



UNIVERSITI PUTRA MALAYSIA

***PESTICIDES CONTAMINATION IN PADDY SOIL AND THEIR
ASSOCIATED DERMAL HEALTH RISK TO PADDY FARMERS IN
TANJUNG KARANG, KUALA SELANGOR***

AMINATUN SOFIA BINTI SALLEHUDDIN

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TANJUNG KARANG, KUALA SELANGOR**

BY

AMINATUN SOFIA BINTI SALLEHUDDIN

**Thesis submitted in fulfilment of the requirement for the degree of Bachelor
Science (Environmental and Occupational Health) from the Faculty of Medicine
and Health Sciences, Universiti Putra Malaysia**

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ABSTRACT

PESTICIDES CONTAMINATION IN PADDY SOIL AND THEIR ASSOCIATED DERMAL HEALTH RISK TO PADDY FARMERS IN TANJUNG KARANG, KUALA SELANGOR

AMINATUN SOFIA BINTI SALLEHUDDIN

Introduction: Tanjung Karang, Kuala Selangor is the third largest paddy field in Malaysia. The pesticide can produce a positive impact on destroying pest that can destroy agricultural activities but it also gives a negative impact on other organisms that act as a biological control and not to mention it exerts health risks on the farmers themselves. **Objective:** To determine the concentration of pesticides in paddy soil samples and their associated dermal health risk among farmers at Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor. **Methodology:** The study was conducted at Kampung Sawah Sempadan in Tanjung Karang. 24 soil samples were collected from 24 paddy blocks that consist of Block A to X. Soil sample was extracted using of acetonitrile (ACN): ultrapure water (1:1) and the aliquot of the extract was injected into ultra high performance liquid chromatography – tandem mass spectrometry (UHPLC-MS/MS). 155 farmers were interviewed using a set of questionnaire to obtain the information such as pesticides exposure, usage of personal protective equipment (PPE) and personal hygiene for dermal health risk assessment. **Result and Discussion:** The Hazard Quotient (HQ) and Hazard Index (HI) for all compounds were less than 1 indicating that the risk of pesticides to the farmers was not significant. The lifetime cancer risk (LCR) for pymetrozine was at a clearly acceptable risk level ($LCR < 10^{-6}$) in the range of 2.03×10^{-14} to 8.67×10^{-14} . **Conclusion:** There was no significant non-carcinogenic and carcinogenic health risk for farmers work in paddy soil for the exposure of 27 years.

Keywords: Pesticides contamination, paddy soil, agriculture, UHPLC-MS/MS, health risk assessment

ABSTRAK

PENCEMARAN RACUN PEROSAK DI DALAM TANAH PADI DAN PENILAIAN RISIKO KESIHATAN TERHADAP DERMAL DALAM KALANGAN PESAWAH DI TANJUNG KARANG, KUALA SELANGOR

AMINATUN SOFIA BINTI SALLEHUDDIN

Pengenalan: Tanjung Karang, Kuala Selangor adalah kawasan sawah padi yang ketiga terbesar di Malaysia. Racun perosak boleh menghasilkan kesan positif terhadap pemusnahan serangga perosak yang boleh memusnahkan aktiviti pertanian tetapi ia juga boleh memberi kesan negatif ke atas organisma lain yang bertindak sebagai kawalan biologi dan juga memberikan risiko kesihatan keatas pesawah sendiri. **Objektif:** Untuk menentukan kandungan racun perosak dalam sampel tanah padi dan menilai risiko kesihatan dermal dalam kalangan pesawah di Kapung Sawah Sempadan, Tanjung Karang, Kuala Selangor. **Metodologi:** Kajian ini telah dijalankan di Kampung Sawah Sempadan di Tanjung Karang. 24 sampel tanah telah diambil dari 24 blok padi yang terdiri daripada Blok A-X. Sampel tanah telah diekstrak dengan menggunakan asetonitril (ACN): air *ultrapure* (1: 1) dan sebahagian ekstrak telah disuntik ke dalam *ultra high performance liquid chromatography – tandem mass spectrometry (UHPLC-MS/MS)*. Seramai 152 orang pesawah telah ditemubual dengan menggunakan satu set borang soal selidik untuk mendapatkan maklumat seperti pendedahan racun perosak, penggunaan peralatan perlindungan peribadi (PPE) dan kebersihan diri untuk penilaian risiko kesihatan terhadap dermal. **Keputusan dan Perbincangan:** *Hazard Quotient (HQ)* dan *Hazard Index (HI)* untuk semua sebatian kurang daripada 1, menunjukkan bahawa risiko racun perosak kepada pesawah tidak signifikan. Risiko *Lifetime Cancer Risk (LCR)* untuk pymetrozine adalah jelasnya boleh diterima ($LCR < 10^{-6}$) dengan julat diantara 2.03×10^{-14} to 8.67×10^{-14} . **Kesimpulan:** Tidak ada risiko kesihatan bukan karsinogenik dan karsinogenik yang ketara bagi petani bekerja di tanah padi untuk pendedahan selama 27 tahun.

Kata kunci: Pencemaran racun perosak, tanah padi, pertanian, UHPLC-MS/MS, penilaian risiko kesihatan

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LIST OF ABBREVIATIONS

ACN	Acetonitrile
C.E.	Collision energy
CAS	Chemical abstract service
CDC	Centers for Disease Control and Prevention
CEC	Cation exchange capacity
ESI	Electro Spray Ionization
FAO	Food and Agricultural Organizational
Fe ³⁺	Oxidized Iron
HCL	Hydrochloric Acid
HI	Hazard Index
HPLC	High Performance Liquid Chromatography
HQ	Hazard Quotient
IRIS	Integrated Risk Information System
ISs	Internal Standards
LCR	Lifetime Cancer Risk
MDL	Method Detection Limit
Mn ²⁺	Manganase
MOA	Ministry of Agriculture
MQL	Method Quantification Limit
MRM	Multiple reaction monitoring
NaCl	Sodium Chloride
Pct	Percent
POPs	Persistent Organic Pollutants

PPE	Personal Protective Equipment
RfD	Reference Dose
rpm	Rotation per minute
RRF	Relative Response Factor
TK	Total potassium
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
UHPLC-MS/MS	Ultra-High Performance Liquid Chromatography-Tandem Mass Spectrometry
UK	United Kingdom
USA	United State of America
USEPA	United State Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, the world's population keeps increasing. Carvalho (2006) states that the population in the world increases about 3.6 billion from 2.5 billion in 1950 to 6.1 billion in 2000. The population in the world will grow from times to times and the estimation of the population in 2050 will be reached to 9.1 billion. Worldwide need for food demands because of the number of people in this world keeps increasing from time to time. In order to increase the food demands, the productivity of the agricultural activity should be increased as well.

Agriculture sector has been identified as the third engine of economic growth in Malaysia after manufacturing and service sector. Agriculture sector classified into food commodities (paddy, meats, fish, fruits, and vegetables) and industrial commodities (rubber, palm oil, and cocoa) (Fahmi, Abu Samah, & Abdullah, 2013).

Paddy is a worldwide demand and planted in vast areas. Rice is the primary staple food for the world community. The highest producer and consumer of paddy (rice) come from the Asian country (Shafie, 2016). Malaysia is suitable for paddy production as their temperature regime and rainfall distribution is suitable for cultivation of rice. In Malaysia, paddy is one of the largest agricultural crops in

Malaysia after oil palm and rubber. Paddy is highly sowed in Peninsular Malaysia such as Kedah, Perak, Selangor, Negeri Sembilan and also in the East of Malaysia, Sabah, and Sarawak. Paddy cultivation is the major food crop enterprise in Malaysia, accounting about 0.67 million hectares for all season (MOA, 2007). Based on the statistic from Food and Agricultural Organization of United Nations (2016) paddy is one of the top ten commodities productions in Malaysia. Department of Statistics Malaysia (2015) stated that in 2014, the production of paddy has increased by 1.6% which is about 41.0 thousand tonnes as compared to the previous year. While the planted area for paddy also increased by 18 thousand hectares which are 2.7% in 2014 as compared to 2013. In Malaysia, paddy cultivation occurs two times per year which is in off season and major season. The major season of paddy plantation in Selangor regions commence between May and November each year. There are four major processes of paddy plantation, which are the clearance of land, crop establishment, management of crop and harvesting the crop (Shafie, 2016).

In order to produce high productivity of paddy, large quantities of pesticides need to be used. Unfortunately, a pesticide can contaminate environment through an intensive or inappropriate dose of pesticide. Various pesticides and its mixture are widely used to prevent pest during the growth period of agricultural plants (Chokeli, Hashim, Ho, Elias, & Mazlan, 2015).

Other than that, a pesticide is to suppress or control a variety of agricultural pests that can damage crops and reduce farm productivity. Pesticide can be naturally derived or synthetically produce substance. A pesticide that commonly applied to agricultural activity are insecticides, herbicides, rodenticides, and fungicides.

Different type of pesticide gives different function. Insecticides are for killing insects, herbicides are for killing weeds, while fungicides are using for control fungi, mould, and mildew.

However, there is no denying that the active usage of this substance can cause major concerns among the communities. The pesticide can produce a positive impact on destroying pest that can destroy agricultural activities but it also gives a negative impact on other organisms that act as a biological control and not to mention it exerts health risks on the farmers themselves.

Moreover, the pesticide is designed to be poisonous, so the exposure to pesticides can be harmful and hazardous to human and other organisms. Multi-residual pesticides can cause many health effects to the community especially farmers. The pesticides also can be harmful to people through occupational use, inhalation (or contact) of pesticide contaminated the air or ingestion of foods or liquids containing pesticide residue. Even in very low levels of exposure to pesticides, it also has an adverse effect on human especially toward susceptible people such as children (Kim, Kabir, & Jahan, 2016). Pesticide can cause health effect because of their nature that consists of the high degree of toxicity. The nature of pesticide that is designed to kill certain microorganism raised some harmful risk and the potential effect on human health and also towards other sensitive ecosystems (Damalas & Eleftherohorinos, 2011). Some of the effects of pesticides are cancer, hormone disruption, asthma, and hypersensitivity. Pesticide exposure also linked with birth defects, reduced birth weight, fatal death and other (Kim et al., 2016).

Health effect of the individual resulting from the exposure to pesticide may be the result of exposure via the oral, inhalation or dermal contact. However, for the pesticide applicator, the most relevant route of exposure is via dermal exposure. Undoubtedly, skin is the main route of exposure to environmental contaminants when the pesticides are applied (How, Hashim, & Omar, 2015). The factors that can contribute to the deposited of the pesticides on the skin are the type of application equipment used, individual work habit, cleaning of pesticide application equipment, usage of personal protective equipment (PPE) and unexpected events such as spills and splashes. Rates of absorption through the skin are different for different parts of the body (Macfarlane, Carey, Keegel, El-zaemay, & Fritschi, 2013).

Because of global concern on the effect of multi residual pesticides to public health, Food and Agricultural Organizational of United Nations (FAO) established an International Code of Conduct on the Distribution Use of Pesticides which acts as a guideline and reference on the management of pesticide.

Furthermore, in Malaysia, Pesticides Act 1974 act as the main legislation in regulating pesticide use. In Pesticides Act 1974, the pesticides that can be distributed and used have been listed.

Some of the common pesticides used in Malaysia, which focused on this study are chlorantraniliprole, difenoconazole and pymetrozine. Information of the target compounds is summarized in **Table 1.1**.

Table 1.1: Information of the compounds chosen.

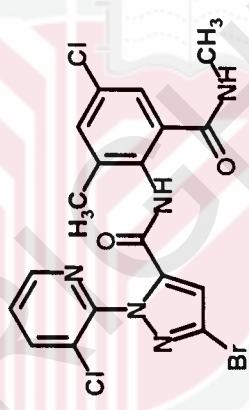
Common Name ^a	Pesticide Type ^a	Chemical Class ^a	IUPAC Name ^a	CAS Number ^a	Molecular formula ^a	Molecular structure ^b	Molecular weight (g mol ⁻¹) ^a	Log Kow ^a	Cancer classification ^c
Chlorantraniliprole									
Insecticide							483.147	2.76	Not Likely to Be Carcinogenic to Humans
					C ₁₈ H ₁₄ BrCl ₂ N ₅ O ₂				
			5-bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chloropyridin-2-yl)pyrazole-3-carboxamide	500008-45-7					

Table 1.1 Continued...

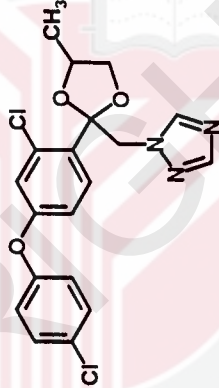
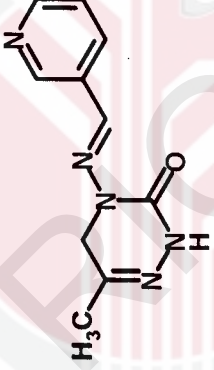
Common Name ^a	Pesticide Type ^a	Chemical Class ^a	IUPAC Name ^a	CAS Number ^a	Molecular formula ^a	Molecular structure ^b	Molecular weight (g mol ⁻¹) ^a	Log Kow ^a	Cancer classification ^c
Difenoconazole	Fungicide	Azole	1-[[[2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole	119446-68-3	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃		406.263	4.2 ^d	Group C. Possible Human Carcinogenic

Table 1.1 Continued...

Common Name ^a	Molecular formula ^a	Molecular structure ^b	Molecular weight (g mol ⁻¹) ^a	Log Kow ^a	Cancer classification ^c
Pymetrozine					
Insecticide					
Triazine (Pyridine Azomethines)					Likely to Be
6-methyl-4-[(E)-pyridin-3-ylmethylideneamino]-2,5-dihydro-1,2,4-triazin-3-one	C ₁₀ H ₁₁ N ₅ O		217.232	-0.18	Carcinogenic to Humans
123312-89-0					

^a Pubchem, 2016. National Center for Biotechnology Information (NCBI). <https://pubchem.ncbi.nlm.nih.gov/> (accessed February 2017).

^b Chempidder, 2016. Royal Society of Chemistry. <http://www.chemspider.com/> (accessed February 2017).

^c USEPA (2016). Chemicals Evaluated for Carcinogenic Potential (Annual Cancer Report 2016). http://npic.orst.edu/chemicals_evaluated.pdf (accessed April 2017)

^d USEPA (1994). Pesticide Fact Sheet: Difenconazole. <https://ntrl.ntis.gov/NTRL/dashboard/searchResults/titleDetail/PB94214525.xhtml> (accessed February 2017).

1.2 Problem Statement

Pesticides usage is common in the agricultural field. Pesticides can be considered as environmental pollutants because of their nature that consists of high toxicity. The half-life of certain pesticides is short and they do not persist at all (Matthews, 2006). Globally, not only is there concern about the environmental impact of pesticides but it also focuses on human health.

Although pesticides give a positive impact on destroying pests and act as the main character in agricultural production, these compounds give some potential risk in soil. The residue that remains in the field gives some adverse effects on rotational crops. The nature of the pesticides themselves are resistant to degradation in soil, leading to contamination by the residual amount and will contaminate the surface and groundwater. Soil contamination will occur if pesticides are resistant to degradation and it will lead to contamination of surface and groundwater subsequently resulting from this situation (Pose-juan, Sánchez-martín, Andrades, Rodríguez-cruz, & Herrero-hernández, 2015).

A widespread use of pesticides in different industries presents a significant health risk to workers involved in the use of pesticides. One of the major groups of workers is farmers that work directly with pesticides in agricultural fields. The majority of pesticides absorbed into the body come from dermal exposure. It has been approved that, the usage of personal protective equipment (PPE) in the form of appropriate clothes and gloves can reduce absorption (Macfarlane et al., 2013).

Pesticides tend to affect human health such as dermatitis, skin irritation, cancer, leukaemia, and asthma. The toxicity of the pesticide's ingredient and the level of exposure to human gives a contribution to the risk of pesticides to human health. Based on Aktar, Sengupta, & Chowdhury (2009), sprayer, mixers, loaders, agricultural workers, formulators, and production workers were the high risk group exposed to the pesticide and has the high tendency toward the effect of pesticides.

