RISK ASSESSMENT AND OCCUPATIONAL EXPOSURE OF PESTICIDES AMONG PADDY FARMERS IN KAMPUNG PERMATANG KERIANG, PULAU PINANG, MALAYSIA

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by

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LIST OF ABBREVIATIONS

ACN	Acetonitrile
ANOVA	Analysis of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
CHAMACOS	Centre for the Health Assessment of Mother and Children of Salinas
ChE	Cholinesterase
CHRA	Chemical Health Risk Assessment
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DMI	Demethylation Inhibitor
DO	Dissolve Oxygen
DOSH	Department of Occupational Safety and Health
ER	Exposure Rating
ERA	Environmental Risk Assessment
EU	European Union
FR	Frequency Rating
GCMS	Gas Chromatography Mass Spectrometry
GHS	Globally Harmonized System
HR	Hazard Rating
IPM	Integrated Pest Management
IUPAC	International Union of Pure and Applied Chemistry
KAP	Knowledge, Attitude and Practice
MeOH	Methanol
MSDS	Material Safety Data Sheet
MR	Magnitude Rating

NGO	Non-Governmental Organizations
OC	Organochlorine
OP	Organophosphate
PID	Photoionization Detector
PPE	Personal Protective Equipment
SAS	Sahabat Alam Sekitar Malaysia
SPE	Solid Phase Extraction
SPSS	Statistical Package for the Social Sciences
USA	United States of America
USECHH	Use of Standard of Exposure of Chemical Hazardous to Health
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
WPS	Worker Protection Standard

LIST OF SYMBOLS

°C	Degree Celsius
LC	Lethal Concentration
LD	Lethal Dose
km	Kilometer
mg/l	Miligram per litre
mg/kg	Milligram per kilogram
ml	Mililitre
min	Minute
m/s	Meter per second
NTU	Nephelometric Turbidity Units
ppm	Part per million
%	Percentage

PENILAIAN RISIKO DAN PENDEDAHAN PEKERJAAN RACUN MAKHLUK PEROSAK DALAM KALANGAN PESAWAH PADI DI KAMPUNG PERMATANG KERIANG, PULAU PINANG, MALAYSIA

ABSTRAK

Matlamat kajian ini adalah untuk menilai potensi risiko, simptom pendedahan racun makhluk perosak dan kaitannya dengan pengetahuan, sikap dan amalan para petani dengan kadar kepekatan sisa racun makhluk perosak (RMP) di dalam medium air. Kajian keratan rentas ini telah dijalankan di Kampung Permatang Keriang, Seberang Perai Utara, Pulau Pinang, Malaysia. Sejumlah 38 daripada 119 petani telah terlibat dalam sesi kaji selidik ini. Kelulusan etika juga diperolehi daripada Jawatankuasa Etika Penyelidikan Manusia dengan nombor rujukan [Ref: USM/JEPeM/279.3]. Penilaian risiko kesihatan kimia (Chemical Health Risk Assessment, CHRA) telah dijalankan terhadap 16 responden dengan memilih empat jenis racun makhluk perosak yang paling kerap digunakan iaitu *buprofezin*, *chlorpyrifos, difenoconazole* dan *lambda cyhalothrin*. Semasa penilaian risiko kesihatan kimia (CHRA), parameter sampel persekitaran seperti halaju udara, suhu persekitaran, kelembapan, karbon monoksida, karbon dioksida dan tahap debu di samping parameter sampel air seperti oksigen terlarut, pH, suhu air dan kekeruhan telah direkodkan. Kepekatan sisa racun makhluk perosak dalam medium air bagi pra-aplikasi dan pasca-aplikasi racun makhluk perosak telah dianalisis menggunakan GC-MS. Daripada kajian ini didapati bahawa 97% adalah lelaki dan 3% adalah perempuan dengan purata umur 36 hingga 40 tahun. Daripada keputusan pengetahuan, sikap dan amalan didapati bahawa sikap menunjukkan skor tertinggi

