STUDIES ON THE BEHAVIOUR OF CERTAIN POLLUTANTS IN THE EGYPTIAN ENVIRONMENT

THESIS

SUBMITTED BY

MAGDY DIAB MADBOULY ALY
THE NATIONAL CENTER FOR SOCIAL
AND CRIMINAL RESEARCH

547.3 M.D

FOR

THE PHILOSOPHY DOCTOR OF SCIENCE

"CHEMISTRY"

Supervised by

~8,124

Prof. Dr. M. F. El-Shahat

Prof. of Inorganic & Analytical Chemistry Faculty of Science, Ain-Shams University Prof. Dr. H. K. M. El-Makkawy
Professor of Applied Organic Chemistry
Hand of the Property of Chemistry

Head of the Branch of Chemical and Biological Aspects The National Center for Social & Criminal Research

Department of Chemistry Faculty of Science Ain Shams University 1994



STUDIES ON THE BEHAVIOUR OF CERTAIN POLLUTANTS IN THE EGYPTIAN ENVIRONMENT

Thesis Advisors

Apporved

- 1- Prof. Dr.Late/ Abdel Maged Samour.
- 2- Prof. Dr. M.F. El-Shahat,
- 3- Prof. Dr. Hussien, K., El-Mekkawi.

Head of Chemsitry Department

Prof. A.F. Fahamy

A. F.M. Falmy



ACKNOWLEDGEMENT

I would like to express my best appreciation to Professor Dr. Late/ Abdel Maged Samour the Former Dean of the Faculty of Science, Ain Shams University for his help. My Sinceer Appreciation to Professor Dr. M.F. El-Shahat, Professor of Analytical Chemistry, Department of Chemistry, Faculty of Science, Ain Shams University for continuons guideness to me throughout this work. Also, my sincere gratitude and deepest appreciation, and debts to my Professor Dr. Hussien, K., El-Mekkawi, Professor of Applied Organic Chemistry, The Head of the Branch of Chemical and Biological Aspects, the National Center for Social and Criminal Reseach, for his advice help and criticism in revising and editing this work.

CONTENTS

	Page
PART I: INTRODUCTION	1
Insecticide studied	<u>5</u>
PART II: Persistence of the studied organophosphorus	•
and pyrethroid insecticides in Nile Water	
- Review of Literature	11
- Experimental	17
- Results and discussion	25
PART III: Persistence and accumulation of the studied	23
insecticides in fish and its aquatic medium	
- Review of literature	86
- Experimental	89
- Results and discussion	93
PART IV: Evaluation of water treatment methods	
1- Adsorption on activated powdered carbon	104
- Review of literature	100
- Material and methods	106
- Procedure	107
- Results and discussion	108
2- Removal of the studied insecticides by	110
chlorine oxidation	
- Review of literature	101
- Experimental	131
- Preparation of chlorine water	134
- Preparation of chloring Water	135
 Preparation of chlorine dioxide solution UV - irradiation 	135
- Ov - Hadiation	137
- Thin - layer chromatography and enzymatic	
inhibition of the oxidation products	138
- Results and discussion	139
3- Removal of the studied insecticides by	
alum coagulation	
- Review of literature	168
- Experimental	170
- Results and discussion	173
SUMMARY	183
REFERENCES ARARIC SIMMADY	192
AKABU SUMMAVY	

INTRODUCTION

INTRODUCTION

Since chemical control of pests is so successful, there has been an explosive expansion in the development of synthetic organic insecticides. The most widely used insecticides, the chlorinated hydrocarbons were generally preferred in the past because they have long residual effects. However, some of these compounds such as DDT and Dieldrin persist amazingly long in soils, water, plants, and animal tissues (1-6).

On the contrary, organophosphorus, and carbamate insecticides are generally unstable and short life in the environment as well as the biological system. They are commonly degraded into nontoxic and water soluble metabolites. The rapid decomposition of these compounds and transformed metabolites have their led to their disappearance from the ecosystem.

Synthetic pyrethroids, have introduced in the Egyptian market since 1978, possessed an excellent and efficient performance against a wide range of pests infesting field crops and vegetables.

Synthetic as well as natural pyrethroids are non-polar compounds and have very small solubility in water. Although they have no systemic or translaminar properties, unlike the organochlorine compounds, they are unstable and non-persistent. The insecticidal activity of pyrethroids is up to four or five times higher than that of the other classes to most insect species. They are both very active against insects and relatively non-toxic to mammales.

The introduction of granular insecticides has opened up new possibilities of application for the control of insects. Granular application of systemic insecticides also, helps to minimise toxic hazards to mammales and birds during application (11).

The increasing demand for pesticides and their massive use for agriculture and vector control have resulted in increased occurrence of these toxic chemicals and their degradation products in the biota e.g. in Egypt the quantity of pesticides used since 1952 to 1984 is 617507 metric tons⁽¹²⁾.

