An Najah National University

Faculty of Graduate Studies

Evaluation of *Imidacloprid* and *Abamectin* Residues in Tomato, Cucumber and Pepper by High Performance Liquid Chromatography (HPLC)

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Dedication

To my beloved parents, wife, brothers, sisters and to my lovely daughters; Maryam and Noor with love and respect

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Evaluation of *Imidacloprid* and *Abamectin* Residues in Tomato, Cucumber and Pepper by High Performance Liquid Chromatography (HPLC)

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Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher´s own work, and has not been submitted elsewhere for any other degree or qualification.

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Abstract

Recently, one of the most indispensable methods is the usage of Imidacloprid (Konfedor®) and Abamectin (Vertimk®) in crops which make great improvement toward this crops such as tomato, cucumber and pepper. On the other hand there are demerits of using such pesticides toward the human health.

In this study, we choose two types of pesticides which mentioned above (Imidacloprid and Abamectin), for many reasons, first of all they are the most common among farmers as shown in questioner, second, this pesticides are the most effective in coming over the spiders and many insects.

Imidacloprid (Konfedor®) and abamectin (Vertimk®) where sprayed on tomato, cucumber and pepper in three greenhouses using the same concentration that farmers used to spray their crops, concentration of imidacloprid (Konfedor®) was 14.5mg /L and concentration of abamectin (Vertimk®) was 29 mg /L.

Samples from different crops and soil were collected of spraying , five days, ten days and twenty days later. Samples were taken from fruits, leaves and roots. After collection of samples they were extracted. Then the extracts were analyzed by high performance liquid chromatography (HPLC) and ultra violet visible spectrophotometer to evaluate the residues of imidacloprid (Konfedor®) and abamectin (Vertimk®).

Results obtained from this study indicates that the residues of both imidacloprid (Konfedor®) and abamectin (Vertimk®) were higher than the quantities of residues that determined by previous researchers. Also results obtained from this study showed that the quantities of residues were higher than the maximum residue levels (MRLs) in the samples that are collected on the first, the fifth and the tenth day of spraying. Also this study showed that the residues of abamectin are higher than imidacloprid, and residues of both abamectin and imidacloprid are higher in soil than plant parts.

Chapter One

1.1 Introduction

Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops (Wang and Liu, 2007) . And Pesticide residues are the very small amounts of pesticides that can remain in or on a crop after harvesting or storage and make their way into the food chain . Not all vegetables contain pesticide residues, and where they do occur they are typically at very low levels. Pesticide residues also include any breakdown products from the pesticide (Hoyu, 2005).

The Environmental Protection Agency sets maximum residue limits (MRLs), or tolerances, for pesticides that can be used on various food and feed commodities. Below are two resources for maximum residue limits (MRLs), or tolerance information. Imidacloprid is a nicotine-based, systemic insecticide, which acts as a neurotoxin and belongs to a class of chemicals called the neonicotinoids. As a systemic pesticide, imidacloprid translocates or moves readily from the soil into the leaves, flowers, fruiting bodies, pollen, nectar, and guttation fluid of plants. Imidacloprid is also mobile and persistent in the environment and has the potential to accumulate in soil (Hughes, 2005).

Abamectin occurs metabolism in plant Avermectins B1a degraded rapidly , thus forming a variety of product. The only residues of toxicological significance were abamectin a mixture of two components, avermectins B1a and B1b, the first being the major component. Many of the derivatives from abamectin include emamectin benzoate and ivermectine , these chemicals are used as acaricides or parasiticides for animals or plants (Valenzuela, *et al*., 2001).

Pesticides residues are affect on health including human and animals (wild life) the effect ranging between very dangerous to slightly, in some times some of pesticides residues affect on hormones on human and cause disturbance to natural hormones in our bodies. These hormone disruptors are said to risk affecting brain development, behavior, and the development of reproductive organs. They have also been associated with such as falling sperm counts and girls entering puberty earlier. The greatest risk from hormone disruptors is that they can cause problems at very low doses. Some block the bodies natural hormones from working, while others mimic the action of natural hormones (Flack, *et al.*, 1992).

Most of the food produced for human consumption is grown using pesticides. Chemical control of weeds, insects, fungi, and rodents has enabled agricultural productivity and intensity to increase. However, these economic benefits are not without their risks to human and environmental health. Small amounts of some pesticides may remain as residues on fruits, vegetables, grains, and other foods. If exposures are great enough, many pesticides may cause harmful health effects, including delayed or altered development, cancer, acute and chronic injury to the nervous systems, lung damage, reproductive dysfunction, and possibly dysfunction of the endocrine (hormone) and immune systems. For some pesticides, residues at levels below detection limits may pose important risks, while for other pesticides detectable levels of residues may not pose a significant health concern.(Ehrich, *et al*, 1990).

In this research we would like to study the pesticides residues (*Imidacloprid and Abamectin)* on some vegetables include tomato, cucumber, and pepper. The method for determine pesticides prepare extraction for previous plant include roots, foliage and fruits and analysis these samples by high performance liquid chromatography (HPLC) and UV-Visible Spectrophotometer to compare results with the two pesticides of the Standards legislation of pesticides residues and maximum residues levels MRLs and the purpose for research identification of apparatus high performance liquid chromatography. And also we studying the soil how contain the residues of the previous pesticides and the fate of two pesticides in soil and the effect by time.

1.2 Background

1.2.1 Agriculture in Palestine

Agriculture remains a dominant sector of the Palestinian economy. It represents a major component of the economy’s GDP, and employs a large fraction of the population. Furthermore, the agricultural sector is a major earner of foreign exchange and supplies the basic needs of the majority of the local population. In times of difficulty, the agricultural sector has acted as a buffer that absorbs large scores of unemployed people who lost their jobs in Israel or other local sectors of the economy.

Palestinian agriculture is constrained by available land and water, as well as access to markets. These constraints have been the object of political conflict, as Israeli authorities have limited available land, water and markets. It is widely recognized that resolution of these conflicts is essential to the establishment of peace in the region (ARIJ,1994). Since Palestinian agriculture is a major potential user of land and water, it is important to establish its needs for these resources. Typically, models for the allocation of water in the region have used a simple derived demand function for water, in which the elasticity of demand is the key parameter (ARIJ,1994).

Agriculture is the backbone of the Palestinian economy, contributing 33% and 24% of the Gross National Products in the West Bank and Gaza strip respectively. West Bank agriculture has, in the last few years, increased in sophistication, and this has had many negative side effects, of which the overuse of pesticides could prove to be the most serious (Saleh *et al.,* 2005).

1.2.2 Status of vegetable production in Palestine

Fruit trees constituted 69.3% of the cultivated area of the Palestinian Territory. While vegetables and field crop comprised 10.2% and 20.5% of the cultivated Palestinian areas respectively, 69.3% of the cultivated area in Gaza Strip rely on irrigation compared with only 7.9% of the West Banks cultivated area that relies on the same source of irrigation (PCBS, 2012).

Vegetables**,** 180 thousand dunums of land are used for vegetable production in the Palestinian Territory of which 71.3% in the West Bank and 28.7% in Gaza Strip. About 73.5% of the vegetables area of the West Bank is irrigated while the rest is rainfed. The area of protected vegetables constitutes 41 thousand dunums which represents 22.6% of the total vegetables area of the Palestinian Territory. Whereas open irrigated area and rainfed area comprises 56.6% and 20.8% respectively. Cucumber, Tomato, and Squash are the main crops of vegetable produce, comprising 44.1% of the total vegetables area of the Palestinian Territory. (Mustafa, 1999).

The total area planted with vegetables in the Palestinian territories during the agricultural year 2006/2007 was approximately 187.8 thousand dunum (Mustafa, 1999).

1.2.3 Pesticides history and classification

Pesticides any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit. Also used as substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport. And Pesticides are chemicals with harmful effects on both the human beings and the environment (Wilson and Tisdell, 2001).

The concept of pesticides is not new. Around 1000 B . C . E . Homer referred to the use of sulfur to fumigate homes and by 900 C . E . the Chinese were using arsenic to control garden pests. Although major pest outbreaks have as potato blight (*Phytopthora infestans*), which destroyed most potato crops in Ireland during the mid-nineteenth century, not until later that century were pesticides such as arsenic, pyrethrum, lime sulfur, and mercuric (Liu and Halterman, 2006).

The first synthetic organochlorine insecticide, DDT (dichlorodiphenyl trichloroethane), discovered in Switzerland in 1939, was very effective and used extensively to control head and body lice, human disease vectors and agricultural pests, in the decades leading up to the 1970s. Benzene hexachloride (BHC) and chlordane were discovered during World War II and toxaphene and heptachlor slightly later (Roberts, 2001). Organophosphate insecticides originated from compounds developed as nerve gases by Germany during World War II (Oates and Cohen, 2009).

Thus, those developed as insecticides, such as tetraethyl pyrophosphate (TEPP) and parathion, had high mammalian toxicities. Scores of other organophosphates including demeton, methyl schradan, phorate, diazinon, disulfoton, dimethoate, trichlorophon, and mevinphos have been registered. In insects, as in mammals, they act by inhibiting the enzyme cholinesterase (ChE) that breaks down the neurotransmitter acetylcholine (Ach) at the nerve synapse, blocking impulses and causing hyperactivity and tetanic paralysis of the insect, then death (Hsieh, *et al.,* 2001).

In recent years, new classes of insecticides have been marketed, none of which are persistent or bioaccumulate. They include juvenile hormone mimics, synthetic versions of insect juvenile hormones that act by preventing immature stages of the insects from molting into an adult, and avermectins, natural products produced by soil microorganisms, insecticidal at very low concentrations. *Bacillus thuringiensis* toxins are proteins produced by a bacterium that is pathogenic to insects (Montiu, *et al.,* 2011).

insecticides a pesticide used against insects. They include ovicides and larvicides used against the eggs and larvae of insects respectively. Insecticides are used in agriculture, medicine, industry and the household (Rodriguez, *et al.,* 2011). The classification of insecticides is done in several different ways as systemic insecticides are incorporated by treated plants. Insects ingest the insecticide while feeding on the plants. Contact insecticides are toxic to insects brought into direct contact. Efficacy is often related to the quality of pesticide application, with small droplets such as aerosols often improving performance. Natural insecticides, such as nicotine, pyrethrum and extracts are made by plants as defenses against insects. Nicotine based insecticides have been barred in the U.S. since 2001 to prevent residues from contaminating foods (Duke, *et al.,* 2010).

Plant-incorporated protectants (PIPs) are insecticidal substances produced by plants after genetic modification. For instance, a gene that codes for a specific Baccilus thuringiensis biocidal protein is introduced into a crop plant's genetic material. Then, the plant manufactures the protein. Since the biocide is incorporated into the plant, additional applications at least of the same compound, are not required (Bates and Drive, 2000).

Inorganic insecticides are manufactured with metals and include arsenates, copper compounds and fluorine compounds, which are now seldom used, and sulfur, which is commonly used. Organic insecticides are synthetic chemicals which comprise the largest numbers of pesticides available for use today (Soriano, *et al,* 2007).

1.3. Types of pesticides

1.3.1 Nematicides

Soil nematocides , such as dichlopropene, methyl isocyanate, chloropicrin, and methyl bromide, are broad-spectrum soil fumigants. Others, aldicarb, dazomet, and metham sodium, act mainly through contact. All have very high mammalian toxicities and can kill a wide range of organisms from both the plant and animal kingdoms. Although transient in soil, they may have drastic ecological effects on soil systems (Olaofe, *et al,* 1993).

1.3.2 Herbicides

Hormone-type herbicides such as 2,4,5-T; 2,4-D, and MCPA; were discovered during the 1940s. They do not persist in soil, are selective in their toxicity to plants, are of low mammalian toxicity, cause few direct environmental problems, but are relatively soluble and reach waterways and groundwater. Contact herbicides, which kill weeds through foliage applications, include dintrophenols, cyanophenols, pentachlorophenol, and paraquat (Lipthay, *et al.,* 2007).

1.3.3 Fungicides

Many different types of fungicides are used, of widely differing chemical structures. Most have relatively low mammalian toxicities, and except for carbamates such as benomyl, a relatively narrow spectrum of toxicity to soil-inhabiting and aquatic organisms. Their greatest environmental impact is toxicity to soil microorganisms, but these effects are short term (Calhelha, *et al*, 2006).