iaitu 83.10% dengan purata nilai 41.55 dan sisihan piawai 4.69. Analisis regresi juga telah dijalankan dan didapati bahawa pengetahuan tidak mempengaruhi amalan petani semasa pencampuran dan pengendalian racun makhluk perosak sebaliknya sikap telah menyumbang kepada amalan petani. Daripada keputusan CHRA didapati bahawa kebanyakan responden berada dalam kategori 3 dan 4 bagi kadar bahaya (HR) dan kadar kekerapan (FR). Bagi kadar magnitud (MR) responden berada dalam kategori 3 hingga 5. Kadar risiko telah dikira berdasarkan matriks risiko dan kebanyakan responden berada dalam kategori 3 hingga 5 iaitu sangat terdedah kepada racun makhluk perosak. Selain itu, analisis CHRA terhadap pengetahuan, sikap dan amalan telah menunjukkan bahawa walaupun responden mempunyai skor yang lebih tinggi dalam pengetahuan, sikap dan amalan namun semasa penilaian sebenar dilakukan, responden sangat terdedah kepada racun makhluk perosak disebabkan pengunaan peralatan pelindungan diri yang tidak sempurna. Daripada analisis kepekatan sisa racun makhluk perosak di dalam sampel air, hanya sisa *difenoconazole* dikesan bagi sampel air pra-aplikasi racun makhluk perosak iaitu sebanyak 4.34 ppm dan 6.64 ppm. Bagi analisis pasca-aplikasi, kesemua sisa racun makhluk perosak dikenalpasti. Bagi analisis pasca-aplikasi, kepekatan sisa racun makhluk perosak bagi *difenoconazole* ialah berjulat daripada 36.00 ppm dan 48.86 ppm, *buprofezin* berjulat daripada 6.70 ppm dan 33.96 ppm, *lambda cyhalothrin* berjulat daripada 6.10 ppm dan 31.80 ppm dan *chlorpyrifos* berjulat daripada 7.47 ppm dan 20.29 ppm. Ini menunjukkan kesemua sisa racun makhluk perosak (pra dan pasca-aplikasi) melebihi had piawai US Environmental Protection Agency (US EPA) dan European Union (EU). Selain itu, semua responden amat terdedah kepada bahaya racun makhluk perosak berdasarkan tingginya kadar risiko (RR) yang diperolehi daripada analisis CHRA dan jumlah kepekatan sisa racun makhluk perosak yang tinggi dalam sampel air. Dalam usaha untuk mengurangkan risiko di kalangan responden, beberapa tindakan perlu diambil ke arah amalan pertanian racun makhluk perosak yang baik seperti pengaplikasian langkah-langkah bahaya dan keselamatan, program pemantauan, program kesedaran dan kaedah alternatif.

RISK ASSESSMENT AND OCCUPATIONAL EXPOSURE OF PESTICIDES AMONG PADDY FARMERS IN KAMPUNG PERMATANG KERIANG, PULAU PINANG, MALAYSIA

ABSTRACT

This study aims to assess potential risks, exposure symptoms of pesticides and their relationship with farmers' knowledge, attitude and practices (K.A.P) and pesticide concentration levels in water samples. This cross-sectional study was conducted in Kampung Permatang Keriang, Seberang Perai Utara, Pulau Pinang. A total of thirty-eight farmers out of one hundred nineteen were involved during the questionnaire session. Demographic information, knowledge, attitude and practices of farmers were collected during questionnaire sessions. Ethical approval was obtained from Human Research Ethics Committee USM [Ref: USM/JEPeM/279.3]. Chemical health risk assessments (CHRA) were conducted to sixteen respondents by choosing four different pesticides that frequent used by farmers which were buprofezin, chlorpyrifos, difenoconazole and lambda cyhalothrin. During CHRA, environmental samples in terms of physical air parameters such as air velocity, ambient temperature, relative humidity, carbon monoxide, carbon dioxide and dust level as well as *in-situ* water parameters such as dissolve oxygen, pH, water temperature and turbidity were collected. Concentrations of pesticide residues in pre-application and post-application waters samples were determined using GC-MS. From this study, it was found that, 97% of the respondents were male and 3% were female with average ages between 36 until 40 years old. From the knowledge, attitude and practices results, attitude showed the highest maximum score which is 83.10% with the mean of 41.55 and standard deviation of 4.69. Regression analysis

