

## Monitoring of multi-class pesticide residues in green grape and their potential risk for Egyptian consumer

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**Abstract:** The residual concentrations of 100 pesticides in 32 fresh grape samples collected from local markets at eight Egyptian governorates during 2011' summer season were monitored based on QuEChERS extraction followed by analysis using liquid chromatography– tandem mass spectrometry (LC-MS/MS) and gas chromatography– tandem mass spectrometry (GC-MS/MS). The potential health risks associated with the exposure to violated pesticides were estimated as well. Mean recoveries ranged between 71 and 96.3%, while the repeatability expressed as relative standard deviation (RSD) was < 19.8%. Limits of quantification (LOQ) was 0.01 mg kg<sup>-1</sup>, which is equal or below the Maximum Residue Limits (MRLs). Of the analysed samples, 81.25% contained detectable residues, of which 21.88% exceeded their MRLs. Out of 35 pesticides that were detected in grape samples, carbendazim, acetamiprid, boscalid,  $\lambda$ -cyhalothrin, profenofos and pyraclostrobin were the most frequently pesticides detected. No residues of organochlorine pesticides and their metabolites were detected in any analysed samples. This study showed also that the estimated daily intake (EDI) of the violated pesticides by the Egyptian population through the consumption of grape did not exceed the toxicological acceptable level.

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**Key Words:** Pesticide residues, QuEChERS, grape, estimated daily intake.

### 1.Introduction

Grape is a nutritionally important fruit crop of international trade significance and consumed both as fresh and processed products (Sinha *et al.*, 2012). It receives frequent application of a huge number of pesticides throughout the cropping season to control a variety of pests. As a result, considerable amounts of harmful pesticide residues often remain in the harvested grape, which may ultimately reach the consumer and slowly cause healthy hazards. The periodical monitoring of pesticide residues in marketed grape has an important role to play by: a) providing data on the pesticide residues status of the fresh produce supply. b) checking on pesticide use by growers, c) checking on compliance with good agricultural practice in the use of pesticides. d) take appropriated advisory or regulatory actions to ensure excessive residues do not recur (Dogheim *et al.*, 1999; Eissa, 2005).

Accordingly, there is a need for rapid, feasible, eco-friendly and reliable analytical technique to analyze pesticides residual levels in grape. Nowadays, the most universal extraction method to analyze a wide range of pesticides is the QuEChERS method which stands for quick, easy, cheap, efficient, rugged and safe. This method was first introduced by Anastassiades *et al.*, (2003). The increase of fruit and vegetable intake contributes to

the prevention of chronic diseases, but could also significantly increase pesticide exposure and may thus be of health concern (Drouillet-Pinard *et al.*, 2011). The effects that result from long-term exposure to low doses of pesticide residues in food are hard to distinguish, detect and quantify. Thus, risk assessment is necessary in order to ascertain the effects due to regular intake of pesticide residues in food (Darko and Akoto, 2008). A causal link between chronic exposure to pesticides and their possible health effects is difficult to establish because consequences appear years after a generally intense exposure or after repeated low-intensity exposures over many years (Multigner, 2005). Current standardized methods of dietary risk characterization for consumers are based on the comparison of exposure data with toxicological reference values that vary widely from one pesticide to another (European Commission, 2010). Similarly, for a given pesticide, dietary exposure greatly depends on the population diet and on residue levels in food, closely correlated to agricultural practices (FAO/WHO, 2008). If potential exposure of consumers to pesticide residues is below the relevant health-based guidance value (acute reference dose ARfD and acceptable daily intake ADI, for acute and chronic exposure, respectively), the use of that pesticide in crop protection is considered acceptable (WHO, 1997;

Boobis *et al.*, 2008). Dietary risk assessment of exposure to pesticide residues is traditionally performed for single compounds (Boon *et al.*, 2008).

Therefore, the aim of this study was to monitor pesticide residues in fresh green grape samples collected from local markets in eight Egyptian governorates during 2011' summer season, and to estimate the potential health risks associated with intakes of each violated pesticide residue on grape.

