

**MONITORING OF PESTICIDAL RESIDUES IN  
CERTAIN COMPONENTS OF AGRO ECO-SYSTEM  
IN KALUBIA GOVERNORATE**

**BY**

***KHALED ABD EL-AZIZ MOHAMED***

**B. Sc. Agriculture (pesticides)**

**Ain Shams University, 1984**

**M. Sc. Agriculture (pesticides)**

**Ain Shams university, 1990**

**A thesis submitted in partial fulfillment  
of the requirements for the degree of**

**DOCTOR of PHILOSOPHY**

**in**

**Agricultural Science**

**"Pesticides"**

**Department of Plant Protection**

**Faculty of Agriculture**

**Ain Shams University**

**1995**







Approval sheet

**Monitoring of pesticidal residues in  
certain components of Agro-ecosystem  
in Kalubia governorate**

by:

Khaled Abd El-Aziz Mohamed

B. Sc. Agriculture (Pesticides)  
Ain Shams University, 1984

M. Sc. Agriculture (Pesticides)  
Ain Shams University, 1990

This thesis for Ph. D. degree has been approved by:

Prof. Dr.: A. M. Marei ..... *A. M. Marei*  
Prof. of Pesticides Chemistry and Toxicology.  
Alexandria University

Prof. Dr.: A. S. H. Kansouh ..... *A. S. H. Kansouh*  
Prof. of Pesticides Chemistry and Toxicology.  
Ain Shams University

Prof. Dr.: A. A. Selim ..... *A. A. Selim*  
Prof. of Pesticides Chemistry and Toxicology.  
Ain Shams University (Supervisor)

Date of examination: *6/9/1995*  
*wed.*



**Monitoring of pesticidal residues in certain components  
of agro- ecosystem in Kalubia governorate.**

*By*

**Khaled Abd El-Aziz Mohamed**

*B.Sc. Agric (Pesticides) Ain Shams University 1984.*

*M.Sc. Agric (Pesticides) Ain Shams University 1990.*

**Under the supervision of :**

**Prof. Dr. A.A.Selim** -----

Prof. of Pesticides Chemistry and Toxicology.

**Prof. Dr. Z.H.Zidan.** -----

Prof. of Pesticides Chemistry and Toxicology.

## **ABSTRACT**

Khaled Abd El-Aziz Mohamed . Monitoring of pesticidal residues in certain component of agro-ecosystem in Kalubia Governorate. Unpublished Doctor of Philosophy dissertation , University of Ain Shams Faculty of Agriculture, Department of Plant Protection: 1995.

Residues of certain organophosphorus and synthetic pyrethroid insecticides on vegetables under plastic house conditions were studied. The initial deposit, degradation behaviour and pre harvest interval (PHI) of the tested insecticides were the criteria of concern. As for  $t_{1/2}$ 's (residue half lives), fenpropathrin, fenitrothion, malathion and pirimiphos-methyl insecticides showed  $t_{1/2}$ 's of (4.326, 3.839, 3.640 and 2.318 days), (6.026, 5.680, 5.372 & 3.960 days) & (6.143, 6.021, 5.457 & 4.559 days) on cucumber, pepper and tomato fruits, respectively. The corresponding calculated PHI were [ $>14$ ,  $>14$ , 4.40 & 7.50 days], [6.40,  $>14$ , 12.75 & 8.80 days] & [8.85, 12.00, 3.30 & 7.85 days] for the same insecticides on treated vegetables, respectively. Also distribution of isoprothiolane (Fuji-one) fungicide residue in an agro eco-system of paddy rice was studied and data indicated that the majority of isoprothiolane deposits were found on rice leaves and surrounding soil. Negligible residues was found in the other components of rice agro-ecosystem especially sediment and irrigation water. Drainage water was found free of fungicide residues within all experimental intervals. At harvest, rice grain contained very low residues of the fungicide. In addition monitoring of insecticide residues in soil, drainage water, milk, cheese, bee honey and certain edible vegetables and fruits in market basket was carried out. Data indicated presence of insecticidal residues of different