results showed that farmers' knowledge did not contribute to the practices during mixing and handling pesticides otherwise attitudes was contributed to the practices of farmers. From CHRA results, most of the respondents fall into categories of 3 and 4 for hazard rating (HR) and frequency rating (FR). For magnitude rating (MR), they fall into categories 3 to 5. Risk rating was calculated based on risk matrix and most of the respondents were within categories 3 to 5 which are highly exposed to the pesticides. Furthermore, analysis of CHRA with knowledge, attitude and practices showed that although respondents had high score in knowledge, attitude and practice; however, in real field situation, respondents were still highly exposed to the pesticides because of the improper use of personal protective equipment (PPE). From the analysis of pesticide residue concentration in water sample, only difenoconazole residue was detectable for pre-application with the concentration of 4.34 ppm and 6.64 ppm. For the post-application analysis, all of the pesticide residues were detected. For post application, concentration of pesticide residues for difenoconazole ranged between 36.00 ppm and 48.86 ppm, buprofezin ranged between 6.70 ppm and 33.96 ppm, while lambda cyhalothrin ranged between 6.10 ppm and 31.81 ppm and chlorpyrifos ranged between 7.47 ppm and 20.29 ppm. It showed that, all of the pesticide residues (for pre and post-application) exceeded the US Environmental Protection Agency (US EPA) and European Union (EU) standard limits. Besides, all the respondents were highly exposed to the dangers of pesticides based on the high risk rating (RR) obtained from the CHRA assessment analysis and high amount of pesticides residue concentration in the water samples. In order to minimize the potential risk among respondents, several actions need to be taken towards good agricultural pesticides practices such as the use of hazard and safety measures, monitoring programme, awareness programme and alternative methods.

CHAPTER 1

INTRODUCTION

1.1 Background

Pesticides can be defined as toxic and hazardous chemicals that have been designed to kill a variety of undesirable living organisms or to control population of pests that live in the areas of concern. Since 1950, pesticides have been the most dominant and famous form of pest management worldwide as a function to kill selected pest organisms (Abhilash and Singh, 2009). In 2006, 5.2 billion pounds of pesticides had been estimated to be used around the world and the same amount was obtained in 2007 (U.S.EPA, 2011). Pesticides can be divided into many different types of chemicals, with more than ten thousand pesticide formulations containing more than eight hundred active ingredients (Hernández et al., 2013).

In developing countries, pesticides have been extensively promoted and applied among farmers in agriculture especially for paddy plantations. Pesticides are universally used in agricultural production to increase their economic potential and enhance productivity of production. Apart from that, they can be used to control the quality of production as well as eliminate or reduce yield losses (Damalas and Eleftherohorinos, 2011). Pesticides are usually classified according to their target organisms, for instance insecticide, fungicide, herbicide, rodenticide, mollucicide, nematocide and others (Aktar et al., 2009).

Although pesticides are good agents for crop protection in ensuring various food supplies, however, they still have potentially hazardous effects on the surrounding environment and human health. Besides, excessive use of pesticides are worrisome to the world (Panuwet et al., 2008). Poorly maintained spraying equipment, incorrect spraying application techniques, inappropriate spraying equipment, as well as use of pesticides that are restricted or banned in other countries are several great problems that the farmers in developing countries face (Asogwa and Dongo, 2009). A small amount of pesticides that are not absorbed by the plants will be transferred or moved to the environment through water, air and soil. It can be infiltrated into animal, human blood, milk, meat and plants. Furthermore, they can also be carried thousands of miles away based on their physico-chemical properties (Igbedioh, 1991).

In addition, vast evidence from previous literature have proven that pesticides pose high potential risk to humans and undesirable bad side effects to the environment and other life forms (Lozowicka et al., 2014). Extensive studies have recognized a few accidents resulting from the exposure of environmental hazards and poisoning cases (Schreinemachers, 2012). Various factors influenced the number of accidents. For example, most of the small-scale farmers lack knowledge in pesticide risks regarding essential precautions, incorrect application during use and handling of pesticides (Recena et al., 2006). Besides, pesticides can enter human bodies either directly or indirectly due to several factors, such as continuous pesticide application and spilled, leaked or dispersed pesticides, which may cause danger to the farmers' health.

Likewise, humans can be exposed to pesticides via several pathways, for instance by residing nearby plantation areas, consuming contaminated water and food, as well as occupational exposures. Dermal contact, inhalation and oral consumption are several kinds of pesticide routes during occupational exposure among pesticide applicators. Moreover, totality of pesticides exposure is essential in determining the pesticide risks by considering all the routes and multiple pathways of exposure (EFSA, 2008). Exposure to some of the pesticides which are suspected as endocrine disrupting chemicals (EDCs) may cause harmful effect when entering the body. It is because these pesticides may disturb the body's hormones. For instances, disruption to the reproductive function in humans and wildlife as well as embryonic development are the some of the adverse effects happened from the endocrine disruptors (Wojciech and Joanna, 2004).