1.4 Fate of pesticides in environment

Pesticides are different types according to fate in the environment, and the fate of pesticides in environment depend on some factors such as soil characteristics, light, temperature and amount of water in the soil. When a pesticide is released into the environment many things happen to it. Sometimes, the leaching of some herbicides into the root zone can give you better weed control. Sometimes, releasing pesticides into the environment can be harmful, as not all of the applied chemical reaches the target site. Pesticide characteristics (water solubility, tendency to adsorb to the soil and pesticide persistence) and soil characteristics (clay, sand and organic matter) are important in determining the fate of the chemicals in the environment (Tiryaki and Temur, 2010).

Many processes affect what happens to pesticides in the environment. These processes include adsorption, transfer, breakdown and degradation. Transfer includes processes that move the pesticide away from the target site. These include volatilization, spray drift, runoff, leaching, absorption and crop removal (Wilde, *et al.*, 2009).

Each of these processes is explained in the following sections (Miles, 1992).

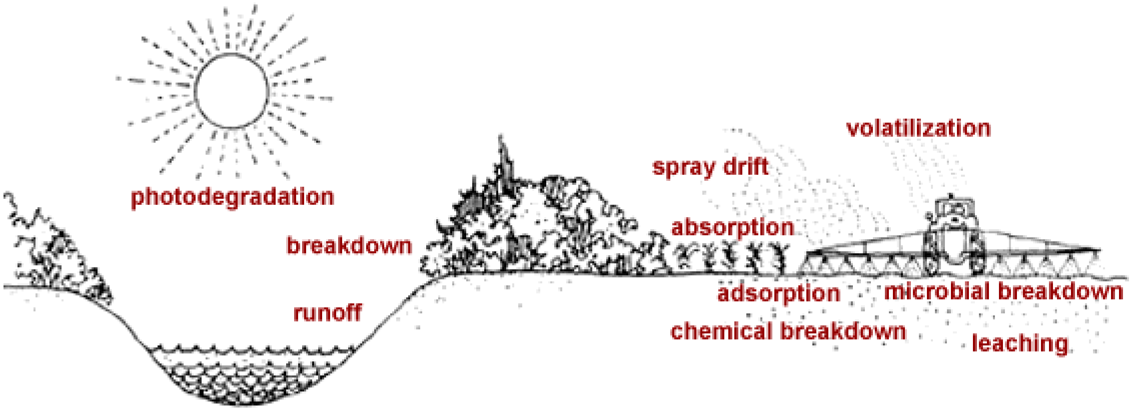

Figure 1.1 Fate of pesticides in Environment

1.5 Current status of pesticides in Palestine

Pesticides use in major quantity in Palestine for application to control pests include fungi, bacteria, mycoplasma and other parasitic plants. And pesticides is also used for veterinary, public health and in household .

The total cultivated area in Palestine is 91.3% which around 2273 thousand dunums in 2008-2009 . In West Bank it is around 2 million dunums, of this only one hundred thousand dunums are under irrigation, while 1.6 million dunums are fallow lands (Ministry of Agriculture, 2011). It is estimated that 96.6 % of irrigated land and 87.0% of rain fed land is treated with pesticides.

A total of 123 pesticides currently being used in the West Bank. Among them, fourteen pesticides are internationally suspended, cancelled or banned . Seven of these pesticides are members of the dirty dozen, namely Aldicarb, Chlordan, DDT, Lindane, Paraquate, Parathion and

Pentachlorophenol. Products marked with asterisks have been internationally suspended, cancelled and/or banned (Brun *et al.*, 2008).

In west Bank as is indicated in Table (1), the total area treated with pesticide is 383.453 dunums, 77% of which under rain fed farming and 23% of which is under irrigated farming. Still, irrigated farming accounts of about 72% of total pesticides consumption. This is due to the intensive nature of cropping methods used in irrigated farming (Saleh *et al.*, 2005). The quantities of pesticide used by district and by cropping pattern shows in Table (2).

Table 1.1. The total area treated with pesticide and the proportion of insecticides, fungicides, herbicides and others* used according to district and cropping type (Saleh *et al*, 2005).

District	Cropping Type	Kg/dunum	Insecticides %	Fungicides %	Herbicides %	Others %
Tulkarem	Open irrig.	1.60	51.0	32.0	10.7	6.30
	Plastic	3.3	42.2	45.5	6.50	5.80
Jenin	Open irrig.	2.10	48.0	26.0	25.5	0.50
	Plastic	4.00	53.0	32.8	9.0	5.20
Jericho	Open irrig.	2.60	55.5	32.9	9.5	2.10
	Plastic	6.00	46.5	33.2	15.5	4.80

**Others kinds of pesticides such as: acaricides, rodenticides, molluscicides,…etc are also used.*

The average seasonal consumption of pesticides was found to be around 4kg/dunum in open irrigated fields and 6.5 kg/dunum under plastic houses in areas Tulkarem, Jenin, and Jericho areas (Saleh *et al*, 2005).

Table 1.2. Areas treated with pesticides in districts according to crop pattern (dunums), (ARIJ, 1995).

District	*Irrigated Farming*				*Rainfed Farming*		
Crop pattern	Vegetables in Plastic Houses	Vegetables in Open Field	Trees	Field Crops	Vegetables	Trees	Field Crops
Nablus	13	1945	1500	0	1650	5535	16450
Tulkarem	5710	8021	13000	0	12000	9260	40000
Jenin	210	12000	1740	0	12000	9260	40000
Ramallah	20	1131	0	0	4100	37560	7000
Hebron	0	526	0	0	9630	74744	12800
Subtotal	6073	53608	22651	6120	33510	168719	92772
Total	88452				295001		

The use of pesticides are different according the type of agriculture and by cropping pattern. It is clear from the table that Jericho, Tulkarem, and Jenin consume about 61% of the pesticides in the West Bank. Irrigated agriculture, for which pesticides are most intensively used, above all in Jericho (ARIJ, 1995).

Table 1.3. Quantities of pesticides used by districts according to cropping pattern(ARIJ, 1995).

District / Crop Pattern	Nablus	Tulkarem	Jenin	Jericho	Ramallah	Hebron	TOTAL
Irrig. Trees	0.780	9.050	1.514	2.735	0.000	0.000	14.079
Irrig. Field Crops	0.000	0.004	0.000	1.281	0.000	0.000	1.285
Vegetables in Plastic Houses	0.084	18.843	0.840	0.720	0.130	0.000	20.617
Vegetables in Open Fields	2.114	12.834	25.200	77.961	0.960	0.288	119.335
Subtotal	2.978	40.731	27.554	82.697	1.090	0.266	155.316
Rainfed Trees	5.958	12.262	1.986	0.000	17.867	45.407	83.480

District / Crop Pattern	Nablus	Tulkarem	Jenin	Jericho	Ramallah	Hebron	TOTAL
Rainfed Field Crops	3.420	3.670	4.000	0.000	1.445	2.740	15.275
Rainfed Vegetables	4.390	1.560	2.500	0.000	6.410	20.888	35.748
Subtotal	13.768	17.492	8.468	0.000	25.722	69.035	134.503
TOTAL	16.476	58.223	36.040	82.697	26.812	69.301	289.819

1.6. Toxicity of Imidacloprid

Imidacloprid is moderately toxic if ingested. And LD50 is defend that standard measure of the toxicity of a material that will kill half of the sample population of a specific test animal in a specified period through exposure via ingestion, skin contact or injection (Hoffmann, *et al*, 2010). Oral LD50 values in rats were estimated to be 450 mg/kg for both sexes in one study and 500 and 380 mg/kg in males and females respectively, in another study in mice, LD50 values were estimated at 130 mg/ kg for males and 170 mg/kg for females. Dermal imidacloprid is very low in toxicity via dermal exposure. The dermal LD50 in rats was estimated at greater than 5000 mg/kg (Kapoor, *et al.*, 2011).

Three case reports of attempted suicides described signs of toxicity including drowsiness, dizziness, vomiting, disorientation, and fever. In two of these cases, the authors concluded that the other ingredients in the formulated product ingested by the victims were more likely to account for many of the observed signs. A 69-year-old woman ingested a formulated product containing 9.6% imidacloprid in N-methyl pyrrolide solution (Jander and Casida, 2002). The woman suffered severe cardiac toxicity and death 12 hours after the exposure. Twenty five Signs of toxicity soon after the ingestion included disorientation, sweating, vomiting, and increased heart and respiratory rates. A 24-year-old man who accidentally inhaled a pesticide containing 17.8% imidacloprid while working on his farm was disoriented, agitated, incoherent, sweating and breathless following the exposure. Pet owners have reported contact dermatitis following the use of veterinary products containing imidacloprid on their pets (Wange, *et al.*, 2009).

1.7. Imidacloprid Residues

Imidacloprid is used to control sucking insects, some chewing insect's includingtermites, soil insects, and fleas on pets. In addition to its topical use on pets, imidacloprid may be applied to structures, crops, soil, and as a seed treatment. Uses for individual products containing imidacloprid vary widely. Imidacloprid applied to soil is taken up by plant roots and translocated throughout the plant tissues. Freshly cut sugar beet leaves contained 1 mg/kg imidacloprid residues up to 80 days following sowing of treated seed although residues were undetectable at harvest 113 days after sowing. In a similar study, sugar beet leaves harvested 21 days after the sowing of treated seeds contained an average of 15.2 μg/g imidacloprid (Utture, *et al.*, 2012).

Researchers grew tomato plants in soil treated with 0.333 mg active ingredient per test pot, and monitored the plants and fruits for 75 days. Plants absorbed a total of 7.9% of the imidacloprid over the course of the experiment, although absorption of imidacloprid declined with time since application.(Alba, *et al.*, 2000).

More than 85% of the imidacloprid taken up by the tomato plants was translocated to the shoots, and only small quantities were found in the roots. Shoot concentrations declined towards the top of the plant. These patterns were also seen in sugar beets grown from treated seed. The tomato fruits also contained imidacloprid, although tissue concentrations were not related to the position of the fruits on the plant. Although tomato fruits contained primarily unmetabolized imidacloprid, the plants' leaves also included small quantities of the guanidine metabolite, a tentatively identified olefin metabolite, and an unidentified polar metabolite in addition to the parent compound. However, sugar beets grown from treated seed appeared to rapidly metabolize imidacloprid in the leaves. On day 97 after sowing, the majority of the radio-label was associated with metabolites, not the parent compound (Schippers and Schwack, 2010).

Researchers sprayed imidacloprid on eggplant, cabbage, and mustard crops at rates of 20 and 40 g/ha when the crops were at 50% fruit formation, curd formation, and pod formation, respectively. The researchers calculated foliar half-lives of 3 to 5 days based on the measured residues. Metabolites detected in the eggplant, cabbage, and mustard plants included the urea derivative [1-(6-chloropyridin-3ylmethil)imidazolidin-2-one] and 6-chloronicotinic acid 10 days after foliar application. Residues of 2.15-3.34 μg/g were detected in the eggplant fruit (Juraske, *et al.*, 2009).

Pesticide Data Program monitored imidacloprid residues in food and published their findings in 2006. Imidacloprid was detected in a range of fresh and processed fruits and vegetables. It was detected in over 80% of all bananas tested, 76% of cauliflower, and 72% of spinach samples. In all cases, however, the levels detected were below the U.S. EPA's tolerance levels. Imidacloprid was also found in 17.5 % of applesauce and 0.9% raisin samples, although percentage of detections were greater in the fresh unprocessed fruit (26.6% of apples sampled, and 18.1% of grapes sampled) (Robson and Wright, 2007).

1.8. Abamectin Residues

Abamectin is a mixture of avermectins B1a (80%) and avermectins B1b (20%). In sunlight the photoisomer 8,9-*Z*-avermectin is produced and becomes part of the residue. It is also described as the *D*-8,9 isomer. Avermectin B1a and 8,9-*Z* B1a produce the same fluorescent compound in the derivatization step of the analytical methods and hence a single peak on an HPLC chromatogram. Avermectin B1b and its photoisomer 8,9-*Z*-avermectin B1b behave in the same way and appear together in a second peak in the chromatogram. Analytical methods that measure the components of the residue involve the HPLC separation and fluorescence detection of derivatives formed by converting the cyclohexene ring to an aromatic ring. Analytical methods for abamectin residues in crops, soil, animal tissues, milk and water were measured (Pozo, *et al.,* 2003).

