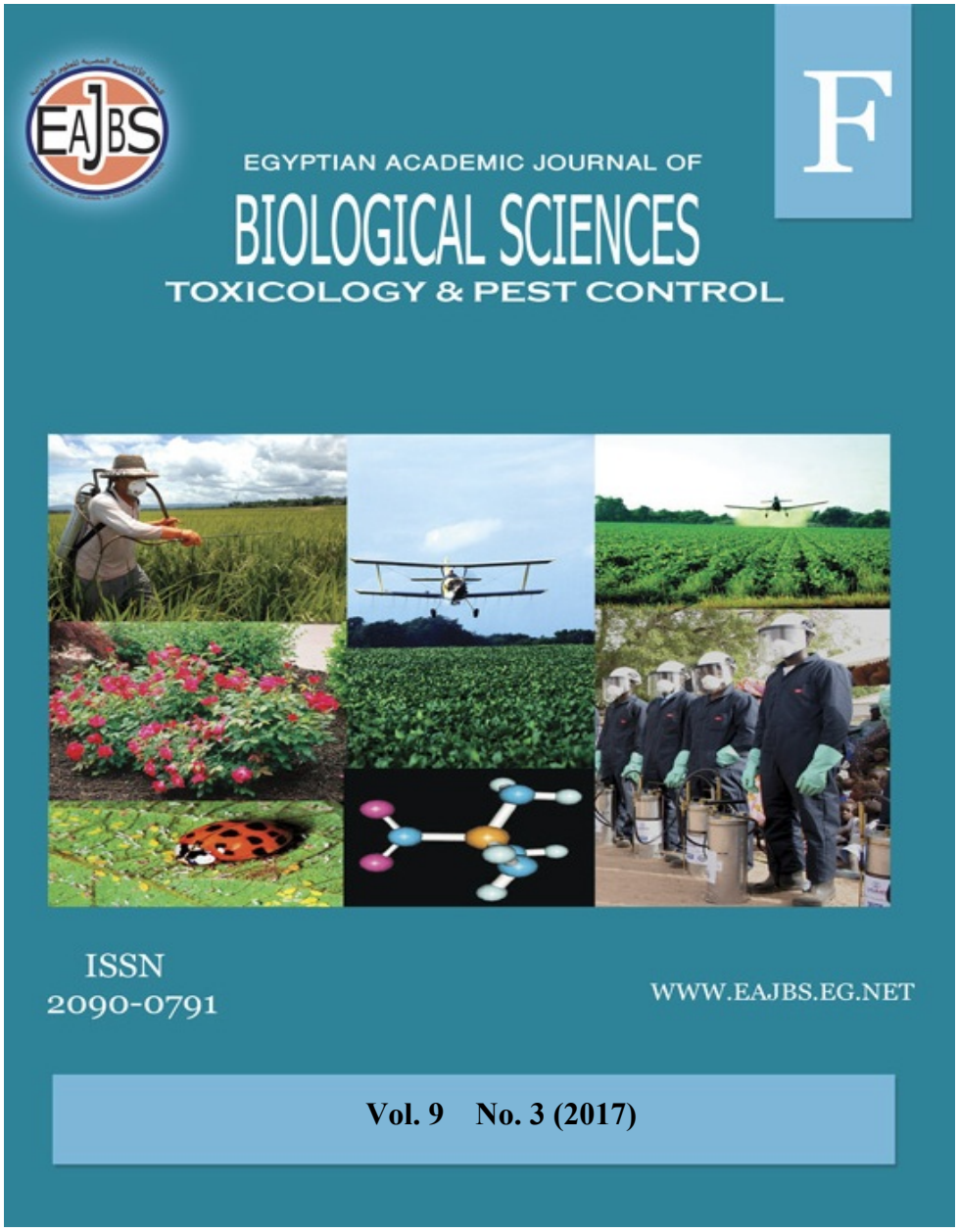

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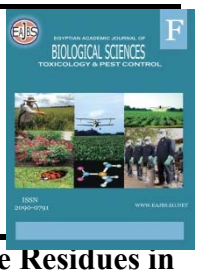