Even though there are many difficulties in assessing risks of pesticides use, especially in human health, the authorization for pesticide commercialization is actively collecting data regarding negative effects of the active ingredients on human health (Damalas and Eleftherohorinos, 2011). In order to assess the risks, risk assessment was promoted worldwide since 1940's. Risk assessment was used as a tool to provide information based on the scientific data analysis which describes the magnitude, form and characteristics of a risk that could cause harm to human and environment (Leeuwen and Vermeire, 2007). Health risk assessment process was implemented to determine the exposure level of chemicals based on the developed framework of guidance as well as strategies for collecting and evaluating valuable data (Van Engelen et al., 2007). Although several studies have been conducted in term of risk assessment, they were limited to focusing on effects of pesticides to users'.

Therefore, it is significant to assess the exposure of pesticide risks to determine the impacts and the circumstances at which they can occur by considering the end-users' knowledge, attitude and practices. It is essential and highly necessary to achieve effective pesticide risk minimization programmes towards good agricultural practices. In order to conduct risk minimization programmes, systematic risk assessment with four important steps is required: (i) hazard identification, (ii) hazard characterization, (iii) exposure assessment and (iv) risk characterization (Damalas and Eleftherohorinos, 2011). Hence, the interaction between end-users' knowledge, attitude and practices with risk assessment between human health and the environment towards risk minimization programme can be seen in Figure 1.1.

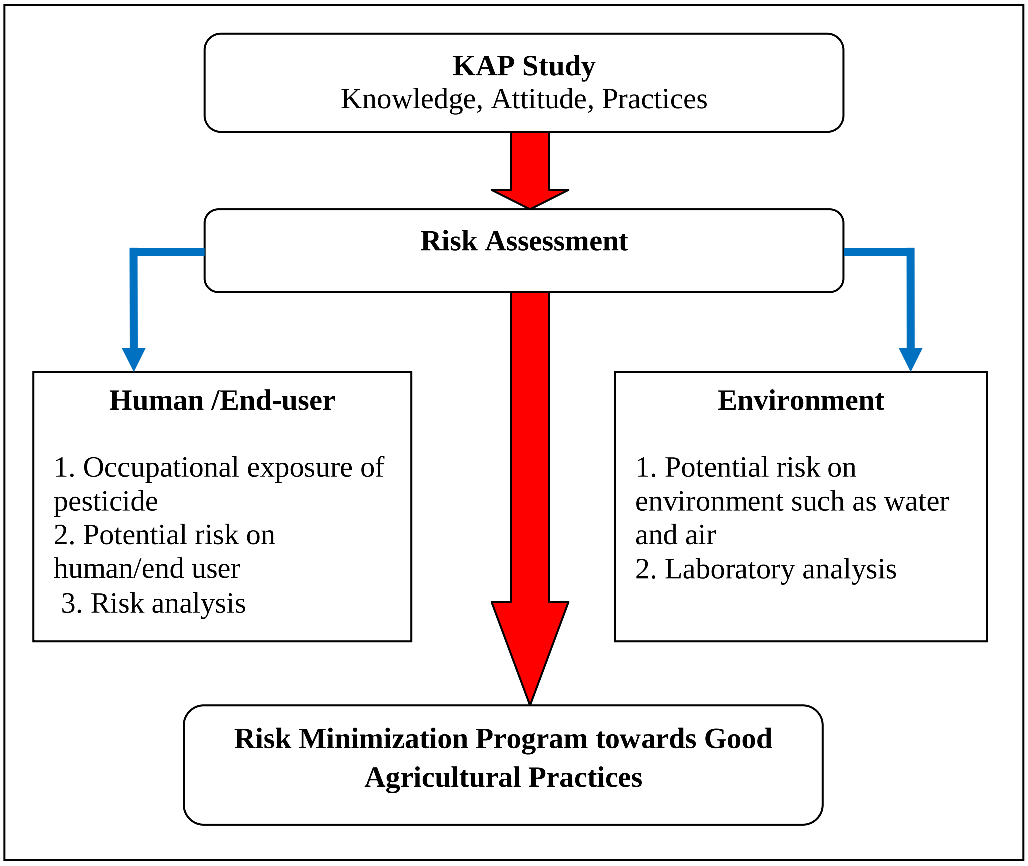

Figure 1.1 Relation between knowledge, attitude and practices (KAP) study and risk assessment towards risk minimization program

1.2 Problem Statement

Pesticides can be hazardous and harmful to humans depending on the dose applied, duration of exposure, exposure route and types of chemical. When compositions of pesticides are mixed together, they can be harmful to humans even in small doses (Tsatsakis et al., 2009). Significant growth in pesticide consumption in agriculture has led to the concern on potential toxicity, risks and adverse effects to environment and human health, particularly in certain countries where farmers' knowledge on safe handling procedures are generally inadequate and regulations are not strictly implemented (Damalas and Eleftherohorinos, 2011). In addition, monitoring and evaluation of pesticides' occupational exposure is critical due to the continuous exposure of pesticides in farming activities which might put farmers' health at risk. Furthermore, various literatures have proven that the use of detailed and complete questionnaires together with a monitoring process; and combining it with other relevant information would provide a more accurate classification of pesticides risks and exposure among farmers (Blair and Zahm, 1995).