1.9. Chemical and Physical Properties of Imidacloprid

Imidacloprid has the molecular formula $C_9H_{10}ClN_5O_2$ (Figure 1.2), with a molecular weight of 255.7 g/mol (Table 1.4). In appearance, it consists of colorless crystals. The insecticide is quite water soluble even at the lowest solubility value reported (510 mg/L) and could potentially leach to groundwater or be transported in runoff. In the literature, some variation exists in reported vapor pressures for imidacloprid (Table 1.4), likely as a result of differences in the formulation of the imidacloprid-containing products. However, according to the comparatively low vapor pressure values , imidacloprid would be relatively non-volatile under field conditions. Imidacloprid did not dissociate when titrated with either acid or base. The octanol / water partition coefficient (log K_{ow}) of imidacloprid is 0.57, would not accumulate in aquatic biota (Donald, *et al.,* 2012).

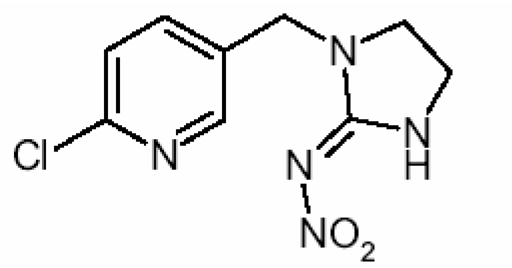

Figure 1.2 Structural formula of imidacloprid

Table 1.4. Physical-Chemical Properties of Imidacloprid (Kaur *et al,* 2011)

Physical- chemical property	Imidacloprid
Appearance	Colorless crystal
Chemical name	IUPAC: 1-(6-chloro-3-pyridylmethyl) Nnitroimidazolidin-2-ylideneamine
Chemical formula	$C_9H_{10}ClN_5O$
Molecular Weight	255.7 g/mol
Water Solubility	0.510 g/L at 20°C
Melting Point	144°C
Partition Coefficient (Kow)	log P = 0.57 @ 21°C

1.10. Physical and Chemical Properties of Abamectin

Abamectin is a white to yellowish crystalline powder. It poses a slight fire hazard if exposed to heat or flame, and a fire and explosion hazard in the presence of strong oxidizers. It may burn but will not readily ignite. Avoid contact with strong oxidizers, excessive heat, sparks or open flame. Thermal decomposition may release toxic oxides of carbon. Workers handling abamectin should wear goggles to prevent eye contact and protective clothing to prevent prolonged skin contact (Ozenci, *et al.,* 2011).

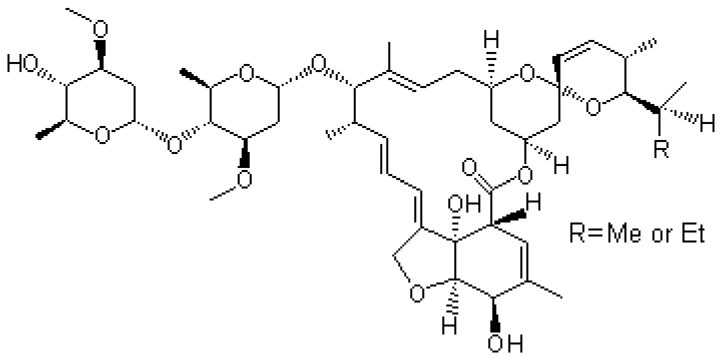

Figure 1.3. Structural formula of abamectin

Table 1.5. Physical properties of abamectin (Novelli, *et al,* 2012)

Physical-Chemical property	Abamectin
Chemical name	Avermectin B1a and Avermectin B1b
Chemical Class/Use	Acaricides and insecticide; macrocyclic lactone disaccharide isolated from the soil bacterium Streptomyces avermitilis.
Density	1.16g/cm^3 at 21 degrees °C
Solubility in water	practically insoluble; 7.8 ppb
Solubility in other solvents	soluble in acetone, methanol, isopropanol and toluene

Chapter Two

Literature Review

2.1. Pesticide Residues Regulation

The US Environmental Protection Agency (EPA) will typically establish a tolerance, representing the maximum permitted residue level. US tolerances are pesticide and commodity specific; the same pesticide may have different tolerances established on different commodities while the same commodity may permit different levels of specific pesticides.

Tolerances exist as enforcement tools to ensure that pesticide applications are made in accordance with regulations, tolerances represent the maximum expected levels of pesticides on food crops resulting from the legal application of a pesticide (Hughes, 2005).

2.2. International Regulation

All world nations possess the sovereign right to establish their own acceptable levels for pesticide residues in foods. Because many nations lack the resources to develop their own pesticide regulatory programs, the majority of the world's countries rely upon a set of international standards developed by the Codex Alimentarius Commission, commonly referred to as Codex. Codex 'maximum residue levels' (MRLs) are analogous to the US 'tolerances' and represent the maximum legal pesticide residues permitted on specific commodities. Codex MRLs, like US tolerances, primarily serve as enforcement tools to determine whether pesticide applications are made according to established directions. Codex MRLs and US tolerances are similar in many cases but differ in others. In cases where the US tolerances and Codex MRLs can be directly compared, 47% are equivalent, 34% of Codex MRLs were lower (more restrictive) than the US tolerances and 19% of Codex MRLs exceeded US tolerances. Some of the differences may be traced to the use of different data sets and/or different methods to regulate pesticide breakdown productions by US and Codex officials. Agricultural production and pest management practices may also differ, leading to differences in the maximum expected residues following pesticide application (Levine, 2007).

2.3 High Performance Liquid Chromatography (HPLC)

HPLC is the term used to describe liquid chromatography in which the liquid mobile phase is mechanically pumped through a column that contains the stationary phase. In general HPLC apparatus consists of injector, pump, column, and detector (Wellings, 2006).

2.3.1 Classification of Liquid Chromatographic Methods

There are two ways to classify liquid chromatographic methods. The first and more common classification is based on the mechanism of retention, and from this the chromatographic modes. The second classification is based on the separation principle (Wellings, 2006).

2.3.2 Classification According to Mechanism of Retention

The most popular classification scheme stems from the manner in which the analyte interacts with the stationary phase. With this approach, chromatography may be divided into five separation mechanisms: adsorption, partition, size exclusion, affinity, and ion exchange, as illustrated in Figure (2.1) (Vidal and Frenich, 2006).

Liquid Chromatography

Adsorption Partition Size Exclusion Affinity Ion

Exchange

Competition Competition Molecular sieving Lock and Competition

Between liquid liquid mobile phase key mechanism between liquid

Mobile phase and liquid stationary phase

mobile

and solid adsorbent phase and ionic

stationary phase

Figure 2.1 Classification of chromatographic modes according to the retention mechanism

2.4 Quantitative determination of Imidacloprid and Abamectin residues:

Many reviews and methods have been published on the quantitative determination of Imidacloprid and Abamectin residues. (Navalon *et.al,* 2001) studied determination of imidacloprid residue in vegetable samples by gas chromatography-mass spectrometry. The applicable concentration range was 12.5 – 250mg/kg, the detection limit was 2.5mg/kg and the relative standard deviation at the 125mg/kg level was 0.7%. the method was applied to the determination of the imidacloprid in vegetables (tomato, cucumber, pepper and green beans). Recovery levels were between 94.3% and 105.8%.

(Navarro *et al.*, 2002) determined the pesticides residues in tomato and cucumber fruits harvest at two hours 1,3, 7, 14 and 28 days after phytosanitary treatment. The determination of residues was carried out by GC – ECD for imidacloprid and HPLC for Abamectin. The residue levels detected imidacloprid in the study immediately after pesticide application were 6.91ppm for tomato, 0.14ppm for cucumber and the residue level for Abamectin in tomato was 0.12ppm, 0.09ppm for cucumber. But these levels fell to 0.14, 0.03ppm after 28 days of the application for Abamectin and imidacloprid respectively. The calculated half –life time were 4.4 and 6.6 days for both pesticides respectively. In the case of imidacloprid, the time necessary to reach the concentration of the corresponding maximum residue limit (MRL) was below their designated days to harvest times. The theoretical initial residue levels of Abamectin (0.12ppm) were below the maximum residue limit (MRL) established for tomato and cucumber Spanish legislation.

(Fernandez *et al.*, 2003), presented an analytical method for the determination of residues of 10 insecticides (imidacloprid one of them) in tomato, it is based on organic solvent extraction with dichloromethane-acetone (75:25,v/v) followed by gas chromatography with spectrometric detection. The applicability of the method was evaluated by analysis of 5 different tomato produced in Rias Baixas area in Galicia (north western

Spain). Results showed that concentration of the insecticides identified in tomato were lower than MRLs established by European legislation.

(Liapis *et al.*, 2003), described rapid, selective and sensitive multi-residue method for determination of six common pesticides in stone fruits samples. The proposed method involves the extraction pesticides with the use of acetone solvent followed by liquid –liquid partition with a mixture of dichloromethane and light petroleum (40-60C°) and subsequent determination by GC-MS system using ion trap technology in negative ion Cl mode. The recoveries of imidacloprid and parathion methyl examined in the concentration range .02-0.2 ppm were 95.5±7.5 to 145±3.6% the highest mean recovery (145%) for imidacloprid is attributed to a matrix enhancement effect. The limits of quantification in apricot were 0.02ppm for imidacloprid. The method was applied successfully to the determination of the target pesticides in 32 samples of stone fruits (apricot and peach).

(Correia *et al.*, 2001), developed a method using SPME and GC-ECD (gas chromatography electron capture detector) for the determination of some pesticides residues in some vegetables (tomato, cucumber, pepper, green beans and lettuce). The procedure only needs dilution as sample pretreatment and is therefore simple, fast and solvent-free. Insecticides (imidacloprid) and acaricides (Abamectin) can be quantified. Good linearity was observed for the two compounds in the range 5-100mg/l .

The reproducibility for the measurement was found acceptable (with residues (RSD) < 20%). Detection limit of µg/L, on average, are sufficiently below the proposed maximum residue limits. The analytical method was applied to the determination of these compounds in some vegetables samples (tomato, cucumber, pepper and green beans) from the Demarcated Region of Alentejo, Portugal.

(Zamboni *et al.*, 2002), developed a SPME GC-MS method for determination of dimethoate residue, such as a imidacloprid. The method has been successfully applied to the analysis of strawberries and tomato samples. The procedure is solvent-free, simple and highly sensitive. Within-day and-to-day residues range between 2-11% and 7-28% respectively. Since the detection limits achieved by this method are well below the maximum residue levels for tomato and strawberries recommended by European Legislation, it can be conveniently used as a low-cost rapid screening method for the contamination of the considered samples.

(Song *et al.*, 2002) have investigated a novel green method using flow injection chemiluminescence´s with controlled-reagent- release technology for the rapid and sensitivity monitoring of sub-nanogram amounts of Abamectin. The rapid analytical reagents involved in the chemiluminescence (CL) reaction, luminal and periodate, were both immobilized on an anion-exchange column. The CL signals produced by the reaction between luminal and periodate, which were eluted from the column through water injection, were decreased in the presences of Abamectin. The decrease of CL intensity was linear over the logarithm of concentration of Abamectin ranging from 0.46 to 489ppm and the limit of detection was 0.19ppm. At a flow rate of 2 ml/min, the determination of

Abamectin including sampling and washing, could be performed in 0.5min with a residue of < 3%. The proposed method was applied successfully in an assay of remnant Abamectin on fruits such as orange and shaddock with the recovery of 94.4-107.4%. The change of concentration of Abamectin in water sample was also investigated, and the variation rate was 99.96% during 35 hours in the open air.

(Schoning and Schmuck, 2003), analyzed dimethoate, imidacloprid and its metabolite omethoate residues in cucumber fruits using gas liquid chromatography (GLC) with a nitrogen phosphorus detector (NPD). Different treatments were used to reduce the residue of dimethoate and imidacloprid from cucumber fruits sprayed with dimethoate 25ml/20liter and 20 ml/20 liter solution. The different removal treatments were evaluated after 1 hour, 2 days, 5 days, and 6 days of treating cucumber fruits with dimethoate and imidacloprid. These treatments included peeling, dipping in tap water with soap for 2 minuets, dipping cucumber for 10 minuets, hand rubbing cucumber fruit under tap water for few seconds. The result showed that the percentages of removal were 52% for peeling 34% for dipping in tap water with soap 1% for 2 minuets, 19% for dipping 10 minuets, 18.6% for hand rubbing and 11.2% for washing cucumber under tap water.

Chapter Three

Materials and Methods

The research experimental work focuses on studying and determining the concentration of pesticides residues of imidacloprid and Abamectin in different vegetables like tomato, cucumber and pepper and soil. Plants samples were collected at different times after spraying the pesticides.

The period of collection was on the first day, fifth day, tenth day and twentieth day of spraying.

