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# Evaluation of Pesticide Residues in some Egyptian Fruits

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## ABSTRACT

A total of 177 fruits samples collected from Egyptian markets during July to December 2010. Samples collected in the season of producing a wide range of fruits in Egypt. Samples were subjected to pesticide residues analysis using multiresidues method (QuEChERs) standard method. The determination of residues carried out using GC-MS/MS and LC-MS/MS. The samples were analyzed using an accredited method that is capable to quantify 251 pesticide residues from different pesticide groups. Fifty one pesticide were detected in all analysed samples. Pesticide residues were not observed in 28.2% of fruit samples (50) and were found in 127 samples (71.7%). In all of the analysed samples; 54.2% (96) were contaminated with pesticide residues below MRLs, while in 17.5% (31) contained residues above safety limits (MRLs) of EU. However, only 2.3% of samples showed violation comparing to codex MRL's. Whereas, the number of samples contained multiple active substances were 69 with a percentage of 39%. The most detected pesticide groups were Pyrethroids, 27.8% followed by Organophosphates (OP's) 24.6%, Benzimidazoles 14.9%. On the other hand, OP's are the most violated group. Data showed that pesticides which not recommended for using in tested fruits were detected in frequency of 76.1% of the findings as well as pesticides revoked by Egyptian authorization.

***Key words:*** Pesticide residues, Fruits, Egypt, Risk assessment, Monitoring

## Introduction

Food safety is an area of growing worldwide concern on account of its direct bearing on human health. The presence of harmful pesticide residues in food has caused a great concern among the consumers. Fruits are essential for a nutritious and healthy diet; they are a particularly rich source of carbohydrates, lipids, vitamins, minerals, antioxidants and other important nutrients. Eating a diet rich in vegetables and fruits as part of an overall healthy diet may reduce risk for many diseases.

Like other crops, fruits are attacked by pests and diseases during production and storage leading to damages that reduce the quality and the yield. The use of pesticides have increased because they have rapid action, decrease toxins produced by ford infecting organisms and are less labor intensive than other pest control methods, (Łozowicka *et al*., 2013).

For several years the use of pesticides has been escalating in the developing countries, however, the heavily use of pesticides may resulted in environmental problems like disturbance of the natural balance, widespread pest resistance, environmental pollution, hazards to non-target organisms and wildlife, and hazards to humans. Control programs for pesticide residues in the developing countries are often limited due to lack of resources and rigorous legislation is not in place. Moreover, training programs for technical personnel and equipment for monitoring pesticide residues are often lacking, (Hjorth *et al*., and 2011).

The use of pesticides during production often leads to the presence of pesticide residues in fruits after harvest. Unfortunately, not all farmers follow legal practices with pesticides during production. Consequently, the monitoring studies are the prime way of ensuring that pesticides are employed in accordance with Good Agricultural Practice (GAP) and yielded the potential risk of pesticides for public health. The surveillance should focus on the proper use of pesticides in terms of authorization and registration (application rates and pre-harvested intervals), and on compliance with established maximum residue limits ( MRLs) that set by different international organization such as, the Codex Alimentarius Commission of the United Nation's Food and Agriculture Organization and the World Health Organization , European commission in a variety of foods. Maximum residue levels (MRLs) are the highest levels of residues expected to be in the food when the pesticide is used according to authorized agricultural practices

Monitoring of food contaminants has been performed by different institutions in Egypt in the past few years. Up to now, content of pesticide residues in fruits and vegetables was not analyzed in a sense that it can be

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dependent on the type of production. However, monitoring of pesticide residues in some conventional and organic crops were studied in some researches (Mansour *et al*., 2009a & b), Sohair Gadalla, *et al*., 2012, 2013 and 2014).

The aim of this study was to determine the presence of pesticide residues in some common Egyptian fruits and evaluate the practices used in subjected fruits such as detected pesticide chemical groups, the allowed pesticides used. Furthermore, compliance with legal regulations concerning the use of plant protection products in crop cultivation was ascertained. Pesticide residue levels were evaluated in relation to: the Maximum Residue Levels (MRLs) of codex and EU. This survey conducted in the summer season of 2010, as higher production and consumption rate of fruits in Egypt.

## Experimental

### *Sampling*

A total of 177 samples of fruits were collected from different local markets from June to December 2010. Thirteen types of fruits subjected for analysis including apple, apricot, banana, cantaloupe, dates, grapes, guava, mangoes, orange, peach, plum, strawberry and water melon. The types selected from the most popularly consumed and locally cultivated fruits in Egypt. The samples were collected from five Governorates, Cairo, Giza, Qualubiya, Ismailia and Fayium, the number of samples analyzed for each fruits is shown in Table (1).

About 2 kilograms (one unit of water melon) from each commodity were thoroughly homogenized and prepared according to the generally recommended method of sampling to achieve a representative part of the material to be analyzed, (Codex Alimentariuos Commission, 1993). Samples analyses were carried out either immediately upon their arrival to the laboratory or the samples were stored at 0-5$^{o}$C for no longer than 2 days before analysis.

### *Pesticide Residues Analysis*

Two hundred and fifteen (215) pesticides of different pesticide chemical groups either currently registered or banned in Egypt were subjected to analysis. The details of the analytical method described by (Emad *et al.,* 2012, Abd El-Moneim *et al.,* 2012 and Sohair *et al.*, 2014).

The method is known as the quick, easy, cheap, effective, rugged and safe (QuEChERS) method was used for analysis of or pesticide residues in fruits. The extraction procedure is based on liquid–liquid partitioning with acetonitrile followed by a cleanup step with dispersive-SPE. The great advantages of this method are the simplicity, the low cost of implementation and the short analysis time. This method nowadays is the official standard method in many laboratories in the world; it's known as the standard method of European Committee for Standardization/Technical Committee 275 (2007) for foods of plant origin: prEN 15662 (QuEChERS).

### *Determination*

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

The method validated for 151 compounds using LC-MS/MS and 64 compounds using GC-MS/MS. The detection and confirmation of pesticides residues in the samples was made using GC-MS/MS and LC-MS/MS.

### *Quality Assurance*

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

The average recoveries of these pesticides at different concentration levels varied between 70-120 %. The reproducibility expressed as relative standard deviation was less than 25%. The limit of quantitation started at 0.01 mg/kg and up depending on the pesticide type and detection module. The measurement uncertainty expressed as expanded uncertainty in terms of relative standard deviation (at 95 % confidence level) is lower than the default value set by the EU (± 50 %).