Kampung Sawah Sempadan has been chosen as a study location because majority of the community in that area involve in paddy farming and exposed to the pesticides.

Interview with the farmers were conducted in order to know the compounds of the commonly used pesticides. The interview was done by enquiring the farmers and the local pesticides supplier on which brands that the farmers most commonly used during spraying season. Based on the interview, there are thirteen compounds of the commonly used pesticides. From the thirteen compounds, three most active compounds have been selected. Three selected compounds are chlorantraniliprole, difenoconazole and pymetrozine.

Based on the field observation in Kampung Sawah Sempadan, the usage of personal protective equipment (PPE) seems neglected. It became worst when the farmers directly in contact with the pesticides and paddy soil without any protection.

1.3 Research Justification

Among the three routes of exposures which are ingestion, inhalation and dermal exposure, this study is focused on dermal health risk among paddy farmers in Kampung Sawah Sempadan, Tanjung Karang. That is because the likelihood of the accidental ingestion of the soil or inhalation of the soil is low compared to dermal exposure. Based on Shenoi, Davis, Rao, Rao, & Nair (2005), the prevalence of skin disease among paddy field farmers in Southern India is high. Pesticides can be reached to the skin directly from the air, by submersion of body parts into the substance or in contact with contaminated surfaces (Schneider et al., 1999). In addition, the Centers for Disease Control and Prevention (CDC) estimates that in the United States more than 13 million workers spanning a variety of occupational industries and sectors, are potentially exposed to chemicals that can be absorbed through the skin.

Pimentel (1995) states that only less than 0.1% of large quantities of pesticides that applied to the crops reach the target pests. The rest of 99.9% of the pesticides will be transported to the environment. In the environment, the pesticides can adversely affect beneficial biota and can contaminate the soil, water and atmosphere.

Pesticides applicator have high tendency to expose with pesticides through dermal exposure. Pesticides can be absorbed through the skin. Other factors such as, the amount and duration of exposure, the presence of other materials on the skin, temperature and humidity and the use of personal protective equipment will take into

account. If the pesticide is concentrated, the hazard becomes increases (Kim et al., 2016).

In addition, according to the interview with the farmers and field observation at Kampung Sawah Sempadan, it was found that some of the farmers did not wear appropriate and complete personal protective equipment (PPE) such as gloves and boots while handling the paddy soil, hence this may increase the risk of exposure to the pesticides that present in the environment. **Figure 1.1** shows the farmers that do not wear appropriate personal protective equipment (PPE) while mixing the pesticides.

Moreover, in Malaysia, there are limited numbers of studies on the pesticides contamination in paddy soil especially on the compounds chosen in this study. Since the farmers did not wear appropriate and full PPE while working, they could be exposed to pesticides that present in paddy soil via dermal contact. Thus, it is important to determine the carcinogenic and non-carcinogenic health risk that is imposed on the farmers by dermal exposure.

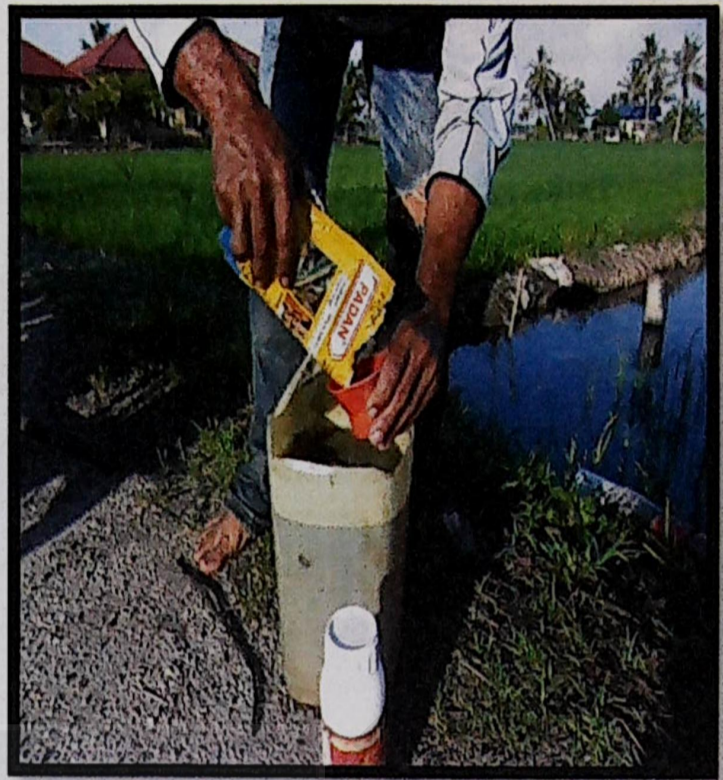
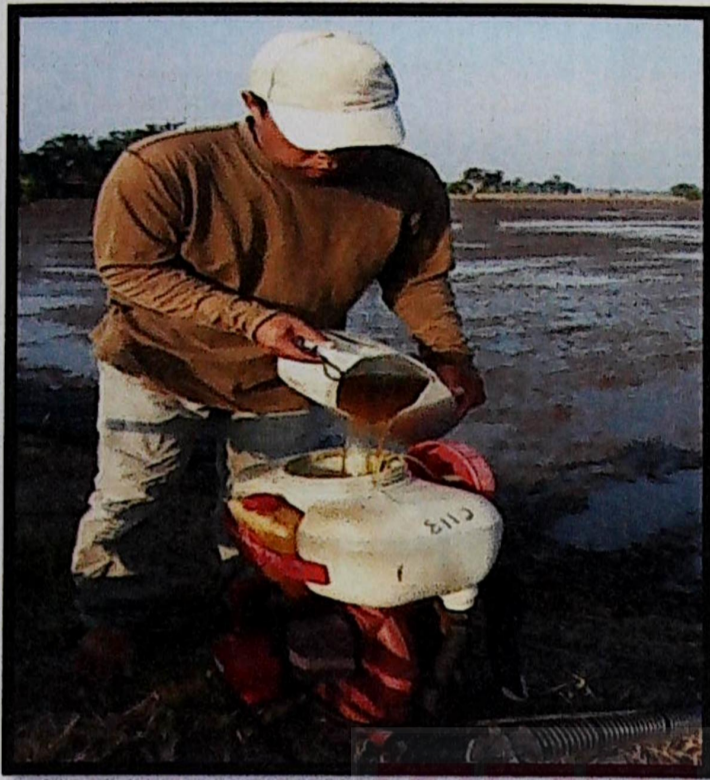


Figure 1.1: Farmers that do not wear PPE while mixing the pesticides.

1.4 Conceptual Framework

This study is focused in two parts which are the concentration of pesticides in soil and the effect of pesticide residues toward human health. The independent variable of this study was the concentration of pesticides while the dependent variables of this study were lifetime cancer risk and hazard quotient. **Figure 1.2** shows the conceptual framework of the study.

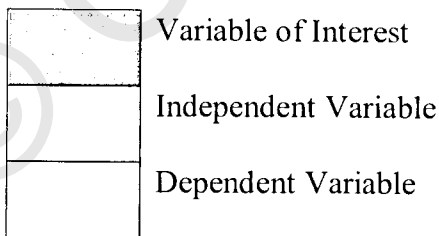
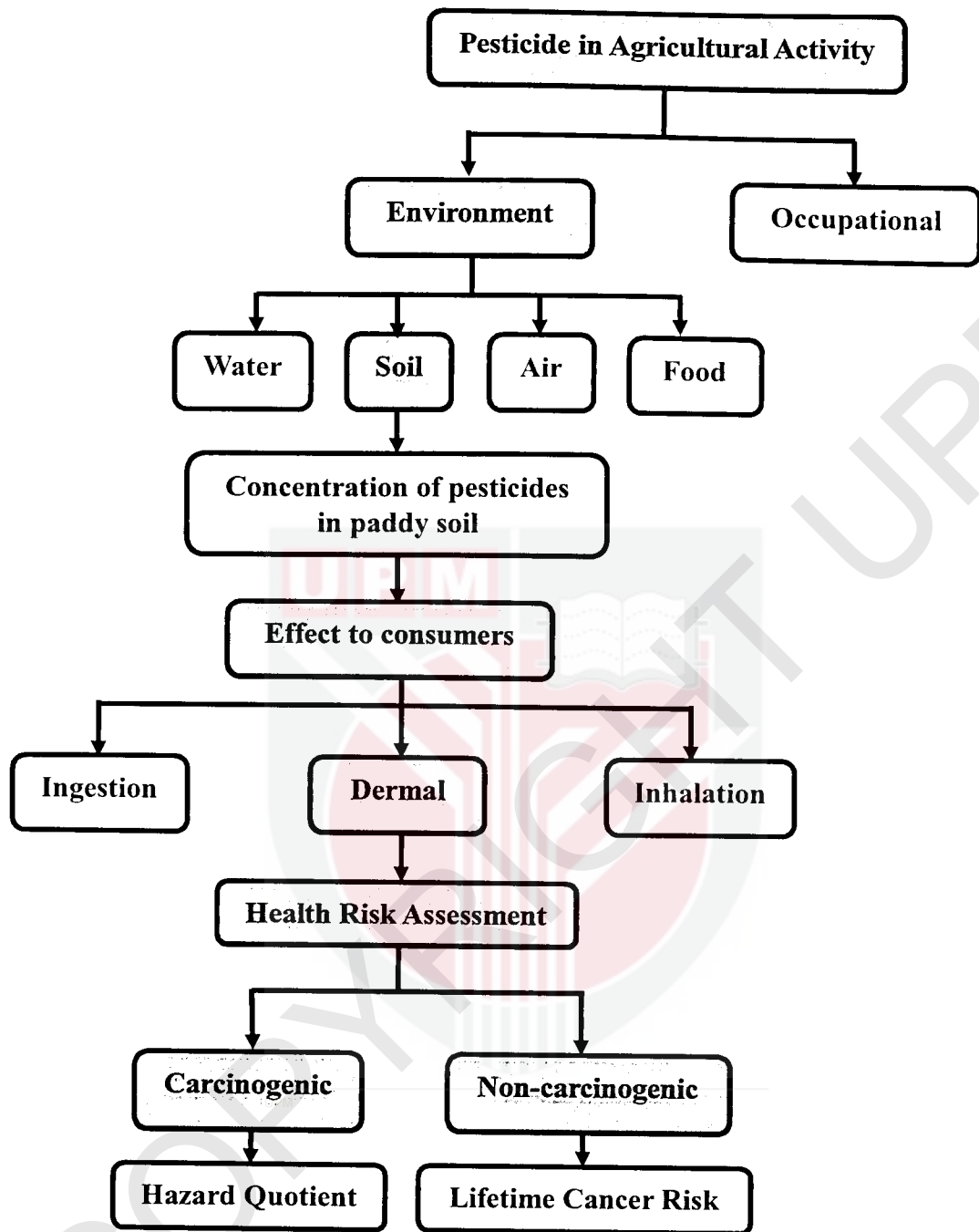


Figure 1.2: Conceptual Framework

1.5 Research Question

Questions arise from this research are as follow:

- i. What is the concentration of chlorantraniliprole, difenoconazole, and pymetrozine in paddy soil in Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor?
- ii. What is the level of personal hygiene and level of using personal protective equipment (PPE) among the paddy farmers in Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor?
- iii. Is there any non-carcinogenic and carcinogenic health risk to the farmers due to the occupational exposure of the pesticides in the soil in Kampung Sawah Sempadan paddy field?

1.6 Research Objective

1.6.1 General Objective

To determine the concentration of pesticides in paddy soil samples and their associated dermal health risk among farmers at Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor.

1.6.2 Specific Objective

- i. To identify the level of personal hygiene and the level of using PPE among the paddy farmers in Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor.
- ii. To quantify the concentration of chlorantraniliprole, difenoconazole, and pymetrozine residue in paddy soil samples collected from Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor.
- iii. To assess the non-carcinogenic and carcinogenic dermal health risk of the farmers due to the occupational exposure of the pesticides in the soil of Kampung Sawah Sempadan.

1.7 Definition of Terms

1.7.1 Operational Definition

Pesticide Contamination

Pesticide may contaminate the paddy soil due to the usage of pesticides in paddy field. In this study, three targeted compound has been selected (chlorantraniliprole, difenoconazole and pymetrozine) out of thirteen compounds. Then, those compounds were analysed through Ultra High-Performance Liquid Chromatography-tandem Mass Spectrometry (UHPLC-MS/MS).

Ultra High Performance Liquid Chromatography-tandem Mass Spectrometry (UHPLC-MS/MS)

The UHPLC-MS/MS will be used to analyse pesticide compound in the soil samples using electro spray ionization in positive method with optimized operating condition.

Health Risk Assessment

This study focuses on the risk assessment through dermal exposure of the paddy farmers. The assessment through the Hazard Quotient for non-carcinogenic effects and Lifetime Cancer Risk for carcinogenic effect were used to estimate the health risk of paddy farmers who were exposed to pesticides through dermal contact.



CHAPTER 2

LITERATURE REVIEW

2.1 Fate of Pesticides

Pesticides are the use of chemicals to control pests which can harm the crops, give annoyance to humans and transmit diseases of both humans and animals. Agricultural production needs pesticides to prevent or control pests, diseases, weeds and other pathogens in order to improve high produce quality and to eliminate yield losses (Fuad et al., 2012). Pesticides residue can be defined as any specific substances in food, agricultural commodities, or animal feed resulting from the use of a pesticide (Pesticide Board Malaysia, 2012). The medium for the pesticides to be spread, move and transfer to the environment is via absorption process, the wind, water, and soil. Certain pesticides can remain in the environment or a medium within hours, week, month and year depend on its characteristic and properties (Fuad et al., 2012).

After pesticides applied to respective crops, it will reach the soil by drifting during application, rain will wash the pesticides off the foliage, leaching and plant material falling to the ground. Each process will contribute to the overall loss of pesticides by referring to the physicochemical properties of the pesticide, characteristics of the soil, environmental conditions and management practices (I. S. Kim, Beaudette, Shim, Trevors, & Suh, 2002). During the application process, a lot

of pesticides lost. Moreover, while using spray equipment, only 25% of the pesticides reach the crop to destroy the pest while the remainder will drift off into the environment rather than reaching the crop or pests (Pimentel, 1995). Based on the research from I. S. Kim et al., (2002) on the environmental fate of the triazole fungicide propiconazole in a rice-paddy-soil lysimeter, propiconazole (fungicides) remained mainly in surface soil. Then, after application of propiconazole, it forms a large fraction of residue in soil because of its persistence in the soil for a long period of time.

When the extraneous compounds accumulate and remain in the environment for a very long period of time, there will be a significant effect on soil and water quality. The distribution of pesticide depends on the characteristics of soils (such as type of soil, temperature, moisture, soil structure and the availability of oxygen) and the chemical structure of the pesticide compound (their half-life, toxicity, solubility, and soil-water partition coefficient) (Harrison, Bull, & Michaelides, 2013).

Each of the compounds has their own half-life. A few study was done in regard of the half-life of certain compounds in pesticides. The half-life was depended on many factors including the physical characteristics of the compounds itself.

Based on USEPA (2008), chlorantraniliprole was categorized as persistent and mobile in terrestrial and aquatic environments. Accumulation of chlorantraniliprole residue in soil is expected to occur from year to year if there is an extended use of chlorantraniliprole. The major route of dissipation is photo-degradation in water, alkaline-catalyzed hydrolysis, leaching and run-off. Referring

to study by Zhang, Chai, & Wu (2012), the degradation rate of chlorantraniliprole in rice straw and water were faster than in soil as their half-life were 16.0 days for soil, 0.85 days for water and 3.50 days for rice straw.