chemical groups, especially organochlorine as major contaminants and organophosphorus, carbamate and synthetic pyrethroids as minors. Organochlorine insecticides were detected in soil, milk, cheese samples, while no or traces monitored in drainage water samples. Bee honey samples were found free of some chlorinated hydrocarbons. In general, the presence of these compounds was found to be less than the maximum residues limits (MRL's). On the other hand O.P's in general were not detected in soil and drainage water system, with few exceptions. Chlorpyrifos-ethyl and fenitrothion were detected in some soil samples at certain periods. Bee honey samples contained malathion . In addition O.P's residues were found contaminating milk and cheese samples. As for synthetic pyrethroids, fenvalerate was detected in soil samples and fluvalinate was detected only in honey samples. Carbamate insecticides carbaryl and methomyl were detected in one of the analyzed soil samples. Market basket survey of vegetable and fruit samples indicated the presence of organochlorine, organophosphorus, carbamate and pyrethroid compounds at different levels higher than MRL's in certain cases which is of much concern. Decontamination of insecticidal residues from vegetables and fruits through laboratory processing indicated that certain technological treatments could free vegetables of insecticidal residues.

#### Key words:

Monitoring - Decontamination - Pesticidal residues - Soil - Drainage water- Milk- Dairy products- Bee honey - Vegetables - Fruits- Kalubia governorate.

\*\*\*\*\*





## ACKNOWLEDGMENT

This work has been carried out at Department of Plant Protection, Faculty of Agriculture, Ain Shams University. The writer wishes to express his deep appreciation and gratitude to Prof. Dr. A. A. Selim, Professor of Pesticides Chemistry and Toxicology for suggesting the problem, supervision, his guidance, and constructive criticism.

The author feels greatly indebted to Prof. Dr. Z. H. Zidan, Professor of Pesticides Chemistry and Toxicology at the same Department and vice Dean for graduate studies and research, for supervising the work, offering facilities of the work, reading the manuscript, helpful suggestion and constructive criticism.

Thanks to Prof. Dr. F. A. Affi, Professor of Pesticides Chemistry and Toxicology at the same Department for his suggestions and advices throughout this study.

Thanks are also due to Dr. M. I. Hussien, Associate Professor, at the same Department for his help to overcome many difficulties met during the field work.

Furthermore, I appreciate all kinds of help given to me by the staff members of Plant Protection Department, Faculty of Agriculture, Ain Shams University.

..



# CONTENTS

	PAGE
LIST OF TABLES	
LIST OF FIGURES	
INTRODUCTION .....	1
REVIEW OF LITERATURE .....	8
 1- Pesticide residues in raw fruits and vegetables. ....	8
2- Pesticide residues in beehoney, beewax and beeworkers .....	18
3- Pesticide residues in milk and dairy products. ....	23
4- Pesticides residues in soil and draining water. ....	31
5- Effect of some technological processes on pesticidal residues decontamination in fruits and vegetables. ....	39
 MATERIAL AND METHODS .....	46
I- Residues of certain insecticides on Cucumber, Pepper and Tomato fruits cultivated under plastic houses during Autumn. ....	46
1. Insecticides used .....	46
2. Experimental work .....	46
3. Gas chromatography determination of insecticidal residue. ....	47
a- Establishment of the studied insecticides calibration curves. ....	47
b- Extraction, clean-up, recovery and G.C determination. ....	49
II- Residues of isoprothiolane fungicide in Rice plants and the surrounding environmental components. ....	49
1. Chemical and physical properties of the fungicide used. ....	49
2. Experimental design. ....	50
3. Analysis of isoprothiolane fungicide in the Rice Agro-ecosystem components. ....	50
a. Establishment of isoprothiolane calibration curve. ....	50
b. Extraction, clean-up, recovery and G.C determination of isoprothiolane residues. ....	52

