Deanship of Graduate Studies
Al-Quds University

Abamectin, β-Cyfluthrin, and Imidacloprid Pesticides Occurrence in the Shallow Aquifer System in Jericho Area

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M.Sc. Thesis

Jerusalem – Palestine

1431/2010

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A thesis Submitted in Partial fulfillment of requirements for the degree of Master of Applied and Industrial Technology Program at Faculty of Science, Al- Quds University.

1431/2010

Al-Quds University
Deanship of Graduate Studies
Applied and Industrial Technology Program

Thesis Approval

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Jerusalem – Palestine
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Dedication

I would like to present this work to my dear father "Mahmoud" and mother "Fatima" for their support, unlimited help, and full understanding; of course I should not fail to extend my sincere thanks to the only love my husband "Ashraf" who did not hesitate to provide all the support, love and patience for me to complete my master's thesis of graduate studies to be well done and highly qualified ....

Ne'mah M. Salah

Declaration:

I certify that this thesis submitted for the degree of Master is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed: ________________

Ne’mah Mahmoud Salah

Date: 20 /12 / 2010

Acknowledgements

Before all and above I would like to express my endless thanks to"ALLA" the merciful for conciliation, and providing patience.

A lot of thanks to Al-Quds University for giving me the opportunity to study the M.Sc., of course I would like to thank my supervisor Dr. Amer Marie for his suggestion and support during my study, besides a special thank to my co-supervisor Dr. Fuad Al-rimawi for his patient and important suggestions.

Also a lot of thanks go to the Environmental lab members in Al-Quds University, for their help and support.

I also extend my sincere thanks to my family and especially my parents for their financial and moral support to get the Master's thesis.

I will never forget my dear husband "Ashraf" for his cooperation and good administration to encourage me to complete the master's thesis.

At the end, for every one helps me to reach this step with a Mater Degree, thank you.

Abstract

Most Palestinians lands are agricultural, that serve many different kinds of crops, fruits and vegetables, in different places in Palestine as Jericho, Jinine, and Qalqelia. So most of the Palestinian people need water to irrigate the fields, and one of the most available sources for this purpose is ground water. In this sense, contamination of groundwater is important to study and to investigate.

Ground water effected with a wide range of pollutants, and the most important of these pollutants that may reach the groundwater through the abuse and ignorance are pesticides, which if found in high concentrations may lead to chronic diseases for human health such as cancer, and perhaps death besides the environmental hazardous. This study focuses on the examination of the concentration of three pesticides are Abamectin, Imidacloprid, and β-Cyfluthrin which are used in large quantities in Jericho district for increasing the crop production and hence effect ground water safety over time.

Water Samples were collected during planting time, two or three days after application of pesticides in the agricultural area, while the other part of the samples were collected after heavy rainfall in the end of winter , and were analyzed for three pesticides Abamectin, Imidacloprid, and β-Cyfluthrin, by using HPLC-UV method. 25 wells were sampled from the three sites of the study area which are Jericho, Al-uja, and Jeftlik to examine the concentration of each pesticide The results of this study show that the concentration of Abamectin ranges between 1.244ppb and 81.71ppb in 11 of 25 sampling wells were detected, and for Imidacloprid between 1.457ppb and 325ppb in 24 of 25 sampling wells were detected, and for β-Cyfluthrin ranges between 0.1000 and 24.46ppb in 7 of 25 sampling wells were detected.

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List of Abbreviations

ND	Not detected
G	Gram
Ml	Milliliter
µL	Micro-liter
ppm	Parts per-million
ppb	Parts per-billion
Rt	Retention time
PWA	Palestinian Water Authority
WHO	Water Health Organization
%	Percentage
DDT	Dichlorodiphenyltrichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDD	Dichlorodiphenyldichloroethane
FL	Fluorescence
MAE	Microwave assisted Extraction
EPA	Environmental protection Agency

List of Abbreviations

PHI	Post harvest interval
HPLC	High-performance liquid chromatography
GC/ECD	Gas chromatography/ Electron Capture Detector
FAO	Food and Agriculture Organization
R^2	Correlation Coefficient
ACN	Acetonitrile
LC-MS	Liquid Chromatography-Mass Spectrometry
SPE	Solid-phase Extraction
MCM	Million Cubic Meter
ICP/OES	Inductively Coupled Plasma - Optical Emission Spectrometer
SD	Standard Deviation
RSD	Relative Standard Deviation

CHAPTER I

INTRODUCTION

I.1 Introduction

Pesticides are used widely in agriculture to kill pests in Palestine as well as in the world, as an effective treatment for many agricultural problems. On the other hand, these pesticides have negative effects on the human health and on the environment e.g. pollution of soil, biological organisms, and even water (especially the ground water).

During recent years, water availability and quality are affected by a wide range of human activities which can be observed clearly in areas with high industrial and agricultural activities. Freshwater was critical and still an issue for the people in the whole world and especially in Middle East. The main water resource in the world is oceans which represent 97% of water supply. Other water recourses are surface water (includes rivers, lakes, and man-made dams) which represent 1% of the world's water supply, and ground water which occurs in different rock types, ranging from ancient crystalline basement rocks (which store small amount of water in their shallow) to alluvial plain sediments (WHO 1996). Water used in agriculture for irrigation is considered the largest source of water consumption which accounts for 60 to 90 per cent of annual water consumption in most countries in the region, as can be seen in Table (1.1) (FAO 2000).

Table 1.1: Water Consumption in the Region & the World (FAO 2000).

	Annual Water Withdrawal by Sector								
	Agricultural		Domestic		Industrial		Total Withdrawal		
Subregion	m^3	% of total	m^3	% of total	m^3	% of total	m^3	% of Asia	m^3 per inhab.
Indian Sub-continent	510.7	92	27.2	5	15.5	3	553.4	38	500
East Asia	418.3	77	26.8	5	95.5	18	540.1	37	428
Far East	73.5	64	23.2	20	18.4	16	115.1	8	674
Southeast	82.1	88	3.9	4	7.0	8	93.0	6	476
Pacific Islands	127.9	90	10.4	7	4.3	3	142.6	10	483
Asia and the Pacific	1 212.5	84	91.5	6	140.2	10	1 444.2	100	476
World	2 310.5	71	290.6	9	652.2	20	3 253.3	100	564
Asia and the Pacific as % of the World	52.2		31.5		21.5		44.4		

In many countries, groundwater represents the main source for irrigation and domestic uses e.g. for drinking, cooking, and personal hygienic supplement. For example in the West-Bank, 20 to 200 liters per person per day were used for domestic usage (ARIJ 2008), and this depends on the number of users and the availability of water.

To get safe water, causes of water pollution must be studied for seeking a solution for this problem. One of those causes of water pollution are pesticides with all types; insecticides, herbicides, fungicides……etc. pesticides can reach to ground water through soil causing hazarders problems for human health especially if high concentrations of pesticides present in ground water. Figure (1.1) shows how pesticides reach the ground water through soil causing contamination.

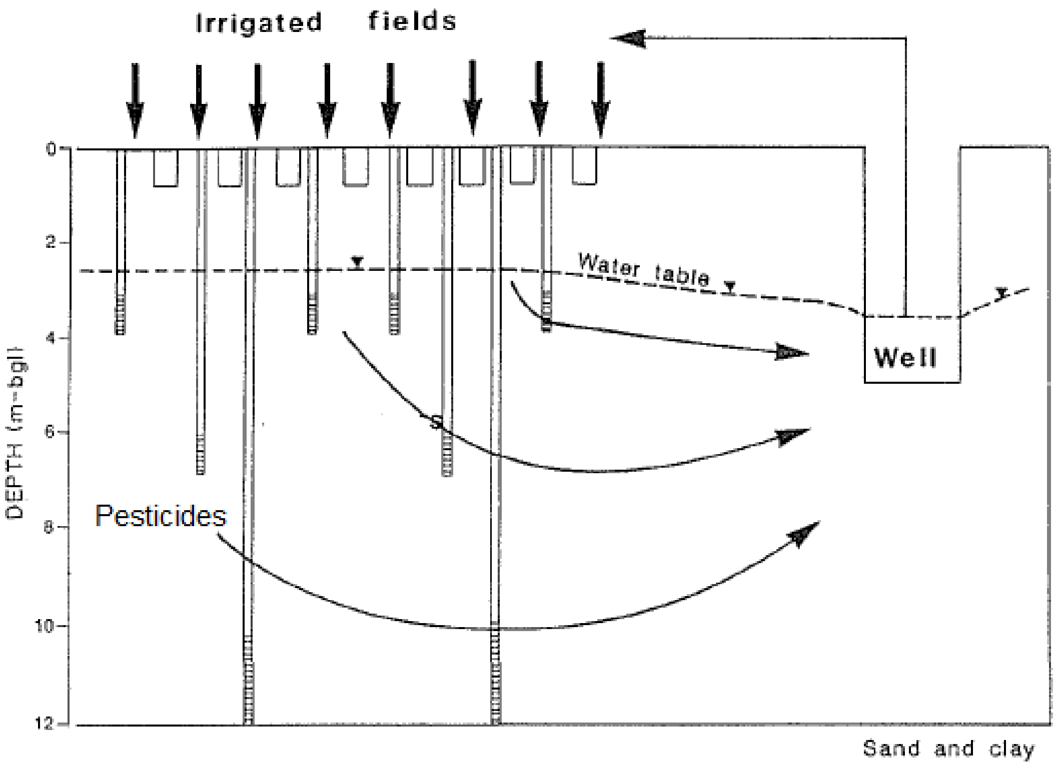

Figure 1.1: General mobility of Pesticides after Irrigation to the Ground water (BGS 1992).

Pesticides include a broad range of organic micro pollutants, and different categories of them have different effects on living organisms, and therefore generalization is difficult. Additionally, pesticides have different degradation rates and consequently different residuals.

Pesticides differ in their half lives (time required for the ambient concentration to decrease by 50%). Furthermore, degradation products of pesticides can be higher or lower hazard than the parent compound (pesticide itself) for instance DDT with a chemical name (Di-chlorodiphenyltri-chloroethane) degrades to DDE with a chemical name (Di-chlorodiphenyldichloroethylene) and DDD (Di-chlorodiphenyldichloroethane) (Hebeberer T. and Dunnbier U. 2000). Despite bad effects of pesticides, more than 10 thousand of new generations of pesticides are used yearly with new effects (Guenzi D. and Beard E. 1976). For instance a list of the 20 most used active ingredients is shown in table (1.2). The table contains information on ten herbicides, eight fungicides, one growth regulator and one desiccant. The desiccant, sulfuric acid, which is applied to potato crops, accounted for 32% of the total weight of active ingredients applied to all crops in Great Britain in 1993 (European Commission 1993).

Table 1.2: Amount (in tones) of the 20 active ingredients, used most by weight, on all agriculture and horticulture crops grown in Great Britain in 1993 (European Commission 1993).

No.	Active ingredient	Weight (tones)
1	Sulfuric acid	10167
2	Isoproturon	2809
3	Chlormequat	2416
4	Mancozeb	1361
5	Chlorothalonil	984
6	Sulfur	740
7	MCPA	730
8	Mecoprop	694
9	Fenpropimorph	650
10	Mecoprop-P	600
11	Chlorotoluron	580
12	Maneb	569
13	Pendimethalin	516
14	Trifluralin	382
15	Glyphosate	312
16	Carbendazim	297
17	Fenpropidin	295
18	Tri-allate	262
19	Metamitron	247
20	Tri-demorph	238

The interaction of pesticides with ground water and with soil and surface water is complex. Pesticides are controlled by numerous simultaneous biological, physical and chemical reactions, and with combination of many processes: a) transformation; refers to a biological and chemical process that change the structure of pesticides or completely degrade it, b) transfer; refers to the way in which pesticide is distributed between solids and liquids e.g. between soil and soil water and c) transport; is the movement from one environmental compartment to another such as the movement of pesticides through soil to ground water, valorization to the air or runoff to surface water (Leonard 1987). Through those interactions, pesticides may degrade in the following degradation processes (Gardner 2006):

1. Photolysis: the degradation of a chemical by light occurs on the plant, soil, water, or any other surface that sunlight reaches.

2. Hydrolysis: water can degrade pesticides by dividing large molecules into smaller ones.

3. Microbiological degradation: microorganisms break down or degrade pesticides after application.

4. Volatilization: a liquid chemical on a plant or soil surface can be converted in to vapors, which escape into the atmosphere.

Laboratory studies show that field trials are essential so that different climatic and soil characteristic can be investigated. The mobility of pesticides after application in the field is important in determining its potential to enter to the ground water because adsorption of pesticides to soil is strongly dependent upon the nature and type of soil to which it has been applied.

I.2 Geography of Jericho (study area)

Jericho is located 258 meters below sea level in an oasis in Wadi-Qelt in the Jordan Valley , and locates in the rain shadow of the West-Bank and receives about 150mm\yr rainfall, during the winter months which extend from October until April. The average temperature is $24C^0$ during winter season and $30C^0$ during the summer season (ARIJ 2004).

Jericho presents about 80% of agriculture production for West Bank market. The low rainfall and the high temperatures spread that area, also Jericho classified as semi-arid, where irrigated agriculture is dominate. Therefore, existence of high agrochemical usage (e.g. pesticides) is uncontrolled for crop protection that increases the chance for environmental pollution, and increases the chances for ground water pollution by pesticides. There are 58 wells located in Jericho area as shown in figure (1.2). These wells consume 2.5 MCM\yr, from the aquifer systems (PWA 2002).

Wells are spread along Jericho, but the focus is concerned more around wells which are located besides the agriculture areas where pesticides are used in large quantities, which may leach to ground water.

I.3 Geography of Al-uja and Jeftlik

Al-uja and Jiftlik are two villages in Jericho district. Al-uja is located 12 km to the north-east of Jericho and has a population of 4132 people. Around the village, there are traditional channels of water which spread up to date aspects of agricultural tourism (ARIJ 2008).

Al-uja is cultivated with vegetables and citrus groves, and greenhouses and that continue to use throughout the year. It is located where the banana plantations and citrus (ARIJ 2008).

Jiftlik village is located on the eastern border of the depths of the North, 100,000 acres and a population of 4000 people, and this number distributed over three localities in the north, south and west of the village, and these groupings based on its agriculture, livestock and livestock development (PWA 2002).

About 550 farms working in agricultural land which is estimated at about 50,000 acres and the cultivated area of about 18.807 acres of agriculture and the cultivation of a variety of open protected cultivation, with an estimated 227 home greenhouses. The number of artesian wells is 22 wells; the rainfall for the past ten years is 180 mm (Directorate of Local Government / Jericho and the Jordan Valley 2005).

I.4 Sampling Wells

Figure (1.2), indicates the wells of the study area (25 wells), with their ID number in the three sites of the study area (Jericho, Al-uja, and Al-jeftlik). The 25 wells were chosen according to particular scientific approach based on:

1. Work on selection operating wells and the exclusion of wells that do not work.
2. Selection of wells, preferably to be in the middle of the field and not far from it.
3. Type of soil surrounding the field of Agriculture that sandy soil is preformed that allows to easily penetration.
4. Wells used continuously and consistently both by farmers for irrigation or for domestic uses.