Zhang et al., (2012), reported the concentrations of chlorantraniliprole in paddy soil were 12.0, 29.0, 22.0, 17.0, 13.0, 10.0 and 6.0 $\mu\text{g kg}^{-1}$ after 2 hours, 8 hours, 1 day, 3 days, 7 days, 14 days and 28 days of pesticides application, respectively. While, Malhat, Abdallah, & Hegazy (2012), also reported that the concentration of chlorantraniliprole in soil were 3193, 2215, 1710, 986, 593, and 165 $\mu\text{g kg}^{-1}$ after 1, 3, 7, 10, 12, and 15 days of pesticides application, respectively.

Next is difenoconazole which is persistent and slightly mobile in the soil environment. Difenoconazole has high potential to reach in soils that are high sand and low organic matter content but it has a low potential to reach ground water. The main route of dissipation on the aquatic environment is partitioning into the bottom sediment and potentially relatively fast to slow aqueous photolysis in clear water conditions (USEPA, 1994). Based on the study on the dissipation of difenoconazole in rice, paddy soil, and paddy water under field conditions by Wang, Wu, & Zhang (2012), there is an increase of difenoconazole residue in paddy soil after two hours of application until 3 days of application in Guangxi and Hubei while in Zhejiang, the residue can be detected until 21 days. Throughout the study, the half-life of difenoconazole were 23.26, 2.82 and 6.61 days in Guangxi, Hubei and Zhejiang, respectively.

A study by He et al. (2016) indicated that the concentrations of difenoconazole in the soil samples in Beijing, Shandong and Anhoi were ranged from 0.2 – 298.0 $\mu\text{g kg}^{-1}$ after spraying.

Based on USEPA (2000), pymetrozine does not pose a risk or contaminate the groundwater. It also expected that there is no major problem in the persistence of soil, mobility and bioaccumulation in fish. From the previous study by Li, Yang, Huangfu, & Wu (2011), the degradation rate of pymetrozine in rice straw and water were faster than in soil as their half-life were 7.0 days for soil, 0.7 days for water and 0.89 days for rice straw.

Li et al. (2011) also reported that the concentrations of pymetrozine in paddy soils were 19.0, 51.0, 44.0, 26.0, 15.0, 6.0 and 2.0 $\mu\text{g/kg}$ after 2 hours, 1, 3, 7, 14, 21 and 28 days of pesticides application, respectively. According to Li et al. (2011), from 2 hours to 1 day, a sharp increase of pymetrozine residues occurred. After 21 days of application, the initial deposit of pymetrozine in paddy soil were declined from 163.0 $\mu\text{g kg}^{-1}$ to 10.0 $\mu\text{g kg}^{-1}$ in Anhui, 163.0 $\mu\text{g kg}^{-1}$ to 9.0 $\mu\text{g kg}^{-1}$ in Beijing, and 242.0 $\mu\text{g kg}^{-1}$ to 13.0 $\mu\text{g/kg}$ in Zhejiang (Y. Zhang, Zhang, Xu, Li, & Wang, 2015).

2.2 Route of exposure

Route of exposure of pesticides toward human is from food, water, air, and soil. It can be distributed by bloodstream throughout the human body and excreted by urine, exhaled air and skin. Three common ways pesticides can enter the human body are from dermal (skin, eye), oral (ingestion), and respiratory pathway (inhalation) (Kim et al., 2016).

Dermal exposure can occur when the body or clothing in touch with the pesticides. While clothing is applied, the pesticides can penetrate the clothing and absorption to the skin will occur. Among three routes of exposure, agriculture workers extensively exposed to the pesticide through the skin (Acquavella et al., 2004; Matthews, 2006). Oral exposure usually happens when accidentally ingest the pesticides due to carelessness and oral exposure may cause a severe health risk. Oral exposure may occur when the farmers did not wash their hand before eating or smoking (Kim et al., 2016). Exposure to the respiratory pathway which is by inhalation is rarely happen compared to dermal exposure because of the efficient filter of the nose, so they can swipe away the particles before reaching the lungs (Matthews, 2006).

2.3 Health Effect of Pesticide

K.-H. Kim et al., (2016) mentioned that exposure to pesticides that are poisonous can be extremely hazardous to human health and other living organisms even though in low doses of exposure. About 51.5% of the farmers' complaints they have difficulty in breathing after spraying pesticide, 26% had itchininess and sore and the other 13.7% had rashes and hand skin peel off. In addition, there are farmers getting poisoned, collapsed, stomach ache and vomiting. As in 2009, there are 24 cases of poisoning and involving two deaths (Fuad et al., 2012). The previous study was carried out by Zare et al. (2015), on 18,782 farmers who use pesticides, shows that there was a link between neurological symptoms in farmers and the number of days when the farmer used pesticides.

Damalas & Eleftherohorinos (2011) stated that the impact of pesticides on pesticides become a serious concern when they mixed and applied the pesticides in their work. All these activities can cause accidental poisoning and expose major health risks to farmers whether in short term or long term. Exposure to pesticides tends to pose various diseases including cancer.

Public becomes concerned about the health of the public in the presence of pesticides residue in the environment as detrimental to life quality. This point of view has been supported by the results of scientific research. The combined effect of xenobiotic chemicals causes suppression of immune response and hypersensitivity to chemical agents even in low concentrations (Rivas, Olea, & Olea-Serrano, 1997).

Baharuddin (2011) mentioned that handler's health are at high risk when exposed to the pesticide repeatedly, and when the pesticides dispersed, leaked or spilled during the process of mixing and application. When dealing pesticides without proper safety consideration, long term exposure to pesticides may lead to several chronic health problems such as cancer, neuro-behavioural changes, liver abnormalities and kidney dysfunction.

Based on Ecobichon (1996), some of the acute health problems that related to organophosphates are headaches, abdominal pain, nausea, vomiting, dizziness, and skin and eye problems. Other studies stated that exposure to pesticides is associated with the chronic health problem such as miscarriage and birth defects, respiratory problem, dermatology condition, memory disorder, cancer, depression, neurologic deficits (McCauley et al., 2006).

Based on USEPA (2005), chemicals are classified into five groups. Group A also known as carcinogenic to human which has an adequate human data to demonstrate the causal association of the agent with human cancer and have sufficient evidence from epidemiologic studies; group B is probably carcinogenic to humans which have sufficient evidence from animal bioassay data, but either have limited human evidence or with little or no human data; group C is possibly carcinogenic to human which have limited animal evidence and little or no human data; group D is not classifiable as to human carcinogenicity which does not have adequate data either to support or refute human carcinogenicity; and Group E is evidence of non-carcinogenicity for humans which show no evidence of

carcinogenicity in at least two adequate animal tests in different species or in both adequate epidemiologic and animal studies.

From the selected active ingredients, chlorantraniliprole was classified as not likely to be carcinogenic to human (USEPA, 2016). Based on USEPA (2008), for all routes of exposure, chlorantraniliprole falls under toxicity category IV and it also acts as a non-sensitizer. As for difenoconazole, it has classified under group C which is possible human carcinogenic due to the existing of animal toxicity studies (USEPA, 2016). Pymetrozine was classified as likely to be carcinogenic to human (USEPA, 2016). Based on USEPA (2000), pymetrozine produce some neurotoxic effects but it is not mutagenic. It also has low acute toxicity and has been classified under Toxicity Category III and IV. Classified under Category III because it gives primary eye irritation and acute dermal irritation while for Toxicity Category IV because it poses primary dermal, acute inhalation and acute oral.

Based on Safety Data Sheet, chlorantraniliprole may give eye irritant and skin irritant to the user. Difenoconazole also can cause eye irritant and skin irritant to the user. However, in a high dose of difenoconazole, kidney and liver may effect. For pymetrozine, it gives slightly irritant to eye and skin. But, when in a high dose, it give effect on liver, spleen, thymus, kidney, muscle, digestive tract, thyroids and blood.

2.4 Legislation and Regulation

Based on Pesticides Act 1974, pesticides can be defined as any substance that can contain an active ingredient or any preparation, mixture or material that contains any one or more of the active ingredients as one of its constituents but does not include contaminated food or any article listed in the Second Schedule of Pesticides Act 1974 (Act 149 Laws of Malaysia, 2015).

Referring to International Code of Conduct on the Distribution and Use of Pesticides, pesticide can be defined as any substance or mixture of substances for destroying, preventing, or controlling any pest that can cause harmful, damage or interfere with the production, processing, storage, transportation or marketing of food, agricultural commodities and others (FAO, 2005).

Regulation, legislation, and guideline have been established around the world to control and oversee the fabrication, distribution and usage of pesticides. In Malaysia, the government establishes Pesticides Act 1974 to control the movement of pesticides in this country. Based on Pesticides Act 1974, Part III, they provide the control of importation and manufacture of pesticides by registration and permit while in Part IV, they provide the control of the manufacture, sale and storage of pesticides by licensing. Then in Part V, they focused on controlling the presence of pesticides in food and in Part VI, they stress out on death and injury that occurs by pesticides (Act 149 Laws of Malaysia, 2015).

Food and Agriculture Organization of the United Nations (FAO) comes up with International Code of Conduct on the Distribution and Use of Pesticides. This Code concerns protecting both human health and environment. This code was established to standardize the public and private entities that involved in the distributions and use of pesticides. It also mentions the responsibility of many sectors to work together in order to sustain the use of pesticide and minimize the potential risk to human health and the environment (FAO, 2005).

2.5 Health Risk Assessment

James (1985a) defined health risk assessment as a methodological approach to identify, characterize, analyse for the dose-response relationship of the chemical toxicities to generate the data that are applied to a mathematical model to produce a numeric estimate representing a guideline or decision concerning allowable exposure. Health risk assessment is risk assessment applied for the assessment of health hazards from the environment.

Health risk assessment can be divided into two, which are qualitative risk assessment and quantitative risk assessment. Quantitative health risk assessment generates a numerical measure of the risk or safety of a chemical exposure while the qualitative health risk assessment merely characterizes or compares the hazard of a chemical relative to others and may not necessarily require a numerical assessment of risk (James, 1985a).

According to USEPA (1989), there are two categories of the potential chronic health risk, which known as non-carcinogenic risk and carcinogenic risk. For the non-carcinogenic risk, there is a level of exposure below which no adverse effects will be observed known as threshold dose. Non-carcinogenic risk can be calculated using the Hazard Quotient (HQ). HQ is a ratio of the average daily dose of the substances to the reference dose (RfD).

According to USEPA (1989b), carcinogenic risk estimates the incremental probability that an individual will develop cancer over a lifetime as a result of specific exposure to a carcinogenic chemical. Carcinogenic risk can be calculated using Lifetime Cancer Risk (LCR) equation.

According to the United States Environmental Protection Agency (USEPA), if the value of HQ is less than one, then there is no significant risk of non-carcinogenic effects. Whereas, when the HQ value exceeds one, then there is a significant non-carcinogenic risk that may increase as the HQ increases.

This three active ingredient that has been selected has never conducted health risk assessment toward paddy farmers especially on dermal risk. But there is study for another pesticide such as for polychlorinated biphenyls and chloro-organic pesticides, classified as persistent organic pollutants (POPs). From the study by Pawełczyk (2013), the carcinogenic risk was detected slightly exceed the unconditionally acceptable risk of 10^{-6} in polychlorinated biphenyls and chloro-organic pesticides.

CHAPTER 3

METHODOLOGY

3.1 Chemicals and Standards

Reference standards of chlorantraniliprole (99.5%), difenoconazole (98.7%), and pymetrozine (99.0%) were purchased from Dr. Ehrenstorfer (Germany). The internal standards (IS) imidacloprid-d4 (99.9%) was purchased from Sigma-Aldrich (Germany). HPLC-grade methanol, HPLC-grade dichloromethane and HPLC-grade acetone were purchased from Fisher Scientific (UK) while HPLC-grade acetonitrile was purchased from Avantor Performance Material (USA). Analytical Reagent Grade dichloromethane, acetone and methanol were purchased from Fisher Scientific (UK). Sodium chloride was purchased from EMSURE (Germany). Hydrochloric acid and formic acid were purchased from R&M Chemicals (UK). Decon 90 was purchased from Decon Laboratories Limited (England). Ammonium formate solution was purchased from Sigma-Aldrich (Switzerland). Dichlorodimethyl-silane was purchased from EMSURE (Germany).

3.2 Study Design

The study design was cross-sectional study design where exposure and outcome were determined simultaneously. This study also involved laboratory

analysis as three compounds (chlorantraniliprole, difenoconazole, and pymetrozine) were quantified. Quantification of the compounds was conducted before their risk to the farmers were assessed.

3.3 Study Location

This study was carried out in the rice farming village of Kampung Sawah Sempadan which located at Tanjung Karang (3° 28' 20.455" N, 101° 17' 51.835" W), the state of Selangor, Malaysia. Tanjung Karang, Kuala Selangor is widely known for its paddy cultivation activity and the third largest paddy field in Peninsular Malaysia. Most of the communities in this area involve in rice farming and exposed to pesticides. Kampung Sawah Sempadan, Tanjung Karang consist of 24 blocks of paddy namely as Block A until Block X, specifically 1468 plots. The total area of the paddy field in Kampung Sawah Sempadan is 2304 hectares. The soil collection was conducted on 19 February 2017, roughly from 11.00 am to 4.00 pm, which was the paddy cultivation period in the study area. The study location is depicted in **Figure 3.1**. There were few considerations that need to be taking care in selecting the location of study. The criteria of the study location were:

- i. Agriculture area with paddy cultivation as the main activity.
- ii. Study location must be nearby or in a short distance from the laboratory which preservation and analysis were conducted.
- iii. The willingness and cooperation of the residents throughout the study.

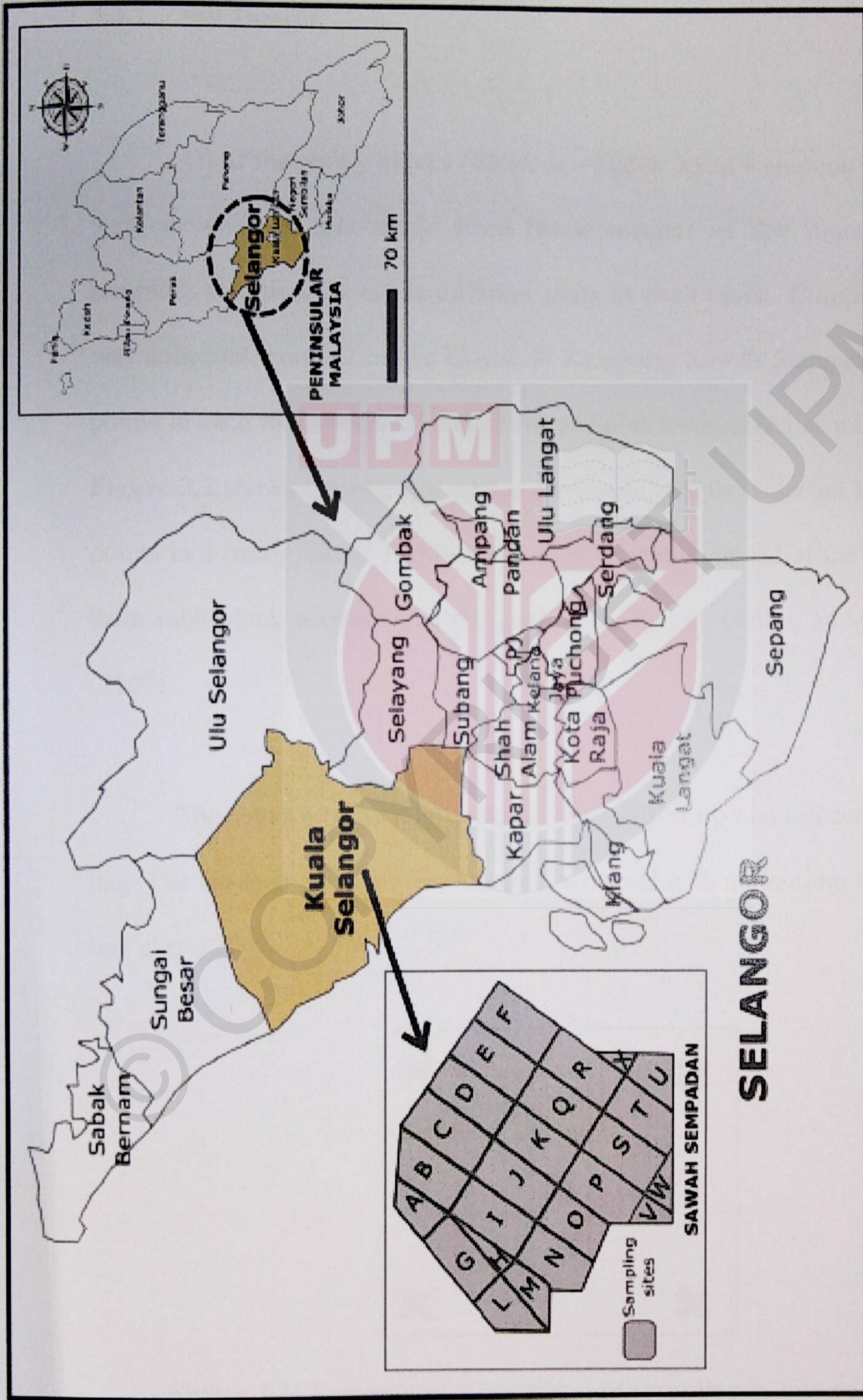


Figure 3.1: Sampling locations in Kampung Sawah Sempadan, Kuala Selangor, Malaysia

3.4 Sampling Technique

3.4.1 Soil Sample

All of the paddy blocks (Block A – Block X) in Kampung Sawah Sempadan were included in this study. Each block consists of few plots. Simple random sampling was used to select different plots of each block. Composite soil samples was collected from all of the blocks in Kampung Sawah Sempadan. Five different points in each block were taken and the samples were mixed as a composite sample. **Figure 3.2** shows the example of the composite sample collected from five different points in a paddy block. Paddy soil samples were collected at the depth of 0-20 cm from each block according to the method by Fenoll, Hellín, M.Martínez, & Flores (2009).