	PAGE
III- Residue of Tau-fluvalinate insecticide in honey, wax and bee workers in treated hives. ....	52
1- Chemical structure and formula . ....	52
2- Experimental work. ....	53
3- Determination of Tau-fluvalinate residues . ....	53
IV. Field monitoring of certain insecticide residues in/on different samples collected from different stations and markets of Kaluhia governorate ....	55
1- Pesticides reference standards. ....	55
1.1- Chlorinated hydrocarbon compounds. ....	55
1.2- Organophosphorus compounds. ....	56
1.3- Carbamate compounds. ....	57
1-4- Synthetic pyrethroids compounds. ....	57
2- Market basket survey. ....	58
2.1- Raw fruits and vegetables. ....	58
2.2- Beehoney ....	58
2.3- Milk and Dairy products. ....	59
2.4- Soil and Draining water ....	59
3- Analysis of Insecticide residues . ....	62
3.1- Establishment of the standard calibration curves of the studied insecticides ....	62
3.2- Extraction, clean-up, recovery and G.C. (Identification & determination). ....	62
V -Effect of some technological processes or treatments on the decontamination of insecticidal residues. ....	70
1- Cucumber fruits. ....	70
2- Pepper fruits. ....	71
3- Tomato fruits. ....	71
4- Potato tubers. ....	72
RESULTS AND DISCUSSION ....	73

	PAGE
<b>PART. I</b>	
Residues of certain organophosphorus and synthetic pyrethroid insecticides on vegetables grown under plastic houses at Kalubia Governorate, Egypt. ....	73
<b>I. Residues of certain insecticides on cucumber, pepper and tomato plant fruits cultivated under plastic houses during Autumn. ....</b>	<b>74</b>
1- Cucumber fruits. ....	74
2- Pepper fruits. ....	77
3- Tomato fruits. ....	79
<b>PART. II</b> .....	<b>85</b>
Distribution of isoprothiolane (fuji-one) fungicide residues in an Agro-ecosystem of paddy rice at Kalubia Governorate, Egypt. ....	85
<b>PART .III</b> .....	<b>92</b>
<b>SECTION. 1</b> .....	<b>92</b>
Monitoring of insecticidal residues in (soil and drainage water), (milk, cheese and bee honey collected in market basket survey) from Kalubia governorate. ....	92
1. Detection of insecticidal residues in soil and drainage water samples collected from Banha, Kalubia governorate. ....	92
2- Detection of insecticidal residues in milk and cheese samples collected from Kalubia governorate markets. ....	96
2.1. Insecticidal residues in raw milk samples. ....	96
2.2. Insecticidal residues in cheese samples. ....	100
2.2.1. Kariesh cheese ....	100
2.2.2 Local hard cheese. ....	103
3. Detection of insecticidal residues in bee honey samples. ....	110
3.1 Fluralinate residues in treated hives. ....	111
3.2 Detection of insecticidal residues in bee honey samples collected from Kalubia governorate. ....	114

	PAGE
SECTION. 2 .....	117
Monitoring of insecticidal residues in market basket of vegetables and fruits surveyed from Kalubia Governorate. ....	117
1. Residues in vegetables. ....	118
1.1. Residues in cucumber. ....	118
1.2. Residues in pepper. ....	118
1.3. Residues in tomatoes. ....	123
1.4. Residues in green beans. ....	123
1.5. Residues in potatoes. ....	129
2. Residues in fruits . ....	137
2.1. Residues in guava. ....	137
2.2. Residues in oranges. ....	137
PART. IV .....	148
Decontamination of insecticidal residues from vegetables and fruit through laboratory processing .....	148
1. Decontamination of insecticidal residues from cucumber .....	148
2. Decontamination of insecticidal residues from green pepper .....	151
3. Decontamination of insecticidal residues from tomatoes. ....	153
4. Decontamination of insecticidal residues from potatoes .....	156
SUMMARY. ....	161
REFERENCES. ....	179
ARABIC SUMMARY	