### *Apparatus*

#### *LC-MS/MS System*

Agilent 1200 series liquid chromatography system equipped with Applied Bio-systems (API 4000 Qtrape) tandem mass spectrometers with electrospray ionization (ESI) interface. Separation was performed on a

C18 column ZORBAX Eclipse XDBC18 4.6 mm x 150 mm, 5 µm particle size. The injection volume was 25 µl. A gradient elution program was at 0.3 ml/min flow rate, in which one reservoir contained 10 mM ammonium formate solution in MeOH:$H_2O$ (1:9, v/v) and the other contained methanol. The ESI source was used in the positive mode, and Nitrogen was used as nebulizer gas, curtain gas, heater gas and collision gas according to manufacturer's settings; source temperature was 300$^o$C, ion spray potential 5500 V, decluster potential and collision energy were optimized using a Harvard apparatus syringe pump. The Multiple Reactions Monitoring mode (MRM) was used in which one MRM was used for quantitation and other was used for confirmation.

*GC-MS/MS System*

Agilent Gas Chromatograph 7980A equipped with tandem mass spectrometer 7000B Quadrupole, EI source was used to perform analysis by using HP-5MS 5% phenyl methyl siloxane capillary column (30 m length x 0.25 mm id x 0. 25 µm film thickness). Samples were injected in a splitless mode and helium was used as carrier gas (1 ml/min). Injector temperature was 250°C, transfer line temperature was 285°C, ion source temperature was 280°C and quadrupole temperature was 150°C. The GC oven temperature was programmed to initially held at 70°C for 2 min then increased to 150°C at 25°C/min (held for 0 min), and raised to 200°C at the rate of 3°C/min (held for 0 min), then went up from 200 to 280°C at 8°C/min (held for 10 min). This resulted in a total run time of 42 min and complete separation of all the analytes.

*Reagents***:** Solvents and chemicals described in the standard method CEN 275, 2007

*Pesticides reference standards*

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

## Results and Discussion

A total of 177 samples of fruits were collected from five local markets in Egyptian Governorates during 2010. All samples were subjected to multiresidues analysis for 215 pesticide residues that are widely used or banned in Egypt using the standard method CEN 275, 2007. The new techniques using LC-MS/MS with GC-MS/MS allowed the detection of a wide range of residues with low quantification levels to achieve the international demands. By this method, it could precisely identify the small quantity (< LOQ) for each compound and the number of pesticides sought in the analytical scope have been increased. The analyzed wide range include many groups of pesticides such as, organophosphorus and nitrogen compounds, organochlorine, pyrethroids, and other groups of pesticide that are widely used or banned in Egypt.

Table (1) showed the number of analyzed fruit samples, the range of detected pesticides, average in mg/kg , number of violated compounds in analyzed samples collected during 2010, as well as the status of each pesticide/ commodity combination in registration system set by the Agricultural pesticide committee (APC).

According to the decree of Agriculture Pesticides Committee (codex+EU) in Egypt, which stated " pesticide residue levels should compare to Codex Alimintarious as it's available and to the EU-MRLs in case of codex MRLs lack". In the current study, the results of the monitoring were evaluated versus to APC decree and to codex Alimentarious MRL's only.

Data in table (2) showed that pesticide residues not observed in 28.2% of fruit samples (50). Whereas pesticide residues were found in 127 samples (71.7%). In all of analyzed samples; 54.2% (96) were contaminated with pesticide residues below MRLs. However, the violation observed in 17.5% (31) in case of comparing the results to (codex + EU limits) according to the APC decree. However, only 4 samples (2.3%) showed violation of MRL's comparing to available MRL's in the codex. therefore, such comparison indicted variation in violation percentages according to the MRL's sources)

In general, the MRLs are always set far below levels considered to be safe for humans. It should be understood that MRLs are not safety limits, a food residue can have higher level than MRL but can still be safe for consumption, (Keikotlhaile, 2010). In this case, MRLs are just indicators of the violation or non-violation of Good Agricultural Practices (GAP), not an indication of health risk, (IFOAM, 2008) i.e legally defined "maximum residue limits" (MRL) are not a guarantee of "zero health risk". Therefore, risk exposure should evaluate based on toxicological end point such as, Acceptable Daily Intake (ADI) or Acute Reference Dose (ARfD).

The obtained data showed, Banana, cantaloupe and water melon are the most free samples, however all analyzed samples of grape, guava, orange and peach are contaminated with pesticide residues (in guava the number of analyzed samples is low). Data in table (2) showed that 69 (39%) out of 127 contaminated fruits

**Table 1:** The number of analysed fruit samples, the range of detected pesticides, average in mg/kg , number of violated compound, the status of registration of each detected pesticide in Egypt in analysed samples collected during 2010.