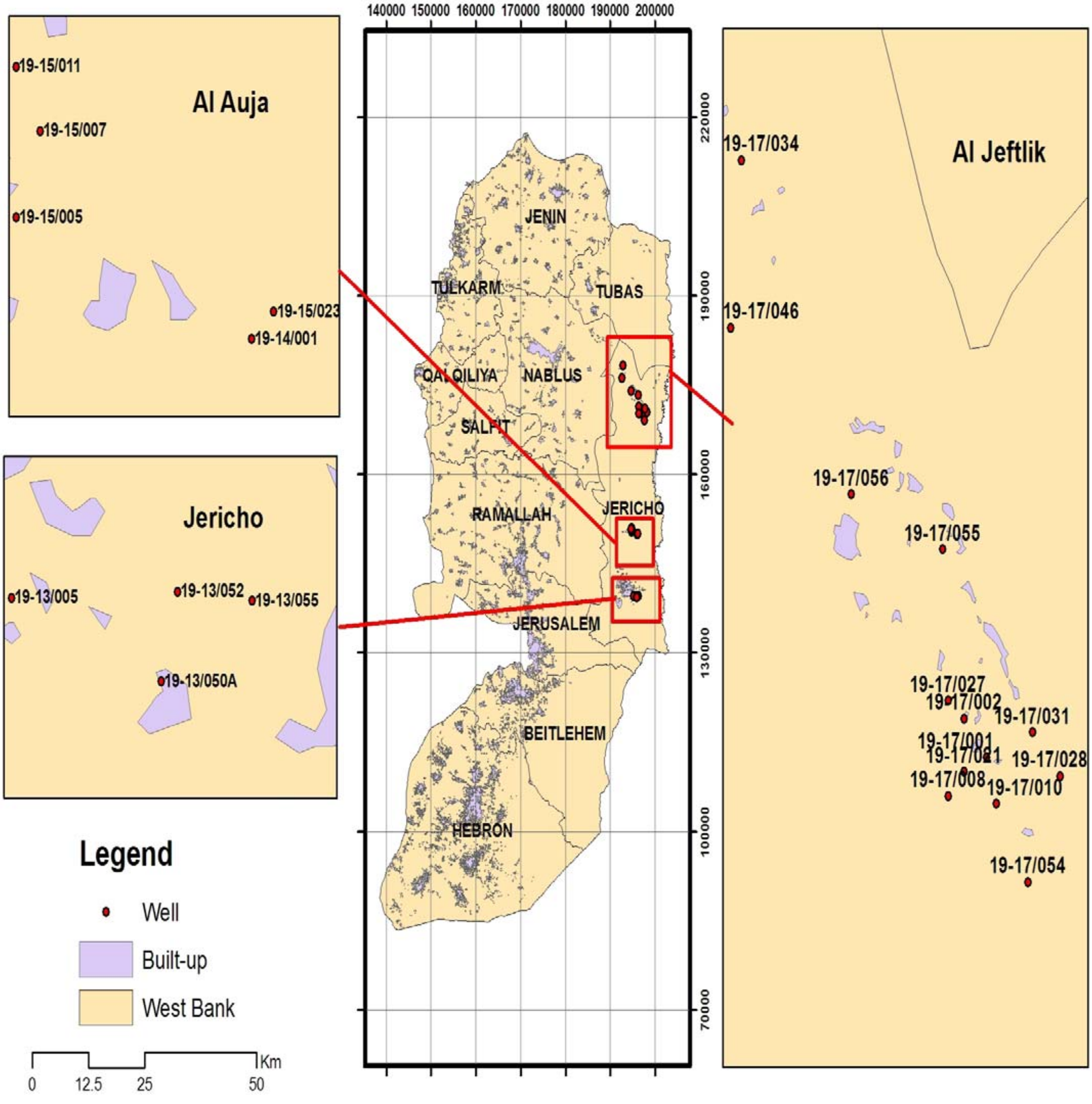

Figure 1.2: Ground water sampling sites in Jericho, Al-uja, and Jeftlik (Environmental lab Research 2010).

I.5 Pesticides

Pesticides can be defined generally as chemicals that are used to kill insects, weeds, and other organisms to protect humans, crops, and livestock. There have been many substantial benefits of the use of pesticides.

The most important benefits of pesticides are (Hallberg 1989):

1. Increases in the production of food because of the protection of crop plants from pathogens, competition from weeds.

2. Prevention of spoilage of harvested, stored foods.

3. Prevention of exhausted illnesses and the saving of human lives by the control of certain diseases.

The earliest pesticides were inorganic substances such as sulfur, mercury, lead, arsenic and ash. Some of these inorganic pesticides are still used today. For example, sulfur is still used as a fungicide, copper is used as an algaecide, lead and arsenic were used as insecticides until World War II, and chromium, copper, and arsenic have been used as wood preservatives to prevent microorganisms from causing wood decay (Hallberg 1989).

There are approximately 400 different active ingredients of pesticides. Pesticides can be divided into four mains types according to the chemical structure (Abrams K. and Hogan DJ. 1991):

1. Organophosphate Pesticides - Most organophosphates are insecticides. They were developed during the early 19th century, but their effects on insects, which are similar to their effects on humans, were discovered in 1932.

All organophosphates contain C-P bonds, some are very poisonous. Organophosphate pesticides degrade rapidly by hydrolysis on exposure to sunlight, air, and soil, although small amounts can be detected in food and drinking water.

2. Carbamate Pesticides- the most common form is carbaryl, they are organic compounds derived from carbamic acid (NH_2COOH), such as Methomyl which has the chemical name [methyl N- {[(methylamino) carbonyl]oxy} ethanimidothioate].

3. Organochlorine Insecticides were commonly used in the past, but many have been removed from the market due to their health and environmental effects and their persistence (e.g. DDT and chlordane).

4. Pyrethroid pesticides- Pyrethrum is a compound extracted from Chrysanthemum flowers. It has been used as an insecticide since the first century. Pyrethroid pesticides are used in agriculture, mosquito control, lawn and garden care. Some representative pyrethroids are Permethrin, β-Cyfluthrin, Sumethrin and Barthrin. However Long-term exposure to pyrethroids may produce anorexia, skin sensitization, and immune system damage. There are indications that some pyrethroids may be carcinogenic.

I.6 Pesticides Usage in the Study Area

Due to different agricultural organisms resulting from large vaiarity of Palestinian agriculture and improvement, about 2.6 million tones of pesticides are used each year (90% for agricultural purposes and 10% for public health purposes) with a high cost of 30 Millar $ each year in the world (PFU 2008). Thus, according to data statistics of agriculture in Palestine that by the year 2009 to 19.7% of the costs of plant production requirements on the disposal of pesticides, while 26.0% of the cost of these supplies is spent on fertilizer (PFU 2008). Table (1.3) shows the amounts (in kg) of pesticides which were used in West Bank in the years 2006-2008.

Table 1.3: Pesticides usage in West-Bank in Kg (The Ministry of Agriculture -Ramallah- West Bank 2008).

Year	**Insecticides**	**Fungicides**	**Herbicides**	**Total**
2006	26789	38955	17458	83202 (83 tons)
2007	27222	39200	17600	84022 (84 tons)
2008	27100	38966	17500	83566 (84 tons)

There are many different kinds of these pesticides with nearly 630 active material and more than 25000 formulations (PFU 2008).

I.7 Abamectin

I.7.1 Abamectin Classification and Properties

Abamectin is an insecticide, a colorless to yellowish crystalline powder, and has a molecular weight of 873.11. It has many different trade names like Affirm, Agri-Mek, Avermectin, Avid, MK936, Vertimic and Zephyr (Boisseau 1996). Abamectin is a highly toxic material, and in concentrated formulations it may causes eye irritation and mild skin irritation. Abamectin belongs to the family avermectins which are macro-cyclic lactones , it is a mixture of avermectins B1a ($C_{48}H_{72}O_{14}$) containing > 80% and avermectin B1b ($C_{47}H_{70}O_{14}$) containing < 20%. These two components (B1a and B1b) have very similar biological and toxicological properties. Figure (1.3) shows the structure of Abamectin. The avermectins are insecticidal or anthelmintic compounds derived from the soil bacterium Streptomyces avermitilis. Abamectin is a natural fermentation product of this bacterium.

Abamectin is used to control pests of a range of agronomic, fruit, vegetable and ornamental crops, it’s used in Jericho in high quantities (field survey) due to its effective in killing pests, also it is used by homeowners to control fire ants (FRANK J. and LAWRENCE H. 1999).

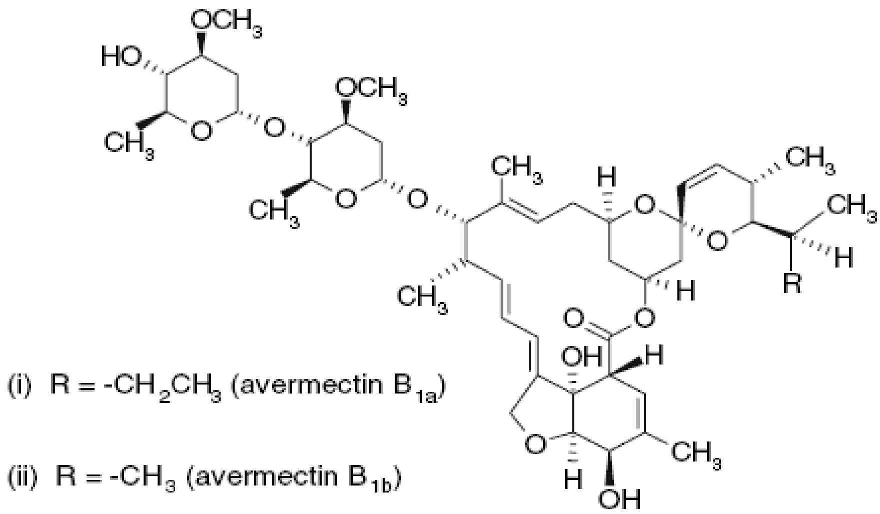

Figure 1.3: Structure of Abamectin (B1a and B1b) (Wislocki 1989).

I.7.2 Mode of Action

Abamectin acts by stimulating the release of amino-butyric acid causing paralysis on insects and by interfering with neural and neuromuscular transmission. It acts on a specific type of synapse located only within the brain and is protected by the blood-brain barrier. However, at very high doses, the mammalian blood-brain barrier can be penetrated, causing symptoms of central nerves system depression such as in coordination, tremors, lethargy, excitation and pupil dilation. Very high doses have caused death from respiratory failure (Ananiev 2002).

Abamectin is not readily absorbed through skin. Tests on monkeys show that less than 1% of dermal applied Abamectin was absorbed into the bloodstream through the skin (Ananiev 2002).

The acceptable daily intake (ADI) for Abamectin in fruits and vegetables was set by WHO at 0.01 mg/kg (body weight) daily and is based on regular consumption of fruit (Ananiev 2002). Environmental exposure to Abamectin and its degradation products may cause serious health risks including fertility and reproductive function (Wislocki 1989).

I.7.3 Degradation

When Abamectin applied to the soil surface, it has a strong tendency to bind to soil therefore the probability of leaching to the ground water is low. However, it can reach the ground water through heavy rain fall or sandy soil. The degradation products of Abamectin have more tendencies to bind to soil than Abamectin itself, therefore they are immobile in soil and unlikely to leach or contaminate ground water. Abamectin soil half-life is about 1 week. Under dark aerobic conditions, the soil half-life is 2 weeks to 2 months (EPA 1990). Loss of Abamectin from soils is thought to be due to microbial degradation. The rate of degradation was significantly decreased under anaerobic conditions. Its half-life in water is 2 to 4 weeks, but this depends on pH for example in pH 5, 7, and 9 Abamectin did not hydrolyze.

I.8 Imidacloprid

I.8.1 Classification

It is an insecticide that was first introduced in the U.S in 1994. It belongs to the chloronicotinyl nitroguanidine class, with IUPAC name 1-[(6-chloropyridin-3-yl) methyl]-N-nitro-4, 5-dihydroimidazol-2-amine, it is colorless and odorless crystal. Figure (1.4) below shows the structure of Imidacloprid (Zheng 1999).

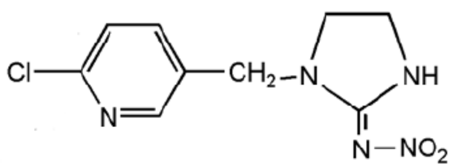

Figure 1.4: Imidacloprid’s Structure (Zheng 1999).

I.8.2 Mode of Action

It works by disrupting the nervous system of an insect. Imidacloprid kills insects by contact and ingestion.

I.8.3 Degradation

Imidacloprid is stable in the soil for several months, which may provide for long term control of termites. However, Imidacloprid tends to break down faster in soil with ground cover compared to bare soil. But there is a potential for Imidacloprid to enter streams and pond via drift during application or in runoff water. (Zheng 2008) found that Imidacloprid did not leach to ground water in their field study. But in recent study conducted in 1998, Bayer Cooperation found this pesticide in ground water concentration ranged from 0.1 to 1 ppb. The hydrolysis half-life can range from 33-44 days at basic pH, that Imidacloprid was found to be stable in acidic and neutral water, but more readily hydrolyzed in alkaline water, and the half-life 39 days at the soil surface (Zheng 2008).

This pesticide is moderately soluble in water and moderately adsorbed by soil, and has a moderate to long half-life in soil. These factors may promote some leaching to ground water (Zheng 1999).

The primary Imidacloprid break-down products in soil as it is shown in figure (1.5) are Imidacloprid urea, 6-hydroxynicotinic acid, 6-chloroniotinic acid, and Imidacloprid guanidine, CO_2 is then formed from 6-chloroniotinic acid which means that the final product of Imidacloprid is CO_2 (Wamhoff 1999).

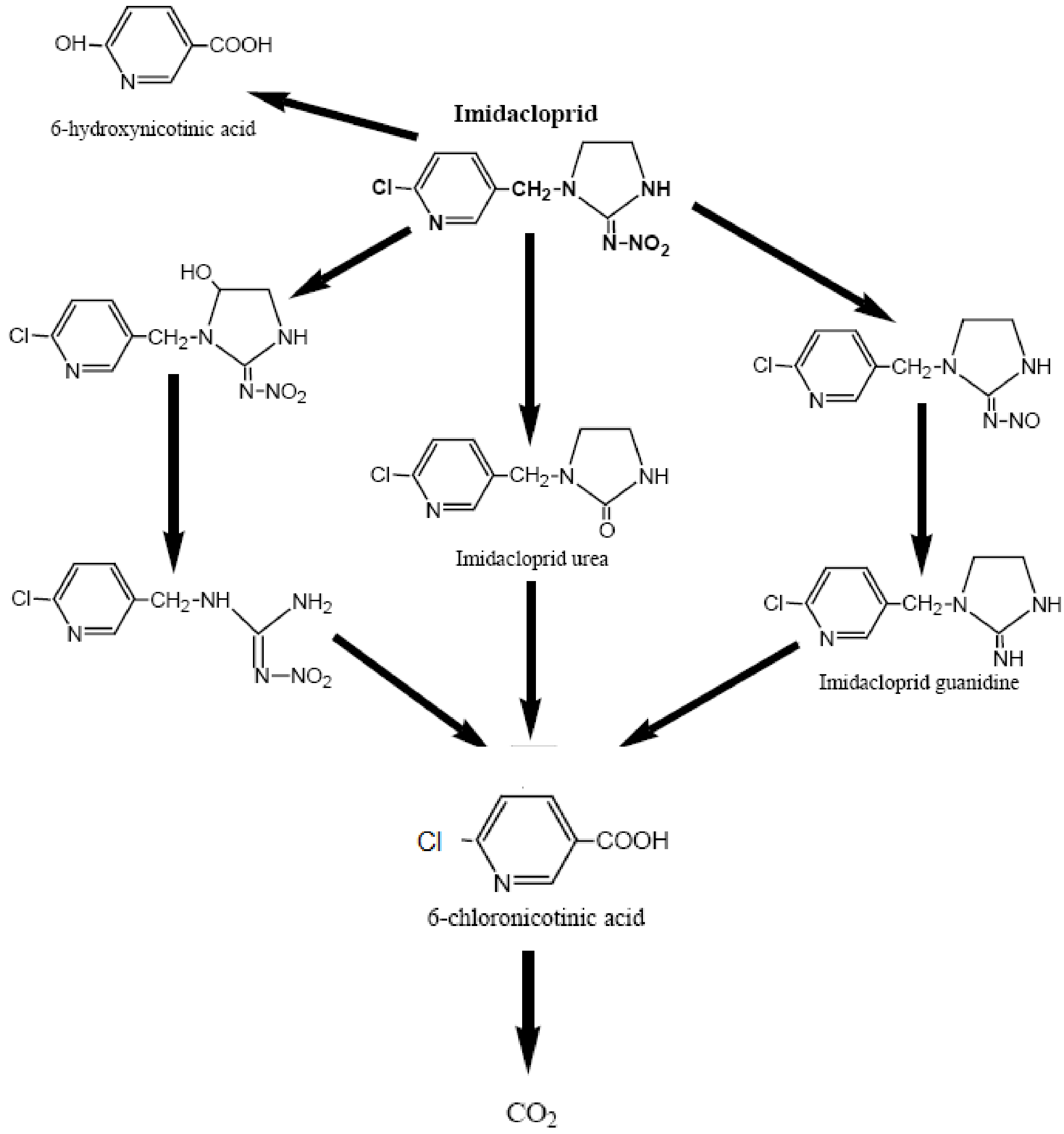

Figure 1.5: Degradation of Imidacloprid (Miles 1993).

