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MONITORING AND RISK EXPOSURE STUDIES OF SOME PESTICIDE RESIDUES DETECTED IN EGYPTIAN FRUIT AND VEGETABLES

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ABSTRACT

A monitoring study of pesticide residues was carried out in Egypt 2010.A 225 samples of different types of fruits and vegetables collected from nine Egyptian local markets located in nine governorates. All samples were examined for residues of 80 pesticides. Overall, results showed that 57.3% of the samples had no detectable pesticide residues, however, 39.1% contained detectable residues without violation, of which 3.6% contained residues that exceeded maximum residue limits (MRLs). Watermelon, banana, mango, cauliflower and potatoes samples were free from pesticide residues. The vegetables samples recorded the highest contamination percentage without exceeding of the levels of MRL' (i.e. 53.2%), followed by fruits (i.e.50.7%), and the leafy vegetables had the lowest percentage (i.e. 29.8%). In contrary, data showed that the leafy vegetables recorded the highest violation % (i.e. 8.5%), followed by fruits (i.e. 2.9%), and vegetables (i.e. 0.01%). The violated samples were apricot, grape, green peas, lettuce, molokhia and watercress. The violated compounds were cypermethrin and dithiocarbamates. The highest frequently detected pesticide was dithiocarbamates, followed by chloropyrifos, lambada-cyhalothrin, profenofos, ethion cypermethrin, fenopropathrin, malathion, chloropyrifos-methyl, dimethoate, diniconazol, dicofol and bromopropylate. However, the lowest frequently detected pesticides, which detected only one time, were phenothoate, malaoxon, imazalil, penconazole, permethrin, chlorfenapyr, iprodione, diazinon and procymidone. The dietary exposures of the most frequently detected pesticides were theoretically calculated to evaluate the risk for Egyptian consumer. As shown by the results, the intake of pesticide residues does not exceed the ADI (Acceptable Daily Intake) in any case. It is found to be below 15% of the ADI for all pesticides. The estimated exposure ranges from 0.00025% of the ADI for malathion on each of molokhia and spinach to 14.6% of the ADI for the ethion on tomato.

Keywords: Monitoring, Pesticide residues, vegetables and fruits, Risk exposure.

INTRODUCTION

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

A lot of studies had been conducted to determine the pesticides residues in plants worldwide include honey (Rissato *et al*., 2007), cabbage (Zhang *et al*., 2007), spring tomato (Gambacorta *et al*., 2005), wine and fruit juices (Zambonin *et al*., 2004), olive (Rastrelli *et al*., 2002), and orange, white cabbage and wheat (Kocourek *et al*., 1998). Environmental Protection

Agency, EPA, (2007) also conducted various studies to determine the maximum levels of pesticides that may introduced into food when harvesting, processing and marketing, and during preparing to be served. The values of pesticide residues are not similar in fruits and vegetables. This may be caused by the climatic condition and also the variation of the plants species (Tariq *et al*., 2007). Norris (1969) indicates that the pesticide enters the plant when it makes a contact with the surface and compatibility with the cuticle and its behavior of pesticides on aerial portions of the plant, on the roots and pesticide residues in food have historically lagged far behind many comparable hazards as a cause for public health concern and action (Correia *et al*., 2000; Eskenazi *et al*., 2008). Pesticide residue contaminating food is the problem focused worldwide because of its direct implications on human health and international trade (Sanborn *et al*., 2004). Reliable residue analysis data resulting from monitoring programs in foods, even if limited, may be of great value indicating the possible risks of pesticide exposure on human health and on international trade (DAF and FSAI, 2006).

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

MATERIALS AND METHODS

Sampling:

A total of 225 samples of different types of fruits and vegetables collected from nine Egyptian local markets located in eight governorates (Great Cairo, Fayoum, Gharbia, Giza, Monufia, Ismailia, Sharkiya, and Qalyubia) during 2010. For residue analysis, 2 kg of each commodity was prepared according to Codex guidelines. The generally recommended method of sampling was used to obtain a representative part of the material to be analyzed. Samples were analyzed immediately upon their arrival at the laboratory, or they were stored at 0–5°C for 4 days before analysis. Samples were analyzed for 80 pesticides, which included organophosphorus, organonitrogen, organochlorine, pyrethroids and dithiocarbamates compounds. The test samples were essentially analyzed immediately after cutting (for dithiocarbamates analysis) to avoid the decomposition of EBDC compounds.

Organophosphorus, organonitrogen and organochlorine analysis:

Chemicals and reagents:

(**a**) *Solvents*.—Acetone, dichloromethane, n-hexane, petroleum ether, acetonitril, (Pestiscan Chromatography grade or similar quality) ethanol 95-96%.

(**b**) *Chemicals* Anhydrous sodium sulphate (Riedel-de haen) sodium chloride, sodium hydroxide, Florisil 60-100 meshes (Merck).

Reference standard:

All pesticides reference materials were certified standard and were provided by Dr. Ehrenstorfer Gmbh, Gogginer str.78 D-8900 Augsburg. Germany, and by the FAO (Food Agriculture Organization of the United Nations, Rome, Italy) and were prepared in n-hexane/acetone mixture.

A) Extraction and cleanup:

Multiresidue method for pesticides: In analyses according to the method described by Luck *et al*. (1975 and 1981), residues were extracted from representative homogenized portion of each non fatty food by blending with acetone or water–acetone. The pesticides were transferred from the aqueous filtrate into the organic phase by shaking with petroleum ether and dichloromethane; after drying, the organic phase is concentrated just to dryness and then dissolved in injection solution for determination by gas chromatography (GCs). The method allows determination of the 80 pesticide residues listed in Table 2, which also shows the commodities, spiking levels, average recoveries, and coefficients of variation (CVs). The cleanup was carried out as described by (Suzuki *et. al.* 1979) using a florisil column, Organic phase was concentrated just to dryness and dissolved in injection solution (hexane/acetone (9:1) for GC-EC detection. This method allows the determination of 80 pesticide residues. The names of analyzed pesticides and their limit of determination is illustrated in table 1.