| Commodity | Total No. of samples | Pesticides detected | Freq | Range mg/kg | | Average mg/kg | MRL mg/kg | Violated comp | Registration in Egypt APC |
|---|---|---|---|---|---|---|---|---|---|
| Apple | 18 | Acetamiprid | 5 | 0.01 | 0.14 | 0.05 | 0.7 | | R-NR1 |
| | | Bromopropylate | 1 | 0.08 | 0.08 | 0.08 | 2 | | R-NR1 |
| | | Carbendazim | 7 | 0.01 | 0.25 | 0.08 | 3 | | R-R1 |
| | | Chlorpyrifos | 2 | 0.02 | 0.07 | 0.05 | 1 | | R-NR1 |
| | | Cypermethrin | 2 | 0.02 | 0.09 | 0.06 | 0.7 | | R-NR1 |
| | | Dimethoate | 6 | 0.01 | 0.05 | 0.02 | 1 | | R-NR1 |
| | | Ethion | 3 | 0.02 | 0.07 | 0.05 | 0.01 * | 3* | R-NR! |
| | | Fenpropathrin | 4 | 0.02 | 0.08 | 0.05 | 5 | | NR |
| | | Flusilazole | 1 | 0.01 | 0.01 | 0.01 | 0.3 | | R-NR1 |
| | | L-Cyhalothrin | 6 | 0.01 | 0.04 | 0.02 | 0.2 | | R-NR1 |
| | | Methomyl | 1 | 0.01 | 0.01 | 0.01 | 0.3 | | R-NR1 |
| | | Myclobutanil | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | R-NR1 |
| | | Profenofos | 2 | 0.01 | 0.53 | 0.27 | 0.05 * | 1* | R-NR1 |
| | | Propargite | 1 | 0.17 | 0.17 | 0.17 | 3 | | NR |
| | | Pyridaben | 1 | 0.01 | 0.01 | 0.01 | 0.5 | | R-NR1 |
| | | Spinosad | 1 | 0.06 | 0.06 | 0.06 | 0.1 | | R-NR1 |
| | | Thiacloprid | 1 | 0.02 | 0.02 | 0.02 | 0.7 | | R-NR1 |
| Apricot | 10 | Acetamiprid | 2 | 0.03 | 0.03 | 0.03 | 0.1 * | | R-NR1 |
| | | Cypermethrin | 3 | 0.01 | 0.1 | 0.06 | 2* | | R-NR1 |
| | | Carbendazim | 3 | 0.06 | 0.98 | 0.39 | 2 | | R-NR1 |
| | | Dimethoate | 4 | 0.02 | 0.03 | 0.02 | 0.02 * | 1* | R-NR1 |
| | | Diniconazole | 1 | 0.01 | 0.01 | 0.01 | 0.1 * | | R-NR1 |
| | | Ethion | 1 | 0.03 | 0.03 | 0.03 | 0.01 * | 1* | R-NR1 |
| | | Fenpropathrin | 2 | 0.04 | 0.1 | 0.07 | 0.01 * | 2* | NR |
| | | Fludioxonil | 1 | 0.01 | 0.01 | 0.01 | 5 | | R-NR1 |
| | | L-Cyhalothrin | 3 | 0.01 | 0.05 | 0.03 | 0.5 | | R-NR1 |
| | | Methomyl | 1 | 0.03 | 0.03 | 0.03 | 0.02 * | 1* | R-NR1 |
| | | Procymidone | 1 | 0.09 | 0.09 | 0.09 | 0.02 * | 1* | R-NR1 |
| | | Profenofos | 1 | 0.25 | 0.25 | 0.25 | 0.05 * | 1* | R-NR1 |
| Banana | 19 | Cyprodinil | 1 | 0.04 | 0.04 | 0.04 | 0.05 * | | R-NR1 |
| | | Iprodione | 2 | 0.08 | 0.28 | 0.18 | 0.02 * | 2* | R-NR1 |
| | | Tetraconazole | 1 | 0.08 | 0.08 | 0.08 | 0.05 | 1 | R-NR1 |
| | | Triticonazole | 2 | 0.03 | 0.03 | 0.03 | 0.01 * | 2* | R-NR1 |
| Cantaloupe | 13 | Dicofol | 1 | 0.03 | 0.03 | 0.03 | 0.5 * | | NR |
| | | Carbendazim | 2 | 0.02 | 0.04 | 0.03 | 0.1 * | | R-NR1 |
| | | Metalaxyl | 1 | 0.01 | 0.01 | 0.01 | 0.2 | | R-NR1 |
| Dates | 2 | Chlorpyrifos | 1 | 0.01 | 0.01 | 0.01 | 0.05 * | | R-R1 |
| | | Cypermethrin | 1 | 0.04 | 0.04 | 0.04 | 0.05* | | R-NR1 |
| Grape | 19 | Acetamiprid | 5 | 0.01 | 0.31 | 0.09 | 0.2 | 1 | R-R1 |
| | | Boscalid | 4 | 0.03 | 1.13 | 0.38 | 5 | | R-NR1 |
| | | Carbendazim | 7 | 0.2 | 2.86 | 1.08 | 3 | | R-NR1 |
| | | Chlorfenapyr | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | R-NR1 |
| | | Chlorpyrifos | 3 | 0.01 | 0.04 | 0.02 | 0.5 | | R-NR1 |
| | | Chlorfluazuron | 1 | 0.02 | 0.02 | 0.02 | NO MRL | | R-NR1 |
| | | L-Cyhalothrin | 3 | 0.01 | 0.26 | 0.12 | 0.2 | 1 | R-NR1 |
| | | Cypermethrin | 4 | 0.02 | 0.16 | 0.09 | 0.2 | | R-NR1 |
| | | Cyprodinil | 1 | 0.02 | 0.02 | 0.02 | 3 | | R-NR1 |
| | | Diazinon | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | R-NR1 |
| | | Dimethoate | 2 | 0.05 | 0.05 | 0.03 | 2 | | R-NR1 |
| | | Diniconazole | 1 | 0.01 | 0.01 | 0.01 | 0.2 * | | R-NR1 |
| | | Fenhexamid | 1 | 0.05 | 0.05 | 0.05 | 15 | | R-NR1 |
| | | Fenpropathrin | 4 | 0.01 | 1.52 | 0.43 | 5 | | NR |
| | | Iprodione | 3 | 0.01 | 0.72 | 0.28 | 10 | | R-NR1 |
| | | Metalaxyl | 2 | 0.01 | 0.01 | 0.01 | 1 | | R-NR1 |
| | | Methamidophos | 1 | 0.49 | 0.49 | 0.49 | 0.01 * | 1* | NR |
| | | Methomyl | 1 | 0.09 | 0.09 | 0.09 | 0.3 | | R-NR1 |
| | | Methoxyfenozide | 1 | 0.01 | 0.01 | 0.01 | 1 | | R-NR1 |
| | | Myclobutanil | 1 | 0.01 | 0.01 | 0.01 | 1 | | R-NR1 |
| | | Piperonyl butoxide | 1 | 0.04 | 0.04 | 0.04 | NO MRL | | NR |
| | | Profenofos | 2 | 0.04 | 0.11 | 0.08 | 0.05 * | | R-NR1 |
| | | Pyraclostrobin | 4 | 0.01 | 2.09 | 0.66 | 2 | | R-NR1 |
| | | Triadimenol | 1 | 0.03 | 0.03 | 0.03 | 0.7 | | R-NR1 |
| Guava | 9 | Acetamiprid | 1 | 0.11 | 0.11 | 0.11 | 0.01 * | 1* | R-NR1 |
| | | Chlorpyrifos | 2 | 0.01 | 0.06 | 0.04 | 0.05 * | 1* | R-NR1 |

