated	%		Min. mg/kg	Max. mg/kg				No.	%	No.	%
14	100	Acetampirid	0.005	0.01	0.007	3	0.01	0	0	8	57
		Carbendazim	0.02	0.28	0.114	4	0.01	4	100		
		Chloropyrifos	< LOQ	0.05	0.126	7	0.01	4	57		
		Malathion	< LOQ	0.07	0.023	10	0.01	2	20		
		Primicarb	0.03	0.05	0.040	2	0.01	2	100		
		Profenofos	0.02	0.09	0.043	4	0.01	4	100		
		Ethion	0.003	0.004	0.004	2	0.01	0	0		
		Azoxystrobin	0.005	0.01	0.008	2	0.01	0	0		
		Dimethoate	0.041	0.041	0.041	1	0.01	1	100		
		Omethoate	0.03	0.03	0.030	1	0.01	1	100		

The limit of quantitation (LOQ) was mg/kg. MRLs: Maximum Residue Limits According to European Union MRLs (EU-MRLs).

Twelve squash samples were analyzed, eight of samples (67%) were free from any pesticide residues. 33% of squash samples contaminated with pesticide residues, and 17% of total samples exceeded the MRL as shown in table (2). Propamocarb exceeded the MRL with mean 0.063 mg/kg, while only one sample violated with chlorpyrifos with mean 0.015 mg/kg, but no violation with carbendazim, thiophanate me, profenofos and acetampirid was found.

This mean that the levels of pesticide residues found in the present study were higher than those observed by Dogheim *et al*. (2001) who analyzed 56 squash samples for the presence of 53 pesticides and detected only dimethoate and vinclozolin residues, and the percentage of contamination was 5.4% without any violated samples. At the same trend Dogheim *et al*. (2002) analyzed 104 squash samples for the presence of 54 pesticides, and detected only dicofol and dimethoate residues and the percentage of contamination was 2.9% without any violated samples. Also, the occurrence of pesticide residues in squash samples from other countries has been reported by Osman *et al.* (2001) who collected 20 squash samples from Al-Qassim region, Saudi Arabia and found that 11 samples were contaminated with pesticide residues, and 7 samples were exceeded MRLs.

Table 2: Monitoring of pesticide residues in squash.

Analyzing samples n=(12)		Detected pesticides	Pesticides level		Mean mg/kg	Frequency	MRL mg/kg	No. of violation compound		No. of violated samples	
Contaminated	%		Min. mg/kg	Max. mg/kg				No.	%	No.	%
4	33	Chloropyrifos	0.01	0.02	0.015	2	0.01	1	50	2	17
		Carbendazim	0.004	0.004	0.004	1	0.01	0	0		
		Thiophenate-Me	0.012	0.012	0.012	1	0.01	0	0		
		Propamocarb	0.015	0.111	0.063	2	0.01	2	100		
		Profenofos	0.009	0.009	0.009	1	0.01	0	0		
		Acetamirid	0.004	0.004	0.004	1	0.01	0	0		

The limit of quantitation (LOQ) was mg/kg. MRLs: Maximum Residue Limits According to European Union MRLs (EU MRLs).

Nine carrot samples were analyzed, five samples (56%) were free from any pesticide residues. 44% of carrot samples contained pesticide residues, and 11% of total samples exceeded the MRL as shown in Table (3).

Omethoate exceeded the MRL with mean 0.04 mg/kg, while no violation residues with chlorpyrifos, profenofos and buprimate was observed.

Table 3: Monitoring of pesticide residues in carrot:

Analyzed samples n=(9)		Detected pesticides	Pesticides level		Mean mg/kg	Frequency	MRL mg/kg	No. of viationl. compound		No. of viol. samples	
Contaminated	%		Min. mg/kg	Max. mg/kg				No.	%	No.	%
4	44	Chloropyrifos	0.01	0.01	0.010	1	0.01			1	11
		Omethoate	0.04	0.04	0.040	1	0.04	1	100		
		Profenofos	< LOQ	< LOQ	< LOQ	2	< LOQ				
		Buprimate	< LOQ	< LOQ	< LOQ	1	< LOQ				

The limit of quantitation (LOQ) was mg/kg. MRLs: Maximum Residue Limits According to European Union MRLs (EU MRLs).