Long term exposure to pesticides may put farmers in dangerous conditions and will cause adverse health effects, for instance respiratory problems, reproductive and development toxicity, neurodegenerative disease, as well as cancer (Bassil et al., 2007, Kanavouras et al., 2011, Parrón et al., 2011, Hernández et al., 2013). Therefore, in relation to these, many researchers have conducted studies pertaining to pesticides particularly on risk assessment (Matthews et al., 2003), environmental health, hazard and exposure (Snelder et al., 2008), toxicology (Curwin et al. , 2007) and pesticide pollution in environment, either in soils or water (Belmonte-Vega et al., 2005). Besides, studies have also been conducted to examine and analyze knowledge, attitude and practices (KAP) in relation to pesticide use and handling around the world for better understanding of occupational setting and work conditions of farm workers (Karunamoorthi et al., 2011).

Although many serious implications of pesticides to the environment and human health were reported across the world, only limited studies have pinpointed the potential risks of pesticides through the establishment of risk assessment procedures with regards to knowledge, attitude and practices among farmers (Yassin et al., 2002) and very limited studies were found in the literature for Malaysia case scenario. With further intensification and expansion in paddy production in Malaysia, a greater extent of research on the pesticides use is critical to help in safe pesticide management practices among farmers in paddy plantation. Therefore, risk assessment is vital to curb these problems from worsening. Keeping the above facts in mind, present study is designed to assess potential risks of pesticides and their relationship with farmers' knowledge, attitude and practices (KAP) as well as the concentration levels in water samples. This study would provide a fundamental basis towards a new direction of scientific management tool for good agricultural practices.

1.3 Research Objectives

With the main aim to assess the potential human health risk, risk assessment and occupational exposure study of pesticides was conducted. The specific objectives of this research are:

- to identify the level of knowledge, attitudes and practices of pesticides use among paddy farmers.
- to examine and evaluate potential risks and occupational exposure of pesticides among paddy farmers in the field.
- to determine and analyze the concentration of pesticide residue in water with risk rating.

1.4 Scope of Research

This research involved questionnaires, field data collection, chemical health risk assessment (CHRA) analysis, laboratory analysis and data analysis. Permatang Keriang village, Seberang Perai Utara, Pulau Pinang, Malaysia was chosen as the sampling site for this research. Field data collection such as environmental data collection, CHRA analysis and water sampling were carried out from April 2013 until March 2014. Finally, laboratory analysis and data analysis were performed.

As for the questionnaire analysis, 25% of the total paddy farmers in Permatang Keriang village were involved in this questionnaire. The questionnaire was divided into four parts, namely, demographic information, knowledge, attitude and practices parts. Subsequently, chemical health risk assessment (CHRA) was conducted on selected farmers by choosing several pesticides that were commonly used by the farmers based on the total pesticides found after analyzing the questionnaires. The chosen pesticides for the CHRA analysis were from insecticide and fungicide groups.

Then, laboratory analysis was conducted. Water samples for pre-application and post-application were taken at 32 different sampling points and were analyzed using solid phase extraction (SPE) method. Next, all the samples were analyzed using GCMS analysis to identify target pesticide residues. Measurement of *in-situ* water characteristics such as dissolved oxygen (DO), turbidity, temperature and pH and physical air parameters including air velocity, ambient temperature, carbon dioxide, carbon monoxide, dust level, photoionization detector (PID) and relative humidity were conducted with three replications. Finally, statistical analysis was conducted using ANOVA to analyze data from this research.

1.5 Importance of Research.

This research helps to identify potential hazards and risks posed especially during handling and usage of pesticides in paddy plantation. By conducting chemical health risk assessment, specific data during assessment allows us to identify pesticides risk. Additionally, hazard risks data for selected pesticides can be used as references for future risk assessment which have similar active ingredients.

Analysis of target pesticide residues can provide essential data on the concentration of pesticides especially in water focusing on paddy field which give high adverse effects to the environment. The data can be used as a guideline to compare with maximum residue limit (MRL) for each pesticide and help other researchers to continue researching about pesticides used in paddy plantation.