Determination of some Carbamat and Synthetic Pyrethroid Pesticide Residues in Vegetables and Fruits in Derna Market at Eastem Part of libya

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ABSTRACT

In this study, the residues of commonly used carbamate and pyrethroids pesticides in Libya, (oxamyl, bendiocarb, carbofuran, carbaryl, methomyl, thiocarb, permethrin, deltamethrin , fenvalerate, esfenvalerate , and cypermethrin) in vegetables (tomatoes, cucumber, green pepper, scald, cabbage, lettuce and squash) and fruits (grape, peach, apple and plume) were determined in different seasons (summer 2013, autumn 2013, winter 2014 and spring 2014). HPLC with UV detector was used for quantification, while the quick, easy, cheap, effective, rugged and safe (QUECERS) extraction and purification method was used to isolate the pesticides found in samples. The mean recovery ranged between 75-95% with relative standard deviations ranged between 15%-25%. Results indicated that pesticide residues were found in some monitored fruits and vegetable samples. In all, 93.71% of fruit and vegetable samples analyzed contained no detectable level of the monitored pesticides, 2.81% of the samples gave results with levels of pesticide residues above the MRL, while 4.11% of the samples showed results below the MRL. Carbofuran and oxamyl appear to have health risk associated with them while rest of tested pesticides were found to be under safe limit. The results suggested that the consumers of the eastern area of Libya are exposed to concentration of pesticides that may cause chronic diseases correlated with carbofuran and oxamyl. A future study in a longer period of time would allow obtaining a deeper knowledge about the fulfillment of vegetables and fruits produced in Libya with respect to the use of pesticides and their presence in them.

INTRODUCTION

Carbamates and Pyrethroid pesticide groups are considered the most widely used classes of agricultural pesticides to control pests also they are repeatedly applied during the entire period of growth and sometimes even at the fruiting stage (Guler *et. al*., 2010). In recent years, many studies showed that carbamates and synthetic pyrethroids have chronic effect such as mutagenic, carcinogenic, teratogenic and immune toxic (Juraske, *et al*., 2009). Many scientists have estimated the carbamate residues in various fruits and vegetables and reported the occurrence of their residues to be even equal or more than maximum residue level (MRL) values recommended by European Union (EU), World health organization (WHO) and Food and Agricultural Organization (FAO) (FAO/WHO, 2004).

For this reason, monitoring of pesticide residues in vegetables and fruits for an extensive evaluation of vegetable quality is a priority objective of pesticide research to avoid possible risks to human health.

To protect consumer's health, many countries have established legal directives to control levels of pesticides in food, through maximum residue levels, MRLs (FAO/WHO, 2004). Highly sensitive and selective analytical procedures to determine residues of these compounds in a variety of food matrices have been developed. Several multi residue methods for determination of carbamate and pyrethroids, organoph-osphorus, organochlorine, pesticides in crops using GC and HPLC for separation of individual compounds, followed by detection with selective and sensitive detectors have been proposed (Berrada *et al*., 2006). Charan *et al*. (2010) collected a total of 182 samples of six vegetables for pesticide residue analysis from different agricultural fields of central Aravalli region, when they were ready for transportation to market. The analysis of samples for different pesticide residues were carried out on GC-ECD and GC-NPD systems. Their results showed that about 40.11% of total analyzed samples were contaminated with different pesticide residues, among which 35.62% were exceeded the maximum residual limit (MRL) values. In Libya use of pesticides is not well controlled as compare to the other developed countries due to ineffective legislation, lack of awareness and in appropriate pesticide management. No data are available on the levels of pesticide residues in vegetables of local markets in Libya. Therefore, the present study was undertaken to monitor carbamate and pyrethroids residues in vegetables and fruit collected from the market located in Eastern area region of Libya (Derna) to provide back ground information on the levels of these residues in this region. It is hoped that the obtained results might exhibit more information that could help to protect the health of consumers, and facilitate international trade to ensure that pesticide residue in fruits and vegetables do not exceed maximum residues levels (MRLs).