Degradation on soil via photolysis has a $t_{1/2}$ of 39 days. In the absence of light, the longest half-life of Imidacloprid was 229 days in field studies and 997 days in laboratory studies (Miles 1993). This persistence in soil, without the presence of light, makes Imidacloprid suitable for seed treatment and incorporated soil applications because it allows continual availability for uptake by roots (Miles 1993). Imidacloprid is not volatile so it has a low potential to be dispersed in air so there is little of a human exposed to this compound in the air (Wamhoff 1999).

I.9 β-Cyfluthrin

I.9.1 Classification

It has a trade name of tempo, The common name is (RS)-a-cyano-4-fluoro-3-phenoxybenzyl(1RS,3RS)-3-(2,2dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate1, with a molecular formula of $C_{22}H_{18}C_{12}FNO_3$, and it has two isomers (Casjens 2002). The structure is shown in figure (1.6).

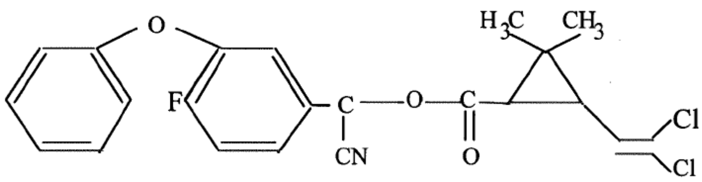

Figure 1.6: Structure of β-Cyfluthrin (Casjens 2002).

This pesticide belongs to the synthetic pyrethroid class which is a broad spectrum insecticide, structurally resembles the organo-chlorine DDT more than other pyrethroids. It is yellow, pasty, and semi-solid of molecular mass 434.3, melting point of the enantiomer pairs ranges from 57-102 C^0 (Arthur 1994).

β-Cyfluthrin has a very low solubility in water and has a very strongly tendency to absorb to soil. Although it is not be readily degradable in water, Anderson (1986) reports a hydrolysis half life in water in about 4 days at pH 8.6, with a significant slowing of degradation after one week. A relatively short aqueous photolysis half-life of 13 days at pH 7 (DPR 2001). In soil, β-Cyfluthrin has a low tendency to leach to ground water; in addition β-Cyfluthrin mobility during runoff events is low, except under conditions of high sediment transport (Casjens 2002). β-Cyfluthrin pesticide is non-volatile pesticides in air (Smith 1995).

I.9.2 Mode of Action

Like DDT, β-Cyfluthrin rapidly accumulates in fatty tissues, including the central nervous system and persists in the environment. In addition, β-Cyfluthrin causes reproductive problems. Like most pyrethroids, β-Cyfluthrin is highly toxic to fish, aquatic organisms and bees. β-Cyfluthrin is used for a wide array of pests in agriculture. As a result β -Cyfluthrin induces salivation, in coordination, muscle trembling, behavioral changes and convulsions.

β -Cyfluthrin causes axonal degeneration in nerves and necrosis in muscle in rats. Besides it causes allergic skin irritation and to the upper respiratory tract which can occur after dermal contact or inhalation (Smith 1995).

I.9.3 Degradation

The persistence of β-Cyfluthrin is varying due to due to various environmental conditions. This pesticide is more toxic at low temperatures. Studies show that it was very persistent with half lifes in soil of 81-191 day depending on the temperature and the soil organic matter content (Smith 1995). Besides that the degradation of this pesticide is more rapid at higher pHs, thus, β-Cyfluthrin was observed to be more persistence in acidic soils than in alkaline soils (Shehata 1987). The main degradation products of β-Cyfluthrin are 4-fluoro-3-phenoxybenz-aldhyde, and 4-fluoro-3-phenoxybenzoic acid (see figure 1.7). The latter being more toxic than parent compound (Shehata 1987).

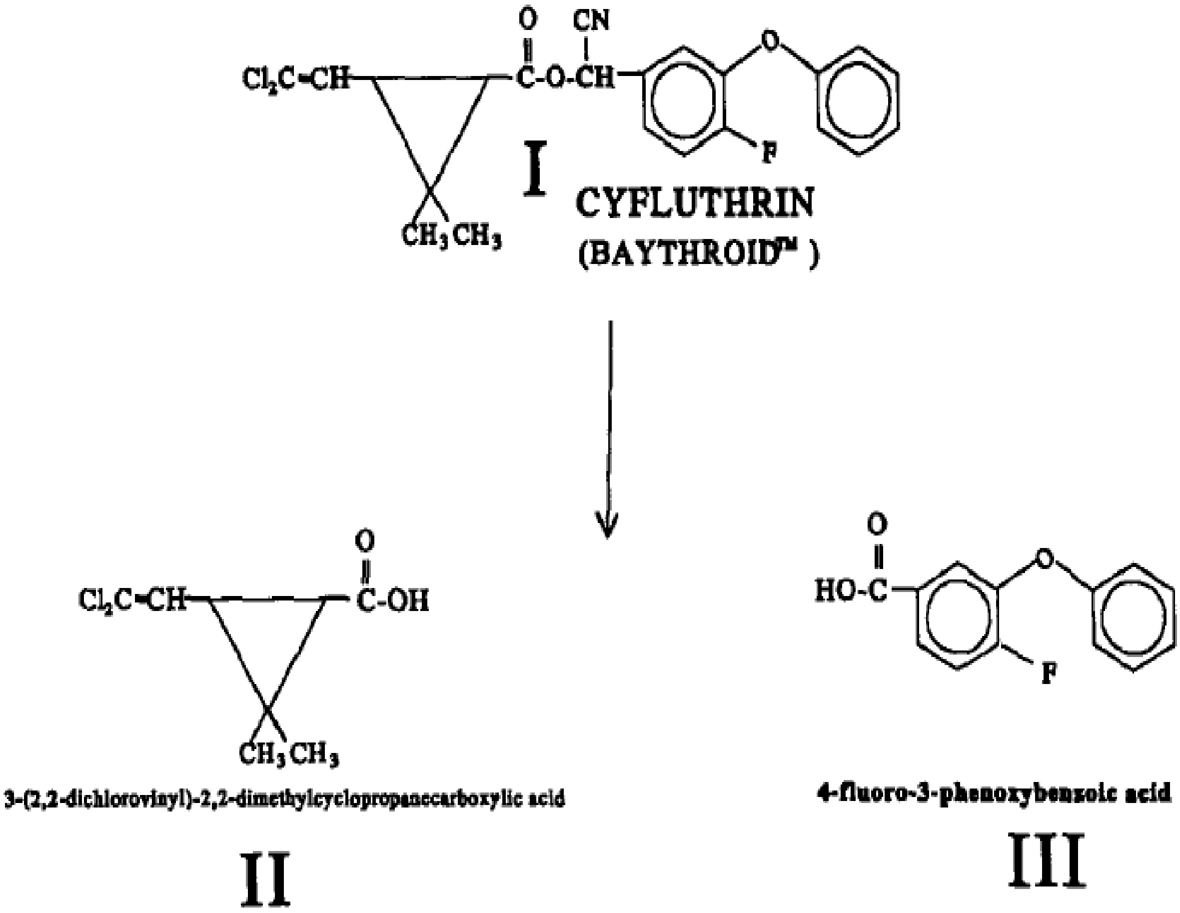

Figure 1.7: Degradation of β –Cyfluthrin (Shehata 1987).

Anaerobic degradation in soil is the result of hydrolysis of the ester linkage by microbial easterase enzyme systems. Such hydrolysis is common to most pyrethroid insecticides in soil; this process is shown in figure (1.8) (Shehata 1987).

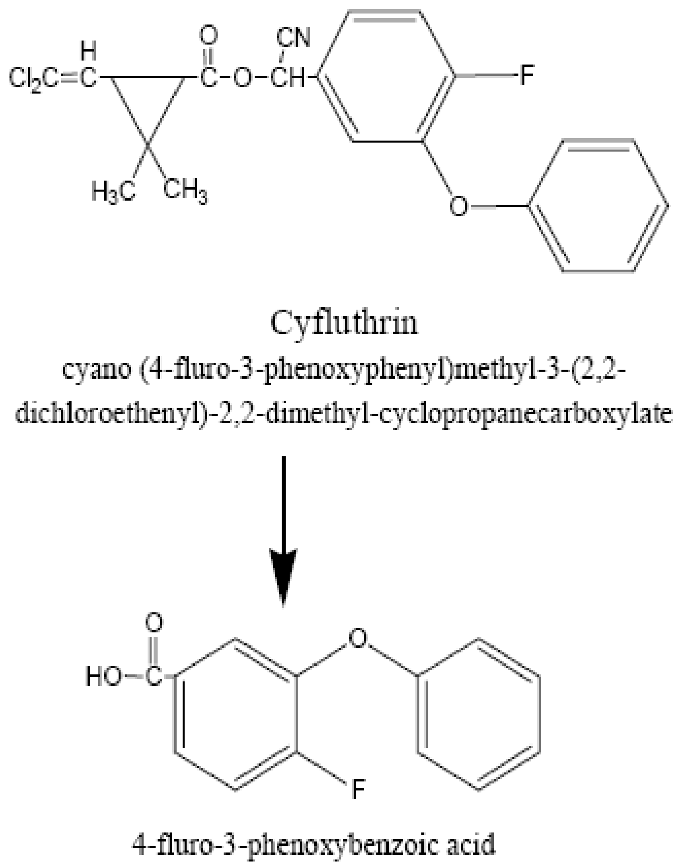

Figure 1.8: Anaerobic soil degradation of β-Cyfluthrin (Bongiorno 2005).

Also β -Cyfluthrin can have an aerobic degradation in soil as shown in figure (1.9).

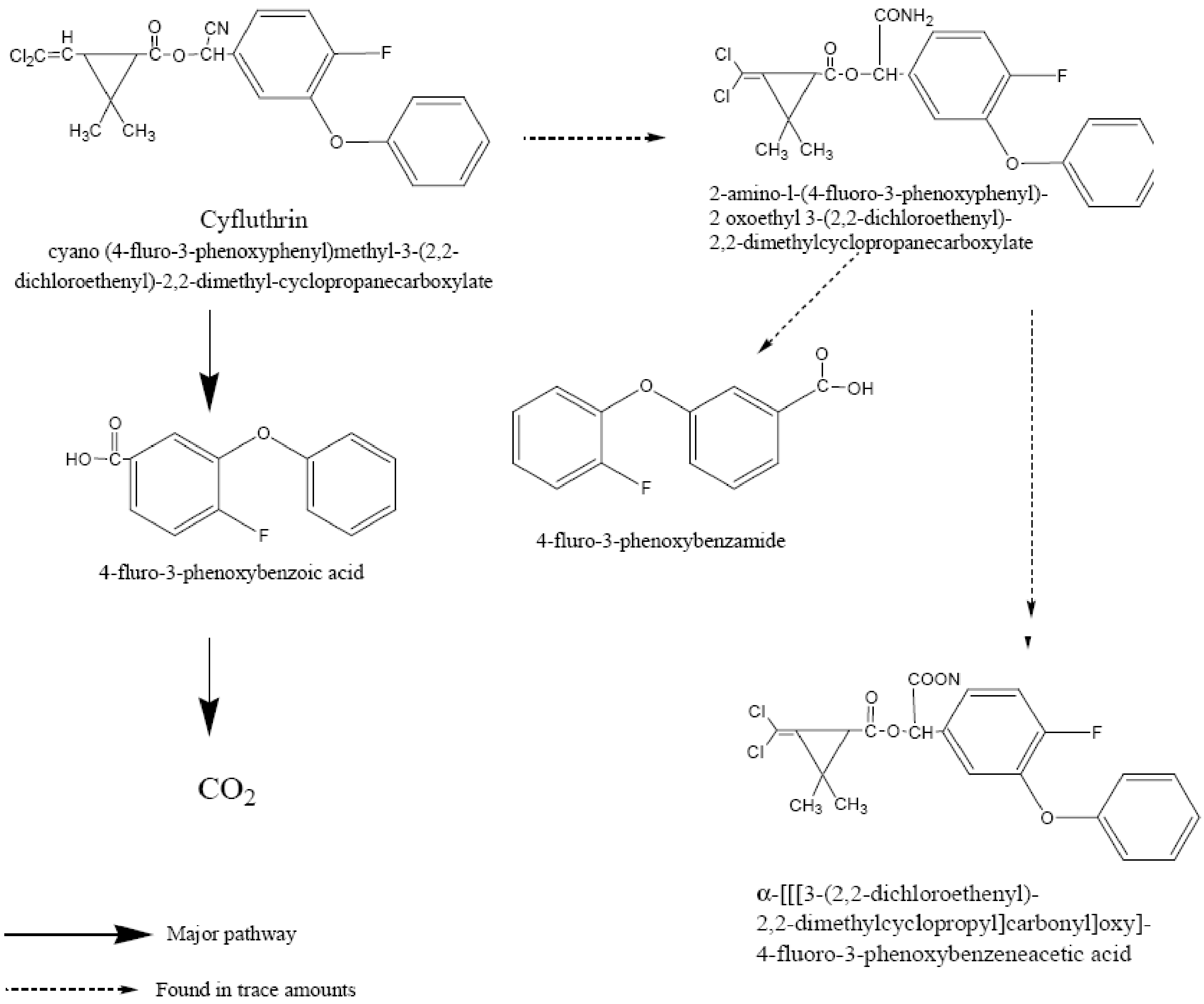

Figure 1.9: Aerobic degradation of β-Cyfluthrin in soil (Bongiorno 2005).

Those degradations products may be more toxic than the parent one if they were available in high concentrations (Bongiorno 2005).

I.10 Objectives:

The overall objective of this study is to determine the quantitative and qualititative pesticides residual in groundwater of the shallow aquifer system in Jericho area.

I.10.1 Specific Objectives:

1. To determine the main pesticide type areal distribution.

2. To determine these pesticides in ground water of the shallow aquifer.

3. To identify sensitive hot spots of pesticides concentration in ground water.

I.10.2 Hypotheses:

The developed hypotheses to serve the objective are summarized in the following points:

1. Pesticides concentration in ground-water varies from one site to another according to residual time in the unsaturated zone.