Eight guava samples were analyzed, four samples (50%) were free from any pesticide residues. 50% of guava samples contained pesticide residues, 50% of total samples exceeded the MRL as shown in Table (4). Chloropyrifos was the most pesticides appeared and also two samples exceeded the MRL with mean 0.072 mg/kg then two samples were contaminated with omethoate only one sample violated with mean 0.018 mg/kg, while two samples were contaminated with profenofos and L-cyhalothrin but only one sample was violated with mean 0.019 mg/kg and 0.02 mg/kg respectively, only one sample was contaminated with carbendazim and methomyl, carbendazim sample without violation but methomyl sample was violated with mean 0.07 mg/kg.

Table 4: Monitoring of pesticide residues in guava:

Analyzed samples n=(8)		Detected pesticides	Pesticides level		Mean mg/kg	Frequency	MRL mg/kg	No. of violation compound		No. of violation. samples	
Contaminated	%		Min. mg/kg	Max. mg/kg				No.	%	No.	%
4	50	Chloropyrifos	< LOQ	0.083	0.072	4	0.01	2	50	4	50
		Omethoate	0.012	0.023	0.018	2	0.01	1	50		
		Profenofos	0.01	0.028	0.019	2	0.01	1	50		
		Carbendazim	0.01	0.01	0.010	1	0.01	0	0		
		Methomyl	0.07	0.07	0.070	1	0.01	1	100		
		L cyhalothrin	0.01	0.03	0.020	2	0.01	1	50		

The limit of quantitation (LOQ) was mg/kg MRLs: Maximum Residue Limits According to European Union MRLs (EU MRLs).

Ten samples of orange were analyzed; all were contaminated and also exceeded the MRL as shown in Table (5). Chloropyrifos, dimethoate and omethoate were the most pesticides appeared and also exceeded the MRL with mean 0.048, 0.392, 0.193 mg/kg with frequencies six for first and second and five for third, then only one sample was contaminated and violated with malathion, while one sample was contaminated with diazinon, imazilil, l-cyhalothrin, and primicarb without violation.

Table 5: Monitoring of pesticide residues in orange

Analyzed samples n=(10)		Detected pesticides	Pesticides level		Mean mg/kg	Frequency	MRL mg/kg	No. of violation compound		No. of viol. samples	
Contaminated	%		Min. mg/kg	Max. mg/kg				No.	%	No.	%
10	100	Chloropyrifos	0.004	0.174	0.048	6	0.01	3	50	10	100
		Dimethoate	0.03	0.65	0.392	6	0.01	5	83		
		Omethoate	0.01	1.176	0.193	5	0.01	5	100		
		Malathion	0.057	0.057	0.057	1	0.01	1	100		
		Diazinon	0.011	0.011	0.011	1	0.01	0	0		
		Imazilil	0.01	0.01	0.010	1	0.01	0	0		
		L cyhalothrin	< LOQ	< LOQ	< LOQ	1	0.01	0	0		
		Primicarb	0.01	0.01	0.010	1	0.01	0	0		

The limit of quantitation (LOQ) was mg/kg. MRLs: Maximum Residue Limits According to European Union MRLs (EU MRLs).

The current study indicated that the number of applied pesticides as well as the rates of contaminated and violated orange samples, were increased. Authors in other countries also reported pesticide residues in orange sample. Berrada *et al.* (2010) detected only methidathion in 36 orange samples collected from Valencia, Spain. However, chloropyrifos, imazalil, thiabendazole, diazinon and methidathion were found in orange samples collected from Croatian local markets, imazalil showed the highest concentration level among the detected pesticides Knezevic *et al*. (2012) and Jardim and Caldas (2012) detected pesticide residues in 28.5% of analyzed orange samples contained non-authorized active ingredients or residues above MRLs.