Soil samples were collected at the same time of collecting plant samples. Samples of plants and soil were analyzed by UV Spectrophotometer and HPLC, the room temperature recorded ranged between 16-27C°.

All glass vessels used were cleaned and dried before measurement and each measurement of this study was the average of four readings to have a representative measurements.

Standard readings were obtained for imidacloprid and Abamectin and were plotted against absorbance readings. Then transformed to concentration using calibration curves.

3.1 Materials and Methods

This section of the research presents how to implement testing and chemicals used and also analyzed by way devices and how to prepare calibration curves.

3.1.1.Chemicals and Reagents

In this experiment, all chemicals and solvents were bought from Aldrich were highly selected and purely chosen.

These chemicals are:

Abamectin.

Imidacloprid.

Distilled water.

Methanol.

Acetonitrile.

Acetone.

Ethyl acetate.

Triethylamine.

3.2.1. Instrumentation

Absorbance readings of imidacloprid and Abamectin were detected using UV-VIS SHIMADZU, Model No: UV-1601 double beam spectrophotometer wave length range from 190- 1100 nm, accuracy ± 0.004.

The detecting wavelengths for pesticides residues compound were confirmed using high performance liquid chromatography (HPLC) (SHIADZU CORPORATION), with Lichoro CART® , C18 Column (150x4.6mm,20µm) Detector FLUROCENCES ARRAY The wave lengths were 270nm and 210nm for imidacloprid and Abamectin respectively.

3.3.HPLC Scanning of Imidacloprid and Abamectin

The usual quick way to determine standard solution for imidacloprid and Abamectin by high performance liquid chromatography (HPLC), The processes for detection of these compound involve two solution preparations (mobile phase and standard solutions).

3.3.1.HPLC Scanning of Imidacloprid

For detection of imidacloprid using UV at 270 nm, chemicals and reagents (acetonitrile solution, triethylamine, distilled water and imidacloprid were used).

In this experiment two solutions were prepared:

Mobile phase solution: solution prepared from 1 ml of triethylamine in 1600 ml of distilled water were added besides 400 ml acetonitrile, with good mixing and adjust the pH to 5.9±0.1.

The standard solution: was prepared by dissolving an accurately weighed quantity of imidacloprid in diluents to obtain concentration of about 0.0292 mg/ml of this solution.

Procedure: inject equal volume (20μ liters) of standard solution into HPLC to take retention time, and then inject equal volume of two sample solutions into HPLC with cleaning by mobile phase after each sample.

3.3.2.HPLC Scanning of Abamectin

For detection Abamectin use UV at 210nm,(chemicals and reagents are methanol, distilled water and abamectin).

Two solutions of mobile phase and standard solutions were prepared

The mobile phase solution was prepared from methanol and distilled water(85:15 v/v) and the standard solution was prepared from 18 mg of Abamectin dissolved in 100ml methanol.

Procedure: inject equal volume (20μ liters) of standard solution into HPLC to take retention time and then inject equal volume of the two samples solutions into same device, with cleaning by mobile phase after each sample.

The following table showed retention time and wavelength for each pesticides

Table 3.1.wavelength and retention time for imidacloprid and abamectin:

Pesticide Name	Wave Length (nm)	Retention Time (minute)
Imidacloprid	270	6.5
Abamectin	210	4.49

3.4.Calibration Curves

Standard calibration curves for imidacloprid and Abamectin were performed by preparing diluted solution to get the concentration of 10 ppm, 8 ppm, 6 ppm, 4 ppm and 2 ppm, using a control concentration of 0 ppm distilled water.

A one ml of imidacloprid was placed in 1liter volumetric flask and filled with distilled water to the mark. A 28.5 ml of this solution to 100 ml volumetric flask and filled to the mark using distilled water. The new concentration became 10ppm, then 80 ml of new concentration was added to 100 ml volumetric flask and filled with distilled water to the mark, the concentration became 8ppm, after this 75ml of the previous solution was taken and transferred to the 100 ml volumetric flask and filled with distilled water to the mark, the concentration became 6ppm. After this, 66.6ml of previous solution was taken and transferred to the 100ml volumetric flask and filled with distilled water to the mark, the concentration became 4ppm.

After this 50ml of the previous solution was taken and transferred to the 100ml volumetric flask and filled with distilled water to the mark, the concentration became 2ppm. Absorbance readings were recorded at 253nm for imidacloprid and 239nm for abamectin using UV-1601 SHIMADZU Spectrophotometer.

Table 3.2 Absorbance Readings of Abamectin Using UV-Visible Spectrophotometer at Wavelength 239nm.

Concentration mg/l	Absorbance
10	1.1337
8	0.8539
6	0.6393
4	0.3600
2	0.1859
0	0

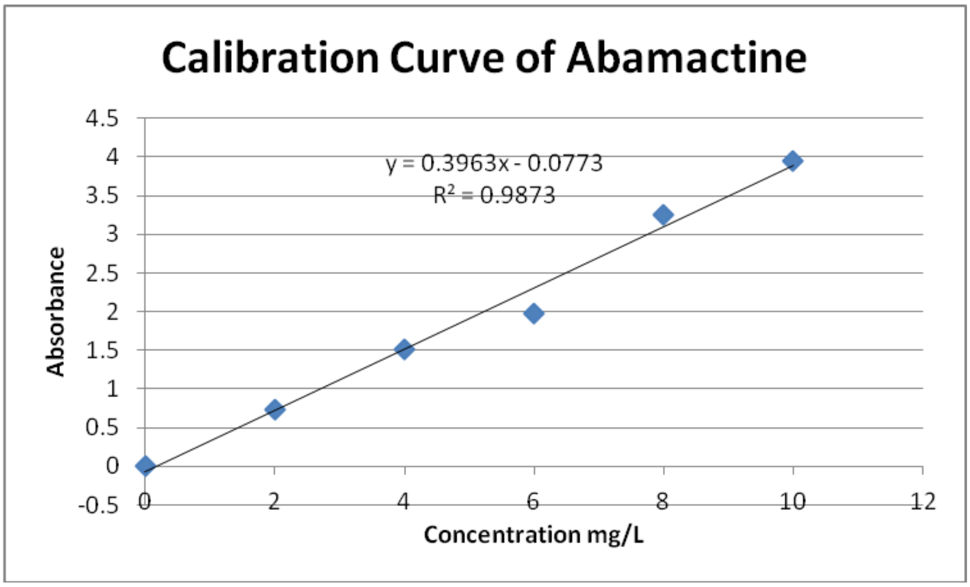

Figure 3.1 Calibration Curve of Abamactin

Table 3.3 Absorbance Readings of Imidacloprid Using UV-Visible Spectrophotometer at Wave length 270 nm.

Concenration mg/l	Absorbance
10	3.945
8	3.256
6	1.976
4	1.508
2	0.740
0	0

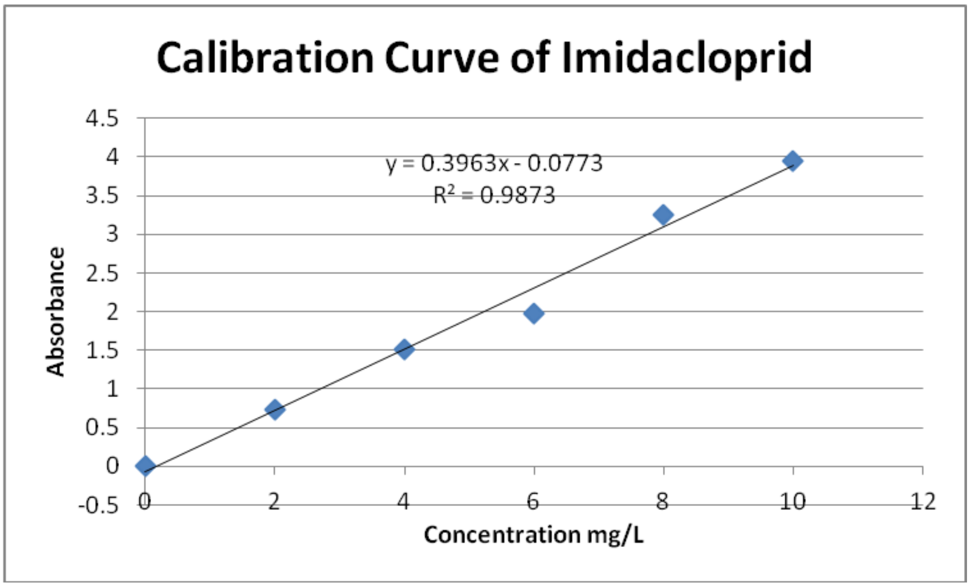

Figure 3.2 Calibration curve of imidacloprid

3.5.1 Farmer Survey

The objective of the survey is to identify more of pesticides used in the study area, and if the farmers use the recommended quantities of pesticides. After answering the questioner, it look like most farmers are using imidacloprid (Konfedor®) as insecticides, and Abamectin (Vertimk®) for acaricides.

3.5.2 Farmer Survey Results

This survey consists of two parts, the first shows the general information about pesticides uses and agriculture, the second part shows the information about control of pests by pesticides. After the survey distributed to fifty farmers the results we obtained.

The first question shows the type of agriculture used by farmers in study area, forty eight farmers answering the type of agriculture used greenhouses, but one farmer answered of rainfed agriculture and one farmer answered plastic spending. The second question shows the type of fertilizers used by farmers in study area forty five answered the type of fertilizers used mixing between chemical fertilizers and organic fertilizers, five farmers answered the fertilizer used organic fertilizer only.

The first question in the part two of survey shows more insecticides used in the study area forty nine farmers answered more insecticides used by farmers was imidacloprid (Konfedor®), but one farmer answered the more insecticides was (Dursban®). The second question in the part two of survey shows more acaricides used in the study area, fifty farmers answered more acaricides used by farmers was abamectin (Vertimk®). Another question in the part two of survey shows the compliance in the recommended amount of pesticides by farmers, forty seven of farmers answered not compliance in the recommended amount of pesticides.

3.6 Equipment

3.6.1 Field Equipment

In this experiment, sprayer with plastic drum (25 liter capacity), and protective clothes, in addition gloves and protective classes. were used in spraying vegetables.

3.6.2 Laboratory equipments

Blender: (model 356D23 (950), 220-240 volts AC, 50-60 Hz, 2.5AMPS, France with a speed of 22000 rounds per minuets (rpm).

High performance liquid chromatography (HPLC): HPLC separates and detect at room temperatures, generally using methanol-water or acetonitrile- water gradient-eluent mixtures and is appropriate for analysis of polar compound. Therefore, HPLC is complementary to GC, because it permits the analysis of thermally labile, non-volatile, and highly polar compounds. HPLC is particularly adapted to multiresidue analysis of pesticides over a wide range of polarity, including their transformation products, without the need to derivative any compound (Wellings, 2006).

3.7. Field Experiments

3.7.1.Location of Experiments

Green house of tomato, cucumber, and pepper located at Burqeen village near Jenin city was used in this study. This green house has moderate climates during the period of growing previous vegetables. Average seasonal temperature was 21C° , average relative humidity was 60% and good water holding capacity for the soil in which the vegetables are planted.

3.7.2. Sampling Procedure

Tomato (2030) that were characterized by-medium-sized fruits and highly roots with fruits suitable for consumption and processing were used in the present work.

Cucumber (Jana) that were characterized by- small to medium-sized fruit and dark green color of fruits and suitable for consumption.

Pepper (Sharabee) that were characterized by-small to medium-sized fruit and light green color of fruit and suitable for marketing and consumption.

Based on the questionnaire distributed to 50 farmers, the results showed that the imidacloprid is the most commonly used insecticides and abamectin is the most commonly acaricides.

The result also showed most farmers do not committed to the recommended amount of pesticides spraying on vegetables, for imidacloprid 1cm^3 of imidacloprid /1Liter water and for Abamectin 2cm^3 of Abamectin /1Liter water. The farmers used imidacloprid to control broad spectrum of insects such as leaf hoppers, whit fleas and other insects.

Protective sprays with imidacloprid (Konfedor®) and Abamectin (Vertimk®) were applied to protect the vegetables (tomato, cucumber, pepper) from some insects such as leaf hoppers, white flies, spiders and other insects. These insects attack the roots, leaves, stems and fruits. Each green house was treated every 3 weeks with imidacloprid (Konfedor®) pesticide (14.5mg/L of spray solution) starting at the beginning of growing season. Abamectin (Vertimk®) was treated every 2 weeks (29 mg/L).