2. Physical and chemical properties of pesticides affect the rate of those pesticides to leach to the ground water.

CHAPTER II

LITERATURE REVIEW

II.1 Literature Review

In 1990, EPA (Environmental protection Agency) released the phase 1 report on its national pesticide survey. This was the first large scale documentation of the extent of ground water contamination by pesticides. After this survey it was clear that pesticide contamination did exist in almost every state. Spurred by these finding, EPA has to better protect the nation's ground water from pesticides. To do this, "pesticides and ground water strategy" was developed including the state management plan concept (EPA 1991).

The issue of pesticides in ground water and their effects to the environment and human health gives the chance of many other studies to occur through the world in different areas with various kinds of pesticides that helps in analysis of many kinds of them with their residuals and this help us also to know how to deal with these pesticides according to the chemical and physical characteristics. The studies below show us the earliest until nowadays studies about pesticides we concern.

Spliid (1998): In this study, 46 compounds of pesticides were studied and analyzed by liquid chromatography mass spectroscopy (LC-MS) with detection limit below 0.01 mg\L in shallow ground water in Denmark (Danish), four sampling sites were included in this study, the sampling sites were equipped with extraction wells with screen 1.5,3 and 5 meters below surface. It was found that many traces of different types of pesticides, herbicides, and fungicides were found, some of them in higher amounts than the acceptable limit for health safety.

Ahmad, et al., (1998): This paper studied the residues of chlorinated hydrocarbon pesticides in rain water, soil and ground water in different areas in Egypt, by sampling from various wells for ground water samples. It was found that many organochlorine pesticides are present in soil and ground water as heptachlor and DDT, besides that it was found that the residual detected in ground water is higher than residuals reported in many European countries (Ahmad M 1998).

Ananiev, et al., (2002): This study described the effect of Abemectin pesticide on the protein and RNA synthesis in primary leaves. It was found that this pesticide preparation plants include Abemectin as the active compound, applied at concentration used in green house practice (0.1%) can stimulate two major biochemical process in plants-biosynthesis of proteins and RNA in the primary leaves of seedling. And these results could be interpreted in view of the ability of Abemectin to act as a membrane-active complexone (Lacorte 1995).

Tomkins (2002): This study focuses on the determination of Atrazin and organophosphorus pesticides in small samples (10ml) of ground water in U.S.A. Solid phase micro-extraction followed by gas chromatography was used. Two independent statistical procedures were used to evaluate the detection limit which range between 2 and 8 mg/L for these analytes.

Yassin M, et al., (2002): The objectives of this study was to assess knowledge, attitude, practice, and toxicity symptoms associated with pesticide use and exposure among 189 farm workers in the Gaza Strip. A cross section of agricultural farm workers in the Gaza Strip were asked to fill in a questionnaire on knowledge, attitudes, practice towards pesticide use, and associated toxicity symptoms. The results concluded of farm workers reported high levels of knowledge on the health impact of pesticides (97.9%). Moderate to high levels of knowledge were recorded on toxicity symptoms related to pesticides. Most farm workers were aware of the protective measures to be used during applying pesticides. However, no one took precautions unless they knew about the measures. So this study proved that Farm workers in the Gaza Strip used pesticides extensively, despite their knowledge about the adverse health impact of the pesticides (Mackay 1992).

Tuncel (2004): In this study organochlorine pesticides in ground water in Turkey were determined by using soild phase microextraction , gas chromatography mass spectroscopy , and polydimethylsiloxane fiber was used as extraction medium.

Shomar (2005): In this study, the occurrence of pesticides in the ground water wells in Gaza was investigated. This study described a 3-year program to monitor types and levels of contamination by 52 pesticides in 94 groundwater wells in Gaza. The analysis was done using chromatographic analytical techniques (GC and HPLC). Water from 63 wells showed no detectable levels of pesticides or levels that were much lower than the allowable limit (0.5µg/L). Atrazine and other pesticides were detected in 4 wells with average concentrations of 3.5, 1.2, 1.5 and 2.3µg/L (Shomar 2005).

Kamel (2006): In this study, degradation of the acaricides Abamectin, flufenoxuron and amitraz on date palms grown in Saudi Arabia was studied during the post-harvest interval (PHI) under the local weather and soil conditions. There are about 400 different species of dates in Saudi Arabia grown in different regions of the Kingdom; the most important regions are: Riyadh, (Central), Eastern, Qassim (Central), Madina (Western), Assir (South Western). The HPLC/FL, GC/ECD methods were used, which shows a highly selective and sensitive for the detection of low amounts of the three acaricides. Results of this study showed that the initial deposit of Abamectin on dates of Nabout Sief type was 0.09 mg/kg and gradually with time the rate of residue decline reached 66% after 7 days and 88% after 14 days of application. This indicates that after 7 days of treatment, which is only 3 days, the amount of Abamectin was 0.03 mg/kg and this exceeded the upper limit of the maximum allowed residue set by the Codex Committee on Pesticide Residues under the Joint WHO Food Standards Program at 0.01–0.02 mg/kg for fruits (FAO/WHO 1997).

Shomar (2006): This study describes the purity of pesticides used in Gaza in terms of trace elements. A semi quantitative technique and quantitative ICP/OES was used to determine the concentrations of Al, As, Ti and Zn in 50 of the most commonly used solid pesticides collected from the five central shops in the Gaza Strip. The results revealed that the pesticides contain considerable amounts of trace elements and do not comply with the expected-theoretical structure of each species. Moreover, they do not reflect the actual constituents mentioned in the trade labels. They may also have been smuggled into Gaza with differing impurities (Rodier 1996).

The results indicate that pesticides should be considered as a source of certain trace metals (particularly Cu, Mn and Zn) and other elements (Sr and Ti), which may affect their mass balances in soil and groundwater as well as their plant uptake.

Herna´ndez Borges (2007): This study has focused on the quantification of Abamectin residues in avocados set by the Spanish and European legislation fruit. The method allows a fast analysis of Abamectin using microwave assisted extraction (MAE), solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) with fluorescence (FL) detection using tri-fluoroacetic anhydride and N-methylimidazole as derivatizing agents. Several avocado samples previously treated with Abamectin were also analyzed 20 days after a single application. No significant quantities of residues were found (Mustafa 2007).

El Bakouri (2007): Studied the pesticide occurrence in ground-water in northwest Morocco. The pesticides which were studied belong to the endosulfon isomers and their degradation products, the traizines and phenyl-ureas. The analyses were done using chromatographic techniques and solid-phase extraction. Endosulfon products and their degradation products were both detected in ground water samples of which the latter presents the highest concentrations.

CHAPTER III

METHODOLOGY

III.1 Instrumentation

III.1.1 HPLC-UV System

The apparatus which was used for analysis of those three pesticides is HPLC with UV detection. It is a form of column chromatography used frequently in biochemistry and analytical chemistry to separate, identify, and quantify compounds. HPLC utilizes a column that holds chromatographic packing material (stationary phase), a pump that moves the mobile phase(s) through the column, and a detector that detect the compound and show its retention time. Retention time varies depending on the interactions between the stationary phases, the molecules being analyzed, and the solvent(s) used (Bidlingmeyer 1992). Figure (3.10) is a schematic representation of HPLC.

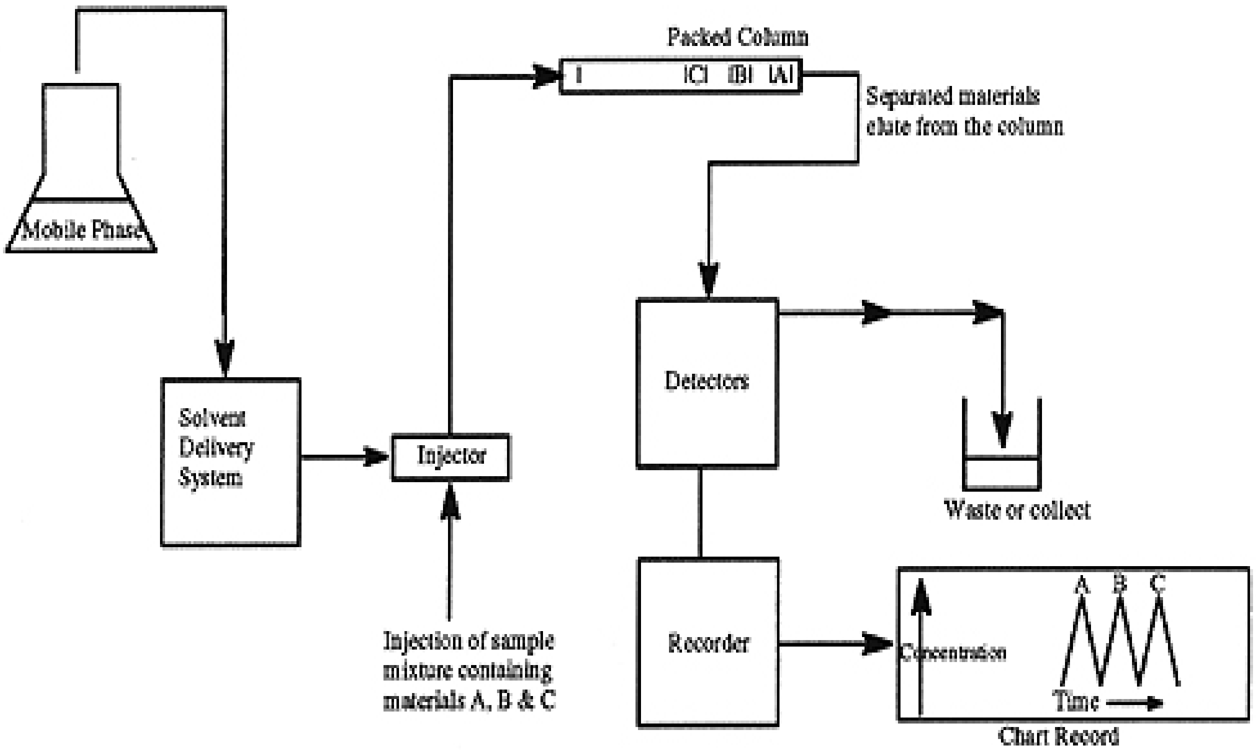

Figure 3.10: Scheme of HPLC Apparatus (Clark 2007).

III.1.2 Multi-Meter

A multi-meter is used to make various electrical measurements, such as AC and DC voltage, AC and DC current, and resistance. It is called a multi-meter because it combines the functions of a voltmeter, ammeter, and ohmmeter (see figure 3.11). This apparatus was used through the sampling procedures to measure the pH of the water wells in the study area, besides measuring the resistivity and the temperature of water; it is an electronic measuring instrument , its principle based on two sensitive electrodes with a small detector to measure the values (Tanuwijaya 2009).

Figure 3.11: Multi-meter (CRUTCHFIELD 1997).

III.1.3 Rotary Evaporator

Rotary evaporator is a specially designed instrument for the evaporation of solvent under vacuum. The evaporator consists of a heating bath with a rotating flask, in which the liquid is distributed as a thin film over the hot wall surfaces and can evaporate easily (BUCHI 1998). The evaporation rate is regulated by the heating bath temperature, the size of flask, the pressure of distillation and the speed of rotation.

This apparatus was the best to use in comparison with any other distillation apparatus because with a vacuum rotary evaporator you can carry out single stage distillation runs quickly and gently. Also the evaporation capacity is about 4 times greater than that of conventional, static distillation apparatus.

Heat transmission in the heating bath as well as inside the flask is greatly improved by rotation of the evaporating flask (BUCHI 1998). Figure (3.12) shows this apparatus.

Figure 3.12: Rotary Evaporator (Aloise 2005).

And in general there is proper operating procedure that should always be followed for more safety and this is done by (Aloise 2005):

1. Rotate the flask
2. Slowly apply the vacuum
3. Use water bath to heat.

III.1.4 Dryer

Simple apparatus was used for sample drying after using the rotary evaporator. The principle of this apparatus is the removal of water moisture or moisture from the sample (see figure 3.13).

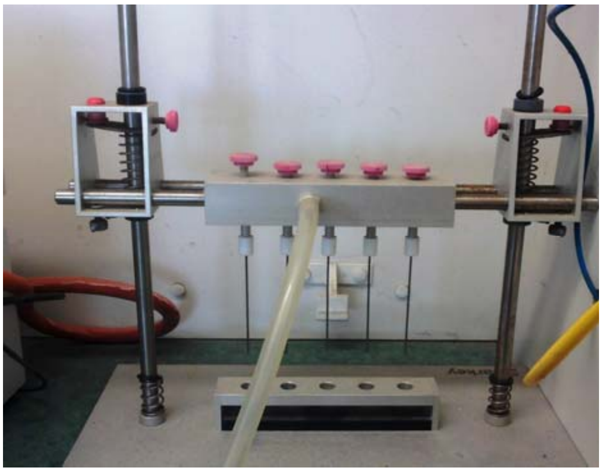

Figure 3.13: Dryer Apparatus (Environmental lab research 2010).

III.2 Chemicals and Materials

III.2.1 Chemicals

Acetonitrile (HPLC grade), n-hexane 95% (HPLC grade), double distilled water, di-chloromethane 99.5% (HPLC grade), phosphoric acid, sulfuric acid. Abamectin (avermectin B1b, 99%, Article no. 31732, assay HPLC grade).

β-Cyfluthrin((RS)-a-cyano-4-fluoro-3-phenoxybenzyl(1RS,3RS)-3-(2,2dichllorovinyl)-2,2dimethylcyclopropane-carboxylate, 99.8%, Article no. 46003, assay HPLC grade), Imidacloprid (1-[(6-chloropyridin-3-yl) methyl]-N-nitro-4, 5-dihydroimidazol-2-amine , 99.9%, Article no. 37894, assay HPLC grade), were obtained from SIGMA-ALDRICH.

Standards of Abamectin, β-Cyfluthrin, and Imidacloprid were prepared in different concentrations, 0.001ppm, 0.01ppm, 0.1ppm, 1ppm, 5ppm, 10ppm, and 100ppm (see table 3.7).

III.2.2 Materials

Separatory funnels 250ml, pipette(25ml, 50ml), beakers 50ml, 100ml, funnels , paper wipes', aluminum foil, markers, vials, labels, gallons (2L, 5L), and large ice containers.

III.3 Methodology

III.3.1 Field Survey

The Ministry of Agriculture in Ramallah has provided our team with the names of the most used pesticides in this area. Some of these pesticides were brought through this Ministry and others from Israel. Table (3.4) lists some of the pesticides used in West-Bank (The Ministry of Agriculture -Ramallah- West Bank 2008). The complete lists of these pesticides are shown in Appendix V.4.

Table 3.4: Some of the Pesticides used in West-Bank (The complete lists of these pesticides are shown in Appendix V.4).

No.#	Chemical Name	Trade Name
1	Fenoxycarb	Insegar
2	Spinosad	Tracer super
3	Chlorpyrifos	Dorsban
4	Methoxyfenozide	Runer
5	Cypermethrin	Cymbush 10
6	Abamectin	Vertimec
7	Imidacloprid	Confidor
8	Carbosulfan	Marshal 25
9	Acetamiprid	Mosblan
10	Oxydemethon methyl	Metasystox
11	β-Cyfluthrin	Tempo
12	Amitraz	Mitac

To determine the number of pesticides which is going to be studied in the area, our team went to Jericho for a survey to determine which pesticides are used often and in large quantities. We have found that different pesticides are used, some of them have the same active material but with different trade names (pictures of Jericho's Survey can be seen in Appendix V.7).