Then, those composite samples were mixed up and collected in the zip-lock bag. The zip-lock bag then was labelled, wrapped with aluminium foil and kept in ice box at 0-4 °C.

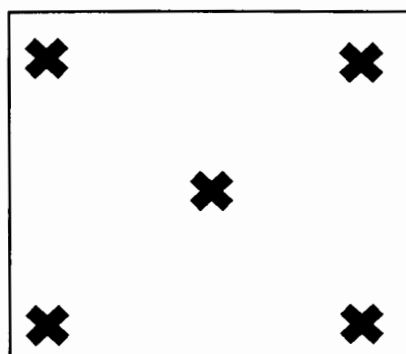


Figure 3.2: Example of composite soil sampling in one paddy block

3.4.2 Determination of Dry Weight Soil Samples

The determination of dry weight in soil samples were carried out in accordance with the USEPA Method 1694 (USEPA, 2007). Determination of dry weight needs to carry out in solid samples prior to the pre-cleaning of reference materials and sample extraction. Five to ten gram of the solids were weighed from the bulk sample to three significant figures in a tared stainless steel container. Then, the solid samples were dried at 110°C for twelve hours and were cooled in in a desiccator. The dried aliquot was weighed and percent solid were calculated as follows:

$$\% \text{ Solids} = \frac{W_a \text{ (g)}}{W_b \text{ (g)}} \times 100 \quad (\text{Equation 3.1})$$

Where,

W_a = Weight of sample aliquot after drying

W_b = Weight of sample aliquot before drying

3.5 Sample Population

The sample frame in this study was the name list of paddy farmers in Kampung Sawah Sempadan that was obtained from Farmers Organization Authority Office, Tanjung Karang. The inclusive criteria were set to determine the farmers that can participate in this study. However, only those who fulfil the inclusion criteria were included in the study. The inclusion criteria were:

- i. Paddy farmers within the age group of 18 to 80 years old
- ii. Paddy farmers who have been working for more than 6 months in the paddy field. Workers than work more than 6 months are expected to have health effect.
- iii. Paddy farmers who exposed directly to the paddy soil in their job task.

Sample size was calculated according to Lemeshow, Hosmer Jr, Klar, & Lwanga (1990). The total population of paddy farmers in the Tanjung Karang as acquired by the District Office of Tanjung Karang was approximately 7679, and the population of the paddy farmers in the study area (Kampung Sawah Sempadan) was 1147. The sample size was calculated using the following equation:

$$n = \frac{Z^2_{1-\frac{\alpha}{2}} P(1 - P)}{d^2} \quad \text{(Equation 3.2)}$$

Where,

n = Sample size

$Z^2_{1-\frac{\alpha}{2}}$ = Standard errors associated with confidence intervals, 95% (1.96)

P = Prevalence, 0.1

d = Desired precision, 0.05

The value of prevalence, P is 0.1 from the study on dermatitis among farmers engaged in peri-urban aquatic food production in Hanoi, Vietnam by Anh et al. (2007). Below is the sample size calculation for this study.

$$n = \frac{1.96^2 \times (0.1)(1 - 0.1)}{(0.05)^2} \quad (\text{Equation 3.3})$$

$$n = 138$$

In order to recover the loss of respondent, 10% of the minimum sample size were added, which is:

$$\begin{aligned} 10\% \text{ of } 138 &= 13.8 \approx 14 \\ &= 14 + 138 \\ &= 152 \text{ respondents} \end{aligned}$$

3.6 Selection of Targeted Compounds

The target pesticides were selected based on the interview with the farmers. The top three pesticides were selected as the target compounds in this study. **Table 3.1** summarized the frequency of the usage of pesticides active ingredients.

Table 3.1: Frequency of the usage of pesticide's active ingredients by farmers in Kampung Sawah Sempadan, Tanjung Karang.

Pesticide active ingredients	Frequency	Percentage (%)
Chlorantraniliprole	44	36
Difenoconazole	44	36
Pymetrozine	43	36
Isoprothiolane	41	34
Propiconazole	38	32
Pretilachlor	31	26
Tebuconazole	29	24
Trifloxystrobin	20	24
Azoxystrobin	27	23
Fipronil	22	18
Tricyclazole	21	18
Imidacloprid	17	14
Buprofezin	13	11

N = 154

3.7 Soil Extraction and Preparation

Soil extraction and preparation procedure was modified according to Fenoll et al., (2009). Upon the arrival to the laboratory, the soil samples were homogenized and passed through a 2 mm sieve. To determine the dry weight and the percentage of solid, aliquot of the homogenized soil samples were used. 10 g of soil samples were weighed into the centrifuge tube. Then, 20 mL of acetonitrile (ACN) : ultrapure water (1:1) were added into the centrifuge tube. The centrifuge tube was extracted by sonication (Elmasonic, Germany) for 15 minutes and followed by salting-out step with 2 g of Sodium Chloride (NaCl). The tube was shaken and centrifuged (Hettich Rotofix 32, Sigma-Aldrich) for 10 minutes at 3000 rpm. An aliquot of the supernatant extract was filtered through 0.45 µm nylon membrane filter. Next, 50 µL of 1 mg/L internal standard (imidacloprid-d4) was spiked into 950 µL extract into an auto sampler vial. Then, the extract was analysed using UHPLC-MS/MS.

3.8 Study Instrument

3.8.1 Questionnaire

A set of questionnaire was distributed among the farmers to obtain the information for health risk assessment. The questionnaire was distributed from 16 January 2017 until 19 January 2017. The questionnaire was divided into four parts which include Section A: information regarding personal information, Section B: exposure to pesticides and personal hygiene, Section C: usage of personal protective equipment (PPE) and Section D: health information.

The information obtained from this questionnaire was used to assess the dermal risk exerted by the farmers. The questionnaire developed was based on Nordic Occupational Skin Questionnaire (2002) and Taneepanichskul et al. (2010).

Fishbowl Draw technique was used to get the human sampling that was selected from a list of farmers in Kampung Sawah Sempadan provided by Farmers Organization Authority Office, Tanjung Karang.

Pre-test of the questionnaire were conducted in Kampung Sungai Burung, Tanjung Karang Kuala Selangor. The questionnaire was distributed to the farmers in Kampung Sungai Burung, Tanjung Karang, Kuala Selangor. The result of the pre-test is 0.8.

3.8.2 Ultra High-Performance Liquid Chromatography-tandem Mass Spectrometry (UHPLC-MS/MS)

The UHPLC-MS/MS (Agilent, USA) method conditions were as follows: chromatographic separation was performed on an Eclipse Plus C18 column (2.1 mm × 50 mm I.D., 1.8 μm particle size) (Agilent, USA). The mobile phase compositions were as follows: A, ultrapure water with 0.1% formic acid and 5 mM ammonium formate, and B, methanol with 0.1% formic acid and 5 mM ammonium formate. The mobile phase was mixed as follows: 0 min 94% A, 6% B; 15 min 2% A, 98% B; 18 min 2% A, 98% B; 18.01 min 94% A, 6% B; and 20 min 94% A, 6% B. The flow rate was 0.5 mL min⁻¹, and the total runtime was 20 minutes. The column temperature was set at 40 °C, and the injection volume was 2.0 μL. All pesticides

were detected using electrospray ionization (ESI) in positive ion mode. The optimized operating conditions were as follows: capillary voltage, 3500 V; gas temperature, 220 °C; gas flow, 11 L min⁻¹; and nebulizer, 30 psi. The optimised ESI and MS/MS parameters, comprising of precursor ions, product ions, collision energy (C.E.) and fragmentation voltage are shown in **Table 3.2**. The optimized ESI and MS/MS parameters were subsequently used for multiple reaction monitoring (MRM) in UHPLC-MS/MS analysis. Data collection, peak integration and linear regression were performed using the QQQ Quantitative Analysis software from Agilent (USA).

Table 3.2: MRM conditions

Compound	Precursor ion,	Product, <i>m/z</i>	Fragmentation, V
	<i>m/z</i>	(Collision energy, V)	
Chlorantranilprole	483.90	452.90 (16), 285.90 (8)	380
Difenoconazole	406.10	337.00 (10), 251.00 (20)	380
Pymetrozine	218.11	78.00 (52), 51.00 (60)	380

3.9 Quality Control

3.9.1 Cleaning of glassware

All glassware were undergone acid wash before used to ensure they are free of any contaminants based on USEPA Method 1699 (EPA, 2007). All glassware were soaked with 5-10% hydrochloric acid (HCL) overnight followed by washed with Decon 90. Then, the glassware was rinsed immediately, first with methanol, then with hot tap water. After that, it was rinsed with methanol again, followed by acetone, and then dichloromethane. After washing, all glassware were dried at 60 °C and capped with solvent rinsed aluminium foil to prevent any accumulation of dust or other contaminants.

3.9.2 Calibration of UHPLC-MS/MS

At a five-point calibration curve, the instrument was calibrated with each analyte. Each calibration point were added the labelled internal standards (ISs) corresponding to the analytes at a concentration of 50 ng mL⁻¹ to generate relative response factors (RRF). A calibration curve was obtained by injecting the standards of chlorantraniliprole, difenoconazole, and pymetrozine range from 0.1 ng mL⁻¹ to 500 ng mL⁻¹.

3.9.3 Extraction Recovery

The extraction recovery was determined in order to validate the analytical procedure by spiking the samples with varied amounts of standard solutions of each compound (Zhuang, McBride, Xia, Li, & Li, 2009). The percentage of recovery was calculated according to Ho, Zakaria, Latif, & Saari (2012), the percentage of recovery was calculated by comparing the concentration of each compound spiked before extraction (C_p) to its concentration spiked after extraction (C_a) in the same sample matrix using **Equation 3.4**, where C_{qc} is the concentration of analyte in the blank sample.

$$\text{Recovery (\%)} = \frac{C_p - C_{qc}}{C_a - C_{qc}} \times 100 \quad (\text{Equation 3.4})$$

3.9.4 Procedural Blank

The soil (blank) collection was conducted on 18 February 2017. The blank sample was collected from a place without any anthropogenic activity. The procedural blank procedure was modified by Fenoll et al., (2009). For every batch of samples, 1 mL of the native standard was spiked into the blank sample, and the sample was allowed to equilibrate for two hours before extraction and instrumental analysis in order to avoid any interference or contamination.

3.10 Health Risk Assessment

3.10.1 Non-carcinogenic Risk

The non-carcinogenic chronic health risk of farmers was assessed using hazard quotient (HQ). Hazard Quotient (HQ) is a ratio of exposure dose to the compounds-specified reference dose (RfD). USEPA (2001) stated that if the value of HQ is less than one, then there is no significant risk of non-carcinogenic effects. Whereas, when the HQ value exceeds one, then there is a significant non-carcinogenic risk that may increase as the HQ increases.

HQ was calculated based on USEPA (2004) as shown in **Equation 3.5**:

$$HQ = \frac{DAD}{RfD} \quad \text{(Equation 3.5)}$$

Based on USEPA (2004), DAD and DA_{event} were calculated using the following equation:

$$DAD = \frac{DA_{event} \times EV \times ED \times EF \times SA}{BW \times AT} \quad \text{(Equation 3.6)}$$

$$DA_{event} = C \times CF \times AF \times ABS_d \quad \text{(Equation 3.7)}$$

$$AT = ED \times 365$$

(Equation 3.8)

The values of each parameter stated in **Equation 3.6, Equation 3.7, and Equation 3.8** are summarized in **Table 3.3**.

The cumulative exposures of pesticides were estimated using a hazard index (HI) by applying the following formula (USEPA, 1989):

$$HI = \sum HQ$$

(Equation 3.9)

Table 3.3 : Values of each parameter stated above.

Parameters	Value	Reference
DAD	Dermal Absorbed Dose ($\text{mg}^{-1} \text{kg}^{-1} \text{day}^{-1}$)	From this study
	Based on calculation	
	Compound	eRfD ($\text{mg kg}^{-1} \text{day}^{-1}$)
	Chlorantraniliprole	1.58 ^a
	Difenoconazole	0.01 ^a
	Pymetrozine	0.008 ^a
RfD	Reference dose ($\text{mg}^{-1} \text{kg}^{-1} \text{day}^{-1}$)	^a USEPA (2010)
DA _{event}	Absorbed Dose (hr event^{-1})	From this study
C	Concentration of pesticides (mg kg^{-1})	From this study
CF	Conversion factor	USEPA (2004)
	Based on calculation	
	Based on laboratory analysis	
	10 ⁻⁶ kg mg ⁻¹	

Table 3.3 *continue...*

Parameters		Value		Reference
	Compound	ABS _d	ABS _d	
ABS _d	Dermal absorption factor	Chlorantraniliprole	0.01 ^a	^a USEPA (2010)
		Difenoconazole	0.75 ^a	
		Pymetrozine	0.001 ^a	
EV	Event frequency (events day ⁻¹)		1	Questionnaire (Question 16)
ED	Exposure duration (years)		27	Questionnaire (Question 9)
EF	Exposure frequency (days year ⁻¹)		220	Questionnaire (Question 16)

Table 3.3 continue...

Parameters	Value	Reference
Recommended Values for		
	Surface area	Mean Solids Adherence (mg cm⁻²)
AF	Hands	0.1595 ^a
	Feet	0.1393 ^a
	Hands and feet	0.2988 ^a
	^a Based on weighted average of geometric mean soil loadings for 69 gardeners, farmers, groundskeepers, landscapers and archeologists (ages 16 to 64 years) for faces, arms and hands; 65 gardeners, farmers, groundskeepers, and archeologists (ages 16 to 64 years) for legs; and 36 gardeners, groundskeepers and archeologists (ages 16 to 62) for feet.	
AT	Averaging time (days)	5949
		From this study

Table 3.3 *continue...*

Parameters	Value	Source
	50th percentile of Surface Area for Adults Male (cm²)	
	Surface Area	
SA	50 th Percentile Skin Area (cm ²)	^a USEPA (2011)
	Hands	1070 ^a
	Feet	1370 ^a
	Hands and feet	2440 ^a
BW	Average body weight (kg)	Questionnaire (Question 4)
		70.68

3.10.2 Carcinogenic risks

Lifetime cancer risk is to estimate the probability of an individual to develop cancer over a lifetime after exposure to a potential carcinogenic substance. Below is the low-dose carcinogenic risk equation that was used for each exposure route (USEPA, 2004).

$$\text{Lifetime Cancer Risk} = \text{DAD} \times \text{SF} \quad (\text{Equation 3.10})$$

Where,

DAD = Dermal Absorbed Dose ($\text{mg}^{-1} \text{kg}^{-1} \text{day}^{-1}$)

SF = Absorbed cancer slope factor ($\text{mg}^{-1} \text{kg}^{-1} \text{day}^{-1}$)

The value for SF was obtained from the USEPA. The value of SF for chlorantraniliprole, difenoconazole, and pymetrozine are stated in **Table 3.4**.