Fruits, leaves and root samples were picked up at 1, 5, 10, 20 days after spraying of two pesticides. The samples were stored in the refrigerator at 2 – 4C° in order to be analyzed for the residues of both pesticides by UV-Visible spectrophotometer. In addition, each sample was represented by 4 replicates used for calculation of the mean value of pesticide residue level for both pesticides. And in the same time the samples of soil were collected and stored by the previous method.

3.7.3 Extraction Procedure

Fifty gram samples of leaves, roots and fruits were blended for 3 minutes with 50ml of acetone and 100ml ethyl acetate. The solution was filtered through Buchner Funnel. Finally, the solution was evaporated to dryness on water bath (70C°), then the residues were diluted with 2ml of ethyl acetate and transferred into a 100ml vial stored at -30 C° until analysis by UV-Visible Spectrophotometer, the procedure was used for both pesticides (Carretero, *et al.*, 2003).

Chapter Four

Results and Discussion

After samples were collected: tomato fruits, leaves, and roots, as well as soil, cucumber fruits, leaves, roots, as well as soil, pepper fruits, leaves, roots and as well as soil. Using the method of extraction and analysis by UV-Visible spectrophotometer illustrated in the section 3.7.3. The following results obtained as.

Table 4.1 Concentration of Abamectin and Imidacloprid at Different Days from Soil Cultivated with Pepper.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	26.92	9.77
5	10.17	5.91
10	0.93	2.32
20	0.05	0.18

- Where day 0 is the original concentration of abamectin and imidacloprid when fall on the pepper soil.

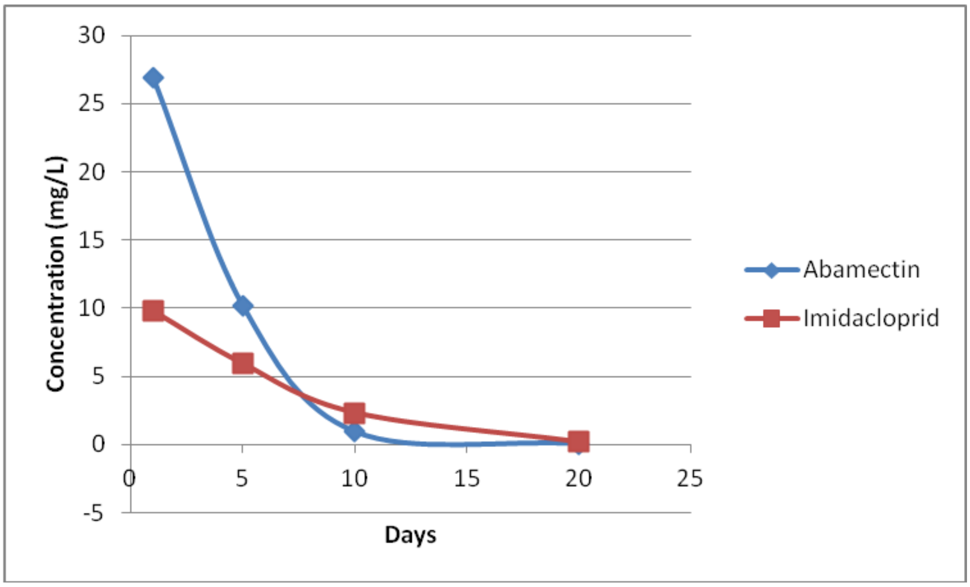

Figure 4.1: Concentration of Abamectin and Imidacloprid Residues in Soil Cultivated with Pepper.

According to figure 4.1 it was noticed that the concentration of abamectin was decreasing by time, due to abamectin degredation by sunlight to many derivtives BHT, avermactin B1a and avermactin B1b (Diserens and Henzelin, 1999) and degredation of abamectin was faster than imidacloprid by time. At the tenth day it was noticed that the concentration of imidacloprid was higher than abamectin; however at the first day it was noticed the concentration of abamectin was higher than imidacloprid due to more drops of spraying solution falled on the soil during doing the expriement, at the fifth day concentration of abamectin was (10.17 mg/L) while the concentration of imidaclprid (9.77 mg/L), it was noticed more decreasing of abamectin concentration between the first to the fifth day of spraying, while imidacloprid concentration was slowly decreasing between the first to the fifth day. The concenration of abamectin and imidacloprid on the first and the fifth day of spraying more than maximum residue levels

(MRLs), and this may refer to quick degradation of abamectin more than imidacloprid. At the tenth day abamectin concentration was less than maximum residue levels (MRLs), while the concentration of imidacloprid at the tenth day was (2.32 mg/L) more than maximum residue levels (MRLs), the concentration of both abamectin and imidacloprid at twentieth day was less than maximum residue levels (MRLs).

Table 4.2 Concentration of Abamectin and Imidacloprid at Different Days from Soil Cultivated with Tomato.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	27	9.63
5	9.48	5.69
10	1.53	2.63
20	0.04	0.15

- Where day 0 is the original concentration of abamectin and imidacloprid when fall on the tomato soil.

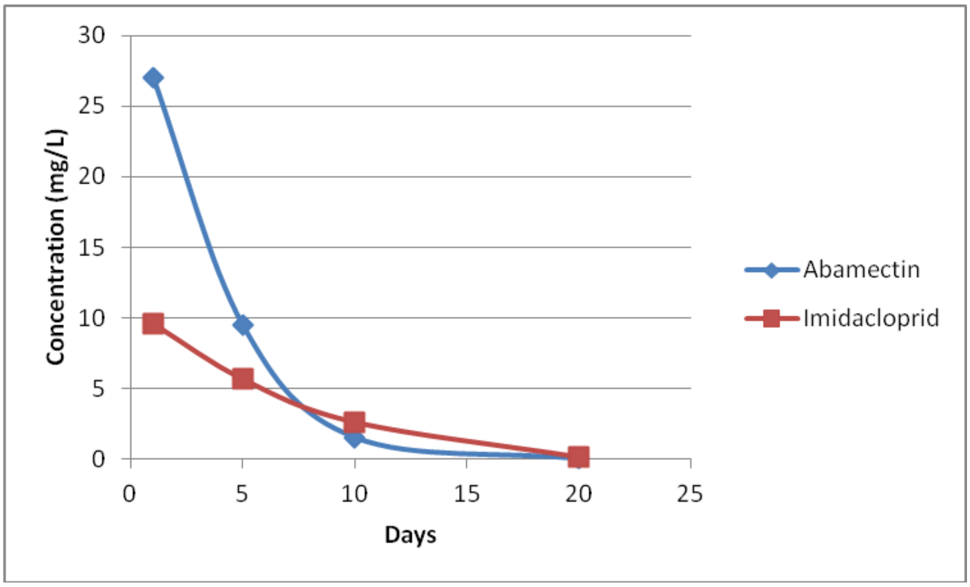

Figure 4.2 : The Concentration of Abamectin and Imidacloprid Residues in Soil Cultivated with Tomato.

From the table (4.2) and figure (4.2) it was noticed that the concentration of imidacloprid was higher than abamectin due to the half life for imidacloprid is more than abamectin. Even the concetration of abamectin at the begining was higher than imidacloprid (Ding, *et al.*, 2011). Also it was noticed from the table (4.2) that at the first day the concentration of abamectin was (27 mg/L), while the concentration of imidacloprid was (9.63 mg/L), the concentration of abamectin was higher than imidacloprid, at the fifth day the concentration of abamectin was (9.48 mg/L) it was noticed more decreasing of abamectin between the first and the fifth day due to more degradation of abamectin due to the effect of sunlight and the abamectin is less persistance in the environment comparing to imidacloprid , concentration of imidacloprid at the fifth day was (5.69 mg/L), it was noticed that the degredation of imidacloprid between the first and the fifth day was very slow comparing to abamectin, may be the imidacloprid molecules are more adsorped by the soil particles comparing to abamectin residues. At the tenth day the concentration of abamectin was (1.53 mg/L); this insures that abamectin residue was faster of degredation comparing to imidacloprid, the concentration of imidacloprid at the tenth day was (2.63 mg/L). Concetration of both imidacloprid and abamectin at the fifth and the tenth day was higher than maximum residue levels (MRLs). At the twentieth day the concentration of abamectin was (0.04 mg/L) less than the maximum residue levels (MRLs), and also the concentration of imidacloprid (0.15 mg/L) was less than maxium residue levels (MRLs).

Table 4.3 Concentration of Abamectin and Imidacloprid at Different Days from Soil Cultivated with Cucumber.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	27.01	10.02
5	17.23	6.19
10	2.25	2.07
20	0.04	0.15

- Where day 0 is the original concentration of abamectin and imidacloprid when fall on cucumber soil

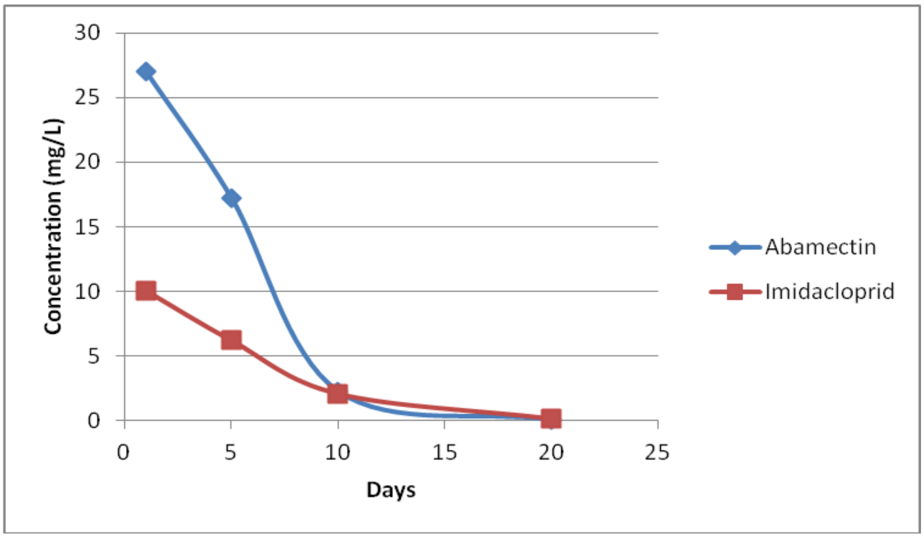

Figure 4.3 : Concentration of Abamectin and Imidacloprid Residues in Soil Cultivated with Cucumber.

From the figure 4.3 it was noticed that the decreasing of concentration of abamectin by time was higher than Imidacloprid due to rapid photo degradation of abamectin with half-lives of 8 and 21 hours or 1 day reported when applied to the soil surface and plants when not shaded, its soil half life was about 1 week, under dark, aerobic conditions the soil half life was 2 weeks to 2 months (Krogh, *et al.*, 2009). And it was noticed the concentration of imidacloprid on the twentieth day was higher than abamectin due to persistence in the environment.

Table 4.4 Concentration of Abamectin and Imidacloprid at Different Days fom Pepper Fruits.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	26.04	6.88
5	1.54	4.03
10	0.09	0.18
20	0.00	0.01

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the pepper fruits.

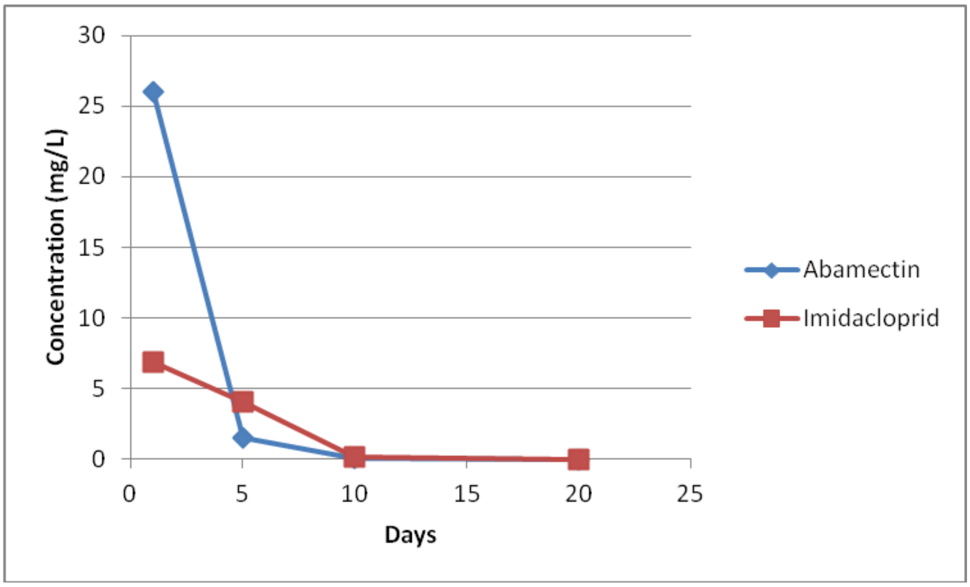

Figure 4.4: Concentration of Abamectin and Imidacloprid Residues from Pepper Fruits.