**Table 1:** Cont.

| Commodity | Total No. of samples | Pesticides detected | Freq | Range mg/kg | | Average mg/kg | MRL mg/kg | Violated comp | Registration in Egypt APC |
|---|---|---|---|---|---|---|---|---|---|
| | | Carbendazim | 2 | 0.02 | 0.08 | 0.05 | 0.1 * | | R-NR1 |
| | | Dimethoate | 1 | 0.12 | 0.12 | 0.12 | 0.02 * | 1* | R-NR1 |
| | | Cyfluthrin | 1 | 0.05 | 0.05 | 0.05 | 0.02 * | 1* | NR |
| | | Cypermethrin | 4 | 0.03 | 0.09 | 0.05 | 0.05* | 1* | R-NR1 |
| | | Imidacloprid | 2 | 0.01 | 0.02 | 0.02 | 0.05 * | | R-NR1 |
| | | L-Cyhalothrin | 2 | 0.02 | 0.03 | 0.03 | 0.02 * | 1* | R-NR1 |
| | | Malathion | 1 | 0.08 | 0.08 | 0.08 | 0.02 * | 1* | R-R1 |
| | | Methomyl | 2 | 0.01 | 0.03 | 0.02 | 0.05 * | | R-NR1 |
| Mango | 18 | Carbendazim | 6 | 0.01 | 0.17 | 0.05 | 5 | | R-NR1 |
| | | Chlorpyrifos | 3 | 0.01 | 0.05 | 0.02 | 0.05 * | | R-NR1 |
| | | Cypermethrin | 1 | 0.05 | 0.05 | 0.05 | 0.7 | | R-NR1 |
| | | Profenofos | 1 | 0.03 | 0.03 | 0.03 | 0.2 | | R-NR1 |
| Orange | 25 | Acetamiprid | 1 | 0.02 | 0.02 | 0.02 | 1 | | R-R1 |
| | | Carbendazim | 3 | 0.01 | 0.03 | 0.02 | 1 | | R-NR1 |
| | | Chlorpyrifos | 4 | 0.01 | 0.02 | 0.02 | 1 | | R-NR1 |
| | | L-Cyhalothrin | 16 | 0.01 | 0.21 | 0.05 | 0.2 | | R-NR1 |
| | | Cyfluthrin | 1 | 0.18 | 0.18 | 0.18 | 0.3 | | NR |
| | | Cypermethrin | 6 | 0.02 | 0.24 | 0.10 | 2 | | R-NR1 |
| | | Diazinon | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | R-NR1 |
| | | Dimethoate | 6 | 0.05 | 0.25 | 0.10 | 5 | | R-NR1 |
| | | Fenitrothion | 3 | 0.03 | 0.38 | 0.18 | 0.01 * | 3* | R-NR1 |
| | | Imazalil | 7 | 0.03 | 2.4 | 0.87 | 5 | | NR |
| | | Malathion | 6 | 0.01 | 0.08 | 0.04 | 7 | | R-R1 |
| | | Methamidophos | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | NR |
| | | 2-Phenyl Phenol | 8 | 0.01 | 1.97 | 0.94 | 10 | | NR |
| | | Piperonyl butoxide | 3 | 0.01 | 0.06 | 0.03 | 5 | | NR |
| | | Phenthoate | 1 | 0.04 | 0.04 | 0.04 | 0.01 * | 1* | NR |
| | | Profenofos | 4 | 0.04 | 0.99 | 0.38 | 0.05 * | 2* | R-NR1 |
| | | Thiabendazole | 8 | 0.02 | 1.5 | 0.61 | 7 | | R-NR1 |
| Peach | 8 | Acetamiprid | 2 | 0.01 | 0.02 | 0.02 | 0.1 * | | R-NR1 |
| | | Azoxystrobin | 1 | 0.01 | 0.01 | 0.01 | 2 | | R-NR1 |
| | | Carbendazim | 3 | 0.01 | 0.04 | 0.03 | 2 | | R-NR1 |
| | | Chlorpyrifos | 1 | 0.08 | 0.08 | 0.08 | 0.5 | | R-NR1 |
| | | Cypermethrin | 5 | 0.03 | 0.31 | 0.19 | 2 | | R-NR1 |
| | | Deltamethrin | 1 | 0.06 | 0.06 | 0.06 | 0.05 | 1 | R-NR1 |
| | | Dimethoate | 2 | 0.3 | 0.33 | 0.32 | 0.02* | 2* | R-NR1 |
| | | Fenpropathrin | 1 | 0.04 | 0.04 | 0.04 | 0.01 * | 1* | R-NR1 |
| | | Fenpyroximate | 1 | 0.02 | 0.02 | 0.02 | 0.3 * | | R-NR1 |
| | | Fenvalerate | 2 | 0.17 | 0.43 | 0.30 | 5 | | NR |
| | | L-Cyhalothrin | 3 | 0.01 | 0.04 | 0.03 | 0.5 | | R-NR1 |
| | | Malathion | 1 | 0.04 | 0.04 | 0.04 | 0.02 * | 1* | R-NR1 |
| | | Methomyl | 1 | 0.04 | 0.04 | 0.04 | 0.2 | | R-NR1 |
| | | Omethoate | 2 | 0.18 | 0.3 | 0.24 | 0.02 * | | NR |
| | | Penconazole | 1 | 0.01 | 0.01 | 0.01 | 0.1 | | R-NR1 |
| | | Piperonyl butoxide | 2 | 0.02 | 0.02 | 0.02 | NO MRL | | NR |
| | | Profenofos | 1 | 0.02 | 0.02 | 0.02 | 0.05 * | | R-NR1 |
| | | Propargite | 1 | 0.02 | 0.02 | 0.02 | 4 | | NR |
| Plum | 6 | L-Cyhalothrin | 1 | 0.01 | 0.01 | 0.01 | 0.2 | | R-NR1 |
| | | Omethoate | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | NR |
| Strawberry | 14 | Bifenthrin | 1 | 0.11 | 0.11 | 0.11 | 1 | | NR |
| | | Boscalid | 2 | 0.09 | 0.13 | 0.11 | 3 | | R-NR1 |
| | | Carbendazim | 4 | 0.03 | 0.25 | 0.10 | 1 | | R-NR1 |
| | | Chlorfenapyr | 1 | 0.03 | 0.03 | 0.03 | 0.05 * | | R-NR1 |
| | | Chlorpyrifos | 1 | 0.02 | 0.02 | 0.02 | 0.3 | | R-NR1 |
| | | Ethion | 2 | 0.04 | 0.06 | 0.05 | 0.01 * | 2* | R-NR1 |
| | | Fenpropathrin | 2 | 0.01 | 0.17 | 0.09 | 2 * | | NR |
| | | Iprodione | 2 | 0.05 | 0.18 | 0.12 | 15 * | | R-R1 |
| | | L-Cyhalothrin | 3 | 0.02 | 0.06 | 0.04 | 0.2 | | R-NR1 |
| | | Methamidophos | 1 | 0.33 | 0.33 | 0.33 | 0.01 * | 1* | NR |
| | | Methomyl | 1 | 0.01 | 0.01 | 0.01 | 0.02 * | | R-NR1 |
| | | Profenofos | 1 | 1.09 | 1.09 | 1.09 | 0.05 * | 1* | R-NR1 |
| | | Propargite | 1 | 0.16 | 0.16 | 0.16 | 0.01 * | 1* | NR |
| | | Pyraclostrobin | 2 | 0.02 | 0.07 | 0.05 | 0.5 | | R-NR1 |
| Water Melon | 16 | Carbendazim | 1 | 0.02 | 0.02 | 0.02 | 0.1 * | | R-NR1 |