Table 3.4: Value cancer slope factor

Compound	Slope factor
Chlorantraniliprole	NA
Difenoconazole	NA
Pymetrozine	0.0119 ^a

^aUSEPA, 2010

N/A: Data not available

3.11 Ethical Consideration

The ethical approval and consent was obtained from the Universiti Putra Malaysia (UPM) Ethical Committee for research involving human subject and can be refer with JKEUPM Ref Number FPSK(EXP16-OSH)U045. Besides that, the consent form and the questionnaire used in this study was explained to the respondents that, and respondents were guided during filling the questionnaire. All information given by the respondents was kept private and confidential and only used for research and scientific publication purposes.



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Quality Control

Calibration curves were obtained for all analytes to determine the concentration of pesticides in the soil samples. Five-point calibration curves for all targeted compounds were derived in the range of 0.1-500 ng mL⁻¹. All calibration curves of the target compounds showed good linearity with regression coefficient (R²) ranges from 0.9988 to 0.9999. The extraction recovery was examined for concentration at 100 ng mL⁻¹ and ranged from 42.08% to 102.19%.

4.2 Information on Questionnaire

The questionnaire consists of Section A (information regarding personal information), Section B (exposure to pesticides and personal hygiene), Section C (usage of PPE and personal hygiene) and Section D (health information).

4.2.1 Socio-demographic background of respondents

One hundred and fifty-four farmers who work in the Kampung Sawah Sempadan paddy field were involved in this study. The socio-demographic information of respondents was summarized in **Table 4.1**.

Table 4.1: Socio-demographic information of respondents (n=154)

Variables	Mean(SD)	Minimum	Maximum
Age (years)	51.36 (13.206)	19	76
Weight (kg)	70.68 (12.933)	45	120

Variables	Category	Frequency	Percentage (%)
Gender	Male	154	100
Race	Malay	154	100

The respondent's age was ranged from 19 to 76 years old, with a mean of 51.36 years old. The average weight of respondent was 70.68 kg and ranged from 45 to 120 kg.

All 154 respondents involved in this study were male and Malay farmers as the majority of the population in Kampung Sawah Sempadan are Malay.

4.2.2 Exposure of respondents to pesticides

To assess the dermal health risk assessment of the farmers, information on exposure of the farmers to pesticides were needed. This information obtained from the interview. All the information of farmer's exposure to pesticides is tabulated in

Table 4.2.

Table 4.2: Information of farmer's exposure to pesticides (n=154)

Parameters	Average
t_{event} (hr event ⁻¹)	2
Event frequency (events day ⁻¹)	1
Exposure duration (years)	27
Exposure frequency (days year ⁻¹)	220
Averaging time (days)	5949

t_{event} is the hour of contact to the pesticides in paddy soil per event. In this study, the average t_{event} was 2 hours. Event frequency (EV) refers to how many times the farmers involve in paddy cultivation activities in a day while the exposure duration (ED) is the number of years the farmers have involved in the activity. In this case, the average ED for the respondents was 27 years. Exposure frequency (EF) refers to number of days per year of exposure and averaging time (AT) is the product of ED and EF.

4.2.3 Personal hygiene and Use of Personal Protective Equipment (PPE)

In order to protect the farmers and minimize the dermal exposure of pesticides in paddy soils, the farmers need to use the personal protective equipment (PPE). The information on the usage of PPE among farmers was recorded in **Table**

4.3.

Table 4.3: Personal Hygiene and Use of Personal Protective Equipment (PPE) among Respondents (n=154)

Variables	Categories	Frequency	Percentage (%)
Wash up / Shower after farming	Yes	129	83.8
	No	25	16.2
Change clothes after farming everyday	Yes	144	93.5
	No	10	6.5
Use Full PPE	Yes	71	46.1
	No	83	53.9

Based on the results obtained from the questionnaire, as a routine of personal hygiene, 129 respondents (83.8%) take a shower after farming, while another 25 respondents (16.2%) do not immediately wash up after farming. About 144 respondents (93.5%) changes the clothes they wear for farming every day while 10 respondents (6.5%) of the farmers use the same clothes for farming. Out of 154 respondents, only 71 respondents (46.1%) use the full set of PPE which consist of boots and gloves, while the remaining 83 respondents (53.9%) do not wear a complete protection.

4.3 Percentage of solids in paddy soil samples

The percentage of solids for paddy soil samples collected from Block A to Block X was ranged from 8.43 to 67.04 %. Details information of the percentage of solids for each Block can be found in **Appendix 4**.

4.4 Pesticides Concentration in Soil Samples

Twenty four paddy block from Block A-X were included in the sampling points that represent each block in Kampung Sawah Sempadan. The concentration of three compounds of pesticides which are chlorantraniliprole, difenoconazole and pymetrozine were determined. The summarized results for the concentration of the selected compounds in soil samples were listed in **Table 4.4**.

Table 4.4: Pesticides concentrations in paddy soil ($\mu\text{g kg}^{-1}$) (n=3).

Block	Chlorantraniliprole	Difenoconazole	Pymetrozine
	Mean \pm SD	Mean \pm SD	Mean \pm SD
A	0.207 \pm 0.045	0.959 \pm 0.146	5.778 \pm 0.032
B	0.412 \pm 0.104	1.526 \pm 0.034	0.125 \pm 0.010
C	0.373 \pm 0.082	2.684 \pm 0.400	0.091 \pm 0.022
D	0.134 \pm 0.012	0.246 \pm 0.056	0.064 \pm 0.012
E	0.586 \pm 0.069	6.087 \pm 0.421	0.168 \pm 0.064
F	0.492 \pm 0.066	7.737 \pm 0.403	0.292 \pm 0.048
G	0.328 \pm 0.072	0.193 \pm 0.041	0.538 \pm 0.047
H	0.188 \pm 0.019	N/D	0.108 \pm 0.040
I	0.643 \pm 0.002	0.494 \pm 0.099	0.207 \pm 0.036
J	1.909 \pm 0.011	2.190 \pm 0.080	0.551 \pm 0.005
K	N/D	0.182 \pm 0.005	N/D
L	1.168 \pm 0.072	12.028 \pm 1.011	0.996 \pm 0.191
M	0.444 \pm 0.120	1.223 \pm 0.099	0.214 \pm 0.052

Table 4.4 continue...

Block	Chlorantraniliprole	Difenoconazole	Pymetrozine
	Mean \pm SD	Mean \pm SD	Mean \pm SD
N	0.473 \pm 0.017	1.638 \pm 0.069	0.228 \pm 0.011
O	0.301 \pm 0.098	0.851 \pm 0.062	0.321 \pm 0.074
P	1.016 \pm 0.023	9.796 \pm 0.676	0.946 \pm 0.015
Q	N/D	N/D	N/D
R	0.180 \pm 0.004	N/D	0.014 \pm 0.007
S	0.273 \pm 0.047	N/D	0.028 \pm 0.019
T	0.474 \pm 0.115	15.108 \pm 2.050	3.214 \pm 0.585
U	N/D	N/D	N/D
V	0.644 \pm 0.060	0.655 \pm 0.044	0.533 \pm 0.215
W	0.112 \pm 0.010	N/D	0.155 \pm 0.002
X	1.076 \pm 0.049	2.831 \pm 0.113	0.651 \pm 0.095

N/D: Not Detected

The average concentration of chlorantraniliprole in the paddy soil was 0.544 $\mu\text{g kg}^{-1}$. Sample W showed the minimum concentration of chlorantraniliprole at 0.112 $\mu\text{g kg}^{-1}$ while sample J showed the maximum concentration at 1.909 $\mu\text{g kg}^{-1}$. The mean concentration of difenoconazole was 3.690 $\mu\text{g kg}^{-1}$. Sample G recorded the minimum concentration of difenoconazole at 0.193 $\mu\text{g kg}^{-1}$ while sample T recorded the maximum concentration at 15.108 $\mu\text{g kg}^{-1}$. On the other hand, the mean concentration of pymetrozine was 0.725 $\mu\text{g kg}^{-1}$. The minimum concentration of pymetrozine was 0.014 $\mu\text{g kg}^{-1}$ from sample R, and the maximum concentration was 5.778 $\mu\text{g kg}^{-1}$ from sample A.

Among these three compounds, the highest mean concentration was difenoconazole ($3.690 \mu\text{g kg}^{-1}$), followed by pymetrozine ($0.725 \mu\text{g kg}^{-1}$), and chlorantraniliprole ($0.544 \mu\text{g kg}^{-1}$).

The average concentration of the pesticides residue in this study was lower compared to other studies. Zhang et al., (2012), reported the concentrations of chlorantraniliprole in paddy soil were 12.0, 29.0, 22.0, 17.0, 13.0, 10.0 and $6.0 \mu\text{g kg}^{-1}$ after 2 hours, 8 hours, 1 day, 3 days, 7 days, 14 days and 28 days of pesticides application, respectively. While, Malhat, Abdallah, & Hegazy (2012), also reported that the concentration of chlorantraniliprole in soil were 3193, 2215, 1710, 986, 593, and $165 \mu\text{g kg}^{-1}$ after 1, 3, 7, 10, 12, and 15 days of pesticides application, respectively.

A study by He et al. (2016) indicated that the concentrations of difenoconazole in the soil samples in Beijing, Shandong and Anhoi were ranged from $0.2 - 298.0 \mu\text{g kg}^{-1}$ after spraying. The results in He et al. (2016) were higher when compared to this study.

Li et al. (2011) also reported that the concentrations of pymetrozine in paddy soils were 19.0, 51.0, 44.0, 26.0, 15.0, 6.0 and $2.0 \mu\text{g/kg}$ after 2 hours, 1, 3, 7, 14, 21 and 28 days of pesticides application, respectively. According to Li et al. (2011), from 2 hours to 1 day, a sharp increase of pymetrozine residues occurred. After 21 days of application, the initial deposit of pymetrozine in paddy soil were declined from $163.0 \mu\text{g kg}^{-1}$ to $10.0 \mu\text{g kg}^{-1}$ in Anhui, $163.0 \mu\text{g kg}^{-1}$ to $9.0 \mu\text{g kg}^{-1}$ in Beijing,

and 242.0 $\mu\text{g kg}^{-1}$ to 13.0 $\mu\text{g/kg}$ in Zhejiang (Y. Zhang, Zhang, Xu, Li, & Wang, 2015).

During the sampling period, most of the block just completed the process of paddy planting. But, there were a few blocks had not started the process of paddy planting. Thus, the concentration of fungicide such as difenoconazole was higher compared to others compounds because the usage of fungicides was essential in this season. According to Azmi, Karim, & Ismail (2005), fungicide needs to apply to the paddy field between 7 to 14 days after the planting process completed to kill weeds.

Whereas, the concentrations of pymetrozine and chlorantraniliprole were lower than difenoconazole because the insecticide used during the season was low. Based on the interview, the farmers mentioned that the application of the insecticide was during the middle phase of the paddy cultivation. According to Ali et al. (2017), an insecticide was applied in a rice field at every 15 days interval after the process of planting completed. As reported in **Table 4.4**, all pesticides were not detected in Block Q and U because these blocks did not start the cultivation process yet.

4.4 Health Risk Assessment among Farmers

According to Alam et al. (2015), pesticides residue can cause both short term and the long term toxic effect that hazardous to health, and can lead to toxicity if applied at a high concentration. Long-term accumulation of pesticide residues in the human body is a severe problem when pesticides commonly used around the world

(Hossain, Rahman, Islam, & Adyel, 2013). Thus, it is important to assess the health risk of the farmers who are exposed to pesticides.

Three different situations were considered to estimate the health risk of farmers. The first situation was that the farmers wore gloves but did not wear boots, hence exposing the feet to the paddy soil and water. Second situation was that the farmers wore boots but did not wear gloves and thus exposing the hands. Meanwhile, the third situation was the farmers did not wear both gloves and boots and consequently exposing their hands and feet in soil and water.

The risk was categorized into non-carcinogenic and carcinogenic risk by calculating HQ and LCR for each pesticides. The HQ and LCR for each compound were listed in **Table 4.5**.

Table 4.5: Hazard Quotient (HQ), Hazard Index (HI) and Lifetime Cancer Risk (LCR) of farmers

Compound	Hand Exposure	Feet Exposure	Hand and Feet Exposure
HQ			
Chlorantraniliprole	8.30×10^{-12}	9.28×10^{-12}	3.55×10^{-11}
Difenoconazole	6.67×10^{-7}	7.46×10^{-7}	2.85×10^{-6}
Pymetrozine	2.18×10^{-10}	2.44×10^{-10}	9.33×10^{-10}
HI			
	6.67×10^{-7}	7.46×10^{-7}	2.85×10^{-6}
LCR			
Pymetrozine	2.08×10^{-14}	2.33×10^{-14}	8.89×10^{-14}

The farmers in Kampung Sawah Sempadan exposed to the paddy soil for average 2 hours per day depending on the weather, peak season and the area of the paddy field they worked on. The average event frequency of the farmers involved in paddy cultivation activities was once in a day. Most of them started to work in the paddy field early in the morning, however, it also depending on the weather.

The average exposure duration of the farmers in Kampung Sawah Sempadan was 27 years. The durations of the farmers involved in paddy cultivation were different due to the age of the respondents was ranged from 19 to 76 years old. The exposure duration was depending on the age of the individual that started working in the paddy field. Majority of the respondents were full-time farmers while some of them worked part-time and only involved in paddy cultivation activities full-time at

the late age. The full term of paddy cultivation was 110 days per season with two seasons per year which make up the exposure frequency of 220 days year⁻¹.

The average body weight of the respondents was 70.68 kg and almost similar to the recommended body weight by USEPA which are 70 kg. Value of 50th percentile body surface area was used to estimate the dermal exposure to the soil (USEPA, 1989). The skin surface areas were considered based on the area that the farmers were exposed while handling the paddy soil. This is due to more than half of the farmers did not wear an appropriate PPE such as boots and gloves while working in the paddy field.

Among the three target compounds, difenoconazole was reported to have the highest HQ with 2.85×10^{-6} for both exposure to hands and feet. Meanwhile, the lowest HQ among the three compounds was chlorantraniliprole with 8.30×10^{-12} , for the exposure to hands.

The HQ calculated for hands exposure, feet exposure and for both hands and feet exposure was less than 1 for each selected compound. Thus, there were no significant health risks due to dermal exposure to pesticides. The HQ value for exposure to hands, feet, and both hands and feet for chlorantraniliprole, difenoconazole and pymetrozine were 8.30×10^{-12} , 9.28×10^{-12} , 3.55×10^{-11} ; 6.67×10^{-7} , 7.46×10^{-7} , 2.85×10^{-6} ; and 2.18×10^{-10} , 2.08×10^{-10} , 9.33×10^{-10} , respectively. Even though the average exposure duration were as long as 27 years, the risk was not significant as the concentration of selected compound in the paddy was in low concentration in the current season.

HI values of this study were below 1, indicating low risk to pesticides related disease. The cumulative risk of exposure to mixtures of pesticides was considered as acceptable when HI values were less than 1.

Among the three target compounds, only pymetrozine was assessed for the cancer health risk due to the unavailability of cancer slope factor for the other two compounds., The LCR calculated were in the range of 2.08×10^{-14} to 8.89×10^{-14} . Thus, it showed that the carcinogenic risk was in the clearly acceptable risk level, which was $<10^{-6}$, and it did not pose significant life cancer risk to the farmers.