## 2. Material and Methods:

### 2.1. Pesticides and chemicals:

Certified reference standards of pesticides were of >98% purity and purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The selected pesticides included most of the insecticides, fungicides and herbicides, which are currently recommended in Egyptian agriculture as well as those, which require monitoring in samples for export. A total of 100 pesticides were thus initially considered for this study, out of which 76 pesticides were analysed using LC-MS/MS (i.e., abamectin, acetamiprid, atrazine, azoxystrobin, benalaxyl, boscalid, bromacil, bupirimate, carbaryl, carbendazim, chlorfluazuron, chlorpyrifos, cyfluthrin, cypermethrin, cyproconazole, cyprodinil, cyromazine, deltamethrin, diafenthiuron, diazinon, difenoconazole, dimethoate, dimethomorph, diniconazole, emamectin, ethion, ethirimol, famoxadone, fenarimol, fenhexamid, fenitrothion, fenpropathrin, fenpyroximate, flusilazole, flutolanil, hexaconazole, hexythiazox, imazalil, imidacloprid, indoxacarb, kresoxim-methyl, lufenuron, malaoxon, malathion, metalaxyl, methamidophos, methomyl, methoxyfenozide, myclobutanil, omethoate, oxamyl, penconazole, permethrin, phenthoate, phosalone, piperonyl butoxide, profenofos, promecarb, propamocarb hcl, propargite, propiconazol, pyraclostrobin, pyridaben, pyriproxyfen, spinosad, spiroticlofen, tetraconazole, thiabendazole, thiacloprid, thiamethoxam, thiobencarb, thiophanate-methyl, tolylfluanid, triadimenol, trifloxystrobin and triticonazole), while the remaining 24 pesticides were analysed using GC-MS/MS (i.e., atraton, bifenthrin, biphenyl, bromopropylate, cadusafos, captan, chlorfenapyr, chlorothalonil, chlorpropham,  $\lambda$ -cyhalothrin, *p,p*'-DDD, *p,p*'-DDE, *p,p*'-DDT, dicofol, fludioxonil,  $\alpha$ -HCH,  $\beta$ -HCH,  $\delta$ -HCH,  $\gamma$ -HCH (lindane), heptachlor, iprodione, ortho phenylphenol (OPP), procymidone and sulfur). All other HPLC-grade organic solvents and chemicals were purchased from standard commercial suppliers.

### 2.2. Sampling:

A total number of 32 green grape samples were collected four times biweekly from local markets in eight Egyptian governorates (i.e., Cairo,

Giza, Kalyobiya, Gharbiya, Sharkiya, Fayoum, Minufiya and Ismailia) during 2011' summer season. Actually, four local fruit markets were selected from each governorate. The samples from each market were collected separately in four packets of approximately 500 g each. The composite samples were prepared by the systematic mixing of the four packets and transferred into the jar of the blender and homogenized for 3 min., then accurately weighed 10 g of homogenized samples from each governorate were extracted.

### 2.3. Extraction and clean up:

Pesticides were extracted from grape using QuEChERS method. In this method ten grams of grape samples were weighed in a 50-ml PFTE tube, and 10 ml of acetonitrile was added and shaken vigorously for one minute. After addition of 4g of magnesium sulfate, 1g of sodium chloride and buffering citrate salts (pH 5 to 5.5), the mixture was shaken intensively and centrifuged at 4000 rpm for 5 minutes for phase separation. An aliquot of the organic phase was injected directly to LC-MS/MS system for analysis.

Another aliquot of the organic phase was 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 primary secondary amine sorbent (PSA) extracts were evaporated and redissolved in injection standard for GC-MS/MS analysis. Quantification was performed using aldrin as an internal standard, which was added directly before injection in GC-MS/MS system.

### 2.4. Determination:

#### 2.4.1. LC-MS/MS analysis:

An Agilent 1200 series liquid chromatograph system equipped with Applied Biosystems (API 4000 Qtrape & API 5500 Qtrape) tandem mass spectrometers with electrospray ionisation (ESI) interface was used. Separation was performed on a C18 column ZORBAX Eclipse XDB-C18 4.6 mm x 150 mm, 5  $\mu$ m particle size. The injection volume was 25  $\mu$ l. A gradient elution program was at 0.3 ml/min flow rate, in which one reservoir contained 10 mM ammonium formate solution in MeOH:H<sub>2</sub>O (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°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 quantitation and other was used for confirmation.