**Table 1:** Cont.

| Commodity | Total No. of samples | Pesticides detected | Freq | Range mg/kg | | Average mg/kg | MRL mg/kg | Violated comp | Registration in Egypt APC |
|---|---|---|---|---|---|---|---|---|---|
| | | Fenpropathrin | 1 | 0.01 | 0.01 | 0.01 | 0.01 * | | NR |
| | | Metalaxyl | 1 | 0.01 | 0.01 | 0.01 | 0.2 | | R-NR1 |
| | | Methomyl | 2 | 0.01 | 0.02 | 0.02 | 0.1 * | | R-NR1 |
| | | Tetraconazole | 1 | 0.03 | 0.03 | 0.03 | 0.05 * | | R-NR1 |
| **Total fruits** | **177** | | **309** | | | | | | |

** MRL of EU, others were of codex Alimentarious, Freq= Number of Pesticides Found on the Commodity*
*APC= Agriculture Pesticide Committee , R= Registered, R1= Recommended, NR= Not Registered,NR1= Not Recommended*

**Table 2:** The number of analysed fruit samples, free, contaminated, and violated and samples with more than two pesticides

| Commodity | Total No. of samples | Free samples | No of Cont. samples * | No of samples <MRL | No of samples >MRL codex + EU | No of samples > MRL codex | No of samples with more than two pesticides |
|---|---|---|---|---|---|---|---|
| Apple | 18 | 2 | 16 | 13 | 3 | | 12 |
| Apricot | 10 | 1 | 9 | 6 | 3 | | 4 |
| Banana | 19 | 13 | 6 | 1 | 5 | 1 | - |
| Cantaloupe | 13 | 8 | 5 | 5 | - | | - |
| Dates | 2 | 1 | 1 | 1 | - | | - |
| Grape | 19 | - | 19 | 17 | 2 | 2 | 13 |
| Guava | 9 | - | 9 | 4 | 5 | | 2 |
| Mango | 18 | 10 | 8 | 8 | - | | - |
| Orange | 25 | - | 25 | 19 | 6 | | 17 |
| Peach | 8 | - | 8 | 5 | 3 | 1 | 6 |
| Plum | 6 | 4 | 2 | 2 | - | | - |
| Strawberry | 14 | 4 | 10 | 6 | 4 | | 9 |
| Water Melon | 16 | 7 | 9 | 9 | - | | 6 |
| **Total** | **177** | **50** | **127** | **96** | **31** | **4** | **69** |
| **%** | | **28.2** | **71.7** | **54.2** | **17.5** | **2.3** | **39.0** |

** The Number of contaminated samples included samples with results <LOQ and >LOQ.*

samples showed contamination with multiple residues (more than 2 pesticides per sample). Total of 75% peach, 68% of each of grape and orange, 66% apple, 64% of strawberry samples contaminated with multiple residues. The obtained results require the need to apply the Integrated Pest Management (IPM) programs to reduce the extensive use of pesticides especially in case of commodities eaten raw.

*Comparison with previous results*

Comparing to values extracted from previous articles, the percentage of free samples were 46.4%, 61.4%, 68.7%, 47% in 1995, 1996, 1997, 2007 respectively, decreasing to 28.2% in 2010. However, the percentages of contamination were 50.7%, 35.11%, 29%, 53%, respectively, increased in 2010 to be 71.5%.

The highest contamination rate in the current study (2010) compared to previous results may attributed to the expanded scope of current analytical procedure with wide range analyzed pesticides; it was 80-90 pesticides with relatively higher LOQ versus 215 pesticides with low LOQ 0.01-0.05 $mg.kg^{-1}$. Whereas, by applying novel instrumental techniques (LC-MS/MS and GC-MS/MS) with the lower limit of detection significant progress has been made for the detection of some recently registered pesticides whose residues could not be detected by previous standard procedures that could be the reason of highest rate of contamination in current work. In addition of wide varieties of new registered pesticide introduce to Egyptian markets in recent years.

The percentages of exceeding the MRL's were 2.7% 3.49% 2.3% in 1995, 1996, 1997 respectively and with the same percentage in 2007 and 2010. MRLs may be exceeded because of pesticide misuse, false positives due to naturally occurring substances, differences in national MRLs, lack of registered pesticides and incorrect pesticide application, (EFSA, 2010). Nevertheless, it is worthy to note that, the violation rates could be changed depending on the MRL sources and issuing date. Whereas, the MRLs setting is based on the national registered good agriculture practice (GAP) data combined with the estimated likely residue from the supervised trials, mean residue (STMR), ADI and ARfD, (Sohair *et al*., 2014).

*Evaluation by pesticides:*

*Detected pesticides groups*

Results identified 51 pesticides in 177 analyzed fruits samples. The detected residues are categorized in groups as shown in table (3) and fig (1).