MATERIALS AND METHOD

Sample Collection and Preparation: Derna city which located in the east of Libya vegetables markets, were selected because it considered the biggest vegetable market in the area. 500 g of each vegetable kind (tomatoes, cucumber, green pepper, scald, cabbage, squash and lettuce) were collected from six vegetable shops. The vegetable samples from each shop were brought in six packets of approximately 500 g each at each season (3kg) (summer, autumn, 2013, spring and winter 2014) (504 samples). Also a total of 198 fruit samples including (grapes, apples, plumes and peaches) were collected during the period of three seasons at summer and autumn (2013) and spring (2014) from the same markets at the same manner. The composite samples were prepared by the systematic mixing of the six packets (3kg). The samles were mixed and divided to three replicates each 1 kg. Each replicate was mixed and ground using a mixer, and 15 g composite samples from each were analyzed by HPLC after extraction.

Extraction:

The QuEChERS method which was developed by Anastassiades *et al.* (2003) and has become widely used in food safety analyses were used. 15 g of a pure mixed vegetable was weighed (Sartorius electronic GMBH balance) with 15 ml acetonitrile in a 50- mL centrifuge tube from the homogenate vegetable sample. Afterwards, 6 g $MgSO_4$ and 1.5 g of sodium acetate were added to the samples above a centrifuge tube. The centrifuge tube was mixed by vortexing for one min and centrifuged at 3700 rpm for 5 min. The aliquot of the acetonitrile phase was transferred into primary secondary amine (PSA) tube containing 125 mg PSA and 750 mg

$MgSO_4$. This centrifuge tube was vortexed for 0.5 min and centrifuged at 3700 rpm for 5 min. All aliquot was then transferred to a clean 15- mL tube and evaporated to complete dryness under a gentle stream of nitrogen at room temperature. The dry residues were reconstituted in 1 mL acetonitrile for HPLC analysis.

Chemicals and active ingredients: Acetonitrile for HPLC gradient grade 99.9 quality were purchased from Sigma Aldrich (Sigma-Aldrich. chemie Gmbh. Germany) Magnesium sulfate Anhydrous was purchased from FLUKA, Germany. Primary secondary amine (PSA) was purchased from VARIAN - (USA). Sodium-acetate from SIGMA-Germany. All active ingredient of pesticide used (oxamyl 98.8% , bendiocarb 96.0%, carbofuran 99.4%, carbaryl 99.4% , methomyl 90.0%, thiocarb 95.4%, permethrin 99.7%, deltamethrin 99.9%, fenvalerate 98.0%,esfenvalerate99.7% and cypermethrin 98.5%) were purchased from (Ridel-Haen Agseelze), Germany.

Stock solutions1-10 mg of interest pesticide (oxamyl, bendiocarb, carbofuran, carbaryl, methomyl, thiocarb, permethrin, deltamethrin, fenvalerate, esfenvalerate, and cypermethrin) were disolved in 10-mL of acetonitrile in volumetric flasks and stored at −20 °C.

Intermidiate solution (1 0µg /mL):- 1 ml of each stock solution pipet in to individual 100 ml volumetric flask.dilute to volume with acetonitrile and stored at −20 °C.

Working solutions:- 5 working standard sets were prepared using the serial dilution method for (oxamyl, bendiocarb, carbofuran, carbaryl, methomyl, thiocarb, permethrin, deltamethrin, fenvalerate, esfenvalerate , and cypermethrin (10, 1, 0.1, and 0.01 µg mL^{-1}) (Barrada *et al.*, 2006) . The standard stored at −20 °C until needed. These standards were then used as standards (i.e., for the determination limits of detection (LOD), limits of quantification (LOQ), the recovery experiment and the linearity experiment).

Preparation of blanks:-

The following vegetables and fruits were used for the spiking experiments: tomatoes, cucumber, green pepper, squash, cabbage, lettuce, scald, grape, apple, plume and peache. All vegetables and fruits were purchased from market. To avoid contamination with pesticides, the samples were extracted with acetonitrile to remove any pesticide residue and were then used as blank samples for the spiking experiments. The extracted samples were fortified with different concentrations from the pesticides and extracted with the same method and tested by HPLC.