Moreover, the detailed data derived from the chemical health risk assessment (CHRA) and knowledge, attitude and practices (KAP) part in this study can be used in the future in terms of bio-monitoring study of pesticide exposure. Research on biological monitoring can be conducted in the future to determine the presence of pesticides in human body. Combination of both studies, which are risk assessment and bio-monitoring, can be a strong evidence and good reference to identify pesticide exposure to human and help fellow researchers to conduct deeper research regarding pesticides exposure in term of human health risk assessment.

1.6 Thesis Outline

There are six chapters in this thesis. Principally, it consists of literature studies, practical field works, scientific results and discussion on the human health risk assessment and pesticide residues analysis, and ends with conclusion and recommendations for future studies. This thesis focuses on knowledge, attitude and practices (KAP) level among farmers, risk assessment on occupational exposure of pesticides among farmers and analysis of pesticide residues in water samples.

Chapter 1 explains overall of the research including background of research, problem statement, objectives of research, scope of research, importance of research and thesis outlines.

Chapter 2 presents literature review of the history of pesticides. Classification of pesticides and their uses in agriculture are elaborated in this chapter. Staple crops, pesticides used in paddy plantation, types of pesticides used and the adverse effects of pesticides on humans and environment are thoroughly discussed. Risk assessment and occupational exposure are explained further in terms of types of risk assessment, elements of risk assessment and steps of risk assessment process. For occupational exposure, route of exposure and significance of safety measures are explained in detail. Studies on risk assessment and occupational exposure in agricultural for fruits, vegetables and staple crops are also discussed in this chapter.

Chapter 3 highlights materials and equipments used; and detailed procedure conditions to perform laboratory analyses that were used in this study. This comprises description of study area, field data collection, which includes questionnaire survey and field measurement, chemical health risk assessment analysis, extraction of target analytes using solid phase extraction (SPE) method, concentration of pesticide residues in water samples, data analysis and statistical analysis for this study. All the laboratory analysis as well as risk assessment analysis are briefly explained. Statistical analysis for this study was performed using ANOVA.

Chapter 4 discusses the research findings from the knowledge, attitude and practices (KAP) questionnaires, chemical hazard risk assessment (CHRA), physical environmental parameters, concentration of pesticide residues in water samples and the association between concentrations of pesticide residues in water samples with risk rating (RR). In addition, comprehensive explanation concerning the relationship between KAP results with CHRA in terms of mixing and handling pesticide during risk assessment are discussed in this chapter. Association between concentration of pesticide residues in water samples with risk rating, frequency rating and exposure rating are also duly explained.

Chapter 5 explains the risk minimization programmes towards good agricultural pesticide practices. The use of hazard and safety measures by paddy farmers including personal protective equipment (PPE), risk minimization programme, monitoring programme and awareness training are several examples of risk minimization strategies to guide paddy farmers towards good agricultural practices. Furthermore, alternative ways such as traditional methods to minimize risk exposure to pesticides were further explained.

Last but not least, Chapter 6 discusses the conclusion that can be summarized based on results and discussion from the previous chapter. Furthermore, recommendations for future research in risk assessment concerning pesticide residues concentration are also included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

In this chapter, two main topics are addressed, which are: (i) history of pesticides and (ii) risk assessment and occupational exposure of pesticides in agriculture. History of pesticides covers classification of pesticides in term of target pests, chemicals group and active ingredients meanwhile for the risk assessment and occupational exposures includes studies of risk assessment in agricultural.

2.2 History of Pesticides

Pesticides were unveiled in the worldwide after the World War II with their plenty of benefits. However, in lines with the changing times, the usage of pesticides nowadays are focusing on the potential hazards to the human health and environment (Chambers et al., 2001). Since 1950, chemical pesticides have overshadowed the traditional methods in agricultural production. Pesticides can be classified into several types, comprising ten thousand pesticide formulations with more than eight hundred active ingredients (Hernández et al., 2013). In the agricultural sector, more than 500 different pesticide formulations are being used worldwide (Azevedo, 1998).

Then, starting from 1940 until 1980, the world had been introduced to synthetic pesticides. For example, organochlorine (OC) pesticide was abundantly used in 1940 until 1950 because of the larger contribution to agricultural outputs and pest control. OC pesticides are capable in controlling diseases like typus or malaria.

Unfortunately, in the year 1960, OC pesticides were restricted or banned especially in advanced countries (Aktar et al., 2009) and developing countries after knowing and understanding the long term adverse effects (Çok et al., 1997). Subsequently, organophosphate (OP) was introduced in 1960 (Aktar et al., 2009). The OP pesticides thrived and became one of the predominant pesticides worldwide until today because of the mechanism action due to the inhibition of acetylcholinesterase in the nervous system of pests (Waddell et al., 2001).