These accumulations lead to several environmental problems such as contaminations of natural waters. Also, fish death caused by various insecticides have been reported

on a global scale. Even if these compounds are present only in very low concentrations, they are hazardous because some species of aquatic life like fish are known to concentrate these compounds 1000 fold or more in their bodies. Thus there is no predictable safe level for insecticides in water where food-chain build-up can occur.

To overcome the problem of the pollutions of the aquatic ecosystems with pesticides, information about the persistence of these compounds under different conditions are of utmost importance. The information also, should include the effects of water treatment methods on the removal of the pesticide residues.

The present investigation aimed to throw light on the persistence and behaviour of two organophosphorus insecticides namely, CYANOX and ACTELLIC, and two pyrethroid ones, namely DANITOL and CYFLUTHRIN, in Nile water under different conditions of pH's and temperatures.

The accumulation of these insecticides in fish tissues head, intestine, liver and edible flesh (muscle) and their rates of disappearence in these tissues and its aquatic medium were concerned. Besides, the effect of fish cooking

on the mentioned insecticides was studied. ALso, studies were carried out to evaluate water treatment methods like adsorption on activated powdered carbon, and oxidation by Chlorine, Chlorine dioxide and/or ultra-violet irradiation and coagulation by alum on the removal of these insecticides from natural water.

INSECTICIDES STUDIED

I- Organophosphorus insecticides:

A- CYANOX (16):-

Common names:-

Cyanophos (BSI, ISO), and CYAP (JMAF).

Other names:

(Former), S 4084.

Action:

Insecticide.

Chemical Name:

0-4-cyanophenyl 0,0-dimethyl phosphorothioate.

CYANOX "Cyanophos"

Chemical properties:-

Clear amber liquid, melting point at 14-15 °C. Miscible with alcohol, ketones, benzene, toluene, xylene and chloroform.

Toxicity:

Acute oral half lethal doses (LD_{50}) for female and male rats were 610 and 580 mg/kg respectively.ively.

Application:

Used on vegetable and fruits, when used in regular schedules, gives excellent control of lepidopterous larvae on apples and vegetables, used also as a grain protectant especially and in house hold insect control cockroaches as a residual spray, taking advantage of its long lasting effectiveness.

B- Actellic(16):

Common name:

Pirimiphos - methyl.

Other names:

Acetellifog, Blex, and PP - 511. (Discontinued name of ICI plant protection), silos on.

Chemical name:

0 - (2-Diethylamino - 6 - methyl pyrimidin -4yl) 0,0- dimethylphosphorothioate.

Action:

Fast acting and broad spectrum insecticide.

Chemical properties:

Miscible with most organic solvents. Solubility in water approx. 5 PPm at 30°C. Vapour pressure 1.1 x 10⁻⁴ torr. at 30°C.

Toxicity:

Acute oral half lethal doses (LD $_{50}$) for female rat > 2000 mg/kg. and acute dermal LD $_{50}$ female rate > 4592 mg/kg.

Application:

For control of a wide range of pests of stored products of domestic and industrial premises, and of fruits, vegetables and other crops.

II Pyrethroid Insecticides:

A- DANITOL(16):

Common Name:

Fenpropathrin.

Other Names:

Meothrin, Ortho Danitol, Rody, S - 3206, SD - 41706, S - 3206, WL - 4706, XE - 938.

Action:

Acaricide and insecticide.

Chemical Name:

(Rs)-α- Cyano-3- Phenoxybenzyl 2,2,3,3 - tetramethylcyclopropanecarboxylate.

Chemical properties:

Yellow to brown liquid or solid melting point 45 - 50°C. Soluble in common organic solvents such as xylene, cyclohexane, chloroform, acetone, and amol methanol. Almost insoluble in water. Stable except in alkaline solution.

Toxicity:

Acute oral half lethal doses (LD₅₀) for male and female rats were 70.6 mg/kg, and 66.7 mg/kg. respectively mg/kg. Acute dermal (rabbit) 2000 mg/kg. Toxic to fish, Mild toxicity to birds.

Application:

For control of various species of mites, white flies, leafminers, cotton bollworms, leafworms, leafrollers, armyworm, cabbage worms, cabbage looper, aphids, fortrixes, psyllas, bugs, fruit moths, tuberworms cutworms, budworms, diamond back moth, mosquito bugs, and stem borer on fruit trees, vegetables ornamentals and other field crops.

B- CYFLUTHRIN⁽¹⁶⁾:

Common Name:

Cyfluthrin.

Other Names:

BAY FCR 1272, Baythroid H and Solfac.

Action:

Nonsystemic synthetic pyrethroid with good insecticidal activity.

Chemica 1 Name:

Cyano (4-fluro- 3-phenoxyphenyl) -3- (2,2-dichloroethenyl) -2-2- dimethyl - cyclopropane carboxylate.

CYFLUTHRIN