Calculating the stander curve:

Five solutions from different concentrations of oxamyl, bendiocarb, carbofuran, carbaryl, methomyl, thiocarb, permethrin, deltamethrin, fenvalerate, esfenvalerate, and cypermethrin, (ranging from 0.00 to 10 µg/ mL) were prepared in acetonitrile using the serial dilution technique for the construction of the linear curve. Peak area and concentration were plotted to draw calibration curve using Excel program. These standard curves were used throughout the study to maintain the accuracy and precision in the sample analysis. The standard deviation and slope of the curve was calculated to all samples using regression static in excel program. LOD and LOQwere calculated as follows (Dolan, 2005)

Where SE= standard error of calibration curve b= slope of calibration curve

LOD = 3.3 *SE / b and LOQ = 10* SE/ b

LOD= limits of detection

LOQ= limits of quantification

Good sensitivity and repeatability were obtained with detection limits of 0.0017- 0.033 µg/g.

The recovery rates for most pesticides in various fruits and vegetables were 75-95% with relative standard deviations < 15%.

Mobil phase: Acetonitrile / water (80 + 2% 1 propanol/20 + 2%1propanol + 1% acetic acid, v/v) was used as the mobile phase. Colum: was C18 Dim. (mm) 250×4.6 particle UV detector: at 210 nm (for pyrothroide pesticide) and at 245nm (for carbamate detection) and the flow rate: was 1ml./min.) Kumari, B., Kumar, R., & Kathpal, T. S., 2001).

Statistical analysis: Data analysis was performed using Costat software. Pesticide data were analyzed in different vegetable samples , different seasons and locations via three -way ANOVA and LSD (The least significant difference) test at $p < 0.05$ levels) Snedecor and Cochran 1990).

RESULTS AND DISCUSSION

The mean levels of six carbamates and five pyrethroids pesticide residues in vegetables samples collected from Derna markets during summer seasons are presented in Table (1). Data showed that oxamyl was detected in squash with concentration 0.02 mg\kg^{-1} and it was less than MRL values, bendiocarb was monitored only in lettuce with concentration 0.03 mg/kg^{-1} and not exceeded the maximum residues limit (MRL) values, thiocarb was monitored in scald and was also less than MRL values.

While carbofuran was detected in the cabbage samples with concentration 0.01 mg/kg^{-1} equal to the value of MRL (0.01mg/kg^{-1}).

Table 1: Residues of different carbamate and pyrethroid pesticides in different vegetables collected from Derna markets during summer 2013 season with MRL.

Pesticides	Tomato		cucumber		Pepper		Squash		Lettuce		cabbage		Scald	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
Oxamyl	ND	0.01	0.01	0.01	ND	0.02	ND	0.03	0.02	0.01	ND	0.01	ND	0.01
Bendiocarb	ND	0.02	ND	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05
Carbofuran	ND	0.01	0.04	0.01	ND	0.01	ND	0.01	ND	0.01	0.05	0.01	ND	0.02
Carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01
Methomyl	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Thiocarb	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Permetrin	ND	0.05	ND	0.05	ND	0.05	ND	0.05	0.004	0.05	ND	0.05	ND	0.05
Deltametrin	ND	0.3	ND	0.2	ND	0.2	ND	0.2	ND	0.5	ND	0.5	ND	0.5
Fenalerata	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Esfenalerate	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Cypermethrin	ND	0.5	ND	0.2	ND	0.5	0.004	0.05	ND	2	ND	2	ND	2

(PPM): Part Per Million
(MRL): Maximum Residue Level

Analysis of vegetable samples from Derna market showed that only 5.19 % from the samples were contaminated with carbamated pesticides and less or equal of MRL values and 94.8% from the samples were free from carbamate and pyrethroid residues (non detected). All vegetable samples from Derna market in this season were free from synthetic pyrethroids and within limit of detection (LOD). Data presented in Table (2) show the results of residues of tested carbamate and pyrethroid insecticides in different vegetables collected from Derna markets during autumn seasons2013. Results showed that from all analyzed samples 92.21% were free from pesticides (not detected) and 7.79 % from the samples were contaminated and among of them two samples (2.59%) were found above the MRLs. Two carbamate insecticides were found in cucumber (Oxamyl and Carbofuran) and in lettuce (Oxamyl and Permethrin from pyrethroids) while for squash and cabbage were contaminated

with only one insecticide. Results also indicated that samples of tomatoes, pepper and scald were not contaminated with any of tested pesticides. Oxamyl was detected in cucumber and lettuce at concentration 0.01 and 0.02 mg/kg^{-1} respectively, Carbofuran was detected in cucumber and cabbage with concentration 0.04 and 0.05mg/kg^{-1} respectively with uper maximum residues limits (MRL). From synthetic pyrethroids only cypermethrin in squash and permethrin in lettuce were detected with concentration less than MRL.