In the following year (1970), carbamate pesticide was introduced followed by pyrethroids in 1980. Carbamate was produced as an insecticide to disturb the pests' nervous system by interrupting the enzyme that controlled acetylcholine. In the area of pesticide production, pyrethroids was also designed to interrupt the nerve system of pests (U.S.EPA, 2012b). In the year of 1970 until 1980, fungicides and herbicides were unveiled (Aktar et al., 2009, N.P.I.C, 2013). Fungicides were used as an agent to inhibit or kill the spore and fungi growth by disturbing energy production within fungal cells and also by destroying membranes of fungal cell when it is applied to plantation (U.S.EPA, 2012b, N.P.I.C, 2013).

On the other hand, herbicides were used to eliminate unwanted plant growth or weeds which became competition to the crops. In the middle of last century, synthetic herbicides expanded rapidly with the existence of auxinic herbicides such as paraquat. From then on, pesticide manufacturers sought to produce herbicides so that the unwanted weeds could be destroyed and killed without affecting crops. During that period until the 20^{th} century, countless selective herbicide classes with various modes were discovered, developed and marketed over the world (Duke, 2005, U.S.EPA, 2012b).

2.2.1 Classification of Pesticides

In general, pesticides can be classified into two categories: (i) target pests and (ii) main groups and their similar chemical structures (U.S.EPA, 2014). Firstly, for classification of pesticides according to target pests, they are classified based on the pests they kill. The suffix "-cide" can be expressed as "to kill". Bactericide, defoliant, desiccant, fungicide, herbicide, insecticide, miticide, molluscicide, nematicide, plant growth regulator, rodenticide and wood preservative are several classification of pesticides that are widely used nowadays (U.S.EPA, 2014). For example, bactericide is used to kill bacteria, whereas, fungicide is used as a tool to kill fungus (Khalidah et al., 2010). Herbicide is extensively used especially in agriculture to control and destroy weeds. Concurrently, insecticide is used to control insects worldwide.

Apart from herbicide and insecticide, miticide or acaricide are used to control mites and ticks. In addition, to control snails and slugs in plantation, molluscicides are normally used. Nematicides are used to control nematodes. Moreover, rodenticide was used to control rodents. Likewise, defoliant and desiccant are used in agriculture to control crop foliage. In addition, wood preservative is used to control wood-destroying organisms. Similarly, plant growth regulator is used as a crop growth process to control pests (Arias-Estévez et al., 2008). Table 2.1 represents classification of pesticides based on target pests.

Table 2.1 Classification of pesticides based on target pests (after Arias-Estévez et al., 2008)

Pesticide Group	Target Pest	Types of Damage
Bactericide (sanitizers or disinfectants)	Bacteria	
Defoliant / desiccant	Crop foliage	
Fungicide	Fungus	
	i. Hawar seludang (*Rhizoctonia solani*)	i. Produce empty rice especially at the bottom of stalk, cause rice collapse
	ii. Bintik perang (*Helminthosporium oryzae*)	ii. Caused by a fungus borne seeds that produce gray or white spots on the leaves or seeds.
	iii. Karah Daun (*Pyricularia oryzae*)	iii. Rice leaves will dry up and die.
	iv. Reput Tangkai (*Pyricularia oryzae*)	iv. Rice stalk rot and no substance in grains and rice plant will fall.
Herbicide	Weeds	
	i. Rumput colok cina (*Ischaemum rugosum*)	i. Live in paddy field and compete with paddy to get nutrients needed by plants
	ii. Rumput padi burung (*Echinochloa crus-galli*)	
Insecticide	Insects	
	i. Lelompat daun (*Empuasca fabae*)	i. Insect adults and nymphs suck the liquid from the surface of the leaves while inserting toxic substances into the leaves.
	ii. Kesing or Pianggang (*Leptocorisa acuta*)	ii. Adult leafhopper and young leafhopper suck the liquid (milk) of rice being formed which will result in smaller fruit rice and half-filled