From the figure 4.4 it was noticed the concentration reading between the fifth to the tenth day was higher of imidacloprid than abamectin. And it was noticed in general the pesticides residue in pepper fruits was lower than the residues in soil due to the soil adsorption of the residues (Andreu and Pico, 2004). At the first day the concentration of abamectin was higher than the concentration of imidacloprid; concentration of both abamectin and imidacloprid on the first day was more than maximum residue levels (MRLs). At the fifth day the concentration of abamectin was (1.54 mg/L); it was noticed very quick decreasing of abamectin concentration in pepper fruits and this due to photodegradation and action of enzymes that degrade abamectin, at the fifth day the concentration of imidacloprid was (4.03 mg/L); it was noticed that the degredation of imidacloprid was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the tenth day the concentration of both abamectin and imidacloprid was less than maximum residue levels (MRLs). It was noticed at the twentieth day the concentration of abamectin was not detectable and less than maximum residue levels (MRLs) while imidacloprid was detectable, but concentration of imidacloprid also less than maximum residue levels (MRLs).

Table 4.5 Concentration of Abamectin and Imidacloprid at Different Days fromTomato Fruits.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	28	14.5
1	24.79	7.2
5	2.27	3.83
10	0.24	0.16
20	0.00	0.01

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the tomato fruits.

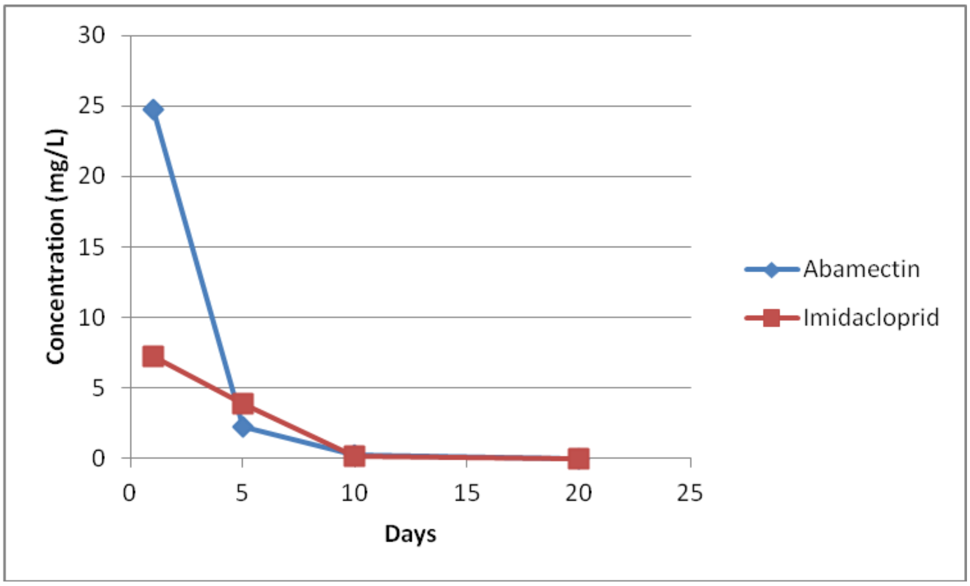

Figure 4.5: Concentration of Abamectin and Imidacloprid Residues from Tomato Fruits

From the figure 4.5 it was noticed that the concentration reading of imidacloprid and abamectin after the tenth day was approximetly equal. And the low concentration of abamectin and imidacloprid refer to tomato fruit decompostion of pesticides residues (Itoiz, *et al.*, 2012). At the first day the concentration of abamectin was higher than the concentration of imidacloprid; concentration of both abamectin and imidacloprid on the first day was more than maximum residue levels (MRLs). At the fifth day the concentration of imidacloprid was (4.08 mg/L); it was noticed that degredation was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the tenth day the concentration of both abamectin and imidaclopid was less than maximum residue levels (MRLs). It was noticed at the twentieth day the concentration of both abamectin and imidacloprid was not detectable, also the concentration of both abamectin and imidacloprid less than maximum residue levels (MRLs).

Table 4.6 Concentration of Abamectin and Imidacloprid at Different Days from Cucumber Fruits.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	23.94	7.39
5	0.99	4.08
10	0.23	0.10
20	0.00	0.00

- Where day 0 is the original concentation of abamectin and imidacloprid when sprayed on the cucumber fruits.

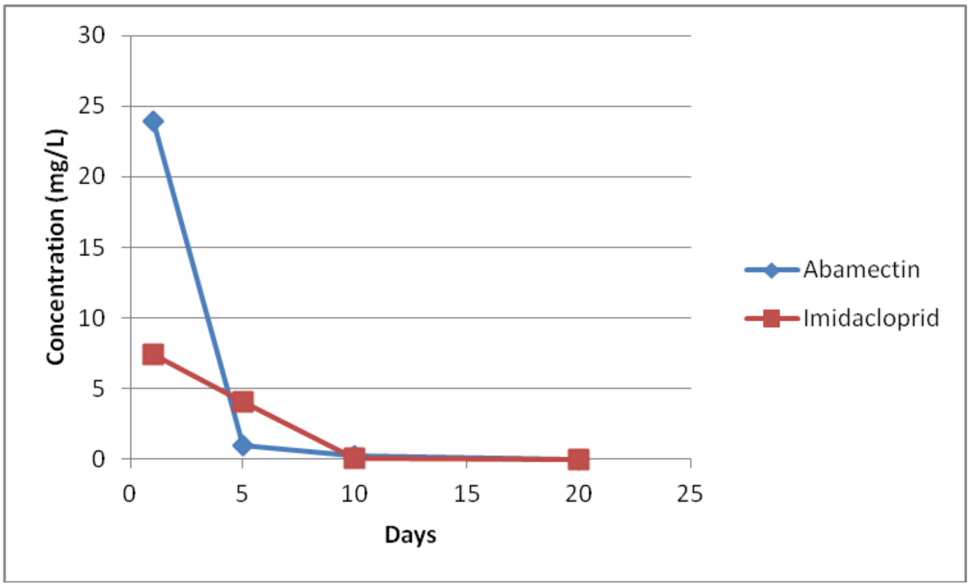

Figure 4.6: Concentration of Abamectin and Imidacloprid Residues from Cucumber Fruits

From the figure 4.6 and table 4.6 it was noticed at the first day the concentration of abamectin was higher than the concentration of imidacloprid; concentration of both abamectin and imidacloprid on the first day was more than maximum residue levels (MRLs). At the fifth day the concentration of abamectin was (0.99 mg/L); it was noticed very quick decreasing of abamectin concentration in cucumber fruits and this due to photodegredation and action of enzymes that degrade abamectin (Rancan *et.al,* 2006). At the fifth day the concentration of imidacloprid was (4.08 mg/L); it was noticed that degredation was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the tenth day the concentration of both abamectin and imidacloprid was less than maximum residue levels (MRLs). It was noticed at the twentieth day the concentration of both abamectin and imidacloprid was not detectable, also the concentration of both abamectin and imidaclopid less than maximum residue levels (MRLs).

Table 4.7 Concentration of Abamectin and Imidacloprid at Different Days from Pepper Leaves.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	26.82	7.46
5	5.77	4.53
10	0.69	0.23
20	0.01	0.02

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the pepper leaves

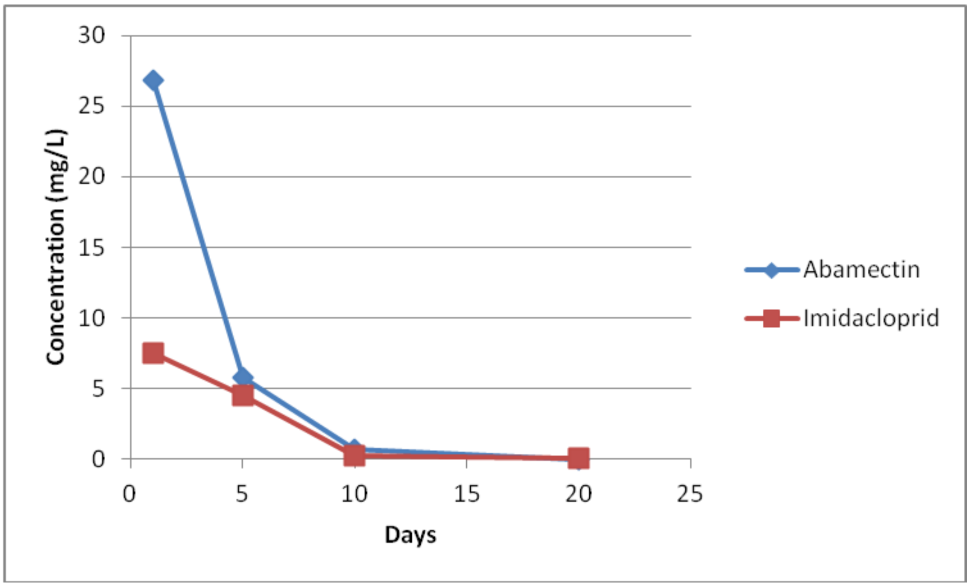

Figure 4.7: Concentration of Abamectin and Imidacloprid Residues from Pepper Leaves

From the figure 4.7and table 4.7 it was noticed that the concentration of abamectin was higher than the concentration of imidacloprid, except on the twentieth day. The concentration of imidacloprid was higher than abamectin due to abamectin more volatization than imidaclopid (Schoning and Schmuck, 2003). And it was noticed the concentration of abamectin and imidacloprid was detectable on the twentieth day. At the first day the concentration of abamectin was higher than the concentration of imidaclopid; concentration of both abamectin and imidacloprid on the first day was more than maximum residue levels (MRLs). At the fifth day the concentration of abamectin was (5.77 mg/L); it was noticed very quick decreasing of abamectin concentration in pepper leaves and this due to photodegredation and action of enzymes that degrade abamectin, it was noticed the concentration of abamectin in pepper leaves was more than the concentration of abamectin in pepper fruits. At the fifth day the concentration of imidaclopid was (4.53 mg/L); it was noticed that degredation was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidaclopid was higher than maximum residue levels (MRLs). It was noticed the concentration of imidaclopid in pepper leaves was more than the concentration of imidacloprid in pepper fruits.

Table 4.8 Concentration of Abamectin and Imidacloprid at Different Days from Tomato Leaves.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	26.92	7.44
5	4.61	4.39
10	0.47	0.21
20	0.01	0.02

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the tomato leaves.

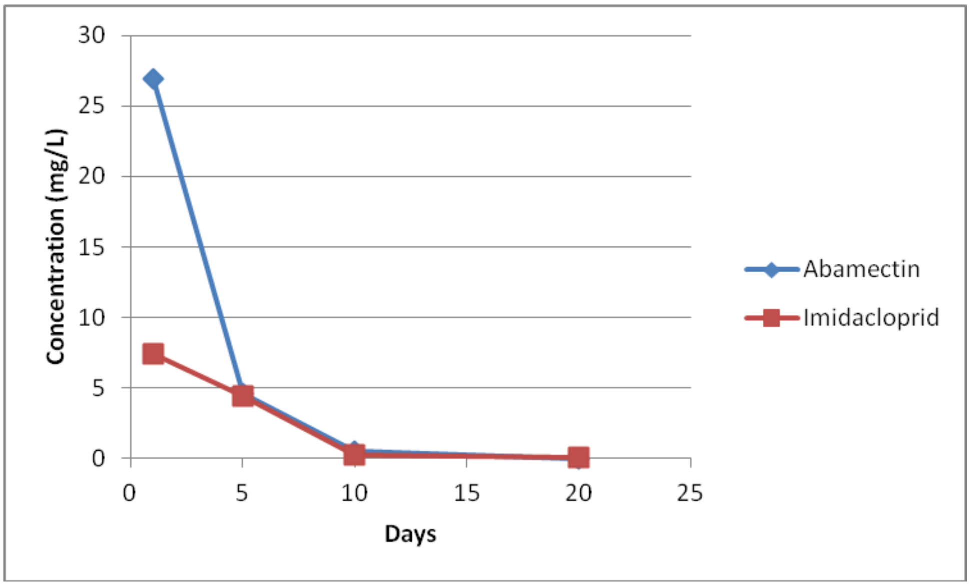

Figure 4.8: Concentration of Abamectin and Imidacloprid Residues from Tomato Leaves .