The investigated pesticides and their limit of determinations in mg/kg were as follows:

Table (1): The names of pesticides analyzed and there limit of determinations

Pesticide	LOD	Pesticide	LOD	Pesticide	LOD
Acephate	0.01	Alachlor	0.02	Atrazine	0.10
Bendiocarb	0.10	Bromopropylate	0.05	Carbaryl	0.50
Carbosulfan	0.10	Captan	0.10	Chlorothalonil	0.02
Chlorpyrifos	0.02	Chorpyrifos-methyl	0.05	Chlordane-transe	0.02
Chlordane-cis	0.02	Cyanophos	0.05	Cyfluthrin	0.10
Cypermethrin	0.10	Lambadacyhalothrin	0.10	Chlorpropham	0.50
DDD-p,p	0.02	DDE-p,p	0.02	DDT-o,p	0.02
DDT-p,p	0.02	Deltamethrin	0.20	Diazinon	0.05
Dichlofluanid	0.05	Dicofol	0.02	Dieldrin	0.01
Dimethoate	0.05	Diniconazole	0.02	Edifenfos	0.10
Endosulfan-alpha	0.02	Endosulfan-beta	0.02	Endosulfan sulphate	0.02
Endrin	0.10	Ethion	0.10	Fenamiphos	0.10
Fenitrothion	0.02	Fenpropathrin	0.05	Fenthion	0.05
Fenvalerate	0.01	HCH-alpha	0.01	HCH-beta	0.02
HCH-delta	0.01	HCH-gamma(lindane)	0.02	Heptachlor	0.01
Heptachlor epoxide.	0.01	Hexachlorobenzene	0.01	Imazailil	0.01
Iprodion	0.50	Malathion	0.02	Metalaxyl	0.20
Metamidiphos	0.05	Metrtibuzin	0.10	Monocrotophos	0.05
Omethoate	0.05	Oxidiazone	0.10	Parathion	0.05
Parathion-methyl	0.05	Pendimethalin	0.10	Permethrin	0.10
Phenthoate	0.10	Phosalone	0.05	Phosphamidone	0.10
Pirimicarb	0.05	Pirimiphos-ethyl	0.02	Pirimiphos-me	0.05
Procymidone	0.05	Profenophos	0.02	Promcarb	0.10
Propiconazole	0.10	Prothiofos	0.02	Pyrazophos	0.02
Terbuconazole	0.10	Tetradifon	0.03	Tolcophos-me	0.02
Triadmefon	0.05	Triadimenol	0.10	Triazophos	0.02
Trifluraline	0.01	Vinclozolin	0.01		

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B) Determinations:

Multiresidue of pesticides: Qualitative and quantitative determination of pesticide residues in food samples depends on the use of two different polarities of chromatography columns. Each GC instrument (NPD, ECD) has its capillary columns with different polarities and consequently two detectors. The injection standard technique was followed for the quantitative determination. Aldrin was used for organochlorine and pyrethroids compounds; Ditalimphos for organophosphorus and organonitrogen compounds; as injection standard.

Quality Assurance procedures: All analytical methods and instructions were carefully validated as a part of the laboratory quality assurance system and were audited and accredited by the Center of Metrology and Accreditation Finnish Accreditation Service (FINAS) ISO/IEC Guide 25. The criteria of quality assurance were described in (Dogheim *et. al.*2002). The recoveries were between 70-120% and CV less than 20%. Low level fortification of all samples with the contaminants of interest has been carried out to ensure that the method performed satisfactory for the particular food examined. Analysis of duplicate of samples represents precision of analysis.

Apparatus and equipment:

- Gas chromatograph HP 5890 equipped with double electron capture detector (ECD) with two capillary column; injector 225^{0}C; detector 280^{0}C, operating conditions; nitrogen carrier gas 2.5 ml /min; 65 ml/ min (carrier + make up) , column head pressure 82 K pa
- Gas Chromatograph, HP 6890 equipped with double nitrogen phosphorous detector (NPD) with two capillary columns; injector 225 ^{0}C detector 280 ^{0}C. Operating conditions hydrogen 3.5 $\pm$ 0.1 ml/min; air 100-110 ml/min; nitrogen carriers gas 2.5 ml/min for both GC's. The specification of chromatography columns are as follows:

1. PAS-5 ECD tested ultra 2 silicon, 25m X 0.32 ml. Film thickness 0.52 μm.
2. PAS –1701 ECD tested 1701 silicon, 25 m X 0.32mm film thickness 0.25μm. Temperature programs of both GC instruments were as follows; Initial temp 90^{0}C for 2 min; ramp (1) 20 ^{0}C /min (to 150 ^{0}C) ramp (2) 6 ^{0}C /min) to 270 ^{0}C hold for 15 min.

Dithiocarbamates analysis:

Chemicals and reagents:

- Ethanol , mass concentration of at least 95%
- Diethanolamine, at least 98% of mass concentration.
- Hydrochloric acid, concentrated 95%.
- Toluene concentration 99.9%.
- Carbon disulphide, colorless, mass concentration of least 99%. If stored at -20°C it is stable for 2 years to 3 years.
- Anhydrous sodium sulphate (Riedel Haen)
- Sodium hydroxide, (Na OH)= 100 g/l
- Copper (II) acetate monohydrate 98%,
- Tin (II) chloride dehydrates, ($Sn\ Cl_2$ .2 H2O) = 40 g/100 ml in conc. HCl acid.