The most occurrence groups were insecticides; 67.3% and fungicides 30.1%, Fig (1). In contrast of our findings, Łozowicka *et al*. (2013), found the fungicides and insecticides with percentages of 82% and 18%,

**Table 3:** The detected pesticide residues and their frequencies in analysed fruits samples, as well as their chemical groups

| SN | Substance classified* | Pesticide | Type [(1)] | Freq [(2)] | Freq % |
|---|---|---|---|---|---|
| 1 | Pyrethroid | L-Cyhalothrin | I | 40 | 12.9 |
| 2 | | Cypermethrin | I | 26 | 8.4 |
| 3 | | Fenpropathrin | I | 14 | 4.5 |
| 4 | | Cyfluthrin | I | 1 | 0.3 |
| 5 | | Fenvalerate | I | 2 | 0.6 |
| 6 | | Bifenthrin | I | 1 | 0.3 |
| 7 | | Deltamethrin | I | 1 | 0.3 |
| | **Total** | | | **85** | **27.8** |
| 8 | Organophosphate | Dimethoate | I | 21 | 6.8 |
| 9 | | Chlorpyrifos | I | 17 | 5.5 |
| 10 | | Profenofos | I | 12 | 3.9 |
| 11 | | Malathion | I | 8 | 2.6 |
| 12 | | Ethion | I | 6 | 1.9 |
| 13 | | Fenitrothion | I | 3 | 1.0 |
| 14 | | Methamidophos | I | 3 | 1.0 |
| 15 | | Omethoate | I | 3 | 1.0 |
| 16 | | Diazinon | I | 2 | 0.6 |
| 17 | | Phenthoate | I | 1 | 0.3 |
| | **Total** | | | **76** | **24.6** |
| 18 | Benzimidazole | Carbendazim | F | 38 | 12.3 |
| 19 | | Thiabendazole | F | 8 | 2.6 |
| | **Total** | | | **46** | **14.9** |
| 20 | Neonicotinoid | Acetamiprid | I | 16 | 5.2 |
| 21 | | Imidacloprid | I | 2 | 0.6 |
| 22 | | Thiacloprid | I | 1 | 0.3 |
| | **Total** | | | **19** | **6.1** |
| 23 | Carbamate | Methomyl | I | 9 | 2.9 |
| | **Total** | | | **9** | **2.9** |
| 24 | DMI: Triazole | Diniconazole | F | 2 | 0.6 |
| 25 | | Tetraconazole | F | 2 | 0.6 |
| 26 | | Triticonazole | F | 2 | 0.6 |
| 27 | | Flusilazole | F | 1 | 0.3 |
| 28 | | Penconazole | F | 1 | 0.3 |
| 29 | | Myclobutanil | F | 2 | 0.6 |
| 30 | | Triadimenol | F | 1 | 0.3 |
| | **Total** | | | **9** | **2.9** |
| 31 | Dicarboximide | Iprodione | F | 7 | 2.3 |
| 32 | | Procymidone | F | 1 | 0.3 |
| | **Total** | | | 8 | 2.6 |
| 32 | DMI:Imidazole | Imazalil | F | 7 | 2.3 |
| | **Total** | | | **7** | **2.3** |
| 34 | Strobilurin type | Pyraclostrobin | F | 6 | 1.9 |
| 35 | | Azoxystrobin | F | 1 | 0.3 |
| | **Total** | | | **7** | **2.3** |
| | **Others** | | | | |
| 36 | Phenylamide :acrylalanin | Metalaxyl | F | 4 | 1.3 |
| 37 | Sulfite ester | Propargite | A | 3 | 1.0 |
| 38 | Diacylhydrazine | Methoxyfenozide | I | 1 | 0.3 |
| 39 | Anilinopyrimidine | Cyprodinil | F | 2 | 0.6 |
| 40 | Carboxamide | Boscalid | F | 6 | 1.9 |
| 41 | Arylepyrrole | Chlorfenapyr | I | 2 | 0.6 |
| 42 | Benzilate | Bromopropylate | A | 1 | 0.3 |
| 43 | Benzoylurea | Chlorfluazuron | I | 1 | 0.3 |
| 44 | Hydroxyanilide | Fenhexamid | F | 1 | 0.3 |
| 45 | Organochlorine | Dicofol | A | 1 | 0.3 |
| 46 | Phenylpyrrole | Fludioxonil | F | 1 | 0.3 |
| 47 | METI | Fenpyroximate | A | 1 | 0.3 |
| 48 | METI | Pyridaben | I | 1 | 0.3 |
| 49 | phenol | 2-Phenyl Phenol | F | 8 | 2.6 |
| 50 | Insecticide/Synergist | Piperonyl butoxide | S | 6 | 1.9 |
| 51 | Spinosyn | Spinosad | I | 1 | 0.3 |
| | | | | 89 | |
| | **Total** | | | **309** | **13.6** |

*1-Types; A, Acarecides- I, insecticide- F, fungicide - – S, Synergist,*
*- Substance classified is referred to : PAN pesticide database, http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC33048 and IUPAC & pesticide manual, 2003-2004*
*2- Freq; The frequencies for the positive samples includes residues at <LOQ and ≥LOQ*

respectively. Lambda-cyhalothrin (12.9%) range of average 0.01-0.12 mg/kg, Cypermethrin (8.4%) 0.04-0.19 mg/kg, Dimethoate (6.8%) 0.02-0.32 mg/kg , and Chlorpyrifos (5.5%) 0.01-0.08 mg/kg were dominated among insecticides. However, Carbendazim (12.3%) was the most detected fungicide with average range 0.02-1.08 mg/kg. This may reflect the extensive use of insecticides than fungicides, which is in contrary with the behavior of fruits pest control, because of the fungal diseases that are expected to affect the fruits, however, the use of many types and large amounts of pesticides resulted of a resistance of insects leading to use more amounts of pesticides.