#### 2.4.2. GC-MS/MS analysis:

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.

#### 2.5. Quality assurance:

Analytical method and instruments were fully validated as part of a laboratory quality assurance system and were audited and accredited by the Centre for Metrology and Accreditation, Finnish Accreditation Service (FINAS), Helsinki, Finland. This quality system is referred to as SFS-EN ISO/IEC 17025:2005. Recovery study was performed in triplicates, by adding known quantities of pesticide standard solutions to aliquots of 10 g of homogenized grape (grapes grown without application of any pesticide). The samples were then analysed according to the aforementioned method in order to calculate the extraction efficiency. The average recoveries of the tested compounds in grape samples varied between 71 and 96.3%. The repeatability expressed as relative standard deviation (RSD) was <20%, while the limits of quantification (LOQ) was 0.01 mg kg<sup>-1</sup>, which is equal or below the Maximum Residue Limits (MRLs). The measurement uncertainty expressed as expanded uncertainty (at 95% confidence level) was found to be within the range of ± 30%.

### 3. Results and discussion:

#### 3.1. Monitoring of multi-class pesticide residues in fresh grape:

The pesticides included in this analytical scope were 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. Of the analysed samples, 81.25% contained detectable residues, of which 21.88% exceeded their Maximum Residue Limits (MRLs). The violated pesticides were chlorflazuron, difenoconazole, dimethoate, λ-cyhalothrin, methamidophos, omethoate, profenofos and pyraclostrobin (Table 1).

Out of 35 pesticides that were detected in grape samples, carbendazim, acetamiprid, boscalid, λ-cyhalothrin, profenofos and pyraclostrobin were the most frequently pesticides detected. Among the detected residues, fungicides effective against grey mould, powdery mildew and downy mildew, followed by the insecticides were prevailed. Fungicides represent one of the most relevant groups of pesticides applied to vineyards. Most of the concentration levels found for the pesticide residues were below MRLs, thus causing no problems in terms of food safety. It is also observed that 15 from the detected pesticides were not registered on grape, and these pesticides were acetamiprid, chlorpyrifos, cypermethrin, deltamethrin, diazinon, dimethoate, chlorflazuron, fenarimol, fenpropathrin, imidacloprid, λ-cyhalothrin, lufenuron, methomyl, methoxyfenozide and profenofos. In addition, three from the detected pesticides were found to be not registered in Egypt. Since the use of methamidophos, hexaconazole and triadimenol is no longer authorized in Egypt, it is recommended to check the possible misuse of the product containing these pesticides at national level.

Multiple residues are expected on grape because various classes of pesticides must be alternated to prevent resistance developing in the pests. The presence of pesticide residues in the marketed fresh grape may be attributed to the excessive use of pesticides on grape for which they were either registered or not registered; disregard of recommended preharvest intervals (PHI); in addition, applied rates often exceeded manufacturers recommendations in the belief that more is better for pest control (Eissa, 2005). It might also be notice 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 for extension officers or reading written directions on the package (Bhanti *et al.*, 2004).

The results of the current study, in which no residues of organochlorine pesticides such as DDT, HCH, and their metabolites were detected in any analysed samples, were comparable with the results of Dogheim *et al.*, (2001). Comparing our findings with those found by Doghiem *et al.*, (2002), revealed that the percentages of the contaminated and violated samples of grape increased from 39.3 and 8.2% in 1997 to 81.25 and 21.88% in the current study, respectively. The results of the current study mainly correspond with the outcomes of other authors. A liquid chromatography–electrospray ionization–tandem mass spectrometry (LC–ESI–MS–MS) was used for the analysis of 10 multi-class pesticides

residues (imidacloprid, thiamethoxam, chlorpyrifos, dimethoate, monocrotophos, metalaxyl, methomyl, hexaconazole, myclobutanil and carbendazim) in fresh grape samples collected from an agricultural area in Hyderabad, South India. The results revealed that the concentrations of studied pesticide residues in grape samples were in the permissible limits except monocrotophos (Venkateswarlu *et al.*, 2007). The residues of cypermethrin, permethrin, chlorpyrifos, metalaxyl and etophenprox were detected in grape samples collected from farm-gates and local markets of Pune district, India at below

MRLs (Dasgupta *et al.*, 2010). 13.3% of grape samples collected from Xiamen, China, during the October 2006 to March 2009 monitoring campaign contained pesticide residues (i.e., chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, dichlorvos, fenvalerate, omethoate and methamidophos) exceeding the MRLs (Chen *et al.*, 2011). The residues of chlorpyrifos were detected in 40% of grape samples harvested directly from five different farms of Nashik, India and the concentrations were below the respective EU-MRL (Banerjee *et al.*, 2013).