- Sodium diethyl dithiocarbamate not less than 95%

Methodology:

Dithiocarbamate fungicides were determined by the spectrophotometric determination of the cupric complex formed with the CS2 evolved from the acid decomposition of dithiocarbamates in the presence of stannous chloride as a reducing agent using either the in-series-2 trap reaction system (Cullen, 1964; Keppel, 1971). The solution of the complex formed from the reaction between CS_2 and the copper (II) acetate monohydrate was measured at 435 nm in spectrophotometer UV (double beam Unicam SP 1800). The results are expressed in mg CS_2/kg.

RESULTS AND DISCUSSION

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

A total of 225 samples of different types of fruits and vegetables were analyzed for 80 pesticide residues. Eleven types of vegetable crops were analyzed (i.e. Molokhia, cauliflower, cucumber, eggplants, g. beans, g. peas, lettuce, pepper, potatoes, Squash and tomato), eleven types of fruits (apple, apricot, watermelon, banana, grape, cantaloupe, guava, strawberry, orange, peach, and mango) and four types of leafy vegetables(watercress, spinach, Molokhia, g. leaf). All samples were examined for residues of 80 pesticides listed in Table 1. The detected pesticides, minimum, maximum, mean detected levels, numbers and percentages of violated samples are shown in Table 2. The MRLs of Codex Alimentarius were used for comparison when those limits were available. In the absence of Codex MRLs, European limits were used.

Overall, 57.3% of the samples were free from any detectable pesticide residues, however, 39.1% contained detectable residues, of which 3.6% contained residues that exceeded maximum residue limits (MRLs). Watermelon, banana, mango, cauliflower and potatoes samples were free from pesticide residues. Fig (1) showed that the percentage of the free samples in the vegetables was higher than that in the leafy vegetables. However, the lowest percentage was in the fruits. Results showed that vegetables recorded the highest contamination percentage without exceeding of the levels of MRL' (i.e.53.2%), followed by the fruits (i.e. 50.7%), and leafy vegetables had the lowest percentage (i.e. 29.8%). Also, results showed that the leafy vegetables recorded the highest violation % (i.e. 8.5%), followed by fruits (i.e. 2.4%) and vegetables (i.e. 0.01%).

Fruits :

A total of 69 fruit samples were subjected to residues analysis. Results showed that 46.4% of all fruit samples analyzed were free from any residues. Only 3 samples of this contaminated samples contained levels of residues exceeded the established MRL's. All banana, mango and watermelon samples were free from any residues.

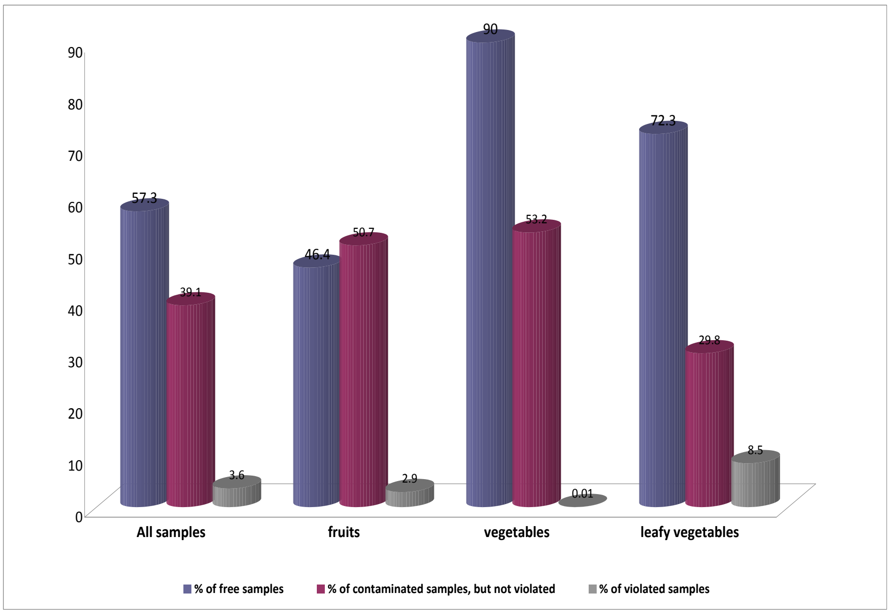

Figure (1): The contamination and the violation percentages in the different types of vegetables and fruits collected from Egyptian local markets during 2010.

Table (2) and Figure (1), showed that 46.4% of all fruit samples analyzed were free from any residues. However, 50.7% of samples were contaminated with detectable amount of pesticide residues without exceeding MRL's while 2.9% of fruit samples analyzed contained levels of residues exceeded the MRL's for each detected pesticide. The violated samples were apricot and grape. The violated compounds were cypermethrin and dithiocarbamates.

Vegetables:

A total of 156 samples of different types of vegetables were subjected to analysis. Data showed that 90% of all samples were free from any pesticide residues. However, 53.2% of samples contained detectable levels of pesticides residues, but without exceeding of MRL established for established for each pesticide. Results showed that 8.6% of samples contained residues at levels above their established MRL's. The violated vegetables were lettuce, Molokhia and watercress. The violated compounds were Chlorpyrifos (4 samples).

Vegetables recorded the highest contamination percentage and also, followed by fruits and finally leafy vegetables; it had the highest violation %. These were in contrary with data represented by Mona A. Khorshed (2012) who found that in monitoring data 2008 leafy vegetables were the highest contaminated with pesticide residues followed by vegetables and finally fruits.

In addition, processing treatments such as washing, dipping. peeling, canning, or cooking that most foods receive before consumption are very important factors leading to a decrease in the levels of show that root vegetable samples had the lowest contamination rate, with none exceeding the MRLs Dogheim *et. al*., (2001).