From the figure 4.8 it was noticed the concetration of abamectin in tomato leaves was higher than the imidacloprid on the first day and the fifth and the tenth day of spraying, but the concentration of imidacloprid on the twentieth day was higher than abamectin, at the fifth day the concentration of abamectin was (4.61 mg/L); it was noticed very quick decreasing of abamectin concentration in tomato leaves and this due to photodegredation and action of enzymes that degrade abamectin (Mingxie, *et al.,* 2006). At the fifth day the concentration of imidaclopid was (4.39 mg/L); it was noticed that degredation was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the tenth day the concentration of both imidaclopid and abamectin was less than maximum residue levels (MRLs). It was noticed at the twentith day the concentration of both abamectin and imidacloprid less than maximum residue levels (MRLs).

Table 4.9 Concentration of Abamectin and Imidacloprid at Different Days from Cucumber Leaves.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	27.09	7.48
5	6.82	4.89
10	0.57	0.21
20	0.00	0.01

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the cucmber leaves.

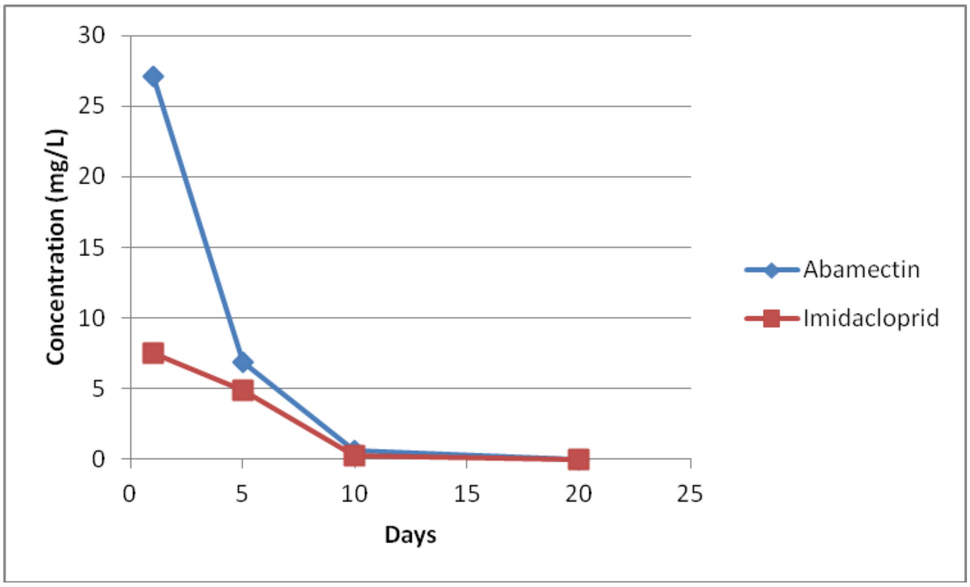

Figure 4.9: Concentration of Abamectin and Imidacloprid Residues from Cucumber Leaves

From the table 4.9 and figure 4.9 it was noticed the concentration of abamectin in cucumber leaves was higher than the imidacloprid on the first day and the fifth and the tenth day of spraying, but the concentration of imidacloprid was on the twentieth day was higher than abamectin, at the fifth day the concentration of abamectin was (6.82 mg/L); it was noticed very quick decreasing of abamectin concentration in cucumber leaves and this due to photodegredation and action of enzymes that degrade abamectin (Mingxie, *et al.*, 2006). At the fifth day the concentration of imidaclopid was (4.89 mg/L); it was noticed that degredation was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the tenth day the concentration of both imidaclopid and abamectin was less than maximum residue levels (MRLs).

It was noticed at the twentith day the concentration of both abamectin and imidacloprid less than maximum residue levels (MRLs).

Table 4.10 Concentration of Abamectin and Imidacloprid at Different Days from Pepper Roots.

Days	Concentration of Abamectin (mg/L)	Concentration of Abamectin (mg/L)
0 *	29	14.5
1	23.38	6.53
5	1.17	4.02
10	0.14	0.18
20	0.00	0.00

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the pepper roots.

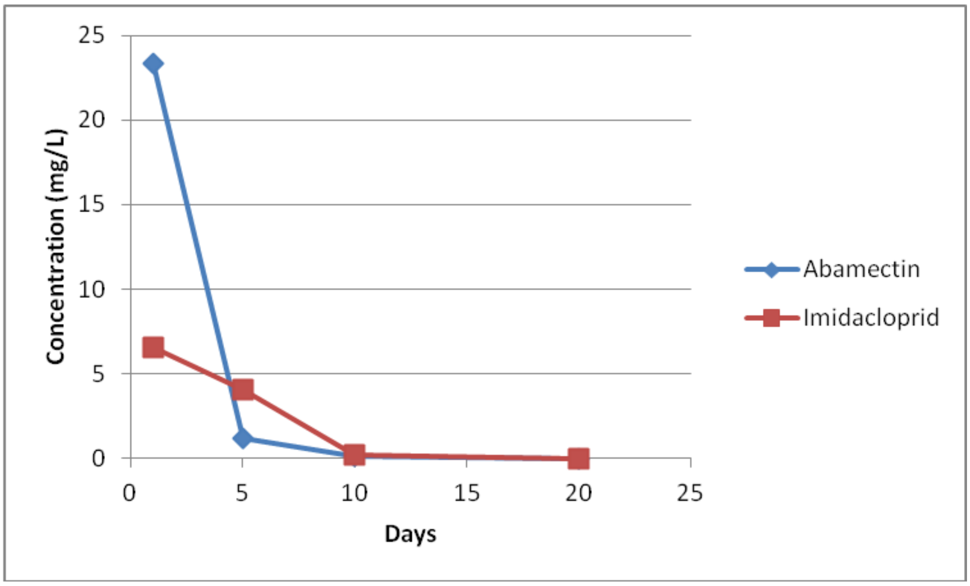

Figure 4.10: Concentration of Abamectin and Imidacloprid Residues from Pepper Roots

From the table 4.10 and figure 4.10 it was noticed the concentration of abamectin in pepper roots was higher on the first day than imidacloprid, but the concentration of abamectin in pepper roots on the fifth day less than the concentration of imidacloprid of spraying. The abamectin and imidacloprid were not detectable on the twentieth day, at the fifth day the concentration of abamectin was (1.17mg/L); it was noticed very quick decreasing of abamectin concentration in pepper roots and this due to action of enzymes that degrade abamectin and effect of fertilizers that used on the pepper. At the fifth day the concentration of imidaclopid was (4.02 mg/L); it was noticed that degredation of imidacloprid was slower than the degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the tenth day the concentration of both imidacloprid and abamectin was less than maximum residue levels (MRLs). It was noticed at the twentieth day the concentration of both abamectin and imidacloprid less than maximum residue levels (MRLs).

Table 4.11 The Concentration Results of Abamectin and Imidacloprid at Different Days from Tomato Roots.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	22.14	6.28
5	1.87	3.95
10	0.21	0.19
20	0.00	0.007

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the tomato roots

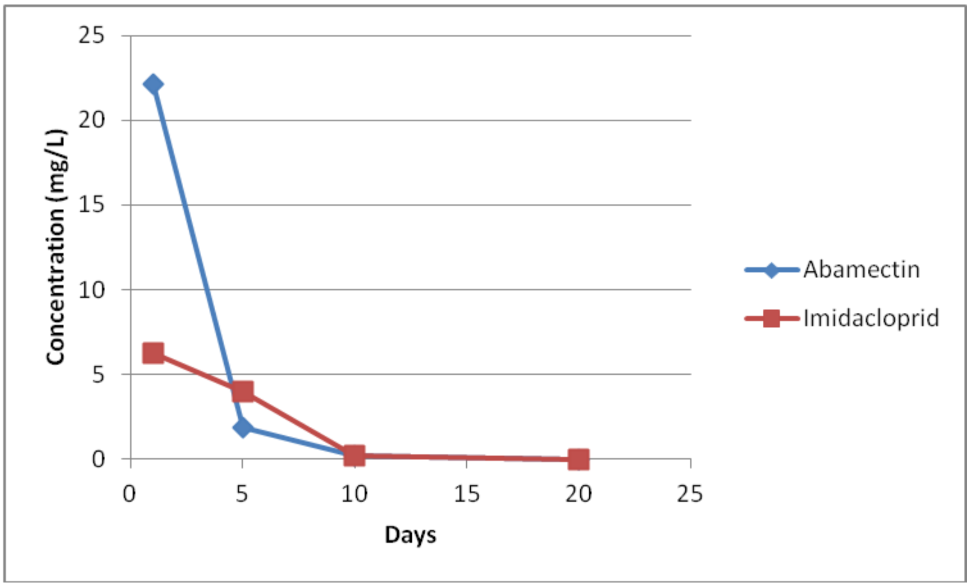

Figure 4.11: Concentration of Abamectin and Imidacloprid Residues from Tomato Roots.

From the table 4.11 and figure 4.11 it was noticed the concentration of abamectin in tomato roots on the first day was higher than imidacloprid, but the concentration of abamectin on the fifth day in tomato roots was less than the concentration of imidacloprid on the fifth day. The concentration of abamectin on the twentieth day in tomato roots was not detcetable but the imidacloprid was detectable due to high concentraction use by farmers (Arora, *et al.*, 2011). At the fifth day the concentration of abamectin was (1.84 mg/L); it was noticed very quick decreasing of abamectin concentration in tomato roots, and this due to action of enzymes that degrade abamectin and the effect of fertilizers on tomato, at the fifth day the concentration of imidacloprid was (3.95 mg/L);it was noticed that degredation was slower than degredation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs). It was noticed at the twentieth day the concentration of both abamectin and imidacloprid was less than maximum residue levels (MRLs).

Table 4.12 Concentration of Abamectin and Imidacloprid at Different Days from Cucumber Roots.

Days	Concentration of Abamectin (mg/L)	Concentration of Imidacloprid (mg/L)
0 *	29	14.5
1	21.28	6.68
5	1.63	4.28
10	0.28	0.23
20	0.00	0.00

- Where day 0 is the original concentration of abamectin and imidacloprid when sprayed on the cucumber roots.

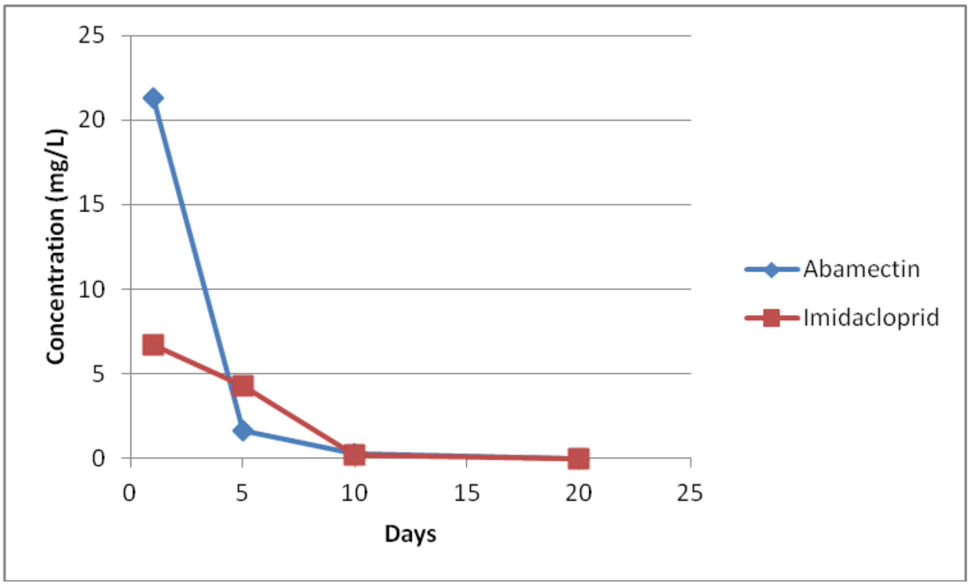

Figure 4.12: Concentration of Abamectin and Imidacloprid Residues from Cucumber Roots.

From the table 4.12 and figure 4.12 it was noticed the concentration of abamectin in cucumber roots on the first day was higher than imidacloprid, but the concentration of abamectin in cucumber roots on the fifth day was less than imidacloprid due to abamectin more volatilization comparing to imidacloprid (Vidal and Frenich, 2006) . The concentration of abamectin and imidacloprid residues on the twentieth day was not detectable. At the fifth day the concentration of abamectin was (1.63 mg/L); it was noticed very quick decreasing of abamectin concentration in cucumber roots and this due to action of enzymes that degrade abamectin, and the use of fertilizers on the cucumber. At the fifth day the concentration of imidacloprid was (4.28 mg/L);it was noticed that degradation was slower than the degradation of abamectin, and it was noticed that the concentration of both abamectin and imidacloprid was higher than maximum residue levels (MRLs).