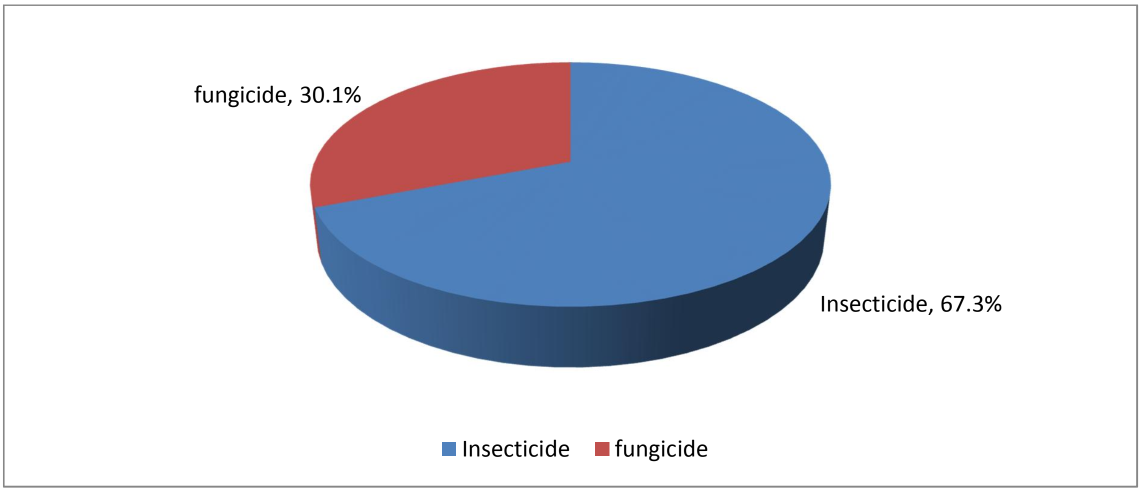


**Fig. 1:** The percentage of detected pesticide residues in fruits samples based on pesticide classification.

*Detected chemical classes*

Fig (2) illustrated the frequencies % of most detected pesticide residues groups in fruit samples showing; Pyrethroids, 27.8% followed by Organophosphates (OP's) 24.6%, Benzimidazole 14.9%, Neonicotinoid 6.1%, Carbamates and Triazoles 2.9%. However, (OP's) is the most violated detected pesticide group with a percentage of 7.7% followed by 2.5%, pyrethroids.

As shown in previous studies, Organophosphates and Pyrethroids are still the predominates detected pesticides groups in Egyptian fruits and vegetables, they were the most group in vegetables samples collected at 2011 with percentages of 41.5 %, 11.8%, (Sohair *et al*., 2014), and also detected in fruits samples collected at 2007 with higher percentages of (29.4%) and (58.8 %) than results of 2010, respectively.

Pyrethroid pesticides are synthetic analogues of pyrethrins, which are natural chemicals found in chrysanthemum flowers. Although synthetic pyrethroids are based on the chemical structure and biological activity of the pyrethrins, the development of synthetic pyrethroids has involved extensive chemical modifications that make these compounds more toxic and less degradable in the environment, (U.S. EPA, 2006 *a*.&b). Therefore, exposure to pyrethroid insecticides is likely to be multi- route throughout agriculture applications as well as via residential control purpose. Despite of being the least toxic pesticides, pyrethroids still have a harmful effects, as chronic exposure to pyrethroids can cause endocrine disrupting effects, liver function impairment and respiratory problems. Oxidative stress, lipid peroxidation and allergy may be some underlying mechanisms of toxicity, (Sahar, *et al*., 2011).

Organophosphate insecticides (OPs) are widely used in Egypt, as are other insecticide groups such as carbamates, pyrethroids and small quantities of organochlorines. OPs are toxic to the nervous system and have been largely removed from agriculture over the past decade from many countries. But they are not banned and still show up on some food crops, the EWG, 2012 considered the OP's as Dirty Dozen endocrine disruptor's pesticides, (The-dirty-dozen-eco-group, 2012).

Roshini and Wickremasinghe (2008) carried out review raises concerns that exposure to OP's pesticides at levels currently regarded as safe have adversely affect human reproductive function and survival. The cheap price and efficacy might be the cause of long period use of OP's and pyrethroids in Egyptian markets and the farmers can't change easily their usage pattern.

Nineteen out of 51 pesticides were found with frequencies higher than 1% of the analyzed samples. The frequencies of the most often found pesticides are shown in Fig (3); they were detected with percentages in descending order, L-cyhalothrin (12.9%), Carbendazim (12.3%), Cypermethrin (8.4%), Dimethoate (6.8%), Chlorpyrifos (5.5%), Acetamiprid (5.2%), Fenpropathrin (4.5%), Profenofos (3.9%) and Methomyl (2.9%) in all of the fruits analyzed samples.

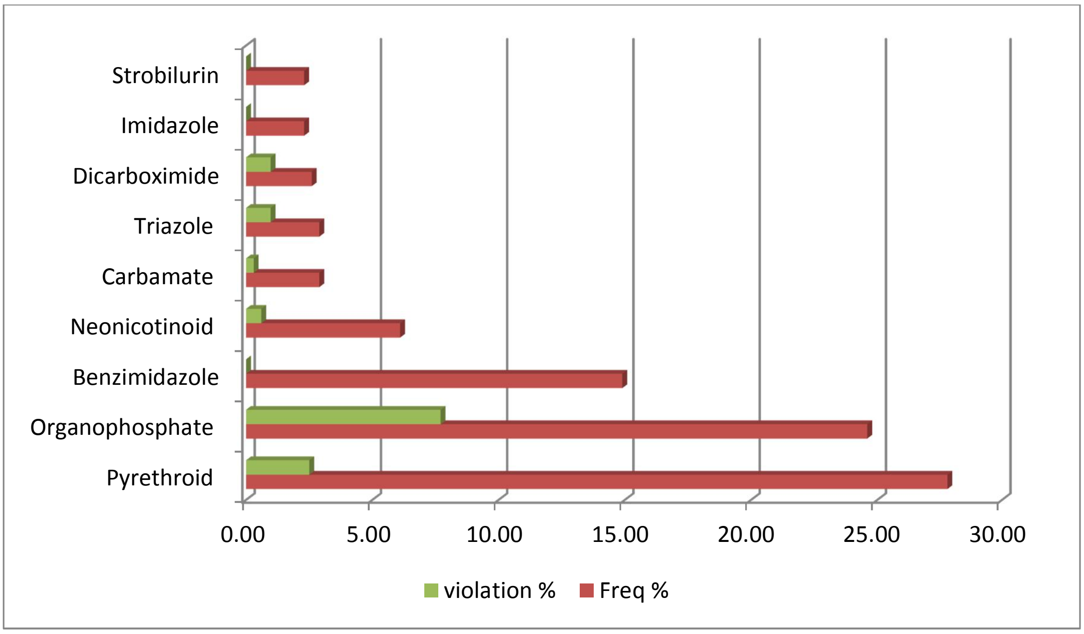


**Fig. 2:** Frequency and violation percentages of most detected pesticide residues based on classified substance groups detected in fruit samples.