The most frequently detected pesticide was chlorpyrifos which found in twenty one samples, ten samples were violated, then eleven samples were contaminated with malathion, only two samples were violated, nine

samples were contaminated with profenofos, five samples were violated, nine samples were contaminated with omethoate all were violated except one sample, seven samples contaminated with dimethoate all samples were violated except one, six samples were contaminated with carbendazim, while four samples were violated, four samples were contaminated with acetampirid with no violation, three samples were contaminated with pirimicarb while two samples were violated, two samples were contaminated with ethion and azoxystorbin without violation, but two samples were contaminated with propamocarb hydrochloride and all were violated, in contrast one sample was contaminated with bupirimate, thiophanate methyl and imazilil without violation, and also one sample contaminated with methomyl, l-cyhalothrin, and diazinon but all were violated. Ten samples of orange were exceeded MRL values followed by eight samples of green beans). In contrast, no violated pesticides were found in sweet potato, potato and banana in samples. On the whole, green beans and orange were the crops with highest percentage of positive samples (all samples were contaminated), followed by guava, carrot and squash were 50%, 44%, 33% contaminated respectively from each commodities. The residual levels differed in between the collected commodities and depended mostly on the time of harvest, size of commodities, and mode of pesticides application.

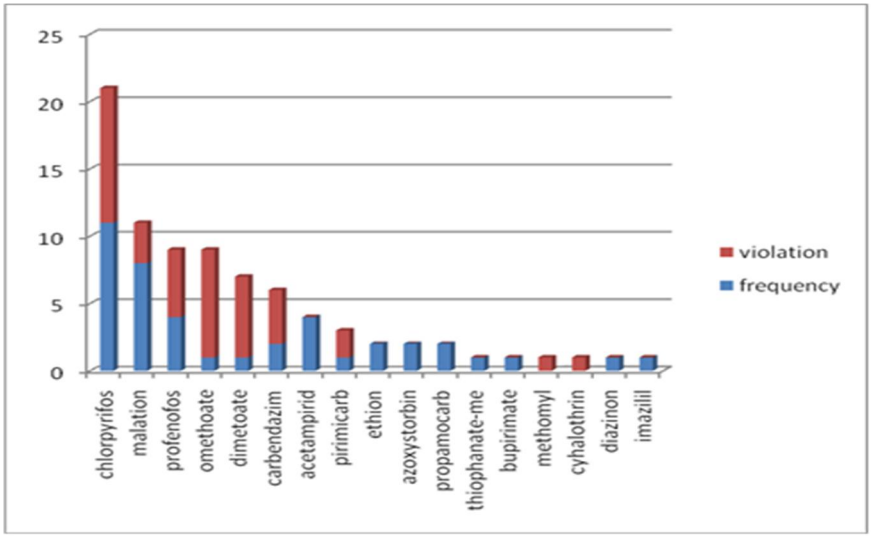

Fig. 1: Shows the most frequently and violated pesticide residues

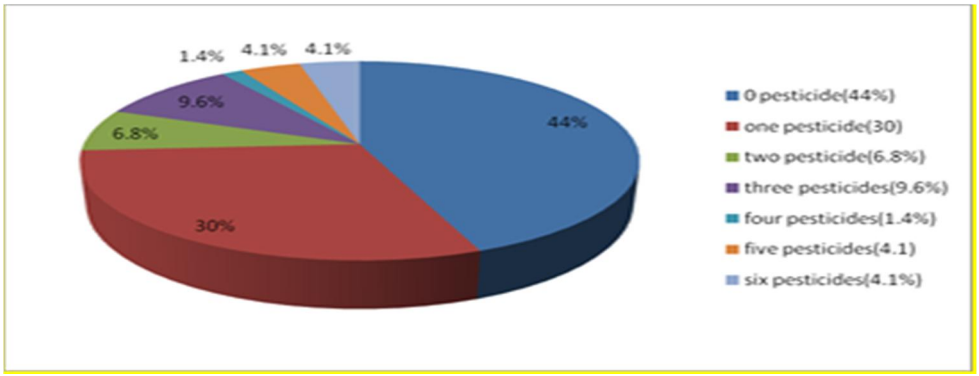

Fig. 2: Distribution (in term of percentage) of the analyzed samples according to the number of target compounds found.

The results showed also that thirty two samples were free from any pesticide (44%) , twenty two contaminated with one pesticide (30%), while five samples contaminated with two pesticides (6.8%), seven samples contaminated with three pesticides (9.6%), one samples contaminated with four pesticides (1.4%), and three samples contaminated with five and six pesticides (4.1%) as shown in figure (2).