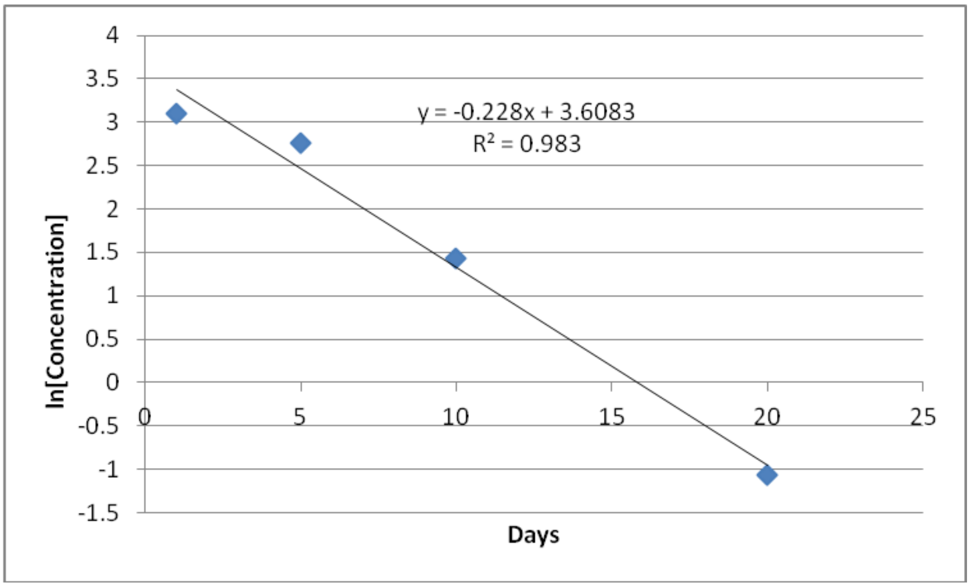

Figure 4.13 Destruction Rate of Abamectin versus Time

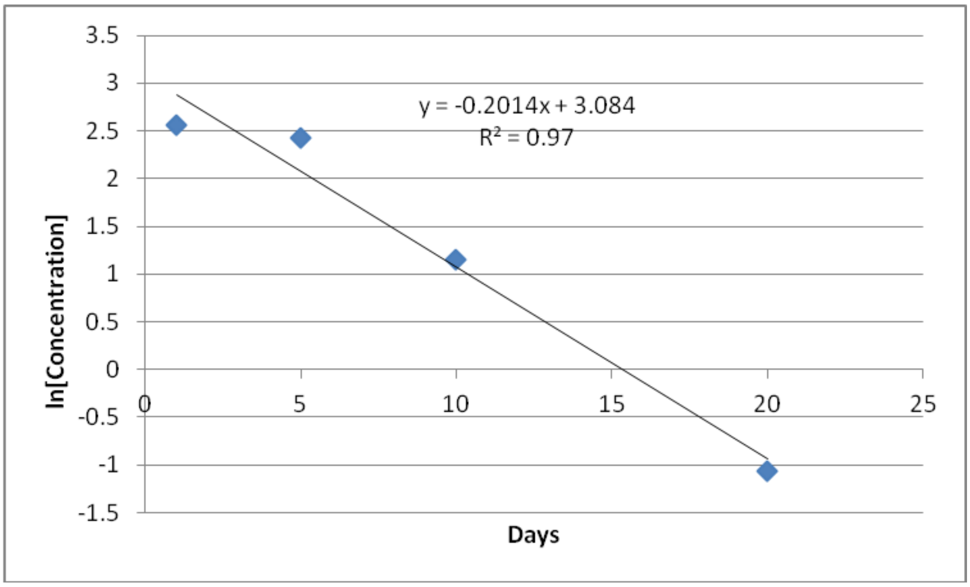

Figure 4.14 Destruction Rate of imidacloprid versus Time

Chapter Five

Conclusion and Recommendation

Detection of pesticides residues in plants and soil contribute a general problem, especially adverse effect on environment and public health.

Results obtained from this study showed that residues of imidacloprid and Abamectin remain in vegetables; tomato, cucumber and pepper especially after few days of spraying of pesticides.

During the study we obtained the following results:

1- Amount of imidacloprid and Abamectin residues were very high after the first day of spraying.

2- Until the fifth day of spraying amounts of residues of two pesticides were high and form a dangerous problem.

3- Quantity of imidacloprid and Abamectin residues in plant parts decrease by time due to photodegradation of pesticides.

4- The reason of high quantities of residues in the first day to the fifth day is due to the high concentration that used by farmers.

5- The ministries of Health and Agriculture should control the harvesting of the products and prevent farmers from selling them before the tenth day of spraying like in cucumber due to existence of pesticide residue.

Recommendations

To decrease the pesticides residues it is recommended to:

1- Invite farmers and the local community for the commitment of recommended amount of pesticides.
2- Use alternative methods of pest control other than imidacloprid and Abamectin to control aphids and other insects.
3- Invite agriculture ministry to educate and guide farmers to use the correct method of using and spraying pesticides.
4- Increasing awareness of farmers by the ministry of Agriculture from the results of pesticide residues.
5- More laws and regulations related to using of pesticides and more management from ministry of Agriculture and ministry of Health.
6- More researches in this regard should be carried out, further investigation into the pesticide residues especially imidacloprid and Abamectin.
7- Reduce the consumption of pesticides and depending on other pathways as integrated pest management that plants can influence other pests such as insects, mites, nematodes and diseases.
8- Unsafe imidacloprid concentration in crop spraying are causing a wide range of health problems. Immediate symptoms that the farmers have reported include respiratory problems, such as asthma attacks, skin rashes, eye irritation and headaches (Kolar, *et al.,* 2008).

Chapter Six

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Appendix

بسم الله الرحمن الرحيم

يهدف هذا الاستبيان المسحي إلى التعرف الى انواع المبيدات الزراعية المستخدمة من قبل المزارعين وكذلك معرفة الكميات التي يستخدمها المزارعين من هذه المبيدات،

نرجو من إخواننا المزارعين تعبئة الاستبيان بكل وضوح ومصداقية.

مع الشكر الجزيل،،،،،

الباحث: سائد المصري

يتكون الاستبيان من قسمين:

1) المعلومات العامة

2) المكافحة المستخدمة (الرش)

القسم الأول: المعلومات العامة

ضع دائرة حول الإجابة المناسبة

1) نوع الزراعة :

أ) مكشوف

ب) بيت بلاستيكي

ت) انفاق بلاستيكية

2) نوع السماد المستخدم :

أ) عضوي بلدي (زبل)

ب) كيميائي (اكياس)

ت) خليط بين النوعين السابقين

3) نوعية المكافحة (الرش) :

أ) بيولوجية (كائنات حية)

ب) كيميائية (مبيدات)

ت) خليط بين النوعين السابقين

4) نوعية المياه المستخدمة في الري :

أ) مياه جوفية (آبار)

ب) سطحية (برك)

ت) مياه مجاري مكررة

5) نوعية البيت :

أ) ملك

ب) أجرة

ت) غير ذلك

6) مدة العمل بالزراعة بالسنوات:

أ) 1 إلى 3

ب) 4 إلى 10

ت) فوق 10

القسم الثاني : المكافحة

ضع دائرة حول الإجابة المناسبة:

1) أكثر المبيدات الحشرية استخداماً:

أ) الكونفيدور

ب) الدروسبان

ت) الميتاك

2) أكثر مبيدات العناكب استخداماً :

أ) نيرون

ب)فيرتميك

ت)مساي

3) عدد رشات المبيدات الحشرية خلال الموسم :

أ) مرتين

ب) 4 مرات

ت) فوق 4 مرات

4) عدد رشات مبيدات العناكب خلال الموسم :

أ) مرتين

ب) 4 مرات

ت) فوق 4 مرات

5) يتم قراءة التعليمات على علبة المبيد :

أ) نعم

ب) لا

ت) غير ذلك

6) يتم الالتزام بالكمية الموصى بها من قبل الشركة المصنعة (التركيز على علبة المبيد)

أ) نعم

ب) لا

ت) غير ذلك

7) يلبس المزارع الكمامات أثناء تحضير المبيد :

أ) نعم

ب) لا

ت) غير ذلك

8) يلبس المزارع القفازات أثناء فترة الرش :

أ) نعم

ب) لا

ت) غير ذلك

9) يلبس نظارات الحماية أثناء فترة الرش :

أ) نعم

ب) لا

ت) غير ذلك

10) هل يتم اضافة السماد بـ :

أ) جرة السماد من خلال شبكة الري

ب) رش السماد على أوراق النباتات

ت) إضافة السماد مباشرة على النباتات .

جامعة النجاح الوطنية
كلية الدراسات العليا

تقييم المتبقيات من مبيد إميدوكلوبريد والأبمكتين في البندورة والخيار والفلفل باستخدام جهاز التحليل الكروماتوغرافي السائل (HPLC)

إعداد
سائد موسى ذياب علي

إشراف
د. شحدة جودة
أ.د. مروان حداد

قدمت هذه الأطروحة استكمالا لمتطلبات نيل درجة الماجستير في العلوم البيئية بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2012

تقييم المتبقيات من مبيد إميدوكلوبريد والأبمكتين في البندورة والخيار والفلفل بإستخدام جهاز التحليل الكروماتوغرافي السائل (HPLC)

إعداد

سائد موسى دياب علي

إشراف

د. شحدة جودة

أ.د. مروان حداد

الملخص

حديثاً من احدى الطرق التي لا غنى عنها هي استخدام المبيدات الزراعية وخاصة مبيدين الأميدوكلوبريد (الكنفيدور) والأبامكتين (الفيرتميك) على المحاصيل الزراعية لتحسين وزيادة إنتاج المحاصيل مثل البندورة والخيار والفلفل وفي الجانب الآخر يوجد أضرار ومشاكل عديدة من إستخدام المبيدات الزراعية وخاصة على صحة الإنسان.

في هذه الدراسة قمنا بإختيار نوعين من المبيدات الزراعية التي تم ذكرها سابقاً وهي (الأميدوكلوبريد والأبامكتين) لأسباب عديدة أولها، أن كلا المبيدين الأكثر إستخداماً بحسب إستبيان تم توزيعه على عدد من المزارعين في منطقة الدراسة، والسبب الثاني أن كلا المبيدين ذات فعالية عالية غي القضاء على العناكب والعديد من الحشرات.

تم رش الأميدوكلوبريد (الكنفيدور) والأبامكتين (الفيرتميك) على البندورة والخيار والفلفل داخل الدفيئات الزراعية وبنفس التراكيز التي يستخدمها المزارعون حيث كان تركيز الأميدوكلوبريد (الكنفيدور) 14.5 ملغم/لتر و والأبامكتين (الفيرتميك) 29 ملغم/لتر.

تم جمع العينات المختلفة من المحاصيل والتربة بعد رشها بعد اليوم الأول ثم الخامس ثم العاشر وأخيراً في اليوم العشري من الرش، العينات التي تم أخذها كانت من ثمار وجذور المحاصيل الزراعية. بعد جمع العينات تم استخلاصها ثم أخذ هذا المستخلص و حلل باستخدام جهاز التحليل الكروماتوغرافي السائل (HPLC) وجهاز الامتصاص الطيفي للأشعة فوق البنفسجية

والضوئي المرئي UV-Visible Spectrophotometer لتقييم المتبقي من مبيد إميدوكلوبريد و أبامكتين.

النتائج التي تم الحصول عليها من هذه الدراسة تظهر أن المتبقي من إميدوكلوبريد وأبامكتين هي أعلى من كميات المتبقيات التي توصل اليها الباحثون السابقون، كما أن النتائج التي تم الحصول عليها من هذه الدراسة تظهر أن المتبقي من إميدوكلوبريد وأبامكتين أعلى من الحد الأقصى المسموح به (MRLs) من المبيدات في العينات التي تم جمعها في اليوم الأول والخامس والعاشر للرش، كما أظهرت النتائج أيضاً أن المتبقيات من الأبامكتين أعلى من المتبقيات من إميدوكلوبريد، كما أن المتبقيات من كلا المبيدين كانت أعلى في التربة منها في أجزاء النبات.