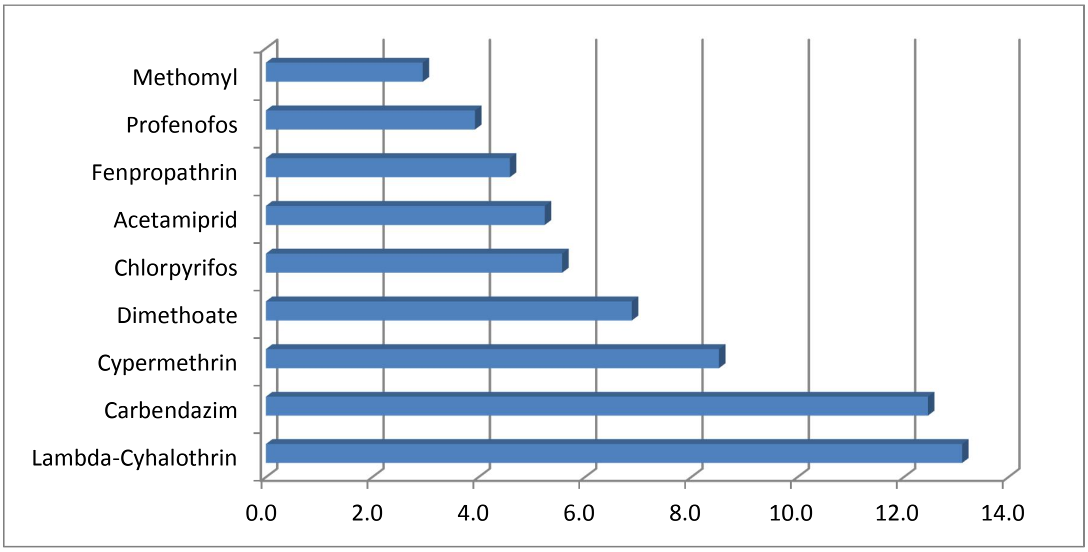


**Fig. 3:** Frequency percentages of most detected pesticide residues in fruit samples

*APC implementation*

The Agriculture of Pesticides Committee (APC), is the Egyptian competent authority responsible of the registration of agricultural pesticides. The committee issued the recommendation of registered pesticides for each crop, (APC, 2010). However, there were cases where not authorized pesticides were found whereas; out of 51 pesticides; 12 pesticides are not registered with frequencies of (16.5%) including, Bifenthrin, Cyfluthrin, Dicofol, Fenpropathrin, Fenvalerate, Imazalil, Methamidophos, Omethoate, Ortho-Phenyl Phenol, Phenthoate, Piperonyl butoxide, and Propargite . Only 7.4% of the findings were registered and recommended on the particular crop i.e. following the recommendation set by APC. However, data investigated that substances not recommended for a given fruits were detected in 235 cases out of 309 with percentage of frequency of 76.1%; Fig (4) indicated misuse and random applications of pesticides by farmers.

However, washing is the most common form of processing and is a preliminary step in both commercial and household preparation of fruits. Peeling is also an effective process for reduction of pesticide residues. Peeling fruits, such, bananas, citrus, mango and water melons, achieves virtually complete removal of residues from the fruit ( González-Rodriguez, Rial-Otero, Cancho-Grande, Gonzalez-Barreiro, & Simal-Gándara, 2011; Kaushik *et al*., 2009 ).

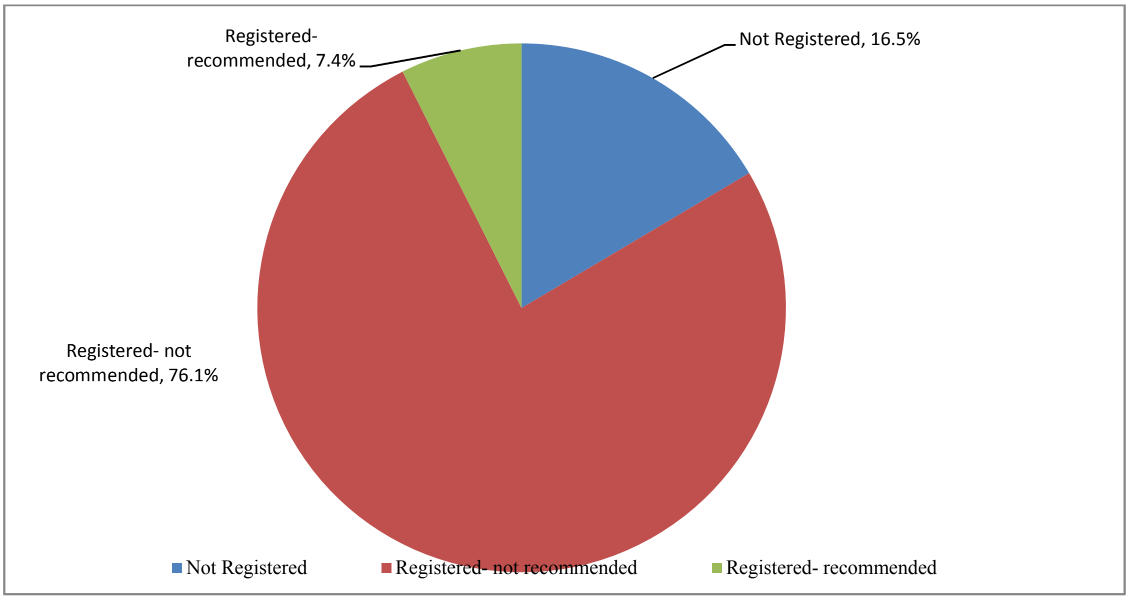


**Fig. 4:** The frequencies (%) of registered, registered and not recommended on particular fruits as well as the non-registered pesticides in analysed fruits samples during 2010.

## Conclusion

- The present study showed high percentages of application of non recommended pesticides on particular fruits in addition of presence of not registered pesticides in fruits samples.
- To prevent exposure to pesticides, it is necessary to reduce and control the use of pesticides in different commodities by enforcement activities. It also calls for improved residue control of production, tighter regulation of pesticide spraying and also tighter regulation on the sale of pesticides as well as for education of farmers and the implementation of integrated pest management system. Nevertheless, monitoring programs are increasingly important and essential to ensure minimal pesticide residue levels in food.

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