According to the team survey in Jericho, three pesticides were found as the most used in this area and each one belong to a different category of pesticide with different chemical and physical properties. These three pesticides are Abamectin, Imidacloprid, and β-Cyfluthrin. The chosen of those three pesticides belongs to several reasons and not randomly according to their physical and chemical properties. These three pesticides have different solubility in water; Imidacloprid has the higher solubility so it is expected that it present in the ground water in higher concentrations than other three pesticides. Other differences between these three pesticides which may affect their presence in ground water are:

- Ability to bind with the soil: Each one of the three pesticides differ in binding to soil according to the organic components of each and to the type of soil and the properties of the pesticide, for example soil with high organic matter content has the ability to bind with hydrophobic (not polar) pesticides. For example β-Cyfluthrin has high tendency to bind with soil particles compared to the other two pesticides, due to the higher tendency of its contents to bind to soil with a small tendency to be dissolved in water (low solubility).

- Half-life of each pesticide to degrade in water and soil: Each pesticide has a half-life to be broken into breakdowns products. Table (3.5) shows the half-life of each pesticide in water and in soil. These half-lives are relative according to the water and soil temperature and according to the pH of the media. β-Cyfluthrin has the highest half-life in soil and in water whereas Abamectin has the smallest.

Table 3.5: Pesticides' Half-life in water and soil (Kollman 1995).

Pesticides	**Hydrolysis Half-life**	**Soil half-life**
Abamectin	2-4 weeks	7 days
Imidacloprid	33-44 days	39 days
β-Cyfluthrin	193 days	81-191 days

The selection of those pesticides (Abamectin, Imidacloprid, and β-Cyfluthrin) was based on a number of reasons, namely:

1. According to the survey, those pesticides were the most used in Jericho area by farmers.

2. The materials and chemicals needed in the laboratory for experimental work were available in the Environmental lab research.

3. The three pesticides have absorption on the UV detector; that each one has a wavelength that can be detected on this detector.

4. Each pesticide has different chemical and physical properties and so these pesticides were chosen to prove those properties on ground water.

III.3.2 Saturated and Unsaturated zone

The saturated zone encompasses the area below ground in which all interconnected openings within the geologic medium are completely filled with water, whereas the unsaturated zone is the zone between the land surface and the regional water table. It includes the capillary fringe and may also include localized perched ground water (Bhattacharya 2010).

The unsaturated zone differs from the saturated zone, in which pores contain water at greater than atmospheric pressure and are almost completely filled with water, see figure (3.14).

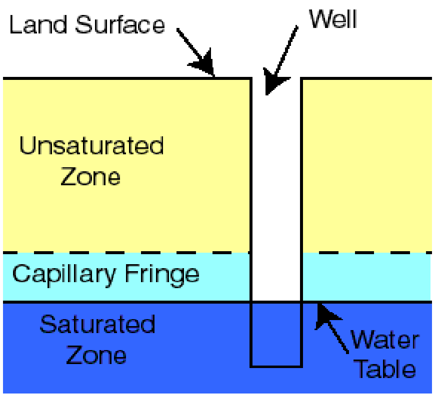

Figure 3.14: Saturated & Unsaturated Zone (Bhattacharya 2010).

Water within the saturated zone moves through the interconnected pores of the geologic material in response to the influences of gravity and pressure from overlying water. Rates of groundwater movement within the saturated zone ranges from a few feet per year to several feet per day depending upon local conditions (Conrad 2007).

In Jericho area the movement of the saturated zone through the ground water depends on the circumstances of that area; Jericho's soil have more desert character to be sandy-soil so easy for penetration.

III.3.3 Water Sampling

III.3.3.1 Information Needed for Sampling

To ensure appropriate methodology for collection of water samples, information is needed before a sample is collected. Some information should be obtained regarding the field activities such as well conditions, construction, water-level information, contaminant types and concentrations, and direction(s) of ground-water flow. Field measurements, such as depth to water and total well depth will be needed prior to purging. Before commencement of all field activities, the field health and safety plan should be consulted under the direction of the site health. The time and date of the measurement, point of reference, measurement method, depth-to-water level measurement and any calculations should be properly recorded. In addition, any known, outside influences (Such as nearby pumping effects, major barometric changes) that may affect water levels should be noted (Michael 1989).

III.3.3.2 Water Sampling Technique

After recording the name and number of the well, the pump in the well has been run for about half an hour, and then the bottles are filled full with water. After this, 5ml of sulfuric acid for each 5 liters water sample, which is used as preservative, is added to the water samples (Barcelona 1985).

The samples are covered with aluminum foil to prevent contamination and moved to the ice containers until moving to the lab.

III.4 Extraction Procedure

In the next day after the collection of water samples, liquid-liquid extraction was used to extract the three pesticides from those samples. Each pesticide has different method of extraction by using different solvent according to the solubility of each pesticide in the solvent used, but the general procedure for this extraction for the three pesticides was done as follows:

Figure 3.15: Extraction Technique (Hoffman 2002).

First of all, the equipment used must be washed and cleaned by distilled water. 100ml of water sample was added to the separatory funnel followed by adding 20 ml of organic solvent (dichloromethane for Abamectin, and n-hexane for Imidacloprid and β-Cyfluthrin) to the sample, after that the separatory funnel was closed tightly with a stopper and shacked well (Mackenzie 2008). The extraction process was repeated three times with three portions of organic solvent to get sure that all the pesticide was extracted to the organic layer. The organic extracts are then collected in a beaker.

III.5 Sample Drying Procedure

After extraction, the extracts are brought to the rotary evaporator to evaporate the organic solvent, to get the total volume of sample after evaporation less than 1ml (few drops), then the dryer system is applied to remove any moisture which may be still present in the sample, after that the sample is pure and ready to be analyzed by HPLC-UV.

III.6 HPLC-UV Analysis

1 ml of Acetonitrile was added to the sample with 1 ml of isopropyl alcohol as an emulsifier to increase the solubility of n-hexane in the ACN used, but for the dichloromethane samples only 1ml of acetonitrile added without any emulsifier due to the miscibility with ACN. Then these

samples are ready to be analyzed in the HPLC. All samples are preserved in the refrigerator until analyzed. At this stage the amount of pesticides in 100ml of water sample was concentrated to 2ml. (concentration factor is 50) or to 1.0 ml (concentration factor is 100).

III.7 Abamectin, β-Cyfluthrin, and Imdacloprid Analysis by HPLC-UV

A method of analysis by HPLC was developed for each pesticide. C_{18} column (25cm, 4.6 mm Inner diameter, 5µm particle size of packing) was used as a stationary phase for analysis. As a mobile phase, a mixture of water and acetonitrile was used (with fixed ratio for each pesticide). Other parameters and HPLC conditions were set for each pesticide (flow rate, wavelength), Injection volume was 20µL for all samples and standards.

Table 3.6: HPLC parameters Used in the Analysis of the Pesticides.

Parameter	**Abamectin**	**β-Cyfluthrin**	**Imidacloprid**
Wave length	245 nm	220 nm	270 nm
Flow rate	1.5 ml/min	1.5 ml/min	1.4 ml/min
% Acetonitrile in the mobile phase	80%	80%	30%
% Water in the mobile phase	20%	20%	70%
Injection volume	20 µL	20 µL	20 µL

III.8 Preparation of Standards

For each pesticide stock standard was prepared by using Acetonitrile as a solvent. From this stock standard, different solutions with different concentrations were prepared for the calibration curve (see tables 3.7) by dilution using mobile phase.

Table 3.7: Pesticide's Standards for Calibration Curve

Pesticide / **Stand. Concentration**	**Abamectin**	**β-Cyfluthrin**	**Imidacloprid**
Standard conc.	100ppm	100ppm	100ppm
Diluted conc.	50ppm	50ppm	50ppm
Diluted conc.	10ppm	10ppm	10ppm
Diluted conc.	5ppm	5ppm	5ppm
Diluted conc.	1ppm	1 ppm	1 ppm
Diluted conc.	0.1 ppm	0.1ppm	0.1 ppm
Diluted conc.	0.01 ppm	0.01 ppm	0.01 ppm
Diluted conc.	0.001 ppm	0.001 ppm	0.001 ppm

Each concentration of these standards was injected into the HPLC (20 μL), and the chromatograms were recorded and the peak areas were plotted versus the concentration.

III.9 % Recovery (Accuracy)

The accuracy of an analytical procedure measures the closeness of agreement between the value, which is accepted either as a conventional true value or an accepted reference value and value found i.e. accuracy is a measure of exactness of an analytical method. Accuracy is measured as the percent of analyte recovered by spiking the analyte in a blind study. For the determination of the accuracy (% recovery) of pesticides in water, these pesticides are spiked in water samples (distilled water). And according to this the following procedure was done.

III.9.1 Spiking of 0.03ppm of Pesticide (Abamectin, Imidacloprid, and β-Cyfluthrin).

<u>% Recovery of Abamectin:</u>

1. 10mg of Abamectin was dissolved in few drops of ethanol and diluted to 100ml with water.
2. 3ml of the above solution was diluted to 100ml with water.
3. 2ml of above solution was diluted to 200ml with water [concentration of this solution = 30ppb].
4. The 200ml solution of Abamectin [0.03ppm] was extracted using the same procedure followed before (section III. 4).

I. <u>% Recovery of Imidacloprid:</u>

1. 10mg of Imidacloprid was dissolved in few drops of ethanol and diluted to 100ml with water.
2. 3ml of the above solution was diluted to 100ml with water.

3. 2ml of above solution was diluted to 200ml with water [concentration of this solution = 30ppb].

4. The 200ml solution of Imidacloprid [0.03ppm] was extracted using the same procedure followed before (section III. 4).

II. <u>% Recovery of β-Cyfluthrin:</u>

1. 10mg of β-Cyfluthrin was dissolved in few drops of ethanol and diluted to 100ml with water.

2. 3ml of the above solution was diluted to 100ml with water.

3. 2ml of above solution was diluted to 200ml with water [concentration of this solution = 30ppb].

4. The 200ml solution of β-Cyfluthrin [0.03ppm] was extracted using the same procedure followed before (section III. 4).

III.10 Precision of the Method

Precision is the measure of the degree of repeatability of an analytical method under normal operation and is normally expressed as the relative standard deviation (RSD) for a statistically significant number of samples. Repeatability is the result of the method operating over a short time interval under the same conditions (injection precision or instrument precision) (Holler, 1991). RSD for replicate injections should not be greater than 10%. Precision of a method can be evaluated by calculating the relative standard deviation (RSD) of peak areas of the studied pesticides in different (e.g. 3-6) samples.

III.11 Limit of Detection (LOD) and limit of Quantitation (LOQ) of the Method

The limit of detection (LOD) of a method is the lowest concentration of analyte of a sample that can be detected, but not necessarily quantitated under the stated experimental conditions (Huber L, 1998). LOD can be determined by preparing a set of low concentrations of analyte that is expected to produce a response that is 3-10 times base line noise. The solutions are injected and the signal to noise ratio (S/N) are recorded. LOD is selected as the concentration of analyte that gives an S/N ratio of 3-10. Limit of quantitation (LOQ) can be determined in the same manner but it is selected as the concentration of analyte that gives an S/N ratio of 10-20.

CHAPTER IV

RESULTS & DISCUSSION

IV.1 Chromatograms of Pesticides Standards

Standard of each pesticide (Imidacloprid, Abamectin, and β-Cyfluthrin) was injected separately in to the HPLC-UV using the conditions described in the previous section (Methodology). Retention times for these pesticides were found as follows: 3.7 and 6.3, minutes for Imidacloprid and Abamectin respectively. For β-Cyfluthrin two peaks appeared at 5.1 and 5.4 minutes (figure 4.18). For the calibration curve and for determination of concentration of β-Cyfluthrin in water samples, the sums of the two peaks of the diasterio-isomers of β-Cyfluthrin were taken.

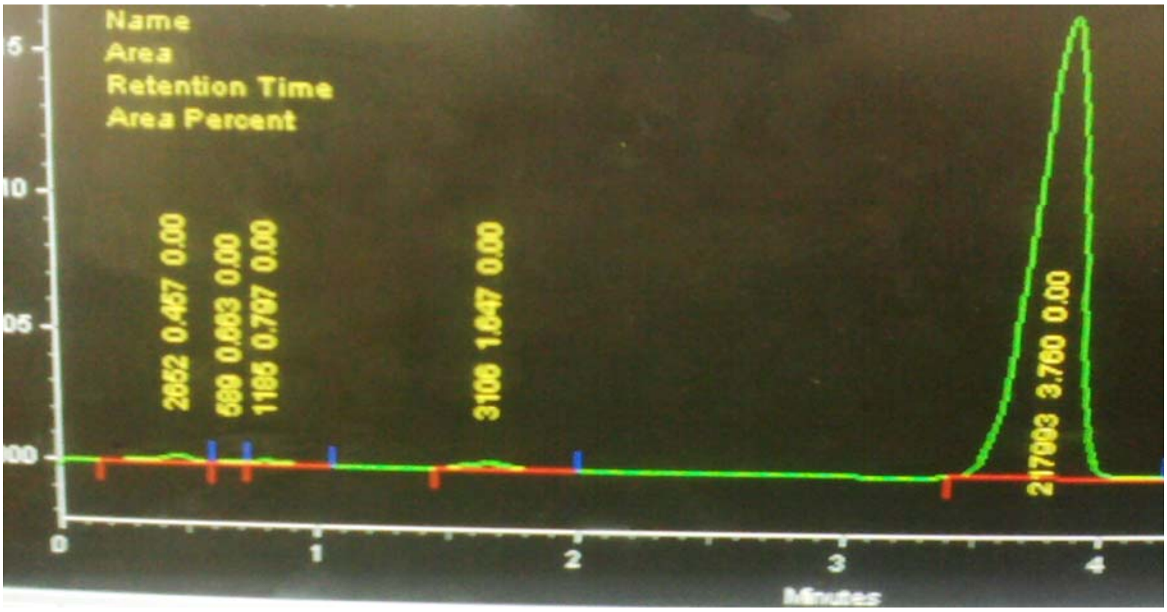

Figure 4.16: Imidacloprid Chromatogram

Figure 4.17: Abamectin Chromatogram.

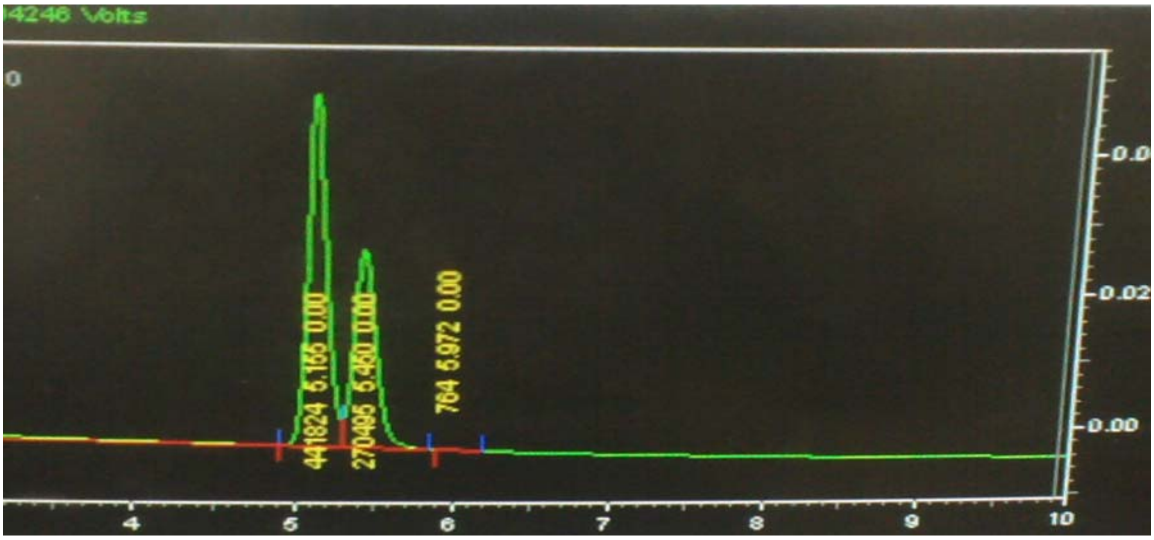

Figure 4.18: β-Cyfluthrin chromatogram (The two peaks are for the diasterioisomers of β-Cyfluthrin)

IV.2 Calibration Curve

To determine the concentration of each pesticide in the ground water samples, a calibration curve for each pesticide was made by analyzing the various solutions of pesticides (with different concentrations) which were prepared in section III.8 (Preparation of standards). The concentrations of the pesticide standards for calibration curve were chosen to cover the concentration of the pesticides in the ground water samples.