A study from Farina, Abdullah, Bibi, & Wan Mohd Khalik (2016), reported that there was no significant non-carcinogenic and carcinogenic health risk due to exposure of pesticides in soil. The HQ due to the exposure of pesticides residue in agricultural soils in Cameron Highlands, Malaysia was found to be less than one, indicating no significant health risk for humans.

To the best of our knowledge, no study has been published on the health risk of these target compounds in soil. Therefore, the risk of the exposure to these target compounds was not compared with other study.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This study showed that the selected pesticides in the paddy soils at Kampung Sawah Sempadan present in low concentration. For all blocks, the concentrations of chlorantraniliprole, difenoconazole and pymetrozine in the paddy soil were ranged from 0.112 $\mu\text{g kg}^{-1}$ to 1.909 $\mu\text{g kg}^{-1}$, 0.193 $\mu\text{g kg}^{-1}$ to 15.108 $\mu\text{g kg}^{-1}$, and 0.014 $\mu\text{g kg}^{-1}$ to 5.778 $\mu\text{g kg}^{-1}$, respectively. Among the three target compounds, the concentration of difenoconazole was the highest, followed by pymetrozine and chlorantraniliprole.

The HQ calculated for all selected compounds were below 1, indicating the risk of non-carcinogenic dermal exposure to pesticides in paddy soil among farmers was not significant. The results also showed that there was no significant carcinogenic health risk for pymetrozine exposure as the LCR obtained was between 2.08×10^{-14} to 8.89×10^{-14} .

There are several limitations of this study that should be considered to improve on further research. The dosage of the pesticides applied in the paddy field at certain season need to be considered as the quantity of the pesticides applied to the field can be the major factor that contributes to cause health effect. Further study on another ten compounds that have been listed in **Table 3.1** is needed because the farmers usually applied different types of pesticides depending on the season.

Another limitation of this study was the physico-chemical parameters such as pH, total organic carbon (TOC), total nitrogen (TN), total potassium (TK), total phosphorus (TP), C/N ratio, cation exchange capacity (CEC) and soil texture was not conducted after sampling.

Next, the health risk assessment of the farmers was only quantified by dermal exposure of pesticides. Another possible exposure pathway for pesticides in paddy soil is oral exposure. As most of the farmer worked in paddy field using bare hands, the farmers may accidentally ingest the pesticides if they are not taking care of good personal hygiene. However, this route of exposure was not assessed in this study as the likelihood of the accidental ingestion of the soil was low compared to the dermal exposure in this case. However, if the oral exposure happens, the concern could be higher than the dermal exposure. Thus, the consideration of this pathway in the further study is recommended.

Other than that, training on the proper usage of PPE and the health promotion on the effect of the pesticides should be provided to the farmers to reduce the risk of exposure to pesticides and create the awareness among the farmers.

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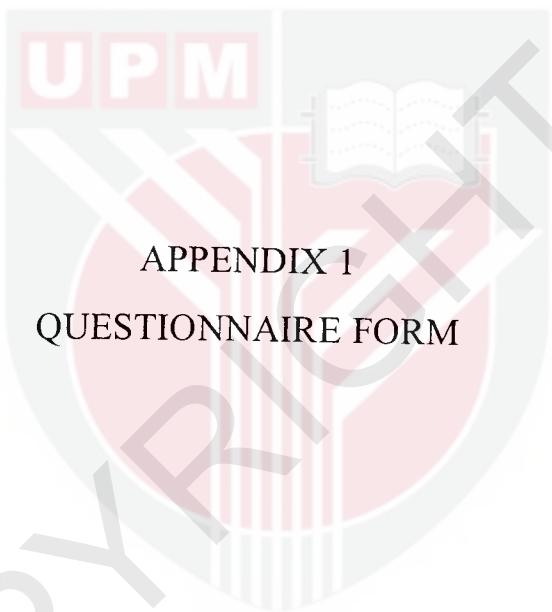
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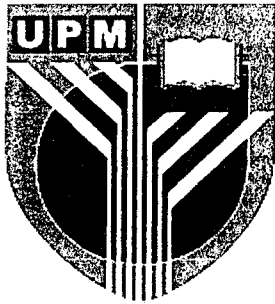
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APPENDIX 1
QUESTIONNAIRE FORM

UPM



JABATAN KESIHATAN PEKERJAAN & PERSEKITARAN

FAKULTI PERUBATAN DAN SAINS KESIHATAN

UNIVERSITI PUTRA MALAYSIA

**PENDEDAHAN KEPADA RACUN PEROSAK DALAM KALANGAN
PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG.**

ARAHAN SOALAN:

1. Borang soal selidik ini mengandungi **Empat (4)** bahagian iaitu:

Bahagian A : Maklumat Diri

Bahagian B : Pendedahan kepada Racun Perosak

Bahagian C : Penggunaan Kelengkapan Pelindung Diri

Bahagian D : Maklumat Kesihatan

2. Anda diminta menjawab semua soalan yang ada dalam buku soalan ini

3. Buku soalan ini hendaklah dikembalikan kepada pengkaji setelah selesai menjawab

PENDEDAHAN KEPADA RACUN PEROSAK DALAM KALANGAN
PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

BAHAGIAN A: MAKLUMAT DIRI

1. Umur: Tahun

2. Jantina:

<input type="checkbox"/>	Lelaki
<input type="checkbox"/>	Perempuan

3. Bangsa:

<input type="checkbox"/>	Melayu
<input type="checkbox"/>	Cina
<input type="checkbox"/>	India
<input type="checkbox"/>	Lain-lain (sila nyatakan):

4. Berat: kg

5. Tinggi: m

6. Jisim berat badan: kg/m²

7. Adakah anda merokok?

<input type="checkbox"/>	Ya
<input type="checkbox"/>	Tidak

PENDEDAHAN KEPADA RACUN PEROSAK DALAM KALANGAN
PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

BAHAGIAN B: PENDEDAHAN KEPADA RACUN PEROSAK

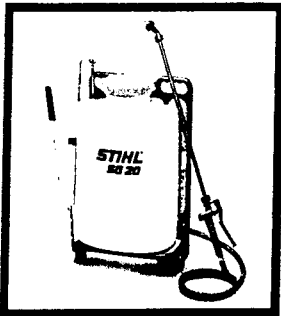
8. Pekerjaan sekarang:
9. Tempoh bekerja di tempat sekarang: bulan/ tahun
10. Pekerjaan terdahulu:
11. Tempoh bekerja di tempat dahulu: bulan/ tahun
12. Adakah anda mandi selepas ke tempat kerja?
- | | |
|--------------------------|-------|
| <input type="checkbox"/> | Ya |
| <input type="checkbox"/> | Tidak |
13. Adakah anda menukar pakaian kerja setiap hari?
- | | |
|--------------------------|-------|
| <input type="checkbox"/> | Ya |
| <input type="checkbox"/> | Tidak |

14. Adakah anda menggunakan racun perosak pada tanaman anda?

Ya

Tidak

15. Jenis alat penyembur racun perosak yang digunakan:



Alat penyembur manual

Alat penyembur bertekanan

Alat penyembur bermotor

16. Nyatakan kekerapan anda menggunakan racun perosak:

..... kali/ hari

atau

..... kali/ minggu

atau

..... kali/bulan

atau

..... kali/ tahun

BAHAGIAN C: PENGGUNAAN KELENGKAPAN PELINDUNG DIRI

17. Adakah anda menggunakan kelengkapan pelindung diri semasa bekerja?

<input type="checkbox"/>	Ya
<input type="checkbox"/>	Tidak

18. Jika “Ya”, apakah jenis kelengkapan pelindung diri yang digunakan semasa bekerja?

a. But	
b. Apron	
c. Baju kalis air	
d. Alat penafasan	
e. Sarung tangan	
f. Cermin mata	
g. Topeng	
h. Penutup kepala	

19. Jika “Ya”, berapa kerapkah anda memakai kelengkapan pelindung diri?

a. Sentiasa (setiap kali turun ke sawah)	
b. Hampir sentiasa (2-4 kali seminggu)	
c. Jarang (sekali seminggu)	
d. Sangat jarang (kurang daripada 4 kali sebulan)	

20. Kekerapan anda menukar kelengkapan pelindung diri:

a. Setiap hari	
b. Seminggu sekali	
c. Dua minggu sekali	
d. Sebulan sekali	
e. Lain-lain (sila nyatakan)	

BAHAGIAN D: MAKLUMAT KESIHATAN

21. Adakah anda mempunyai masalah kulit?

<input type="checkbox"/>	Ya
<input type="checkbox"/>	Tidak

22. Adakah keluarga anda mempunyai sejarah penyakit kulit? Jika "Ya", nyatakan ahli keluarga yang mempunyai masalah kulit tersebut.

<input type="checkbox"/>	Ya
<input type="checkbox"/>	Tidak	

SULIT

PENDEDAHAN KEPADA RACUN PEROSAK DALAM KALANGAN PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

KEGUNAAN PENYELIDIK

23. Adakah anda mempunyai alahan kulit?

<input type="checkbox"/>	Ya
<input type="checkbox"/>	Tidak

24. Nyatakan gejala – gejala masalah kulit anda:

a. Gatal	
b. Ruam	
c. Kulit merah	
d. Gelembung kulit	
e. Kulit kering	
f. Kulit merekah	
g. Sakit	
h. Kulit membengkak	

25. Adakah anda menerima rawatan untuk masalah kulit anda? Jika "Ya", nyatakan.

<input type="checkbox"/>	Ya sila nyatakan:
<input type="checkbox"/>	Tidak

26. Bagaimanakah keadaan masalah kulit anda di waktu tidak bekerja?

a. Seperti biasa	
b. Semakin pulih	
c. Semakin teruk	

SULIT

PENDEDAHAN KEPADA RACUN PEROSAK DALAM KALANGAN PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

KEGUNAAN PENYELIDIK

27. Bilakah kali terakhir anda menghidapi penyakit kulit?

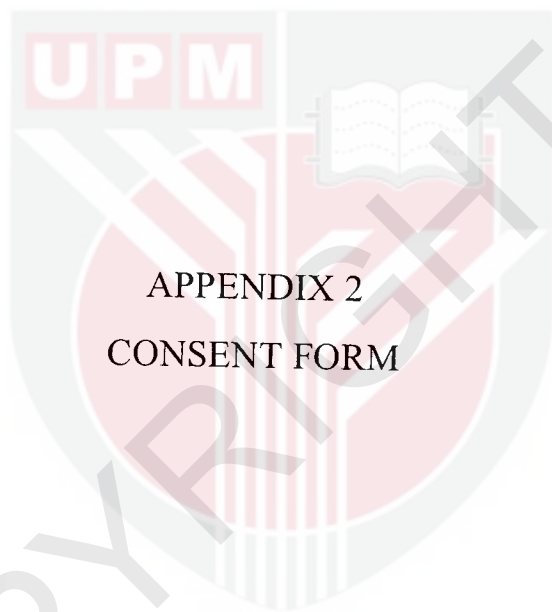
a. sekarang	
b. dalam tempoh 3 bulan yang lalu	
c. 4 – 12 bulan yang lalu	
d. lebih daripada 12 bulan yang lalu	

28. Adakah anda mempunyai masalah kesihatan lain seperti berikut:

SIMPTOM	Ya, setiap hari	Ya, selalu (3-4 kali/minggu)	Ya, Kadang-kala (1-2 kali/minggu)	Tidak
Keletihan				
Peluh Berlembihan				
Degupan Jantung Laju				
Sakit Kepala				
Lemah Otot				
Loya				
Hilang selera makan				
Cirit- birit				
Lain-lain (sila nyatakan)				

~Tamat-soal-selidik-

SULIT



APPENDIX 2
CONSENT FORM

UPM

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BORANG B1: PENERANGAN DAN PERSETUJUAN RESPONDEN

Sila baca maklumat berikut dengan teliti. Sekiranya anda mempunyai sebarang pertanyaan, sila kemukakan kepada penyelidik.

1. TAJUK KAJIAN

Kesan pendedahan kepada tanah yang dicemari dengan racun perosak kepada kesihatan di kalangan pesawah padi di kawasan sawah padi Tanjung Karang, Kuala Selangor, Selangor.

2. PENGENALAN

Pada masa kini, jumlah populasi di dunia meningkat dari samasa ke semasa dan anggaran penduduk pada tahun 2050 akan mencecah 9.1 bilion. Oleh kerana bilangan populasi kian meningkat, permintaan makanan turut meningkat. Dalam usah Malangnya, racun perosak boleh memberi kesan kepada alam sekitar dan kesihatan penduduk sekiranya kuantiti dos racun perosak yang digunakan berlebihan daripada yang dihadkan. Kawasan kajian yang menjadi pilihan di dalam kajian ini ialah kawasan sawah padi Kampung Sawah Sempadan, Tanjung Karang, Kuala Selangor. Penanaman padi di kawasan kajian ini telah menjadi identiti penduduk setempat kerana penduduk di kawasan ini kebanyakan merupakan petani yang mengusahakan tanaman padi di sekitar kawasan Kampung Sawah Sempadan. Kawasan ini telah di pilih untuk menjadi kawasan kajian kerana pemerhatian bahawa hampir semua petani yang mengusahakan tanaman padi di kawasan ini tidak menggunakan kelengkapan pelindung diri semasa menjalankan aktiviti di sawah padi. Penilaian risiko kesihatan merupakan satu proses dimana penyelidik akan menganggar kebarangkalian terjadinya penyakit berbahaya jika terdedah kepada bahan kimia di persekitaran yang tercemar. Pesawah merupakan golongan yang paling terdedah kepada racun perosak melalui aktiviti membancuh, menyembur dan sebagainya menyebabkan mereka lebih cenderung kepada pendedahan ini daripada penduduk sekitar. Terdapat kajian yang dijalankan sebelum ini membuktikan pendedahan kepada beberapa jenis racun perosak boleh mengakibatkan penyakit kulit yang kronik. Oleh itu, kajian ini dilakukan untuk mengkaji kesan pendedahan kepada tanah yang dicemari dengan racun perosak kepada kesihatan di kalangan pesawah padi di kawasan sawah padi Tanjung Karang, Kuala Selangor, Selangor.

3. APAKAH YANG PERLU ANDA LAKUKAN?

Responden dikehendaki untuk menjawab semua soalan yang terdapat di dalam borang kaji selidik yang dibekalkan oleh penyelidik. Selain itu, berat badan responden juga akan di ambil oleh penyelidik.

4. SIAPA YANG TIDAK BOLEH MENYERTA KAJIAN INI?

Penduduk Kampung Sawah Sempadan yang tidak terlibat dalam aktiviti pertanian padi dan pesawah yang tidak menggunakan racun perosak dalam tanaman. Selain itu, kanak-kanak yang di bawah umur 18 tahun juga tidak dibenarkan terlibat dalam kajian ini. Kajian ini melibatkan pesawah yang berumur diantara 18 tahun sehingga 60 tahun.

5. APAKAH FAEDAH MENYERTA KAJIAN INI?

a) KEPADA ANDA SEBAGAI PESERTA?

Kajian ini akan menilai jika terdapatnya risiko kesihatan kulit atau tidak apabila anda terdedah kepada racun perosak. Selepas selesai kajian, anda akan diberitahu sekiranya penggunaan bahan racun perosak berisiko atau tidak berisiko untuk mendapat penyakit kanser atau bukan kanser.

b) KEPADA PENYELIDIK?

Penyelidik akan dapat mengumpul maklumat mengenai kehadiran racun perosak dalam tanah di kawasan sawah padi Kampung Sawah Sempadan dan seterusnya mengkaji kesan kehadiran racun perosak dalam tanah ini kepada kesihatan pesawah padi yang terdedah kepada tanah yang dicemari dengan racun perosak ini.