Fig (2) showed the frequency numbers of the pesticide residues detected in the samples. The highest frequently detected pesticide was dithiocarbamates which detected in 87 samples, followed by lambada-cyhalothrin which detected in 21 samples, profenofos (i.e. 17 samples), ethion detected in 12 samples whereas, cypermethrin and fenopropathrin each detected in 10 samples, and the Chlorpyrifos detected in 8 samples, chloropyrifos methyl detected three times, dimethoate,,diniconazole, dicofol and fenarimol detected two times. However, the lowest frequently detected pesticides, which detected only one time were phenothoate, penconazole, malaoxone, permethrin, imazalil, iprodione, diazinon, and diflufenican.

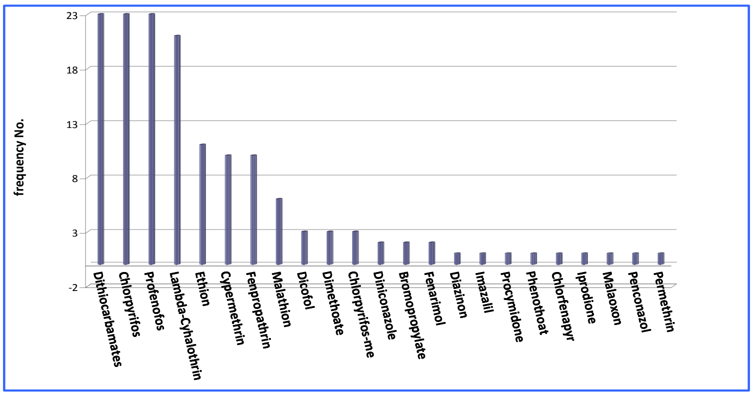

Figure (2): Frequency numbers of residues found over all concentration ranges in fruit and Vegetable samples collected from Egyptian local markets during 2010.

The percentage of contaminated samples with residues of □12 pesticides are listed in Fig (3), results showed that 2.2% of all samples analyzed, contained residues of 12 pesticides, 5.3% contained residues of 11 pesticides, 3.1% contained residues of 10 pesticides, 2.22% contained residues of 9 and 8 pesticides, 3.6% contained residues of 7 pesticides, 5.3% contained residues of 6 pesticides, 4% contained residues of 5 pesticides, 1.3% contained residues of 4 pesticides, 2.7% contained residues of 3 pesticides, 7.6% contained residues of 2 pesticides and 1.8% contained residues of one pesticides Multiple residues are expected on fruits and vegetables because various classes of pesticides must be alternated to prevent resistance from developing in pests. In addition to this reason for multiple residues justified by agricultural practices, other possible reasons for the occurrence of multiple residues are residues resulting from uptake via soil in cases where pesticides have high persistence in soil; contamination during storage; mixing of lots which were treated with different pesticides, either during the sampling or in the course of sorting the commodities; residues resulting from spray drift from neighboring plots or cross contamination in the processing of crops (e.g. by washing practices) (EFSA,2010)

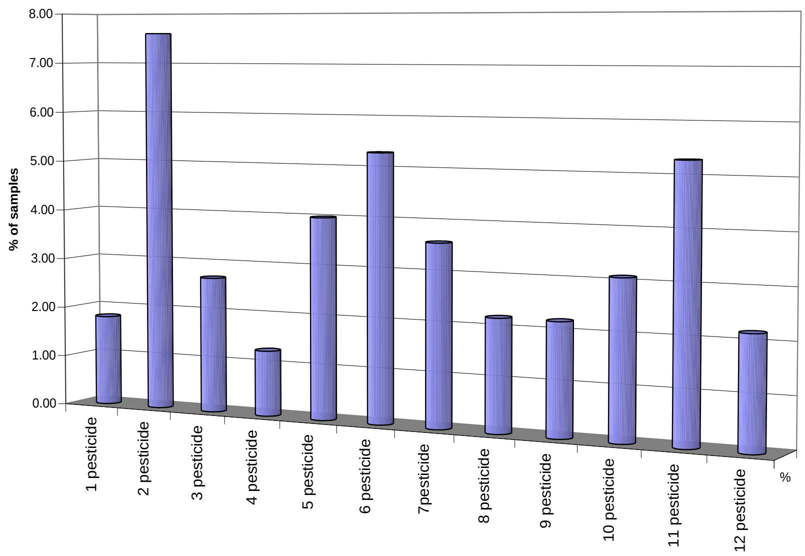

Figure (3): The percentage of samples with residues pesticides

Dietary exposure and dietary risk assessment:

Dietary exposure assessment is defined by Codex Alimentarius as "the qualitative and/or quantitative evaluation of the likely intake of chemical agents via food as well as exposure from other sources, if relevant" (FAO 2006). Exposure is basically a function of the amount of consumed food and the concentration of the chemical (e.g. pesticide residue concentration) and can be expressed by the following equation:

Dietary exposure = Σ (residue concentration x *food consumption)Body weight*

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

The estimation of the exposure to pesticide residues in the Egyptian population was performed, using recent residue data generated by the monitoring program (2010) and food consumption data obtained from GEMS food consumption (cluster C, 2006) data, C, in kg/day/ body weight, based on a 60 kg person (WHO, 1997). The calculated Theoretical Acceptable Daily Intake TADI's were compared with the acceptable daily intake for the compounds, ADI (Codex, 2010), and expressed as % ADI.

% ADI = (TMDI / ADI) X 100

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

As shown by the results in table (3), the intake of pesticide residues does not exceed the ADI in any case. The estimated exposure ranges from 0.00028% of the ADI for the profenofos on lettuce to 14.6%% of the ADI for the ethion on tomato.