Table 2: Residues of Carbamate and Pyrethroid pesticides in vegetables collected from Derna market during Autumn 2013 season with MRL.

Pesticides	Tomato		cucumber		Pepper		Squash		Lettuce		cabbage		Scald	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
Oxamyl	ND	0.01	0.01	0.01	ND	0.02	ND	0.03	0.02	0.01	ND	0.01	ND	0.01
Bendiocarb	ND	0.02	ND	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05
Carbofuran	ND	0.01	0.04	0.01	ND	0.01	ND	0.01	ND	0.01	0.05	0.01	ND	0.02
Carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01
Methomyl	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Thiocarb	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Permetrin	ND	0.05	ND	0.05	ND	0.05	ND	0.05	0.004	0.05	ND	0.05	ND	0.05
Deltametrin	ND	0.3	ND	0.2	ND	0.2	ND	0.2	ND	0.5	ND	0.5	ND	0.5
Fenalerata	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Esfenalerate	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Cypermethrin	ND	0.5	ND	0.2	ND	0.5	0.004	0.05	ND	2	ND	2	ND	2

(PPM): Part Per Million
(MRL): Maximum Residue Level

Carbamate and pyrethroid pesticide residues in vegetables were found from Derna markets during winter season. Data presented in Table (3) show the result of analysis of vegetable samples collected from Derna markets during winter season 2014 indicated that oxamyl was determined in the quantity of 0.006 mg/kg^{-1} in lettuce samples. Carbofuran was determined in the quantity of 0. 07 mg/kg^{-1} in squash samples and exceeded MRL values in the both two crops.

Table 3: Carbamate and Pyrethroid pesticides residues in vegetables from Derna during winter season 2014 and their MRL valuse

Pesticides	Tomato		cucumber		Pepper		Squash		Lettuce		cabbage		Scald	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
Oxamyl	ND	0.01	ND	0.01	ND	0.02	ND	0.03	0.006	0.01	ND	0.01	ND	0.01
Bendiocarb	ND	0.02	ND	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05
Carbofuran	ND	0.01	ND	0.01	ND	0.01	0.07	0.01	ND	0.01	ND	0.01	ND	0.02
Carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01
Methomyl	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Thiocarb	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Permetrin	ND	0.5	ND	0.05	ND	0.05	ND	0.05	0.004	0.05	ND	0.05	ND	0.05
Deltametrin	ND	0.3	ND	0.2	ND	0.2	ND	0.2	ND	0.5	ND	0.5	ND	0.5
Fenalerata	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Esfenalerate	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Cypermethrin	ND	0.5	ND	0.2	ND	0.5	ND	0.2	0.002	2	ND	2	ND	2

(PPM): Part Per Million
(MRL): Maximum Residue Level.

From synthetic pyrethroids only cypermethrin was detected in Lettuce with concentration 0.002 mg/kg^{-1} which not exceeded the maximum residue limits

MRL (FAO / WHO 2004). In general only three samples were found contaminated with one or more from tested pesticides.

Among all samples carbofuran was found above MRL in squash. From all the analyzed samples there were 97.1% free from tested carbamate and synthetic pyrethroids and 3.89 % were found contaminated where 1.29% of these exceeded MRLs. Carbamate and pyrethroid pesticide residues in vegetables during spring season 2013 were shown in Table (4). All tested pesticides were not detected in samples of tomatoes, pepper, squash, cabbage, and scald while cucumber was contaminated with oxamyl and cypermethrin at concentration of 0.01 and 0.008 mg / kg^{-1} and the residues of oxamyl was equal to the value of MRL in cucumber. Samples of lettuce were contaminated with bendiocarb with concentration of 0.1 mg / kg^{-1} and exceeded the value of MRL limit. From all samples only 3.89 % were contaminated and 96.1% from the samples were free from tested pesticides where 2.59 % from the sample were more or equal to MRLs values.