**Table (1): Pesticide residues detected in 32 grape samples collected from local markets located in eight Egyptian governorates during 2011' summer season.**

Contaminated samples (n=32)		Detected pesticides	Pesticide level (mg/kg)		Mean mg/kg	Frequency		MRLs (mg/kg)	No. of violated compound		No. of violated samples	
No.	%		Min. mg/kg	Max. mg/kg		No.	%		No.	%	No.	%
26	81.25	Acetamiprid	0.01	0.31	0.0771	7	21.88	0.5			7	21.88
		Azoxystrobin	0.11	0.22	0.165	2	6.25	2				
		Boscalid	0.01	1.13	0.386	7	21.88	5				
		Carbendazim	0.05	2.86	0.883	13	40.63	3				
		Chlorfenapyr	0.01	0.01	0.01	1	3.13	0.05 *				
		Chlorfluazuron	0.02	0.02	0.02	1	3.13	0.01 *	1	100		
		Chlorpyrifos	<LOQ	0.04	0.02	5	15.63	0.1				
		Cypermethrin	0.02	0.16	0.076	5	15.63	0.2				
		Cyprodinil	0.02	0.1	0.06	2	6.25	3				
		Deltamethrin	0.04	0.04	0.04	1	3.13	0.2				
		Diazinon	0.01	0.01	0.01	1	3.13	0.01 *				
		Difenoconazole	0.33	0.33	0.33	1	3.13	0.1	1	100		
		Dimethoate	0.05	0.05	0.05	1	3.13	0.02 *	1	100		
		Diniconazole	0.01	0.01	0.01	1	3.13	0.2 *				
		Fenarimol	<LOQ	<LOQ	<LOQ	1	3.13	0.3				
		Fenhexamid	0.04	0.05	0.045	2	6.25	15				
		Fenpropathrin	<LOQ	1.52	0.433	5	15.63	5				
		Fludioxonil	0.07	0.07	0.07	1	3.13	2				
		Flusilazole	<LOQ	0.02	0.02	2	6.25	0.2				
		Hexaconazole	<LOQ	<LOQ	<LOQ	1	3.13	0.1				
		Imidacloprid	0.1	0.1	0.1	1	3.13	1				
		Iprodione	0.01	0.8	0.413	4	12.5	10				
		$\lambda$ -cyhalothrin	<LOQ	0.26	0.078	7	21.88	0.2 *	1	14.28		
		Lufenuron	<LOQ	<LOQ	<LOQ	1	3.13	1 *				
		Metalaxyl	<LOQ	0.01	0.01	3	9.37	1				
		Methamidophos	0.49	0.49	0.49	1	3.13	0.01 *	1	100		
		Methomyl	0.09	0.14	0.115	2	6.25	0.3				
		Methoxyfenozide	0.01	0.17	0.06	4	12.5	1				
		Myclobutanil	<LOQ	0.11	0.06	3	9.37	1				
		Omethoate	0.05	0.05	0.05	1	3.13	0.02 *	1	100		
		Penconazole	<LOQ	<LOQ	<LOQ	1	3.13	0.2				
		Profenofos	<LOQ	0.4	0.178	7	21.88	0.05 *	3	42.86		
Pyraclostrobin	0.01	2.09	0.655	6	18.75	2	1	16.67				
Sulfur	0.01	0.69	0.33	4	12.5	N.S.						
Triadimenol	0.03	0.03	0.03	1	3.13	2 *						

The limit of quantification (LOQ) was 0.01 mg kg<sup>-1</sup>. MRLs: Maximum Residue Limits According to Codex Alimentarius Commission (FAO/WHO, 2004) and \* for European Union MRLs (EU MRLs) N.S. means MRL has not been established.