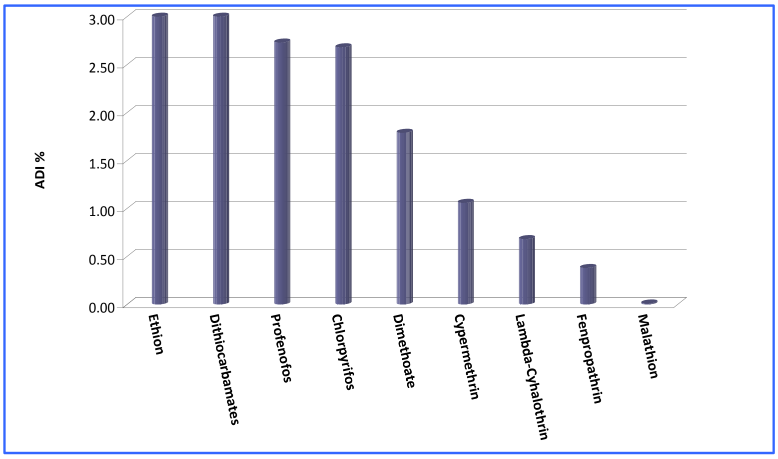

Figure (5): Total intake of selected pesticides calculated in % of the ADI

Fig (5), demonstrated that the total intake of ethion was higher than that of dithiocarbamates, followed by profenofos, chloropyrifos, dimethoate, cypermethrin, lambada-cyhalothrin, fenopropathrin and malathion. This is due to their wide range of using on fruits and vegetables to control a wide range of the diseases. While all of them still below 15% of the ADI for all pesticides.

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

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

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

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

Because the residual build up of a pesticide is so long-term, it's difficult to prove it's happening, but many Egyptian people prefer not to risk exposure to pesticides.

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

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

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

Conclusion:

From the calculated data of risk exposure according to monitoring of pesticide residues in Egyptian fruits and vegetables all the contaminated samples including that exceeded MRL was about 15% of the Acceptable Daily Intake (ADI) which insure that no risk will be found from consuming these types of fruits and vegetables.

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دراسات على تقصى و مدى التعرض للخطر لبعض متبقيات المبيدات فى الخضراوات و الفاكهة المصرية

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المعمل المركزى لتحليل متبقيات المبيدات و العناصر الثقيلة فى الأغذية. مركز البحوث الزراعية- الدقى- وزارة الزراعة- مصر

تم عمل دراسة لتقصى متبقيات المبيدات فى مصر سنة 2010 فتم جمع 225 عينة من الأنواع المختلفة من الفاكهة و الخضراوات من 9 أسواق محلية فى 9 محافظات. تم تحليل كل العينات لعمل تقصى ل80 مبيد. أظهرت كل النتائج ان 57.3% من العينات الكلية كانت خالية تماما من متبقيات المبيدات فى حين تم رصد 39.1 % من العينات بها متبقيات المبيدات من غير اى تعدى للحدود القصوى و كان 3.6% من العينات تحتوى عل متبقيات المبيدات متعدية للحدود القصوى. و قد وجد ان عينات البطيخ و الموز و المانجو و القرنبيط و البطاطس كانت خالية من متبقيات المبيدات. و قد سجلت الخضراوات اعلى نسبة من التلوث بمتبقيات المبيدات ولكن دون تعدى للحدود القصوى للمبيدات (53.2%) يليها الفاكهة (50.7%) ثم الخضراوات الورقية (29.8%) بينما سجلت الخضراوات الورقية اعلى نسبة من التعدى للحدود القصوى (8.5%) يليها الفاكهة (2.9%) ثم الخضراوات (0.01%). لقد أظهرت النتائج ان العينات المتعدية هى المشمش و العنب و البسلة و الخس و الملوخية و الجرجير بمبيدات السيبرميثرين و الدايثيوكاربامات. و أظهرت النتائج ان المبيدات الأكثر تواجدا فى العينات هى الدايثيوكاربامات يليها الكلوربيريفوس ثم لمبادا سيهالوثرين و برفينوفوس و إثيون و سيبرميثرين و فينوبروباثرين و ملاثيون و كلوربيريفوس- ميثيل و دايميثوات و دينيكونازول و دايكوفول و أخيرا بروموبروبيلات و كانت المبيدات الأقل تواجدا و التى تواجدت مرة واحدة فقط هى فينوثوات و ملاؤكسون و إيمازليل و بنكونازول و بيرميثرين و كلورفينبير و إبرديون و ديازينون و بروسيميدون. تم تقدير الخطر الذى يمكن ان يتعرض له المستهلك المصرى نتيجة لتناول الخضراوات و الفاكهة الملوثة عن طريق حساب التعرض اليومى لهذه المبيدات حسابيا و قد اظهرت النتائج ان المتناول اليومى من متبقيات المبيدات فى العينات الملوثة لم يتعدى المتناول اليومى المسموح به حيث وجد انه اقل من 15% من المتناول المسموح به يوميا لكل المبيدات محل الدراسة. و تراوحت نسب التعرض ما بين 0.00025% من المتناول اليومى المسموح به وذلك للملاثيون فى الملوخية و السبانخ الى 14.6% من المتناول اليومى المسموح به و ذلك للإثيون فى الطماطم.