Table 4: Carbamate and Pyrethroid pesticides residues in vegetables from Derna during spring season 2014 and their MRL valuse

Pesticides	Tomato		cucumber		Pepper		Squash		Lettuce		cabbage		Scald	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
Oxamyl	ND	0.01	0.01	0.01	ND	0.02	ND	0.03	ND	0.01	ND	0.01	ND	0.01
Bendiocarb	ND	0.02	ND	0.05	ND	0.05	ND	0.05	0.1	0.05	ND	0.05	ND	0.05
Carbofuran	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.02
Carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01	ND	0.01
Methomyl	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Thiocarb	ND	0.1	ND	0.1	ND	0.2	ND	0.1	ND	0.3	ND	0.3	ND	0.3
Permetrin	ND	0.05	ND	0.05	ND	0.05	ND	0.05	0.004	0.05	ND	0.05	ND	0.05
Deltametrin	ND	0.3	ND	0.2	ND	0.2	ND	0.2	ND	0.5	ND	0.5	ND	0.5
Fenalerata	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Esfenalerate	ND	0.1	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02
Cypermethrin	ND	0.5	0.008	0.2	ND	0.5	ND	0.2	0.002	2	ND	2	ND	2

(PPM): Part Per Million
(MRL): Maximum Residue Level

A total average of the concentrations of different pesticide residues was computed using analysis of variance and costat programme (Tables 5 and 6). It was observed that carbofuran has the highest contaminant in all the season. Bendicarb and methomyl shows lowest contamination in summer and autumn seasons. In winter the lowest contamination has been found with Methomyl, Oxamyl and Bendicarb. Based on the results of analysis of variance all seasons, maximum contamination was found in winter vegetables followed by spring vegetables while it was minimum in autumn season. The probable reason of higher residues in winter may have been due to low temperature and short day lengths where these compounds may be photodegredaded with temperature and light. In autumn season the lowest contamination may be attributed to the washing out of the external surfaces of vegetables due to rain and arise of temperature like summer. Another reason of higher residues in winter and spring may have been due to these vegetables comes from greenhouses in the winter where vegetables were treated repeatly with pesticides specially systemic pesticides like carbofuran and oxamyl to control sucking pests which infested crops in green houses (Barkat *et al*.,

2012) and these insecticides can be used to control nematodes pests with high concentration (Kumari, *et al*., 2001). Similar results were reported for pesticide contamination in different season by Bhanti and Taneja (2005). Low-level pesticides contaminations in summer vegetables as shown in the present study were also reported by Kumari *et al.* (2001).

Table 5: Analysis of variance of different seasons and different vegetables crops residues of Carbamates

Source of variance		Average of residual PPM	F value	No. of samples
Seasons	Spring	0.00063	1.438ns	105
	Summer	0.00008		105
	Autumn	0.000047		105
	Winter	0.00073		105
Vegetables	Tomato	0.000066	1.172ns	60
	Pepper	0.0001		60
	Squash	0.00061		60
	cucumber	0.000103		60
	cabbage	0.000066		60
	Scald	0.0		60
	Lettuce	0.00079		60

Table 6: Residues of Carbamate and synthetic Pyrethroids in fruits collected from Derna markets during summer 2013 with the values of MRL.

Pesticide	Grape		Apple		plume		peaches	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
oxamyl	ND	0.01	0.03	0.01	ND	0.01	ND	0.01
bendiocarb	ND	0.02	0.02	0.02	0.02	0.02	ND	0.02
carbofuran	ND	0.01	ND	0.01	ND	0.01	ND	0.01
carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01
methomyl	ND	0.5	ND	0.2	ND	0.5	ND	0.2
thiocarb	ND	0.5	ND	0.2	ND	0.5	ND	0.2
permethrin	ND	0.05	ND	0.05	ND	0.05	ND	0.05
deltamethrin	ND	0.2	ND	0.2	ND	0.1	ND	0.1
Fenvalerate	ND	0.3	ND	0.1	ND	0.2	ND	0.2
esfenvalerate	ND	0.3	ND	0.1	ND	0.2	ND	0.2
cypermethrin	ND	2	ND	1	0.007	2	0.001	2