6. ADAKAH IA BERISIKO?

Tidak, responden hanya perlu mengisi borang kaji selidik yang dibekalkan oleh penyelidik dan juga memberi kerjasama untuk membenarkan penyelidik mengambil berat badan responden.

7. ADAKAH MAKLUMAT DAN IDENTITI SAYA KEKAL RAHSIA?

Ya, segala maklumat dan identiti responden adalah sulit dan akan kekal rahsia dan hanya akan digunakan untuk tujuan kajian sahaja.

8. SIAPA YANG SAYA PERLU HUBUNGI SEKIRANYA SAYA MEMPUNYAI SOALAN TAMBAHAN SEMASA MENGIKUTI PENYELIDIKAN INI?

Responden boleh menghubungi penyelidik kajian ini :

0179417918
AMINATUN SOFIA BINTI SALLEHUDDIN
JABATAN KESIHATAN PERSEKITARAN DAN PEKERJAAN,
FAKULTI PERUBATAN DAN SAINS KESIHATAN,
UNIVERSITI PUTRA MALAYSIA,
43400 UPM SERDANG,
SELANGOR, MALAYSIA.

0126140221/0389472396
HO YU BIN, Ph.D
JABATAN KESIHATAN PERSEKITARAN DAN PEKERJAAN,
FAKULTI PERUBATAN DAN SAINS KESIHATAN,
UNIVERSITI PUTRA MALAYSIA,
43400 UPM SERDANG,
SELANGOR, MALAYSIA.

Sila tandatangan di sini sekiranya anda telah membaca dan memahami kandungan halaman ini _____

9. PERSETUJUAN

Saya..... No Kad Pengenalan.
beralamat.....
.....dengan ini bersetuju untuk mengambil bahagian secara sukarela dalam penyelidikan yang tersebut di atas *(kajian klinikal/percubaan ubat-ubatan/rakaman video/kumpulan sasaran/temuduga/ soal selidik).

Saya telah diberi penjelasan secara menyeluruh mengenai penyelidikan ini dari segi metodologi, risiko dan komplikasi (seperti tertulis pada Helaian Penerangan Responden). Saya memahami bahawa saya berhak menarik diri dari penyelidikan ini pada bila-bila masa tanpa memberi sebarang alasan. Saya juga memahami bahawa sebarang maklumat yang berkaitan identiti saya akan dirahsiakan.

Saya* berminat / tidak berminat untuk mengetahui keputusan kajian yang melibatkan saya.

I setuju/tidak bersetuju untuk imei/gambar/rakaman video/ rakaman suara digunakan dalam apa jua bentuk penerbitan atau pembentangan. (sekiranya berkaitan).

*potong yang tidak berkenaan

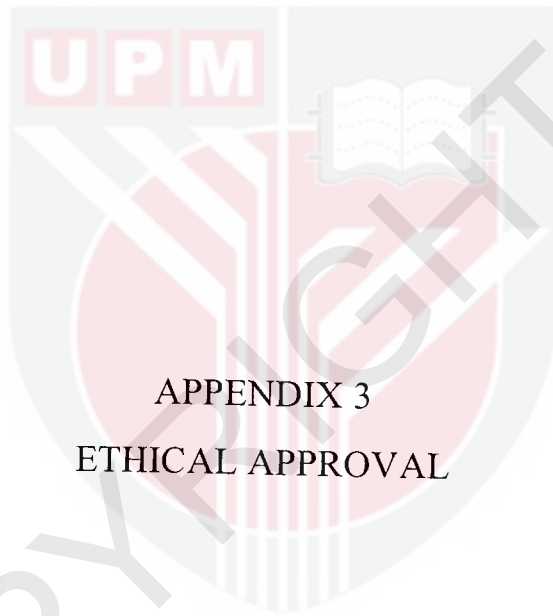
Tandatangan Tandatangan
(Responden) (Saksi)

Tarikh : Nama :

No. K/P:

Saya mengesahkan bahawa saya telah menerangkan kepada responden ini sifat dan tujuan penyelidikan yang tersebut di atas.

Tarikh Tandatangan
(Penyelidik)



APPENDIX 3
ETHICAL APPROVAL

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**ETHICS COMMITTEE FOR RESEARCH INVOLVING HUMAN SUBJECTS
(JKEUPM)
UNIVERSITI PUTRA MALAYSIA**

Research title	: Pesticides Contamination In Paddy Soil And Their Association Health To Paddy Farmers In Tanjung Karang Kuala Selangor
Study Site	: Tanjung Karang Kuala Selangor
JKEUPM Ref No.	: FPSK(EXP16-OSH)U045
Researcher	: Aminatun Sofia Binti Sallehuddin
Supervisor	: Dr. Ho Yu Bin

Documents received and reviewed with reference to the above study:

1. Ethics Application Form, Version 1 dated 18/10/2016
2. Respondent Information Sheet & Consent (Malay) Version 1 dated 18/10/2016
3. Proposal (English), Version 2 dated 23/1/2017
4. Questionnaire (Malay), Version 1 dated 18/10/2016
5. Curriculum Vitae of:
 - a. Dr. Ho Yu Bin
 - b. Dr. Sarva Mangala Praveena

The University Research Ethics Committee, Universiti Putra Malaysia (JKEUPM) operates in accordance to the ICH-GCP Guidelines.

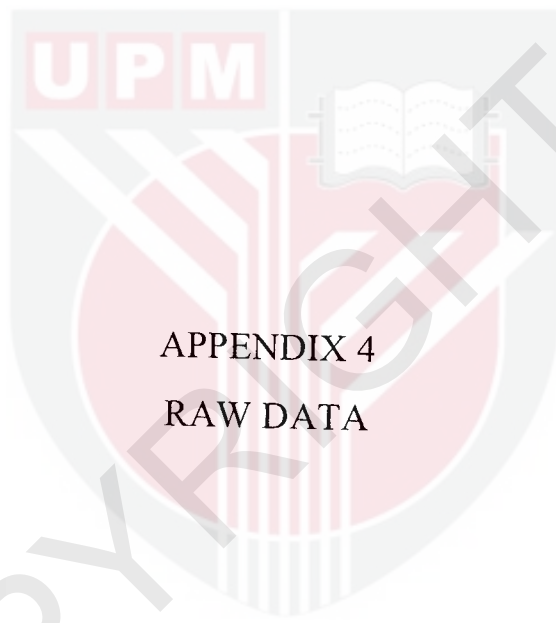
Decision by JKEUPM:

- Approved
- Permission MUST BE OBTAINED from the respective hospitals/ institutions before conducting the research**
- Disapproved

Please note that the approval is valid until 7 February 2018

Researchers should comply with the following:

- I. Complete a Study Final Report upon study completion (Form D).



APPENDIX 4
RAW DATA

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Table 1: Concentration for each replication

Block	Chlorantraniliprole (ng/mL)	Difenoconazole (ng/mL)	Pymetrozine (ng/mL)
A1	2.3904	10.622	57.5537
A2	1.7566	8.5544	58.0034
B1	3.3854	15.0165	1.1746
B2	4.8511	15.4937	1.3186
C1	3.1485	24.0127	1.0715
C2	4.3044	29.6652	0.7549
D1	1.4254	2.8571	0.7273
D2	1.2494	2.0584	0.5605
E1	6.3444	63.8523	2.1341
E2	5.3684	57.8928	1.2346
F1	5.3851	80.2196	3.2613
F2	4.4504	74.5244	2.5883
G1	3.7928	2.2243	5.7126
G2	2.7703	1.6415	5.0501
H1	1.7394	ND	1.3578
H2	2.0151	ND	0.7943
I1	6.4410	4.2462	1.8156
I2	6.4153	5.6432	2.3298
J1	19.0102	21.3262	5.4764
J2	19.1688	22.4645	5.5403
K1	ND	1.7836	ND

Block	Chlorantraniliprole (ng/mL)	Difenoconazole (ng/mL)	Pymetrozine (ng/mL)
K2	ND	1.8482	ND
L1	12.1871	113.1316	8.6059
L2	11.1711	127.4269	11.3137
M1	5.2886	11.5308	2.5092
M2	3.5926	12.9333	1.7725
N1	4.8490	15.8870	2.2024
N2	4.6029	16.8692	2.3584
O1	2.3144	8.9465	3.7356
O2	3.6971	8.0639	2.6876
P1	10.3200	93.1806	9.5610
P2	10.0010	102.7442	9.3556
Q1	ND	ND	ND
Q2	ND	ND	ND
R1	1.8262	ND	0.0898
R2	1.7676	ND	0.1886
S1	2.4008	ND	0.1468
S2	3.0627	ND	0.4147
T1	3.9292	136.5804	36.2775
T2	5.5607	165.5766	28.0100
U1	ND	ND	ND
U2	ND	ND	ND
V1	6.8469	6.2353	6.8514
V2	6.0191	6.8576	3.8162

Block	Chlorantraniliprole (ng/mL)	Difenoconazole (ng/mL)	Pymetrozine (ng/mL)
W1	1.0541	ND	1.5667
W2	1.1930	ND	1.5430
X1	10.4090	27.5117	7.1793
X2	11.1045	29.1038	5.8383

ND: Not Detected



Table 2: Percentage of solid in soil samples

Block	Weight of sample aliquot before drying (g)	Weight of sample aliquot after drying (g)	Percentage solids (%)
A	10	2.797	27.97
B	10	6.698	66.98
C	10	3.328	33.28
D	10	6.704	67.04
E	10	6.292	62.92
F	10	4.18	41.8
G	10	1.313	13.13
H	10	1.045	10.45
I	10	2.533	25.33
J	10	5.101	51.01
K	10	4.576	45.76
L	10	2.631	26.31
M	10	4.508	45.08
N	10	6.162	61.62
O	10	0.843	8.43
P	10	2.758	27.58
Q	10	5.585	55.85
R	10	5.265	52.65
S	10	4.575	45.75
T	10	3.068	30.68

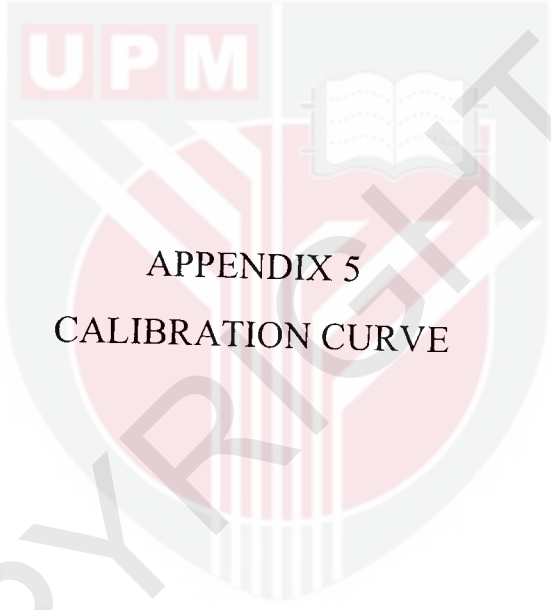
Block	Weight of sample aliquot before drying (g)	Weight of sample aliquot after drying (g)	Percentage solids (%)
U	10	1.317	13.17
V	10	3.862	38.62
W	10	5.086	50.86
X	10	4.613	46.13
Reference Soil	10	9.792	97.92

Table 3: Linear range and R² for each compound

Analyte	Linear range (ng mL ⁻¹)	R ²
Chlorantraniliprole	1.0-500	0.9990
Difenoconazole	1.0-500	0.9988
Pymetrozine	0.1-500	0.9999

Table 4: Recovery (%) and the relative standard deviation (RSD, %) of each compounds in paddy soil (n=3)

Analyte	Recovery	Relative Standard Deviation (RSD)
Chlorantraniliprole	102.194	5.743
Difenoconazole	115.044	7.867
Pymetrozine	42.081	6.178



APPENDIX 5
CALIBRATION CURVE

UPM

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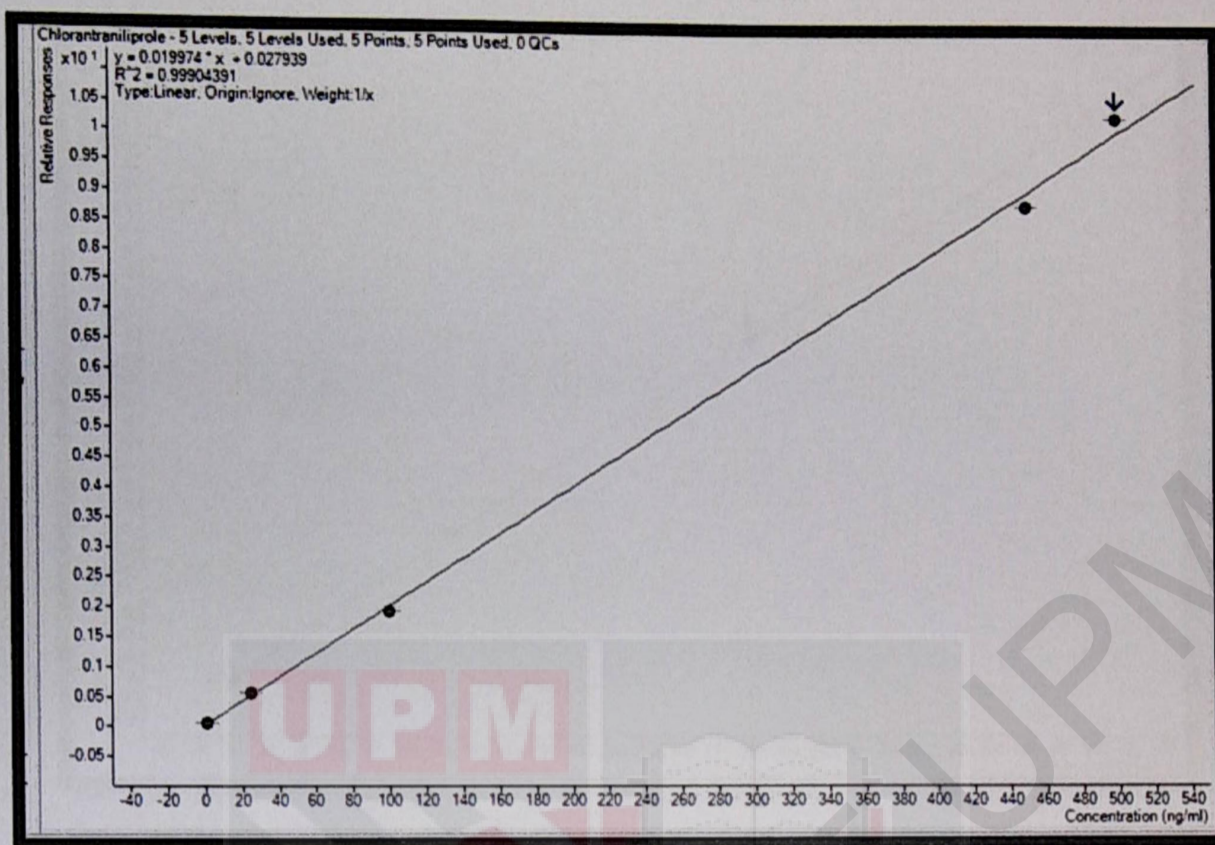