The highest numbers of pesticide residues were found in four samples of green beans two of them have six pesticides and another two have five pesticides. Most of samples (33 samples) of positive samples contained organphosphorus (45%). The pesticides included in this analytical scope prioritized in relation to their high frequency of application, high toxicity and detection in previous monitoring programs. Moreover, most of the pesticides identified as those that are commonly in use were included.

Estimated daily intake: (EDI)

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 this equation:

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

The health risk indices were obtained by dividing the EDI by their corresponding values of ADI (FAO/WHO, 2010); assuming average baby's body weight. 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).

Then HRI of the residues was computed using the equation,

HRI = EDI/ADI, EFSA (2013).

The mean body weight for baby from six months to one year is 8.6 kg calculated according to Nabil (2012).

Table 6: Consumption rate of analyzed commodities in g/day based on GEMS/food total diet food balance sheet and Egyptian food balance sheet in g/person/day.

Type	Consumption g/day
Green beans	4.1
Squash	11.4
Carrot	8.1
Guava	22.8
Orange	38

Table (7) showed the estimated average daily intake (EDI) and the hazard index (HI) for each pesticide residues (the ratio of EDI to ADI) in green beans. None of individual HI of pesticides detected in green bean samples exceeded one indicates no risk associated with consumption of green beans.

Table 7: Estimated daily intake of violated pesticides on green beans:

Pesticides	Mean Conc. (mg/kg)	EDI (mg/kg body weight)	ADI (mg/kg)	Hazard Index (EDI as a % of ADI)
Acetampirid	0.017	0.000008	0.07	0.0001
Carbendazim	0.246	0.000117	0.03	0.004
Chloropyrifos	0.126	0.00006	0.01	0.006
Malathion	0.107	0.000051	0.3	0.0002
Primicarb	0.055	0.0000262	0.035	0.00075
Profenofos	0.148	0.00007	0.03	0.0024
Ethion	0.006	0.0000029	0.002	0.000
Azoxystrobin	0.010	0.0000048	0.2	0.0000
Dimethoate	0.041	0.0000195	0.002	0.0098
Omethoate	0.030	0.000014	0.0003	0.047

Food consumption 4.1 g/person/day; Body Weight 8.6 kg

Risk assessment of daily intake of pesticides by Squash based on pesticide residue data and a daily Squash consumption for baby of 8.6 kg for average weight for baby from 6-12 months the (HI) values of all pesticides did not exceeded the value of 1 and results indicate that there is a negligible risk associated with the exposure via the consumption (11.4 g/person/day) of selected agricultural products as calculated and presented in Table (8).

Table 8: Estimated daily intake of violated pesticides on Squash.

Pesticides	Mean Conc. (mg/kg)	EDI(mg/kg body weight)	ADI (mg/kg)	Hazard Index (EDI as a % of ADI)
Chloropyrifos	0.025	0.000033	0.01	0.003
Carbendazim	0.004	0.000005	0.03	0.000
Thiophenate-Me	0.012	0.000016	0.08	0.000
Propamocarb	0.119	0.000157	0.4	0.000
Profenofos	0.009	0.000012	0.03	0.000
Acetamirid	0.004	0.000005	0.07	0.0000

Food consumption 11.4 g/person/day; Body Weight 8.6 kg

Table (9) showed the estimated average daily intake (EDI) and the hazard index (HI) for each pesticide residues (the ratio of EDI to ADI) in carrot. None of individual HI of pesticides detected in carrot samples exceeded one indicates no risk associated with consumption of carrot.

Table 9: Estimated daily intake of violated pesticides on Carrot:

Pesticides	Mean Conc. (mg/kg)	EDI (mg/kg body weight)	ADI (mg/kg)	Hazard Index (EDI as a % of ADI)
Chloropyrifos	0.010	0.000009	0.01	0.0009
Omethoate	0.040	0.000038	0.0003	0.13

Food consumption 8.1 g/person/day; Body Weight average for infant 8.6 kg

Table (10) showed the estimated average daily intake (EDI) and the hazard index (HI) for each pesticide residues (the ratio of EDI to ADI) in guava. None of individual HI of pesticides detected in carrot samples exceeded one indicates no risk associated with consumption of guava.