قام بتحكيم البحث

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Table (2): Contamination samples number, contamination %, frequency, minimum, maximum and mean of pesticide residues monitored in vegetables and fruits in Egypt during 2010

Commodity	Total no. of analyzed samples	The detected pesticide	Cont. no.	Cont. %	frequency	min	max	mean	MRL	Viol. no	Viol %
Fruits: Apple	5	Chlorpyrifos	5	10.9	3	<LOQ	<LOQ	<LOQ	0.05	0	0
		Cypermethrin			1	<LOQ	<LOQ	<LOQ	-	-	-
		Dicofol			1	0.27	0.27	0.27	-	-	-
		Ethion			2	0.05	0.46	0.255	1	0	0
		Fenpropathrin			3	<LOQ	0.05	0.045	-	-	-
		L- Cyhalothrin			4	<LOQ	0.17	0.11	-	-	-
		Phenthoate			1	<LOQ	<LOQ	<LOQ	-	-	-
		Profenofos			2	<LOQ	<LOQ	<LOQ	-	-	-
		Dithiocarbamates (CS2)			5	<LOQ	0.55	0.29	3	0	0
Peach	7	Chlorpyrifos	7	15.2	2	<LOQ	0.03	0.03	1	0	0
		Chlorpyrifos -methyl			1	<LOQ	<LOQ	<LOQ	-	-	-
		Cypermethrin			3	<LOQ	0.57	0.57	1	0	0
		Dimethoate			1	0.04	0.04	0.04	3	0	0
		Diniconazole			1	<LOQ	<LOQ	<LOQ	-	-	-
		L- Cyhalothrin			4	<LOQ	0.1	0.12	-	-	-
		Malaoxone			1	<LOQ	<LOQ	<LOQ	-	-	-
		Malathion			1	0.18	0.18	0.18	-	-	-
		Profenofos			1	1.3	1.3	1.3	-	-	-
		Dithiocarbamates (CS2)			7	<LOQ	0.45	0.25	3	0	0
Strawberry	6	Chlorpyrifos	5	10.9	1	<LOQ	<LOQ	<LOQ	0.05	0	0
		Ethion			1	0.08	0.08	0.08	-	-	-
		Fenpropathrin			3	<LOQ	0.23	0.19	-	-	-
		L- Cyhalothrin			2	0.04	0.04	0.04	-	-	-
		Profenofos			1	<LOQ	<LOQ	<LOQ	-	-	-
Apricot	5	Chlorpyrifos	5	10.9	1	0.03	0.03	0.03	1	0	0
		Cypermethrin			2	<LOQ	1.3	1.3	1	1	2.2
		Ethion			1	<LOQ	<LOQ	<LOQ	1	0	0
		Fenpropathrin			1	0.08	0.08	0.08	-	-	-
		L- Cyhalothrin			3	0.03	0.14	0.07	-	-	-
		Dithiocarbamates (CS2)			4	<LOQ	1.7	5.1	3	1	2.2
Grape	7	Chlorpyrifos	5	10.9	1	0.06	0.06	0.06	1	0	0
		Cypermethrin			1	0.05	0.05	0.05	0.05	1	4.3
		Ethion			1	0.08	0.08	0.08	2	0	0
		Fenarimol			1	<LOQ	<LOQ	<LOQ	0.1	0	0
		L- Cyhalothrin			1	<LOQ	<LOQ	<LOQ	-	-	-
		Penconazole			1	0.06	0.06	0.06	0.1	0	0
		Permethrin			1	<LOQ	<LOQ	<LOQ	-	-	-
		Dithiocarbamates (CS2)			6	<LOQ	0.94	0.16	-	-	-

Table (2): Continued

Commodity	Total no. of analyzed samples	The detected pesticide	Cont. no.	Cont. %	frequency	min		max	mean	MRL	Viol. no	Viol %
Guava	3	Dicofol	2	6.5	1	0.75		0.75	0.75	-	-	-
		L- Cyhalothrin			1	<LOQ		<LOQ	<LOQ	-	-	-
orange	10	Bromopropylate	7	15.2	1	<LOQ		<LOQ	<LOQ	-	-	-
		Cypermethrin			2	<LOQ		0.05	0.03	-	-	-
		Dimethoate			1	<LOQ		<LOQ	<LOQ	5	0	0
		Imazilil			1	<LOQ		<LOQ	<LOQ	10	0	0
		L- Cyhalothrin			2	0.02		0.19	0.11	-	-	-
		Malathion			4	<LOQ		0.05	0.03	4	0	0
Cantaloupe	6	Ethion	1	2.2	1	0.29		0.29	0.29	-	-	-
Total no. of fruits	69										3	8.7
Vegetables: Cucumber	12	Chlorpyrifos	3	2.3	1	<LOQ	<LOQ	<LOQ		0.01	0	0
		Ethion			1	<LOQ	<LOQ	<LOQ		-	-	-
		Profenofos			1	<LOQ	<LOQ	<LOQ		-	-	-
		Dithiocarbamates (CS2)			10	<LOQ	0.25	0.08		2	0	0
Grape Leaves	9	Chlorpyrifos	4	3.2	2	<LOQ	0.3	0.15		0.01		
		Profenofos			2	<LOQ	<LOQ	<LOQ		-	-	-
		Dithiocarbamates (CS2)			9	<LOQ	0.37	0.17		5	0	0
Green Beans	11	Chlorfenpyr	5	4	1	<LOQ	<LOQ	<LOQ		-	-	-
		Chlorpyrifos			3	<LOQ	0.35	0.32		0.01		
		Diazenon			1	<LOQ	<LOQ	<LOQ		0.7	0	0
		Dicofol			1	0.23	0.23	0.23		5	0	0
		Diniconazole			1	<LOQ	<LOQ	<LOQ		-	-	-
		Ethion			1	<LOQ	<LOQ	<LOQ		-	-	-
		Fenarimol			1	<LOQ	<LOQ	<LOQ		-	-	-
		Fenpropathrin			1	<LOQ	<LOQ	<LOQ		-	-	-
		Iprodione			1	<LOQ	<LOQ	<LOQ		0.1	0	0
		Malathion			1	<LOQ	<LOQ	<LOQ		2	0	0
		Profenofos			1	<LOQ	<LOQ	<LOQ		-	-	-
		Dithiocarbamates (CS2)			8	<LOQ	0.31	0.12		2	0	0