(PPM): Part Per Million
(MRL): Maximum Residue Level

From these results it can be observed that level of contamination of vegetables with Carbamate are less than MRL in majority of consumed vegetables in eastern Libya except carbofuran, thiocarb and oxamyl. The average residue concentrations of different pesticides in vegetables of different seasons (winter, autumn, spring, and summer) are summarized in Tables (5and 6). It is obvious that scald, cabbage and lettuce were contaminated with Carbufuran, Oxamyl, Thiocarb and Cypermethrin abve MRL values. We observed that the leafy vegetables could be considered a source of contamination more than the other vegetables. Carbofuran, Oxamyl and Thiocarb have the highest contamination in all the season. Bendicarb, carbaryl and methomyl and synthetic pyrethroids have the lowest contamination levels in summer, autumn, spring and winter. The low contamination of synthetic pyrethroids may be due to their broken by sunlight and the atmosphere in one or two days Metcalf (2002).

Farag *et al*. (2011) analyzed one hundred thirty two samples of fruits, vegetables, herbs and spices collected from Egyptian local markets for pesticide residues. Contamination with pesticide residues reached 54.55% while samples free from contamination were 45.45%. Only one sample from 132 analyzed samples was more than the Maximum Residue Limits (MRLs).

Carbamates and pyrethroids pesticides residues in fruits collected from Derna markets during summer 2013 are shown in Table (7). Results indicated that from all tested samples 88.64 % were not contaminated and 11.36 % were contaminated and from these samples 6.81% exceeded or were equal to MRLs limits. Oxamyl was detected in apple with concentration of 0.03 mg\kg^{-1} and it was high than MRL value. Bendiocarb was detected in apple and plume with concentrations of 0.02 mg\kg^{-1} in both and equal to MRL values while only cypermethrin was found in peaches and plume at 0.001and 0.007 mg\kg^{-1} respectively, and were less than MRL value.

Residues of carbamate and pyrethroid pesticides in fruits from Derna Markets during autumn season 2013 are shown in Table (8). It was observed that only thiocarb was detected in apple and plume at concentration of 0.08 and 0.03 mg\kg^{-1} respectively. Among pyrethroids, cypermethrin only was detected in apple and plume at concentration of 0.003 and 0.002 mg\kg^{-1}, respectively. From all analyzed samples all in this season 90.9 % were found not contaminated while 9.09% were contaminated but not exceeded MRL value.

Table 7: Residues of Carbamate and synthetic Pyrethroids in fruits collected from Derna markets at autumn 2013 with their MRLs values.

Pesticide	Grape		Apple		plume		Peache	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
oxamyl	ND	0.01	ND	0.01	ND	0.01	ND	0.01
bendiocarb	ND	0.02	ND	0.02	ND	0.02	ND	0.02
carbofuran	ND	0.01	ND	0.01	ND	0.01	ND	0.01
carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01
methomyl	ND	0.50	ND	0.2	ND	0.5	ND	0.2
thiocarb	ND	0.50	0.08	0.2	0.03	0.5	ND	0.2
permethrin	ND	0.05	ND	0.05	ND	0.05	ND	0.05
deltamethrin	ND	0.20	ND	0.2	ND	0.1	ND	0.1
Fenvalerate	ND	0.30	ND	0.1	ND	0.2	ND	0.2
esfenvalerate	ND	0.30	ND	0.1	ND	0.2	ND	0.2
cypermethrin	ND	2.00	0.003	1	0.002	2	ND	2

Table 8: Residues of Carbamate and synthetic Pyrethroids in fruits collected from Derna markets at spring 2014 with their MRLs values.