Figure 1: The calibration curve for chlorantraniliprole

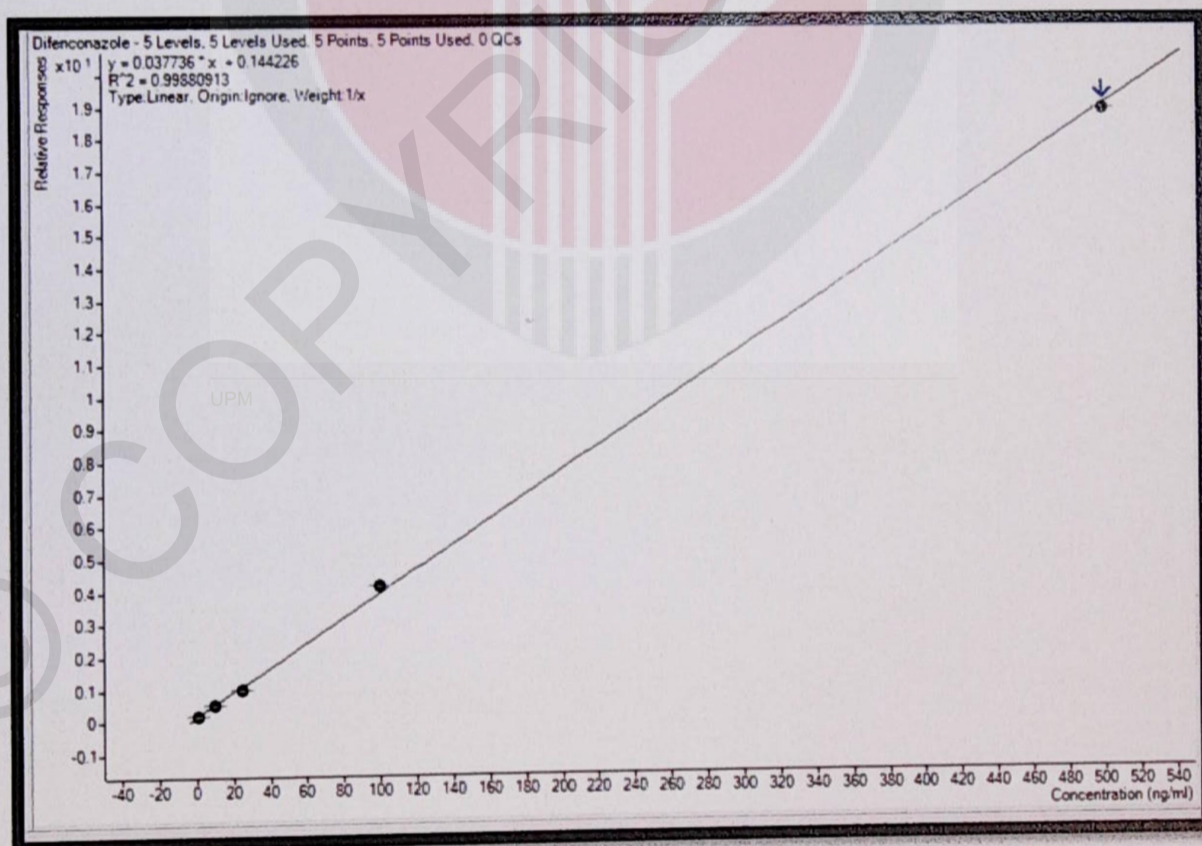


Figure 2: The calibration for difenoconazole

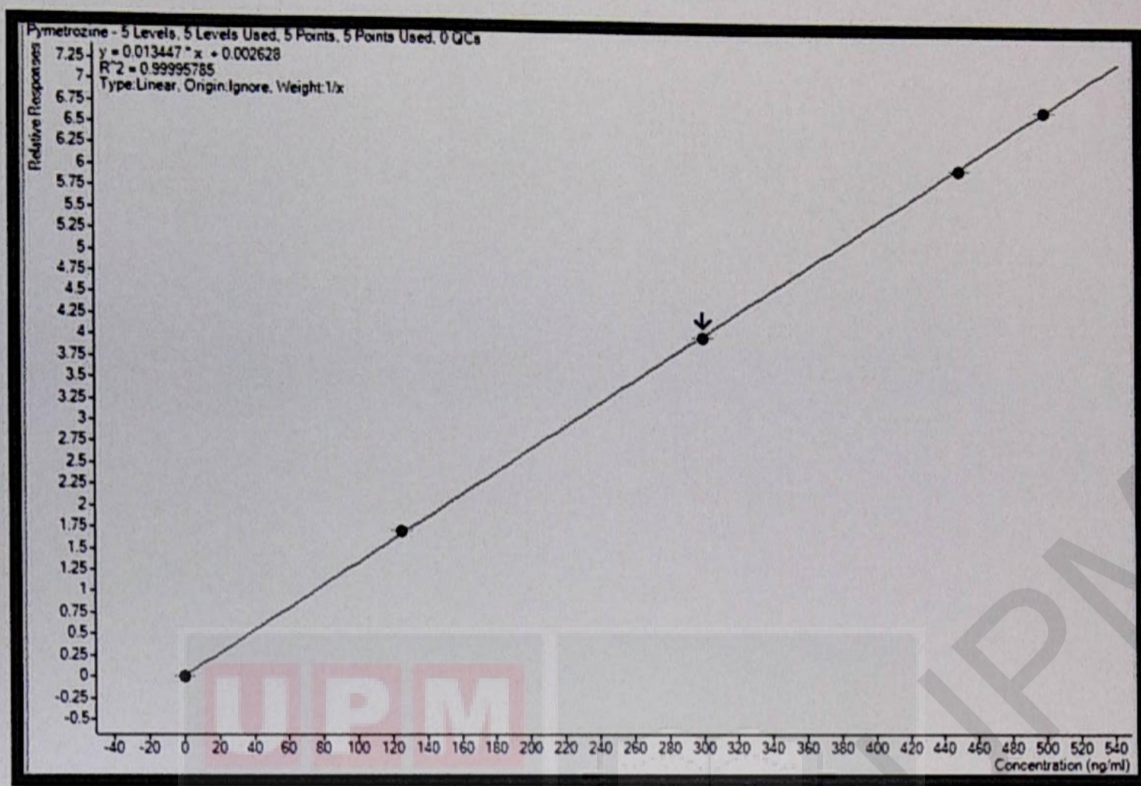


Figure 3: The calibration curve for pymetrozine

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APPENDIX 6
CHROMATOGRAM GRAPH

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Figure 4: Chromatogram for pymetrozine

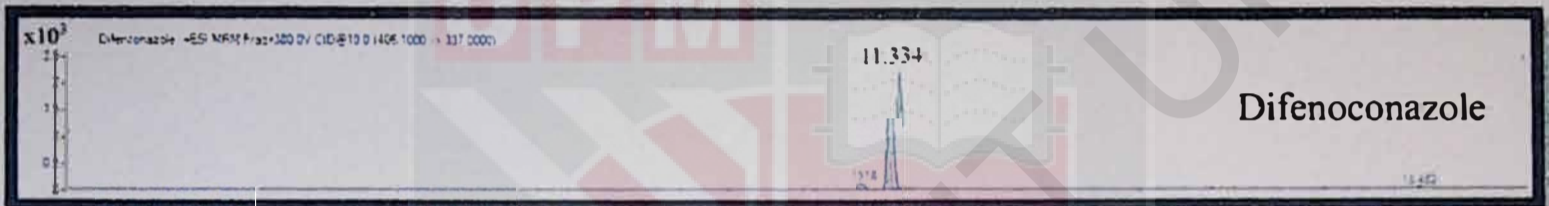
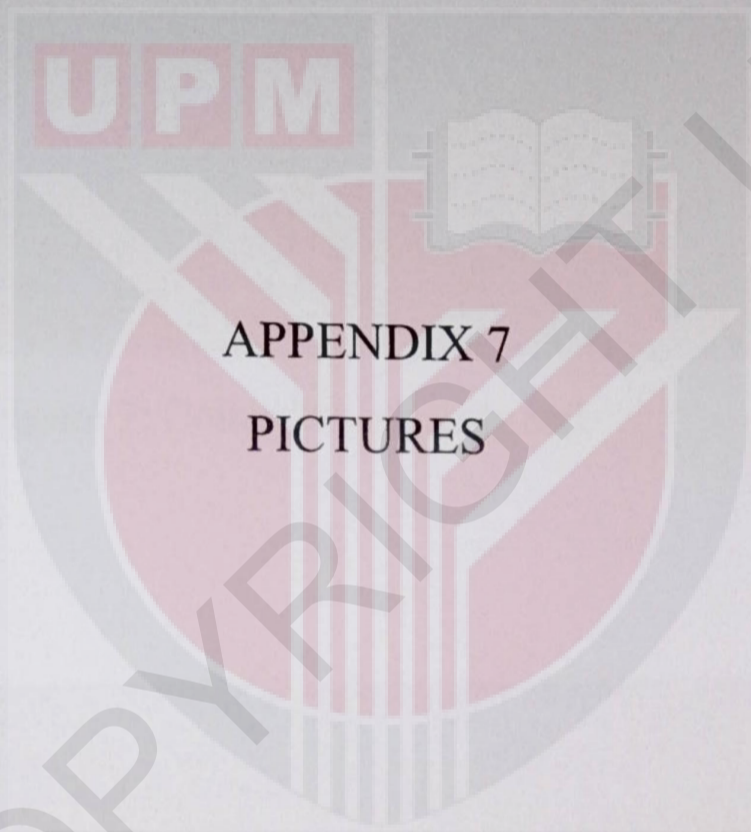


Figure 5: Chromatogram for difenoconazole



Figure 6: Chromatogram for chlorantraniliprole



APPENDIX 7
PICTURES

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Figure 7: Collection of paddy soil

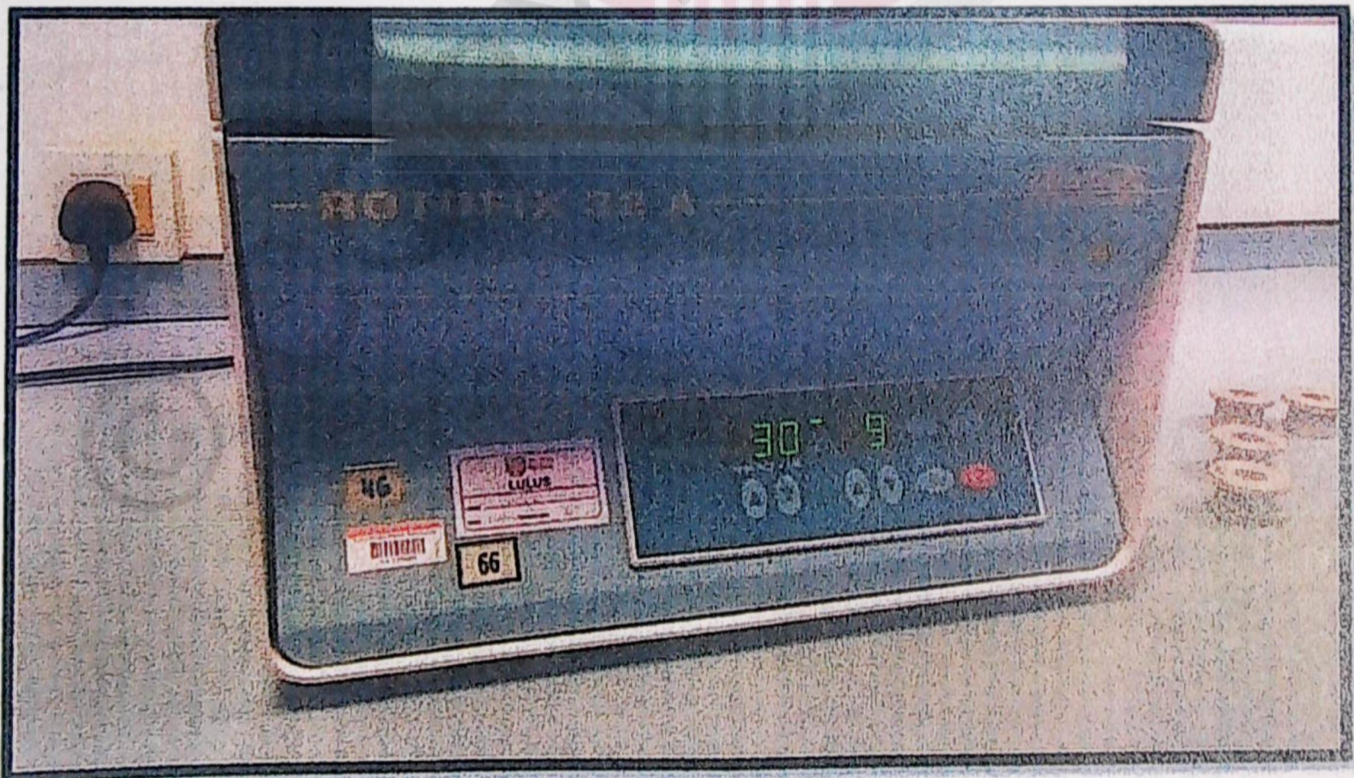


Figure 8: Centrifuged at 3000rpm for 10 minutes

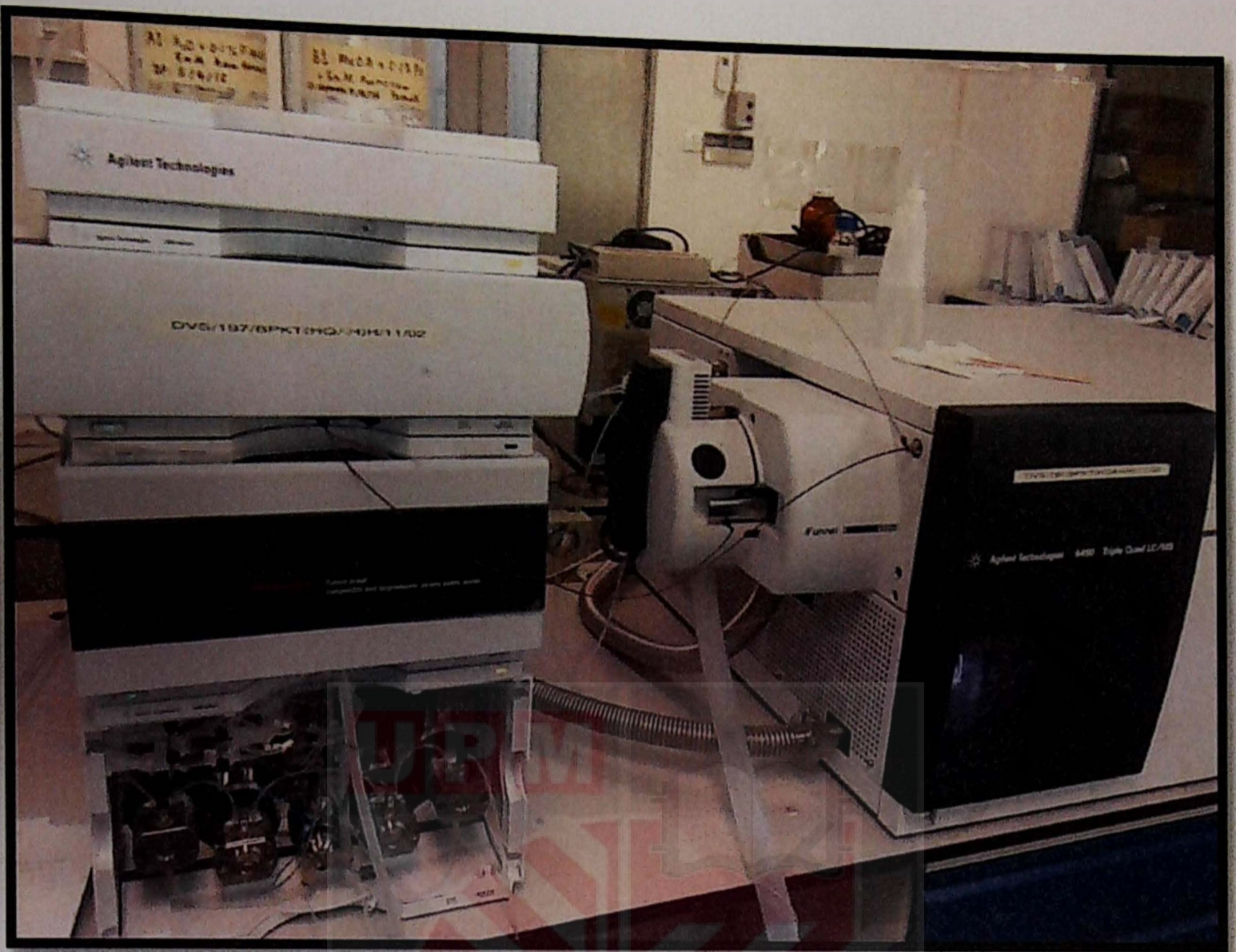


Figure 9: Analysed with UHPLC-MS/MS

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