Table (2): Continued

Commodity	Total no. of analyzed samples	The detected pesticide	Cont. no.	Cont. %	frequency	min	max	mean	MRL	Viol. no	Viol %
Green Peas	7	Bromopropylate	4	3.2	1	<LOQ	<LOQ	<LOQ			
		Chlorpyrifos			1	<LOQ	<LOQ	<LOQ	0.01	0	0
		Malathion			1	<LOQ	<LOQ	<LOQ	2	0	0
		Profenofos			1	0.18	0.18	0.18	-	-	-
		Dithiocarbamates (CS2)			5	<LOQ	4.3	0.93	2	1	0.8
Lettuce	10	Chlorpyrifos	2	1.6	1	0.05	0.05	0.05	0.01	1	0.8
		Profenofos			1	0.05	0.05	0.05	-	-	-
		Dithiocarbamates (CS2)			6	<LOQ	0.15	0.6	2	0	0
Pepper	13	Chlorpyrifos	8	6.3	4	<LOQ	0.04	0.02	1	0	0
		Ethion			1	0.52	0.52	0.52	-	-	-
		Fenvalerate			1	0.05	0.05	0.05			
		L- Cyhalothrin			2	0.08	0.08	0.08	-	-	-
		Procymidone			1	0.19	0.19	0.19			
		Profenofos			4	<LOQ	0.51	0.14	-	-	-
		Dithiocarbamates (CS2)			10	<LOQ	0.58	0.08	3	0	0
Spinach	6	Chlorpyrifos	1	0.8	1	<LOQ	<LOQ	<LOQ	0.01	0	0
		Dimthoate	8	6.3	1	<LOQ	<LOQ	<LOQ	5	0	0
Squash	8	Dithiocarbamates (CS2)			8	<LOQ	0.17	0.04	2	0	0
Tomato	14	Chlorfenpyr	12	9.5	1	0.03	0.03	0.03	-	-	-
		Chlorpyrifos			5	<LOQ	0.08	0.04	0.5	0	0
		Chlorpyrifos-me			2	0.05	0.2	0.13	-	-	-
		Cypermethrin			1	<LOQ	<LOQ	<LOQ	0.5	0	0
		Diflufenican			1	<LOQ	<LOQ	<LOQ	-	-	-
		Ethion			1	0.17	0.17	0.17	-	-	-
		Fenpropathrin			1	0.05	0.05	0.05	-	-	-
		Fenvalerate			1	<LOQ	<LOQ	<LOQ	0.2	-	-
		L- Cyhalothrin			1	<LOQ	<LOQ	<LOQ	0.02	0	0
		Profenofos			6	<LOQ	1.3	0.32	-	-	-
		Dithiocarbamates (CS2)			9	<LOQ	0.378	0.09	5	0	0
Molokia	8	Chlorpyrifos	2	1.6	2	<LOQ	7	3.5	0.01	1	0.8
Water cress	14	Chlorpyrifos			2	0.03	0.05	0.04	0.01	2	2.2
		Profenofos			5	<LOQ	3.4	0.72	-	-	-
Egg plant	14	Chlorpyrifos	5	4	1	<LOQ	<LOQ	<LOQ	0.01	0	0
		Ethion			2	<LOQ	<LOQ	<LOQ	-	-	-
		Fenpropathrin			1	0.07	0.07	0.07	-	-	-
		L- Cyhalothrin			2	<LOQ	<LOQ	<LOQ	-	-	-
		Profenofos			1	0.89	0.89	0.89	-	-	-
Total of vegetables	156									3	3

Table (3): Estimated dietary intake for chronic risk for those 9 pesticides, which were the highest frequently detected in the samples.

Compound	commodity	Mean conc. mg/kg	food consumption g/day	Estimated Acceptable daily intakes (EADI) mg/kg	Estimated Acceptable daily intakes (EADI) mg/kg.bw /day	Acceptable Daily Intakes (ADI) mg/kg.bw /day	Highest calculated EADI in % of the ADI
Chlorpyrifos	Apple	0.01	18.5	0.000185	0.0000030833	0.01	0.03083%
	Peach	0.03	3.3	0.000099	0.0000016500	0.01	0.01650%
	Strawberry	0.01	2	0.00002	0.0000003333	0.01	0.00333%
	Apricot	0.03	3.9	0.000117	0.0000019500	0.01	0.01950%
	Grape	0.06	27.1	0.001626	0.0000271000	0.01	0.27100%
	Cucumber	0.01	5.9	0.000059	0.0000009833	0.01	0.00983%
	Grape leaves	0.15	43.9	0.006585	0.0001097500	0.01	1.0975%
	Green beans	0.01	4.5	0.000045	0.0000007500	0.01	0.00750%
	Green peas	0.01	6	0.00006	0.0000010000	0.01	0.01000%
	Lettuce	0.05	0.1	0.000005	0.0000000833	0.01	0.00083%
	Pepper	0.02	3.2	0.000064	0.0000010667	0.01	0.01067%
	Spinach	0.01	1.1	0.000011	0.0000001833	0.01	0.00183%
	Tomato	0.03	102.8	0.003084	0.0000514000	0.01	0.51400%
	Molokhia	3.50	1.1	0.00385	0.0000641667	0.01	0.64167%
	Water cress	0.04	3.3	0.000132	0.0000022000	0.01	0.02200%
	Egg plant	0.01	12.3	0.000123	0.0000020500	0.01	0.02050%
Cypermethrin	Apple	0.01	18.5	0.000185	0.0000030833	0.02	0.01542%
	Peach	0.57	3.3	0.001881	0.0000313500	0.02	0.15675%
	Apricot	1.30	3.9	0.00507	0.0000845000	0.02	0.42250%
	Grape	0.05	27.1	0.001355	0.0000225833	0.02	0.11292%
	Orange	0.03	38	0.00114	0.0000190000	0.02	0.09500%
	Tomato	0.03	102.8	0.003084	0.0000514000	0.02	0.25700%
Ethion	Apple	0.26	18.5	0.00481	0.0000801667	0.002	4.00833%
	Strawberry	0.08	2	0.00016	0.0000026667	0.002	0.13333%
	Apricot	0.01	3.9	0.000039	0.0000006500	0.002	0.03250%
	Grape	0.06	27.1	0.001626	0.0000271000	0.002	1.35500%
	Cantaloupe	0.29	22.6	0.006554	0.0001092333	0.002	5.46167%
	Cucumber	0.01	5.9	0.000059	0.0000009833	0.002	0.04917%
	Green beans	0.01	4.5	0.000045	0.0000007500	0.002	0.03750%
	Tomato	0.17	102.8	0.017476	0.0002912667	0.002	14.5633%
	Egg plant	0.01	12.3	0.000123	0.0000020500	0.002	0.10250%