Pesticide	Grape		Apple			Plume	Peache	
	PPM	MRL	PPM	MRL	PPM	MRL	PPM	MRL
oxamyl	ND	0.01	ND	0.01	ND	0.01	ND	0.01
bendiocarb	ND	0.02	ND	0.02	0.04	0.02	ND	0.02
carbofuran	ND	0.01	ND	0.01	ND	0.01	0.07	0.01
carbaryl	ND	0.01	ND	0.01	ND	0.01	ND	0.01
methomyl	ND	0.50	ND	0.2	ND	0.5	ND	0.2
thiocarb	ND	0.50	ND	0.2	ND	0.5	ND	0.2
permethrin	ND	0.05	ND	0.05	ND	0.05	ND	0.05
deltamethrin	ND	0.20	ND	0.2	ND	0.1	ND	0.1
Fenvalerate	ND	0.30	ND	0.1	ND	0.2	ND	0.2
esfenvalerate	ND	0.30	ND	0.1	ND	0.2	ND	0.2
cypermethrin	ND	2.00	ND	1	ND	2	ND	2

Residues of Carbamate and pyrethroid pesticides in fruits during spring season 2013are shown in Table (9). Residues were found in plume with Bendiocarb at 0.04 mg/kg^{-1} and in peaches at 0.07 mg/kg^{-1} which exceeded MRLs values. From all tested samples at this season 95.46% were not contaminated and 4.54 % were contaminated and exceeded MRLs limits. The probable reason of lowest residues in summer and spring may have been due to increasing of temperature and long photoperiod which had a significant effect on degradation of these pesticides. Similar results were reported for by Kumari *et al.* (2001). In majority of the cases, pesticides concentrations found in our study were below the Maximum Residue Limits (MRL) set by the European Union legislation (EU-Pesticides Database, 2009). The pesticides found in fruits more than MRL., values were Carbofuran in grapes, Bendiocarb in plums and Thiocarb and Oxamyl in apples. These insecticides are common known to control nematode pests, Lepidopteran and sucking insects.

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RABIC SUMMERY

رصد متبقيات بعض مبيدات الكاربامات والبيروثريدات الصناعية في الفاكهة والخضر في منطقه درنه شرق ليبيا

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اجريت هذه الدراسه لرصد متبقيات بعض المبيدات المستخدمه في ليبيا oxamyl, bendiocarb, carbofuran) carbaryl, methomyl, thiocarb, permethrin, deltamethrin , fenvalerate, esfenvalerate , and cypermethrin) على بعض الخضر (طماطم، خيار، فلفل، فيورى ، لفه، الكوسه) وبعض من الفاكهه (العنب، خوخ، تفاح، وعوينه) الموجوده في الأسواق في مناطقه درنه شرق ليبيا في المواسم المختلفة ومقارنتها بالحدود القصوي للمتبقيات المسموح بها عالميا. وذلك باستخدام جهاز الكروماتوجرافي السائل العالي الأداء HPLC المزود الاشعه تحت البنفسجيه وتم إجراء الاستخلاص والتنقية بطريقة QuEChERS، واستخدام طريقة التقدير المتعدد للمتبقيات multiresidues وكانت قدره الكشف للجهاز ما بين٠.٠٠٣٣-٠.٠٠٧ mg|kg وكانت نسبه الاسترجاع ٧٥-٩٥ % . اوضحت النتائج ان العينات التي تم جمعها من درنة في صيف ٢٠١٣ ان % ٩٣.٧١ من العينات خالية من متبقيات المبيدات في حدود التقدير . بينما أظهرت نتائج فصل الخريف ٢٠١٢ أن ٩٢.٢١ ٪ كانت خالية من متبقيات المبيدات المختبرة وان ٢.٨١% وان ٤.١١% من العينات كانت ملوثه باقل من الحدود القصوى للمتبقيات المسموح بها. وبنا على نتائج تقدير مخاطر السميه فان مركبى الكابوفيوران ولاكسميل يبدو ان لهم مخاطر صحيه بينما باقى المركبات لازالت تحت الحدود القصوى المسموح بها وبنا على هذه النتائج يجب رصد كافه متبقيات المبيدات في معظم السلع الغذائيه لكى نستطيع حمايه المستهلكين من اخطار هذه المركبات السامه وعليه نوصى بتعميق هذه الدراسات لوقت اطول فى الخضر والفاكهه لكى نحصل على معلومات وافيه تساعدنا على معرفه المتبقيات بها.