The resulting chromatograms of the pesticide were recorded and the peak areas were plotted versus concentration of that pesticide (in ppm), and a linear fit was made. For each calibration curve, the linearity equation y=mx+b (y: peak area, m: slope, x: concentration in ppm, b: y-intercept), as well as correlation coefficient (R^2) were obtained using the Excel software. Figures (4.19-4.21) show the calibration curves for Abamectin, Imidacloprid, and β-Cyfluthrin, respectively.

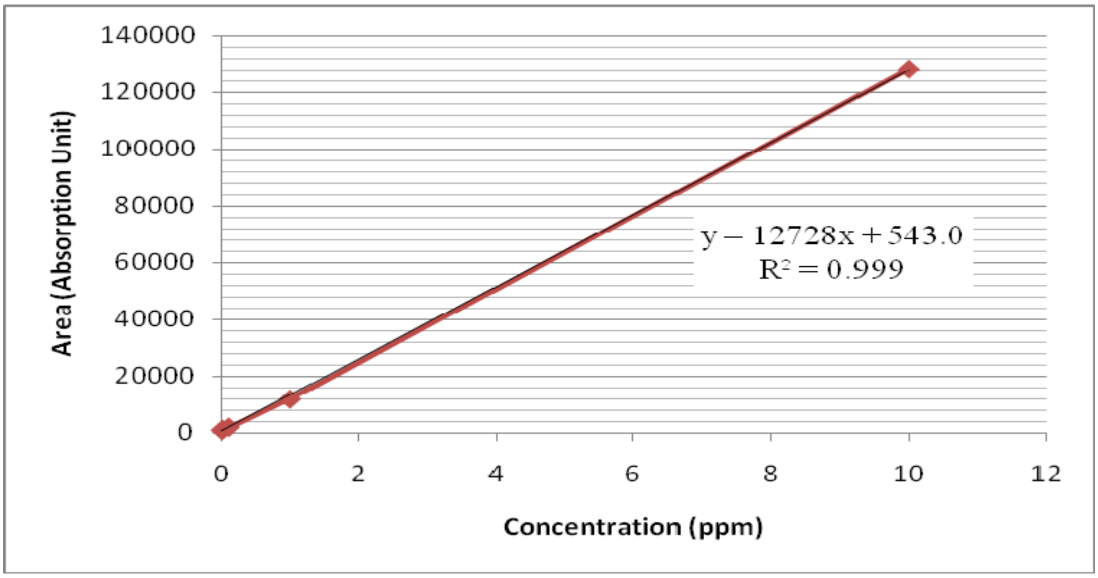

Figure 4.19: Calibration curve for Abamectin.

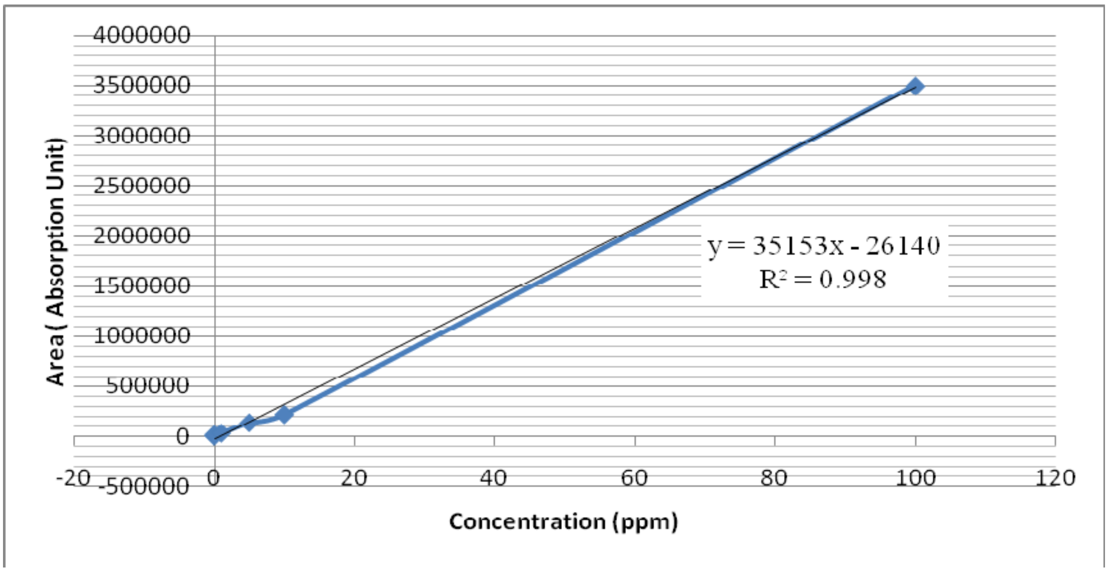

Figure 4.20: Calibration curve for Imidacloprid.

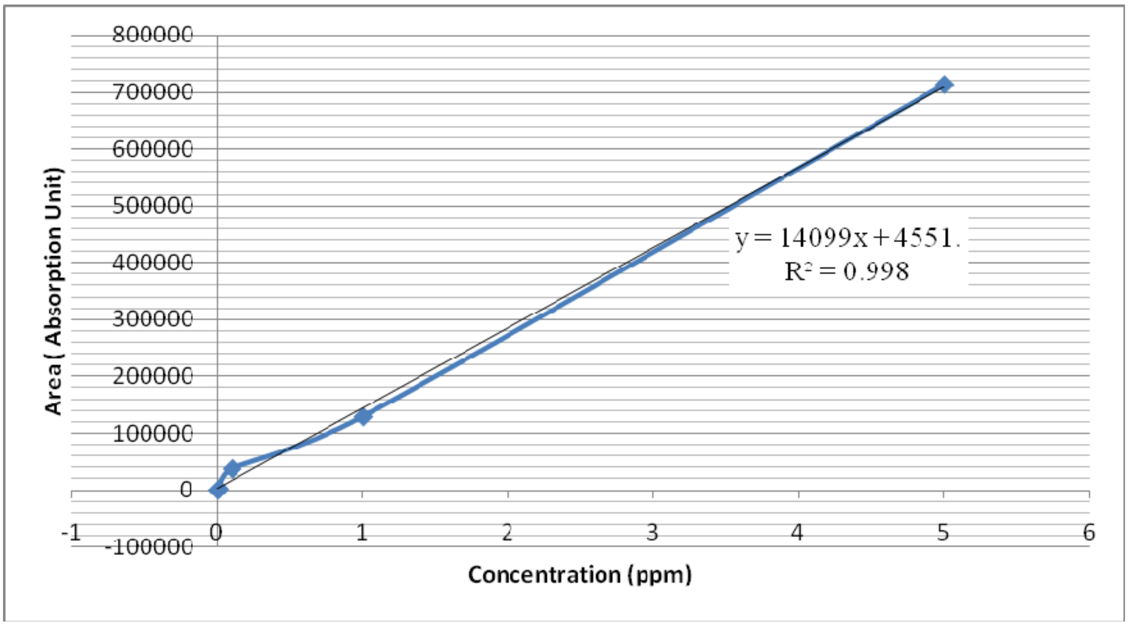

Figure 4.21: Calibration curve for β-Cyfluthrin.

The following tables show the areas of the peaks of each pesticide standard.

Table 4.8: Pesticide's Standards Peak Areas.

	Areas		
Standard's concentration	**Imidacloprid**	**Abamectin**	**β-Cyfluthrin**
0.001	5130	969.0	760.0
0.01	19831	1943	3303
0.1	…..	2049	38442
1	34881	11920	129529
5	138869	…..	712319
10	222905	127956	…..
100	3499699	…….	……

The peak's areas of each pesticide (Abamectin, Imidacloprid, and β-Cyfluthrin) found in water samples are shown in the following tables (4.9- 4.11):

Table 4.9: Peaks Areas for Well's Samples of Imidacloprid.

No.	Well's No.	Peak's Area	No.	Well's No.	Peak's Area
1	19-17/010	10855	**8**	19-17/054	1942
2	19-17/027	2485			
3	19-17/034	544200	**9**	19-13/005	7608
4	19-17/055	16684	**10**	19-13/52	2550
5	19-17/056	4878	**11**	Ismail Deik	7298
6	19-15/011	5797	**12**	19-15/012	2400
7	19-17/028	3575	**13**	19-17/008	18354
14	19-17/031	276	**21**	19-17/021	2446
15	19-17/046	5766	**22**	19-17/023	5258
16	19-14/001	3743	**23**	19-14/046	3788
17	19-15/005	3081	**24**	19-13/50A	141045
18	19-15/23	ND	**25**	19-13/55	5916
19	19-17/001	3544			
20	19-17/007	1817			

Table 4.10: Peaks Areas for Well's Samples of Abamectin

No.	Well's No.	Peak's Area	No.	Well's No.	Peak's Area
1	19-17/010	ND	**15**	19-17/031	10002
2	19-17/027	ND			
3	19-17/034	18139	**16**	19-17/046	ND
4	19-17/055	2126	**17**	19-14/001	ND
5	19-17/056	2126	**18**	19-15/005	ND
6	19-15/011	ND	**19**	19-15/23	16650
7	19-17/028	ND	**20**	19-17/001	647
8	19-17/021	ND	**21**	19-17/007	1817
9	19-17/054	ND	**22**	19-17/023	2399
10	19-13/005	ND	**23**	19-14/046	4666
11	19-13/52	34253	**24**	19-13/50A	ND
12	Ismail Deik	ND	**25**	19-13/55	8233
13	19-15/012	2899			
14	19-17/008	ND			

Table 4.11: Peaks areas for well's samples of β-Cyfluthrin.

No.	Well's No.	Peak's Area	No.	Well's No.	Peak's Area
1	19-17/010	2971	**16**	19-14/001	ND
2	19-17/027	ND	**17**	19-15/005	2517
3	19-17/034	22517	**18**	19-15/23	ND
4	19-17/055	3755	**19**	19-17/001	ND
5	19-17/056	2478	**20**	19-17/007	ND
6	19-15/011	ND	**21**	19-17/023	ND
7	19-17/028	ND	**22**	19-14/046	11420
8	19-17/054	ND	**23**	19-13/50A	ND
9	19-13/005	ND	**24**	19-13/55	ND
10	19-13/52	ND	**25**	19-17/021	ND
11	Ismail Deik	10083			
12	19-15/012	2127			
13	19-17/008	5238			
14	19-17/031	19828			
15	19-17/046	21794			

IV.3 Concentration of Pesticides in the Ground Water Samples

All of the extracted samples were injected (20µL) separately into the HPLC-UV and peak areas of the pesticide (if detected) were recorded. The concentration of the pesticide in the 2ml concentrated samples (or 1ml) was calculated from the linearity equation $y=mx+b$ found for each calibration curve. Then the concentration of each pesticide's water samples was calculated as follows:

Illustrative example: concentration of Abamectin in sample No. 19-17/034
Using the equation $y=12728x+543.0$ for Abamectin, with area equals 18139, so the concentration of Abamectin in the extracted sample (1ml) was found to be 1.382ppm

(1.382mg/L). This means that 1ml contains (1.382)*(1)/1000=0.001382mg of Abamectin. This also means that the 100ml of the water sample (No.19-17/034) contains 0.001382mg of Abamectin.

To convert this value to ppm: (0.002764)*(1000)/100=0.01382ppm.

Therefore this water sample (19-17/034) has 0.01382ppm (or 13.82ppb) of Abamectin. Following concentrations of Abamectin,Imidacloprid, and β-Cyfluthrin pesticides were found in the water samples (in ppb) (table 4.12).

Following concentrations of Abamectin, Imidacloprid, and β-Cyfluthrin pesticides were found in the water sample (in ppb):

Table 4.12: Pesticides concentrations in samples (in ppb).

No.	Sample No.	Abamectin	Imidacloprid	β-Cyfluthrin	Total (ppb)
1	19-17/010	ND	21.04	ND	21.04
2	19-17/027	ND	16.29	ND	16.29
3	19-17/034	13.82	325.0	2.540	341.4
4	19-17/055	1.244	24.36	ND	25.61
5	19-17/056	1.244	17.65	ND	18.90
6	19-15/011	ND	18.17	ND	18.17
7	19-17/028	ND	16.91	ND	16.91
8	19-17/054	ND	16.00	ND	16.00
9	19-13/005	ND	19.20	ND	19.20
10	19-13/52	26.48	16.32	ND	42.80
11	Ismail Deik	ND	20.00	7.840	27.84
12	19-15/012	1.882	1.457	1.238	4.577
13	19-17/008	ND	25.32	0.1000	25.42
14	19-17/031	7.432	15.03	21.68	44.14
15	19-17/046	ND	18.15	24.46	42.61
16	19-14/001	ND	17.002	ND	17.22
17	19-15/005	ND	16.63	ND	16.63
18	19-15/23	12.65	ND	ND	12.65
19	19-17/001	81.71	16.89	ND	98.60
20	19-17/007	ND	16.00	ND	16.00
21	19-17/021	ND	16.26	ND	16.26
22	19-17/023	1.458	17.86	ND	19.34
23	19-14/046	3.240	17.03	10.00	30.27
24	19-13/50A	ND	95.12	ND	95.12
25	19-13/55	6.042	18.24	ND	24.28

The chromatograms below (Figures 4.22, 4.23, and 4.24), show the presence the three pesticides in some water samples.

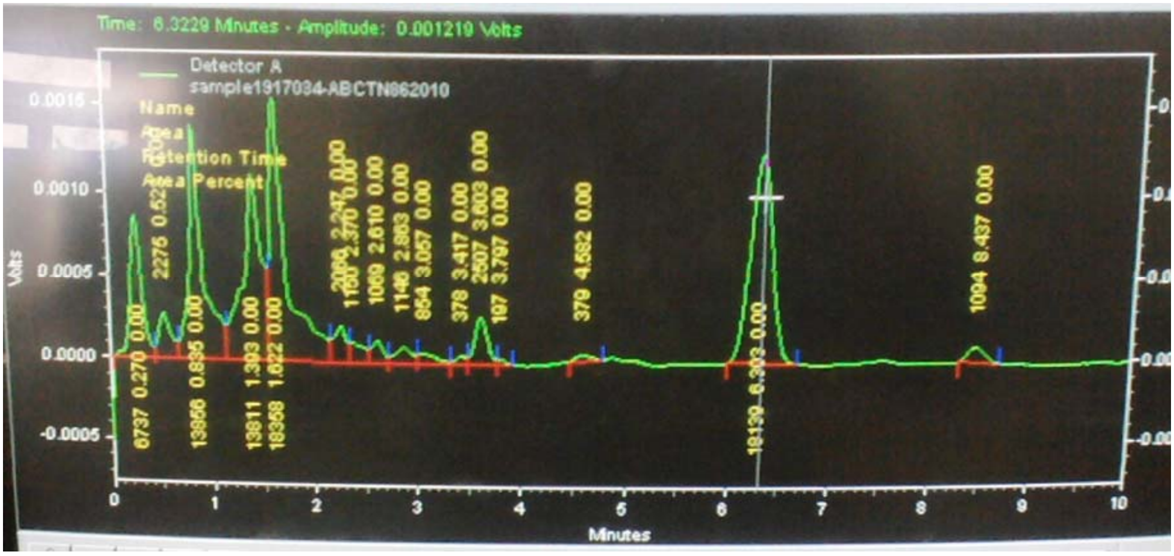

Figure 4.22: Water sample with Abamectin detected.