Table 10: Estimated daily intake of violated pesticides on Guava:

Pesticides	Mean Conc. (mg/kg)	EDI (mg/kg body eight)	ADI (mg/kg)	Hazard Index (EDI as a % of ADI)
Chloropyrifos	0.113	0.0002995	0.01	0.03
Omethoate	0.029	0.00007688	0.0003	0.256
Profenofos	0.033	0.000087	0.03	0.0003
Carbendazim	0.010	0.000027	0.03	0.0009
Methomyl	0.070	0.00019	0.02	0.009
L cyhalothrin	0.035	0.00009	0.005	0.019

Food consumption for 22.8 g/person/day; Body Weight 8.6 kg

Risk assessment of daily intake of pesticides based on pesticides residue data and a daily consumption for baby of 8.6 kg (6-12 months) in orange samples showed that the highest EDI of omethoate followed by Dimethoate The (HI) values of Omethoate and Dimethoate were exceeded the value of 1 and it was 13.9 and 5.1 respectively and the results indicate that there was risk associated with the exposure via the consumption of selected agricultural products (38 g/person/day) in contrast as the (HI) values of Primicarb, Malathion and L-cyhalothrin did not exceeded the value of 1and the results indicate that there was a negligible risk associated with the exposure via the consumption of selected agricultural products as calculated and presented in Table(11). Multiple residues are expected on crops because various classes of pesticides must be alternated to prevent resistance developing in the pests. The presence of pesticide residues in the marketed fresh commodities may be attributed to the excessive use of pesticides on commodities either they were registered or not, besides, disregard of recommended pre-harvest interval (PHI). In addition applied rates often exceed manufacturer's recommendations in the belief that more is better for pest control (Eissa, 2005). It might also be noticed that farmers literacy rate is very low which lead to the improper and non judicious use of pesticides, whereas the majority of the farmers relied on pesticides seller or on their own experiences, and little of them give attention foe extension officers or reading written directions on the package (Bhanti *et al*., 2004).
It also may be due to lack of awareness of farmers about application dose, method of application and randomly combination of pesticides of different groups which may lead to contamination with pesticides residues (Latif *et al*., 2011).

Table 11: Estimated daily intake of violated pesticides on Orange:

Pesticides	Mean Conc. (mg/kg)	EDI(mg/kg body weight)	ADI (mg/kg)	Hazard Index (EDI as a % of ADI)
Chloropyrifos	0.281	0.0012	0.01	0.12
Dimethoate	2.308	0.01	0.002	5.1
Omethoate	0.943	0.00416	0.0003	13.9
Malathion	0.057	0.00025	0.3	0.0008
Diazinon	0.011	0.0000486	0.002	0.002
Imazilil	0.010	0.000044	0.025	0.002
L cyhalothrin	0.010	0.000044	0.005	0.0088
Primicarb	0.010	0.000044	0.035	0.0013

Food consumption for 38 g/person/day; Body Weight 8.6 kg

This misuse of pesticides by growers came also from their decisions regarding which pesticides to use rely strongly on their previous experience, on costs, and product availability on the farm (Jardim and Caldas, 2012), as well as inadequate management and regulation of these chemicals in developing countries (Waichman *et al*., 2007). In all cases, violated pesticides exposure through foodstuffs consumption were far below the

acceptable daily intake (ADI) as established by FAO/WHO which suggested that consumption of foodstuffs was at little risk to human health at present in term of pesticides. The most critical pesticides were dimethoate, omethoate and diazinon to the hazard index (HI).

Conclusion

Risk analysis revealed that daily intake levels of pesticide residues including dimethoate and omethoate in present study are higher than the recommended permissible levels that pose a great threat to the end consumers. Although you must understand the meaning of sustainable development which means that meets the needs of the present without compromising the ability of future generations to meet their own needs, we have to use pesticides but should to rationalization of consumption so does not affect the accumulation of pesticides on health so in terms of the routine monitoring to be maintaining the health of children who are the future. Moreover, these findings suggest creating awareness in the farmer community and general public regarding the avoidance of pesticide residues in food.

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