### 3.2. Estimated daily intake of violated pesticides:

The results of the monitoring in combination with food consumption data were taken into consideration to evaluate whether the estimated daily intake (EDI) of violated pesticides through grape consumed by the local inhabitants is a cause of toxicological concern according to the recommended dose by the FAO/WHO. The calculated daily intakes were obtained by multiplying the mean concentrations of violated pesticides detected and the amount of grape consumed based on WHO/Global Environment Monitoring System-Food Contamination Monitoring and Assessment Program average consumption cluster C diets (WHO/GEMS/FOODS, 2006). The long-term risk assessments of the intakes compared to the pesticide toxicological data were performed by calculating the hazard index (HI), by dividing the estimated daily intake with the relevant acceptable daily intake (ADI) (EFSA, 2007).

The estimated daily intakes (EDIs) ranged from 0.18% of the ADI for chlorfluazuron to 2.26% of the ADI for dimethoate and 7.53% of the ADI for omethoate. The most critical pesticide is methamidophos, contributing 22.13% to the hazard index (HI) (Table 2). The results show that despite a high occurrence of pesticide residues in grape, it

could not be considered a serious public health problem.

In other words, an exposure assessment, based on pesticide residues levels detected in the grape analysed in this study, confirms that the intake of the violated pesticides through grape consumption in Egypt does not represent a health risk to consumers, i.e., the estimated daily intake (EDI) is less than the acceptable daily intake (ADI). Česnik *et al.*, (2008) analysed 47 grape samples at harvest from Slovenia for the presence of 67 pesticides by gas chromatography-mass spectrometry (GC-MS). Results revealed that folpet (97.9%), cyprodinil (51.1%), dithiocarbamates (44.7%), chlorothalonil (23.4%), chlorpyrifos (19.1%) and pyrimethanil (14.9%) were the most frequently found pesticides in grapes. Risk assessment showed also that the exceeded concentrations of cyprodinil and fludioxonil did not represent any risk for consumer's health (the national estimate of short-term intake as a percentage of the acceptable daily intake was below 100%). On the contrary to our results, Sinha *et al.*, (2012) showed that chlorpyrifos, triazofos, imidacloprid, fenitrothion and quinalphos were detected in all the samples of grapes collected from Hyderabad, India, and people eating grapes are at high risk due to exposure to these pesticides.

**Table 2: Estimated daily intakes (EDIs) of violated pesticides residues found in grape.**

Pesticides	Mean Conc. (mg/kg)	EDI (mg/kg body weight)	ADI (mg/kg)	Hazard index (EDI as a % of ADI)
Chlorfluazuron	0.02	9.03333E-06	0.005	0.180666667
Difenoconazole	0.33	0.00014905	0.01	1.4905
Dimethoate	0.05	2.25833E-05	0.001	2.258333333
λ-cyhalothrin	0.078	0.00003523	0.005	0.7046
Methamidophos	0.49	0.000221317	0.001	22.13166667
Omethoate	0.05	2.25833E-05	0.0003	7.527777778
Profenofos	0.178	8.03967E-05	0.03	0.267988889
Pyraclostrobin	0.655	0.000295842	0.03	0.986138889

Grape food consumption 27.1 g/person/day; Body weight 60 kg

It should be emphasized that dietary pesticide intakes estimated in this study considered only exposures from grape and did not include other food products such as vegetables, fruits, grains, dairy, fish, and meats. As such, estimates are not considered as total dietary exposure to the pesticides, nor do we consider drinking water, residential, or occupational exposures. It should also be noted that not all registered pesticides in Egypt were measured in this study due to budget constraints. Therefore, it is an underestimation of the total exposure of pesticides studied. On the other hand, processing factors were ignored, resulting in an overestimation of the actual exposure to pesticide residues.

### 4. Conclusions

It could be concluded that the use of permitted pesticides, the consideration of pesticide concentrations and the pre-harvest interval importantly diminish the health risk for consumers. The data suggest the need for regular monitoring of the pesticide residue levels in marketed fruits, which should be extended periodically and the number of samples analysed per item needs to be increased for a better representation of contamination in the markets. Although the consumption data used here is the most updated available, there is a need for data which reflects real food consumption patterns in Egypt. The

effect of grapes washing as the standard procedure before consumption on the residue concentration is required to assess real consumer exposure.

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