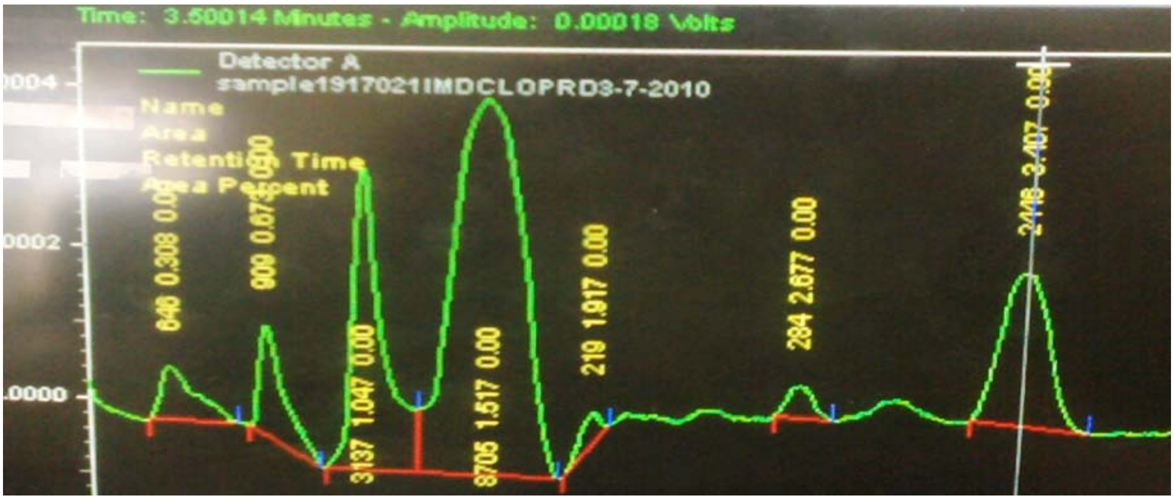

Figure 4.23: Water sample with Imidacloprid detected.

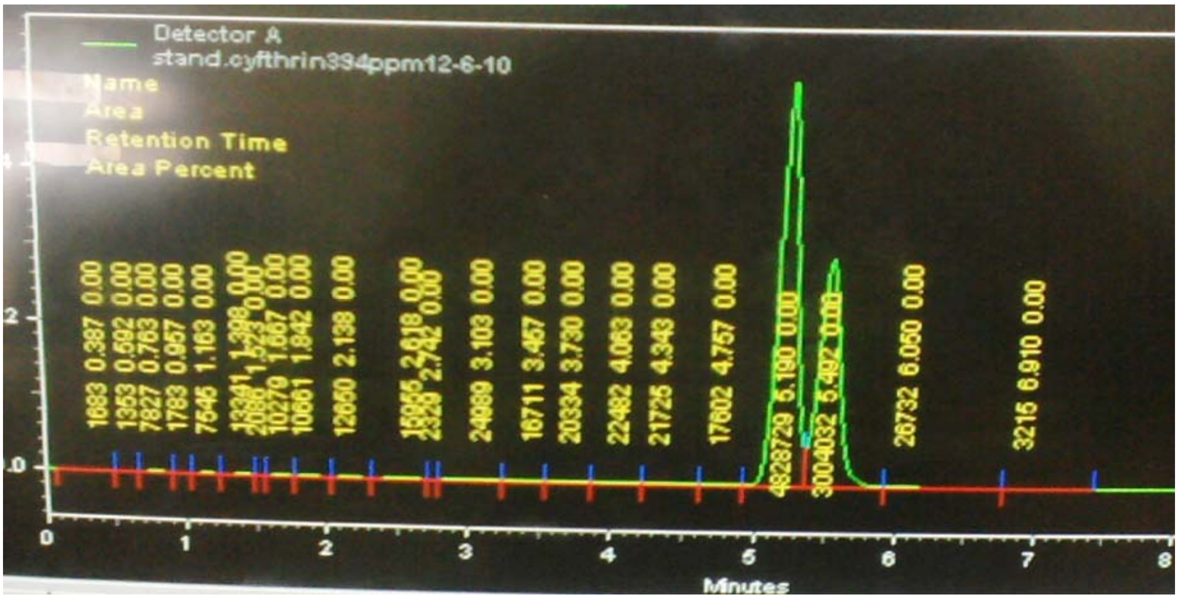

Figure 4.24: Water sample with β-Cyfluthrin detected.

IV.4 % Recovery

The percentage recovery of the three pesticides from 0.03 ppm spiked solutions (100ml) was calculated as follows:

1. The 200ml solution of 0.03ppm contains 0.006mg of Abamectin.
2. So the concentration of Abamectin in 1ml solution after evaporation is 6ppm.
3. And the concentration for Imidacloprid and β-Cyfluthrin in 2ml solution after evaporation (due the addition of Isopropyl-alcohol) is 3ppm.
4. So the calculated concentrations of each pesticide in the final evaporation sample (1ml, 2ml) are 6ppm for Abamectin and 3ppm for Imidacloprid and β-Cyfluthrin.

5. The percentage recovery for the pesticides can be calculated as follows:

$$\% \text{ Recovery} = \frac{\text{concentration of pesticide from the calibration curve} \quad \text{X } 100\%}{\text{Theoretical concentration}}$$

After injection the three pesticides sample into the HPLC (20 μL from each), the obtained Areas for each pesticide are shown in table below:

Table 4.13: Peak's Areas.

Pesticide	**Area**
Abamectin	78605
Imidacloprid	74128.5
β-Cyfluthrin	404584

Using the calibration curves, the concentrations of each pesticide in spiked sample was calculated and results are as follows:

Table 4.14: Concentrations of Pesticides.

Pesticide	**Concentration in ppm**
Abamectin	6.13
Imidacloprid	2.85
β-Cyfluthrin	2.83

The % Recovery for each pesticide was calculated and the results are shown in the table (4.15).

Table 4.15: Recovery Values.

Pesticide	% Recovery
Abamectin	6.13/6 *100 = 102.2%
Imidacloprid	2.85/3*100 = 95.0%
β-Cyfluthrin	2.83/3*100 = 94.6%

These results show that this analytical method used for analysis of these pesticides by HPLC-UV has a good recovery according to the directives laid down by the European Commission that the limit of recovery for pesticides is 70-110% (Holler 1991).

IV.5 Precision of the Method

The precision of this method was evaluated by calculating the relative standard deviation (RSD) of the peak areas of the pesticides in three water samples (from the same well, # 19-15/012). Results have shown that the RSD of the peak areas of Abamectin, Imidacloprid, and β-Cyfluthrin for the three samples is less than 10%, (see tables 4.16, 4.17, and 4.18), which reflect the good precision (repeatability) of the current method.

Table 4.16: Peak Areas of Abamectin for 3 Samples (Repeatability of the Method).

No. #	**Abamectin**	**Peak's Area**
1	19-15/012	2650
2	19-15/012	2460
3	19-15/012	2883
4	Average Area	2664
5	Standard Deviation	211.8
6	Relative Standard Deviation	7.9%

Table 4.17: Peak Areas of Imidacloprid for 3 Samples (Repeatability of the Method).

No. #	**Imidacloprid**	**Peak's Area**
1	19-15/012	2532
2	19-15/012	2477
3	19-15/012	2668
4	Average Area	2559
5	Standard Deviation	98.3
6	Relative Standard Deviation	3.8%

Table 4.18: Peak Areas of β-Cyfluthrin's for 3 Samples (Repeatability of the Method).

No. #	**β-Cyfluthrin**	**Peak's Area**
1	19-15/012	2322
2	19-15/012	2454
3	19-15/012	2048
4	Average Area	2275
5	Standard Deviation	207.1
6	Relative Standard Deviation	9.1%

IV.6 Pesticides Acceptable limit

The presence of pesticides in groundwater even in low concentrations is enough to affect human health and the environment (Chilton 1993). In other studies, however, a certain limit is specified for each pesticide and for total pesticides. The limit of each pesticide in ground water is 0.1µg/L (0.0001 ppm) (Kamble 2005), where in another study it is 0.5µg/L (0.0005 ppm) for the limit of total pesticides in ground water (American Chemical Society 2001).

IV.7 Limit of Detection (LOD) and limit of Quantities (LOQ) of the Method

Results showed that LOD and LOQ of the three pesticides are shown in table (4.19).

Table 4.19: LOD and LOQ of Abamectin, Imidacloprid, and β-Cyfluthrin.

Pesticides	**LOD (ppm)**	**LOQ (ppm)**
Abamectin	0.0005	0.0015
Imidacloprid	0.0001	0.0003
β-Cyfluthrin	0.0001	0.0003

Results showed that the LOD and LOQ of the studied pesticides (Abamectin, Imidacloprid, and β-Cyfluthrin) are low which enables the detection and quantitation of these pesticides in ground water using this HPLC-UV method at low concentrations.

IV.8 Discussion

According to this study which was conducted in West Bank/Jericho, the results showed the presence of pesticides residuals in water samples of some wells, while these pesticides are not detected in other wells. However, this does not guarantee that these wells have no pesticides, but it may be that this current method (HPLC-UV) cannot detect very low concentrations (less than 0.0001ppm) of the pesticides (traces).

The presence of these pesticides in the ground water in the study area can be attributed to the following reasons:

1. Quantity of pesticides used: In the study area, most farmers do not adhere to guidance and to the quantities specified on the pack of pesticide bottles, and they use usually higher amounts of pesticides randomly.

2. Site of the well: It has been found that the wells which are located in the middle of agricultural areas contain higher amounts of pesticides compared to wells located around the agricultural area or not near to it. Most of the sampling wells were found in the middle of the agricultural area and this increases the ability of pesticides to arrive to the ground water due to the small distance between the sprayed field and the well, this explained the existence of pesticides in high amounts in ground water of the sampling wells.

3. Type of soil: Type of the soil plays an important role in the arrival of pesticides to the ground water. Soil with high amount of clay particles and organic matter tend to retain the pesticides (i.e the pesticides are held by the soil) and therefore the pesticides become immobile and the probability of their arrival to the ground water is low. On the other hand, soil with low organic matters and clay or soil which has desert-character (like the soil in the study area) do not retain (hold) the pesticides (weak interaction with soil) and therefore pesticides in such soil tend to leach to the ground water. The soil in the study area

(Jericho) has a desert character and therefore the probability of arrival of pesticides to the ground water is high (ZHAO-YANG LI 2003).

4. Polarity of the pesticides: polarity of the pesticide plays also a role in the arrival of pesticides to the ground water. Pesticides with low polarity (high hydrophobicity) tend to be retained in the soil (strong interaction with soil) and so their probability to arrive ground water is low, while pesticides with high polarity (low hydrophobicity) do not interact strongly with the soil and their probability to reach the ground water is high. β-Cyfluthrin is non-polar (and more hydrophobic than Abamectin and Imidacloprid) and this may explain why it was detected in small number of wells (7 of 25 wells) and in low concentrations. Imidacloprid which is polar, on the other hand, was detected in most of the wells and in higher concentrations compared to β-Cyfluthrin and Abamectin.

5. Type of pesticide used: Certain pesticides have strong interaction with the soil which decreases the probability of the arrival of the pesticide to the water, while other type of pesticides have weak interaction with the soil which increases the likelihood of leaching of pesticides to the ground water .

6. The distance from the surface of the earth to the ground water: The greater the distance between groundwater and surface of the earth, the more time the pesticides needs to reach the ground water. For the wells in study area, the distance is from 60 to 120 meters.

7. Time of water collection: This has a very big role in the concentration of pesticides in groundwater, since each pesticide has a certain half-life in soil and water (see table 3.5) that explains the half-life of each, where the half-life of pesticides depends on the pH of the media; in basic media (pH=8.3) hydrolysis increases. For the three pesticides in this study, (some with soil half-life of few days), water samples were taken within few days of pesticide application, to check if they are stable in soil or water.

8. Rain water: Rain has a big role where it increases the probability of the arrival of pesticides to the ground water. Most of the samples in this study were taken in the period after winter, it is known that pesticides dissolved or suspended in runoff water may quickly reach surface waters such as lakes and rivers, and highly soluble pesticides will tend to readily leach into groundwater (National Water Quality Assessment Program 2001).

9. Type of fertilizers added to the soil: Since fertilizers are organic matters, pesticides bind strongly to these organic matter and prevent them to leach into the ground water.

The number of detected wells with these pesticides is found as follows: Abamectin 11 of 25 wells, Imidacloprid 24 of 25 wells, and β-Cyfluthrin 7 of 25 wells. It was also found that the highest concentration of these pesticides found in the studied wells is for Imidacloprid with 325ppb followed by Abamectin 81.7ppb and finally β-Cyfluthrin with a concentration of 24.46ppb, (see table 4.12).

These results can be explained by the weather in the study area and the physical and chemical properties of the three pesticides. Below is the explanation (justifications) of these results.

1. Imidacloprid is polar and has higher solubility compared to the other pesticides (see table 4.20), and therefore it was found that it has the highest concentration in the ground water and also it has been detected in large number of wells (24 out of 25). It was also found a positive (direct) correlation between the solubility of the pesticide in water and concentration of pesticide in the ground water, and anther direct relationship between the solubility of pesticide in water and the number of wells which are contaminated with the pesticide.

Table 4.20: Solubility of Pesticides in water (Jack 2006).

Pesticide's Name	Solubility in water (ppm)
Imidacloprid	514
Abamectin	0.54
β-Cyfluthrin	0.02

2. Time of sampling; not all the wells were sampled at the same time, some of the samples were collected directly after farmers applied the pesticides, while others were collected after the rain fall in winter, and this is documented in the Appendix chapter. Pesticides application increases the probability of finding pesticides in the ground water, while the samples which were collected after rain fall increases the probability of finding the pesticides in ground water especially the pesticides with high water solubility.

3. Interaction with the soil: β-Cyfluthrin bind strongly to the soil (Gioia 2005) and this decreases the possibility of leaching of this pesticide to the ground water.

4. Weather condition of Jericho city: Jericho city has a very hot climate at morning and cool weather at night (desert climate), and this play a big role in the degradation of pesticides in water or in soil before leaching to the ground water. Each pesticide has a different soil photolysis half-life and hydrolysis half-life. β-Cyfluthrin takes 193 days to degrade in water, but in soil photolysis of β-Cyfluthrin takes 16 days in the same temperature ($30C^0$) (DPR Pesticides chemistry database 2001). On the other hand Imidacloprid takes 30 days to degrade in water and Abamectin takes 1 day to degrade in soil in photolysis conditions. But in Jericho the temperature reach more than $30C^0$ and so faster degradation takes place. (Wislocki 1989).