Table (3): Continued

Compound	commodity	conc. mg/kg	food consumption g/day	Estimated Acceptable daily intakes (EADI) mg/kg	Estimated Acceptable daily intakes (EADI) mg/kg.bw /day	Acceptable Daily Intakes (ADI) mg/kg.bw /day	Highest calculated EADI in % of the ADI
Malathion	Orange	0.03	38	0.00114	0.0000190000	0.3	0.00633%
	Green beans	0.01	4.5	0.000045	0.0000007500	0.3	0.00025%
Lambda-Cyhalothrin	Apple	0.11	18.5	0.002035	0.0000339167	0.02	0.16958%
	Peach	0.01	3.3	0.000033	0.0000005500	0.02	0.00275%
	Strawberry	0.04	2	0.00008	0.0000013333	0.02	0.00667%
	Apricot	0.03	3.9	0.000117	0.0000019500	0.02	0.00975%
	Grape	0.01	27.1	0.000271	0.0000045167	0.02	0.02258%
	Guava	0.01	0.6	0.000006	0.0000001000	0.02	0.00050%
	Orange	0.11	38	0.00418	0.0000696667	0.02	0.34833%
	Pepper	0.08	3.2	0.000256	0.0000042667	0.02	0.02133%
	Tomato	0.01	102.8	0.001028	0.0000171333	0.02	0.08567%
	Egg plant	0.01	12.3	0.000123	0.0000020500	0.02	0.01025%
Fenpropathrin	Apple	0.05	18.5	0.0008325	0.0000138750	0.03	0.04625%
	Strawberry	0.19	2	0.00038	0.0000063333	0.03	0.02111%
	Apricot	0.08	3.9	0.000312	0.0000052000	0.03	0.01733%
	Green beans	0.01	4.5	0.000045	0.0000007500	0.03	0.00250%
	Tomato	0.05	102.8	0.00514	0.0000856667	0.03	0.28556%
	Egg plant	0.01	12.3	0.000123	0.0000020500	0.03	0.00683%
Profenofos	Apple	0.01	18.5	0.000185	0.0000030833	0.03	0.01028%
	Peach	0.18	3.3	0.000594	0.0000099000	0.03	0.03300%
	Strawberry	0.01	2	0.00002	0.0000003333	0.03	0.00111%
	Cucumber	0.01	5.9	0.000059	0.0000009833	0.03	0.00328%
	Grape leaves	0.01	43.9	0.000439	0.0000073167	0.03	0.02439%
	Green beans	0.01	4.5	0.000045	0.0000007500	0.03	0.00250%
	Green peas	0.18	6	0.00108	0.0000180000	0.03	0.06000%
	Lettuce	0.05	0.1	0.000005	0.0000000833	0.03	0.00028%
	Pepper	0.14	3.2	0.000448	0.0000074667	0.03	0.02489%
	Tomato	0.32	102.8	0.032896	0.0005482667	0.03	1.82756%
	Water cress	0.72	3.3	0.002376	0.0000396000	0.03	0.13200%
	Egg plant	0.89	12.3	0.010947	0.0001824500	0.03	0.60817%

Table (3): Continued

Compound	commodity	conc. mg/kg	food consumption g/day	Estimated Acceptable daily intakes (EADI) mg/kg	Estimated Acceptable daily intakes (EADI) mg/kg.bw /day	Acceptable Daily Intakes (ADI) mg/kg.bw /day	Highest calculated EADI in % of the ADI
Dimethoate	Peach	0.04	3.3	0.000132	0.0000022000	0.002	0.11000%
	Pepper	0.12	13	0.00156	0.0000260000	0.002	1.30000%
	Orange	0.01	38	0.00038	0.0000063333	0.002	0.31667%
	Squash	0.01	7.3	0.000073	0.0000012167	0.002	0.06083%
Dithiocarbamates**(CS_2)**	Apple	0.29	18.5	0.005365	8.94167E-05	0.03	0.29806%
	Peach	0.25	3.3	0.000825	0.00001375	0.03	0.04583%
	Apricot	5.1	3.9	0.01989	0.0003315	0.03	1.10500%
	Grape	0.16	27.1	0.004336	7.22667E-05	0.03	0.24089%
	Cucumber	0.08	5.9	0.000472	7.86667E-06	0.03	0.02622%
	Grape leaves	0.17	43.9	0.007463	0.000124383	0.03	0.41461%
	Green beans	0.12	4.5	0.00054	0.000009	0.03	0.03000%
	Green Peas	0.93	6	0.00558	0.000093	0.03	0.31000%
	Lettuce		18.5	0.005365	8.94167E-05	0.03	0.29806%