5. Well's depth relation: When the distance of ground water from the earth surface increased, pesticides take more time to reach, so the concentration of pesticides in ground water will be also decreases, but this factor is minor; that type of soil and amounts of pesticides used effect the concentration of pesticides to be high or low more than the distance of ground water is. So in some of the sampling wells the correlation between the well depth and the concentration of pesticides found is inverse relation as in the figure below (for selective wells 19-17/034 and 19-17/001)

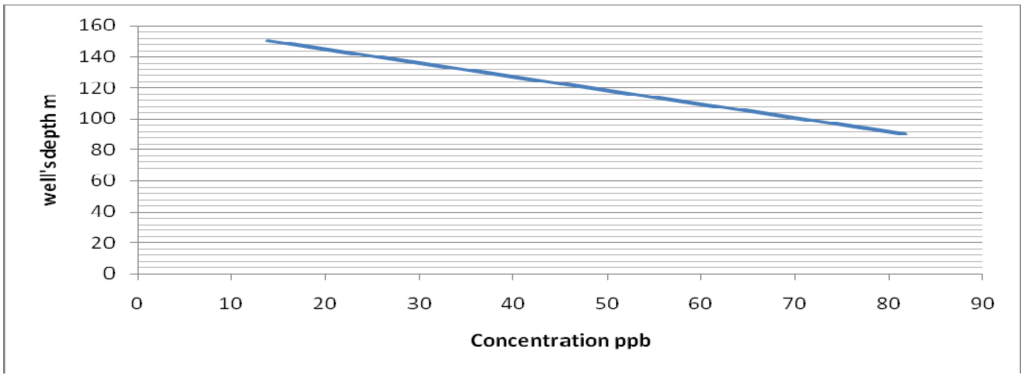

Figure 4.25: Abametin concentration versus 2 well's depth.

When all the sampling wells for Abamectin correlated with their Abamectin's concentrations, the curve will be irregular as shown in figure below.

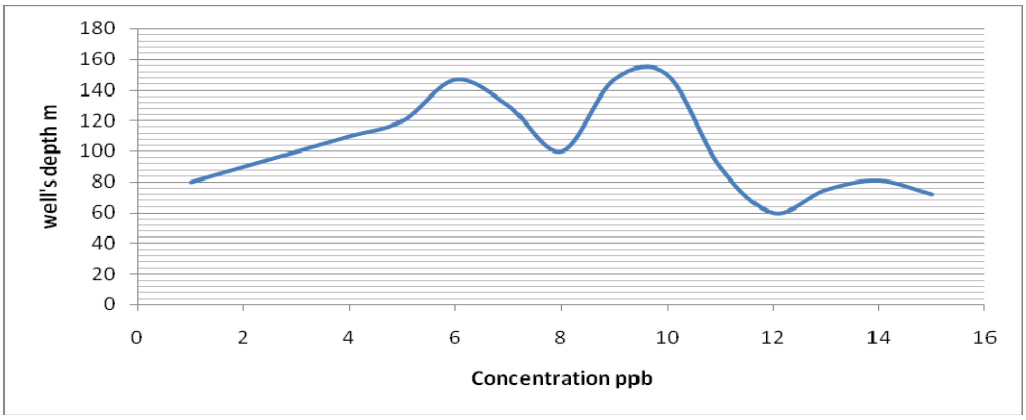

Figure 4.26: Abamectin's concentration versus 25 well's depth.

According to the acceptable limits of the pesticides in ground water (0.1 or 0.5 ppb), the ground water in the study area is contaminated with the three pesticides, in higher amounts than the acceptable limit (The presence of pesticides in groundwater enough to affect human health and the environment). This result can be attributed to many reasons:

1. The use of pesticides by farmers without care and control.

2. Poor management of the Ministry of Agriculture in pursuing the type of pesticides used by farmers and quantity used to spray plants and agricultural crops.

3. Failure to follow the instructions and guidance stated in the bottle of insecticide by many farmers regarding the amounts of pesticides for applications. Furthermore, most of farmers do not follow safety rules before using the pesticide due to the ignorance of the farmers about the effects of pesticides on human health in the short and long run.

4. Throw empty jars or bottles of pesticides on agricultural land. These bottles contain residual of these pesticides and this may lead to the accumulation of these pesticides on the soil and therefore leaching to the ground water.

5. pH of water: pH of water affects the solubility of the pesticides in water. For example, the three pesticides investigated in the current study are stable in acidic and neutral media while their degradation rate increases in basic media. The pH of the wells in the study area was measured and found to be neutral (from 6.89-7.41; see table 4.21) and therefore these pesticides are considered stable in this ground water.

Table 4.21: pH for the Water Wells Samples.

Well's No.	pH's	Well's No.	pH's
19-17/010	7.04	19-15/005	7.13
19-17/027	7.16	19-15/23	7.30
19-17/034	7.40	19-17/001	7.06
19-17/055	7.05	19-17/007	7.05
19-17/056	6.97	19-17/021	7.06
19-15/011	7.35	19-17/023	7.41
19-17/028	7.25	19-14/046	7.00
19-17/054	6.98	19-13/50A	7.07
19-13/005	7.01	19-13/55	7.15
19-13/52	7.11		
Ismail D3ek	6.89		
19-15/012	7.23		
19-17/008	6.91		
19-17/031	7.13		
19-17/046	7.10		
19-14/001	7.10		

IV.8.1 Site of the Wells

Site of the well has an important role in the presences of pesticides in ground water. Some of those wells surrounded with a lot of empty bottles of pesticides used by farmers and that increase the chance of existing pesticides in water well samples.

IV.8.2 Comparison of the Results with Recent Studies

The recent study of the “occurrence of pesticides in ground water of Gaza strip “in 2005, (Shomar 2005) showed that 31 wells of the 94 sampled wells contain detectable level of pesticides while the remaining sixty three wells had pesticide concentration less than the instrumental detection limit. In that study, one or more of 14 types of pesticides in ground water supply were detected in 8 wells mainly Atrazin, DDT, DDD, and DDE. Also it was found that DDT was detected in wells in Rafah area and two in Khan Yunis (Supported by European Commission). Comparison of the results of the study in Gaza strip (in 2005) with the current study shows that the number of wells of ground water which were contaminated with pesticides is higher in Jericho (study area in this work) compared to Gaza strip; 24 wells of 25 in Jericho were found to contain one or more of the three pesticides while only 31 of 94 wells in Gaza strip found to contain one or more pesticides of the 14 types of pesticides studied. This difference (results) can be attributed to the geology Gaza strip which is different from Jerich’s.

Other study was done in Northwest Morocco titled as “pesticides in ground water northwest Morocco” in 2007 (El Bakouri 2007). In this study, the occurrence of pesticides in ground water, as well as in soil of the field was studied. This study has focused also on the presence of some anions that may be a proof of existing some of pesticides where these anions may be produced from these pesticides such as nitrates. In my study, I ‘am interested only in the pesticides in ground water and it is interesting that other student may extend this research for the occurrence of these pesticides in soil.

IV.9 Recommendations

According to the survey which showed that high amounts of pesticides are used in the West-Bank in a wrong and unsafe way, and according to the results of this study that showing the leach of pesticides to the ground water in low concentrations to high concentrations (above the acceptable limit). According to the results above there are some recommendations which have to be addressed:

1. Much care and attention should be given to the wells which found to have high concentrations of pesticides, and limit the use of the water only for external uses and not for personal uses.

2. The pesticides which cause high health hazard should be identified and used in very low amounts or not at all if possible.

3. The use of pesticides should be controlled and the instructions on the sheet of guideline of the pesticide should be followed carefully, especially in the areas I found the level of pesticides and even if very few in their wells of those areas because they may increase the hazard.

4. Regular analysis of water (ground water) for the presence of pesticides.

5. Farmers should follow the instructions of the Ministry of Agricultural regarding the use of pesticides, their effect on health and environment, how to use them …etc.

6. Use only the pesticides which are permitted by the Ministry of Agriculture and to punish the farmers who use banned pesticides, or who smuggles the pesticides from Israel.

7. Public awareness.

8. To locate a place for disposal of the empty bottle of pesticides and the remaining pesticides after use by the municipality or the village council or the Ministry of Agriculture and these places are dedicated and far from agricultural land.

9. I recommended students or researchers interested in this field to investigate the presence of these three pesticides and other pesticide in soil and to correlate it with the pesticide concentrations in ground water.

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V APPENDICES

V.1 Appendix

Jericho well's information, which were collected on 21/10/2009 in after direct pesticides application to the field.

Well's No.#	Well's ID	Coordination East North	Well's depth (m)	Water use
1	19-13/52	195880…139670	120	Agriculture
2	19-13/50A	195810…139380	100	Agriculture
3	19-13/55	196200…139640	110	Agriculture
4	19-13/005	195170…139650	80	Agriculture
5	ISMAIL DEIK	197312…137860	90	Agriculture

V.2 Appendix

Jeftlik's well information, which were collected on 26/5/2010.

Well's No.#	Well's ID	Coordination East North	Well's depth (m)	Water use
6	19-17/056	194600…174100	147	Agriculture
7	19-17/055	196150…173400	130	Agriculture
8	19-17/031	197680…171060	100	Agriculture
9	19-17/046	192560…176230	147	Agriculture
10	19-17/034	192740…178370	150	Agriculture
11	19-17/001	196900…170740	90	Agriculture
12	19-17/027	196250…171470	60	Agriculture
13	19-17/054	197600…169150	75	Agriculture
14	19-17/021	196520…170560	81	Agriculture
15	19-17/008	196250…170250	72	Agriculture
16	19-17/023	194200…175230	150	Agriculture
17	19-17/028	198150…170500	72	Agriculture

V.3 Appendix

Al-uja's well information, which were collected on 19-20/5/2010 after rainfall.

Well's No. #	Well's ID	Coordination East North	Well's depth (m)	Water use
18	19-15/005	194750…150440	108	Agriculture
19	19-14/001	195910…149990	59	Agriculture
20	19-15/23	196020…150090	41	Agriculture
21	19-15/007	194870…150760	105	Agriculture
22	19-15/012	194590…150940	103	Agriculture
23	19-15/011	194750…151000	95	Agriculture
24	19-17/010	197060…170150	77	Agriculture
25	19-17/007	194080….161002	110	Agriculture

V.4 Appendix

Most usable Pesticides used in Jericho/ West-Bank on 2008-2009.

No. #	Chemical Name	Trade Name
1	Fenoxycarb	Insegar
2	Pyriproxyfen	Tiger
3	Spinosad	Tracer super
4	Chlorpyrifos	Dorsban
5	Deltamethrin	Decis
6	Dichlorvos	Divipan 100
7	Methoxyfenozide	Runer
8	Cypermethrin	Cymbush 10
9	Abamectin	Vertimec
10	Imidacloprid	Confidor
11	Carbosulfan	Marshal 25
12	Acetamiprid	Mosblan
13	Oxydemethon methyl	Metasystox
14	Amitraz	Mitac

V.5 Appendix

Most usable fungicides in Jericho/West-Bank by the year 2008-2009.

No.	Chemical Name	Trade Name
1	Fenbuconazole	Indar
2	Hexaconazole	Anvil
3	Penconazole	Ofir
4	Triadimenol	Bayfidan
5	Propanocarp HCL	Previcur
6	Carbendazim	Bavistin
7	Myclobutanil	Rally
8	Fenarimol	Rubigan
9	Kresoxim methyl	Stroby
10	Copper hydroxide	Champion

V.6 Appendix

Most usable herbicides in Jericho/ West-Bank by the year 2008-2009.

No.	Chemical Name	Trade Name
1	Oxyfluorfen	Amcogol
2	2,4-D	Albur super
3	Glyphosate Trimesium sulfate	Touchdown
4	Trifluralin	Trifluran
5	Cloquintocet + Clodinafop Propargyl	Topik
6	Oxyfluorfen	Galigan
7	Oxyfluorfen	Goal FN
8	Glyphosate isopropy amine salt	Roundup
9	Oxadiazon	Ronstar
10	Clethodim	Select Supr
11	Linuron	Linurex

V.7 Appendix

Pictures below explain the empty pesticides bottles around Jericho’s field, these pictures were taken through the team survey.

Pesticide bottles around farms in Jericho

المبيدات الحشرية الثلاث التي انحصرت الدراسة عليها هي امبماكتن (Abamectin) و ايميداكلوبرايد (Imidacloprid) و بيتا-سايفلوثرين (β-Cyfluthrin) . حيث تمت الدراسة على ٢٥ بئر ارتوازي تم اختيارهم بشكل عشوائي في مناطق الجفتلك والعوجا وأريحا، حيث أظهرت الدراسة بوجود بعض هذه المبيدات في مياه الآبار المستخدمة للري وبنسب متفاوتة نتيجة الاستخدام المفرط للمبيدات الحشرية من قبل المزارعين مما أدى إلى وصول بعضها إلى المياه الجوفية وبعدت تراكيز معينه مما قد تتسبب الأذى الذي قد يمتد إلى المدى البعيد للإنسان والبيئة حيث أظهرت الدراسة أن نسبة تواجد الامبماكتن في عينات مياه الآبار تتراوح ما بين ١.٢٤٤ إلى ٨١.٧١ جزء من البليون في ١١ عينة بئر من أصل ٢٥، أما نسبه تواجد الايميداكلوبرايد فتتراوح ما بين ١.٤٥٧ إلى ٣٢٥ جزء من البليون في ٢٤ عينة بئر من أصل ٢٥ عينه، بينما ألبيتا-سايفلوثرين فتتراوح نسبة تواجده ما بين ٠.١٠٠٠ إلى ٢٤.٤٦ جزء من البليون في ٧ عينات من أصل ٢٥ عينة بئر، إذ أن هذه القيم ليست بالنسب القليلة مقارنة مع الحد المقبول عالميا (٠.١ -٠.٥) لتواجد المبيدات الحشرية في المياه الجوفية وعليه فان بعض الآبار وخصوصا الآبار التي تتواجد فيها هذه المبيدات الحشرية التي تم الدراسة عليها تشكل خطرا يهدد صحة الإنسان والبيئة سواء على المدى القريب أو البعيد وبناء عليه تم اقتراح بعض التوصيات تشير إلى كيفية التعامل مع هذه الآبار للحد من انتشار الأمراض والتلوث البيئي.

المبيدات الحشرية في طبقة المياه الجوفية الضحله في منطقة أريحا

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إشراف: د. عامر مرعي

د. فؤاد الريماوي

الملخص:

تعد المبيدات الحشرية مهمة بالنسبة للمزارعين في الوطن العربي والعالم، حيث أن لهذه المبيدات غرض أساسي ومهم في المحافظة على المحاصيل الزراعية من التلف من قبل الحشرات وبعض الفطريات الضارة والقوارض التي تقضي على المحصول وتسبب خسارة كبيرة للمزارع وبالتالي لاقتصاد الدولة. إلا أن لهذه المبيدات أخطار كبيره على صحة الإنسان والبيئة ، فهي مكونه من مواد كيميائيه مثل النحاس والكبريت وغيرها الكثير والتي تسبب أمراض خطيرة ومزمنة للإنسان إذا تعرض لها مباشرة أو استنشقها بكميات كبيرة، ،ومثل هذه المبيدات تتصف بترسباتها الخاملة التي يمكن لها أن تتراكم في التربة ملوثة إياها لتغسل فيما بعد إما بالأمطار الهاطلة أو بواسطة الري بالمياه ،محمولة إلى جدول الماء والأنهار مؤدية إلى موت الطحالب والأسماك بالاضافه إلى وصولها للمياه الجوفية .

منطقه اريحا في فلسطين من المناطق الزراعية الهامة والتي تعتمد في زراعتها على المياه الجوفية والآبار الارتوازية بشكل كبير بالاضافه للاستخدام الكبير للمبيدات الحشرية وبكميات هائلة حسب الإحصائيات الفلسطينية والتي وردت في نص الرسالة، بالتالي فان هذه الدراسة تتضمن حصر الكميات الهائلة من المبيدات الحشرية المستخدمة إلى ثلاثة مبيدات حشرية عن طريق المسح الميداني الذي تم في منطقه أريحا لفحص سلامه المياه الجوفية في الآبار الارتوازية من المبيدات الحشرية أم لا.