Table 2.1 Continued

Pesticide Group	Target Pest		Types of Damage	
Insecticide	Insects			
	iii.	Bena Hijau or Green leafhopper (*Nephotettix virescenes*)	iii.	Green leafhopper damage the rice plants either by sucking liquid from rice plants or carrying the virus that causes red
	iv.	Bena Perang (*Nilaparvata lugens*)	iv.	Rice plant becomes yellow and dry
	v.	Bena belakang putih (*Sogatella furcifera*)	v.	Adult and young white leafhopper will suck fluids from rice plants and cause leaves to wither and slowly turn red.
	vi.	Ulat lipat daun /ulat guglung daun (*Cnaphalocrosis medinalis*)	vi.	Larvae will attack during rice growth by winding up the leaves and combine them at the end of growing process. They also will chew the green leaf.
	vii.	Ulat ratus (*Nymphula depuntalis*)	vii.	Caterpillars feed on green tissues of the leaves and leaves become whitish and papery
	viii.	Kepinding nyamuk or Nyamuk hijau (*Helopeltis antonii*)	viii.	Sucking on mouth parts, they pierce plant tissues and cause damage ranging from leaf destruction and fruit blemishes.
Miticide (acaricide)	Mites and ticks			
Molluscicide	Slugs and snails			
Nematicide	Nematodes			
Plant growth regulator	Crop growth processes			
Rodenticide	Rodents		i.	Rodent infestation will cause effects such as cut rice stalks. Rice fields appear yellow and dry.
Wood preservative	Wood- destroying organisms			

Secondly, for the classification of pesticides based on main groups with similar chemical structures, pesticides which have same main groups normally have similar active compounds with same chemical structures (Arias-Estévez et al., 2008). However, not all the groups are equal in terms of application amount, compound and usage. For instance, organophosphorus compounds have more than 80 different active ingredients with different sub-groups such as phosphonate, phosphate, phosphorodithionate, phosphorothiolate, and so forth. Mean while, some pesticides compounds contain very few active ingredients such as imidazolinones (Barcelo and Hennion, 1997).

Pesticide compounds of pyrethoids, organophosphorus and organochlorine are normally used as acaricides, insecticides or nematicides. In addition, triazole and conazole are the sub-groups of pesticides from azole group which are mainly used as fungicide. Carbamates can be used as two different functions such as insecticide or herbicide. Moreover, carbamates, amides and triazines are the pesticide groups that are widely used as herbicide and normally applied on crops such as rice, soybean and maize (Barcelo and Hennion, 1997). According to Arias-Estévez et al. (2008), classification of pesticides based on chemical structure normally have the same characteristics and same mode of action to kill pests. Table 2.2 shows classification of pesticides based on main pesticides groups and sub-groups.

Table 2.2 Classification of pesticides based on main pesticides groups and sub-groups (after, Barcelo and Hennion, 1997)

Groups	Related sub-groups
Amide	Chloroacetanilide, acylanaline, dichloroanilide
Aryloxyalkanoic acid	Phenoxacetic acid and salts
Azole	Conazole, Triazole
Carbamate	Carbamate, dithiocarbamate, dimethyldithiocarbamate
Diazine	Pyrazine, pyridazine
Dinitroaniline	Benfluralin, butralin, chlorinidine
Diphenyl – ether	Hydroxylation, sulfonation
Imidazolinone	Imazapyr, imazapic, imazethapyr
Organophosphorus	Phosphonate, phosphate, phosphorodithionate, phosphorothiolate, phosphoroamidate
Organochlorine	DDT, chlordane, toxaphene
Pyrimidine	Cytosine
Pyrethroid	Permethrin, cypermethrin, deltamethrin
Triazine	1,3,5- triazinone, 1,3,5-triazine, 1,2,4 - triazine
Sulfonylurea	Azimsulfuron, bensulfuron-methyl
Urea	Phenylurea
Various	Single structure, no specific structure (benzoic acid derivatives).

On the other hand, the World Health Organization (WHO) also introduced the classification of pesticides which has been used as a guideline. The WHO classification follows the acute toxicity hazard categories from The Globally Harmonized System (GHS) of Classification and Labelling of Chemical (U.N, 2011). The GHS was accepted in the classification of pesticides system because it complied with the extensive international consultation. In addition, the WHO classification of pesticides is being widely used due to the consistent updates from time to time by the consultation with regional bodies, international agencies and countries around the world (WHO, 2011). Table 2.3 shows the classification of pesticides according to WHO guideline based on different classes.

Table 2.3: Classification of pesticide toxicity (after WHO, 2011)

WHO Class		**Hazard Statement**	**Band Colour**	**Hazard Symbol**	**LD_{50} for rats (mg/kg body weight)**			
					Oral		**Dermal**	
					Solid	**Liquid**	**Solid**	**Liquid**
Ia	Extremely hazardous	Very toxic	Red		5 or less	20 or less	10 or less	40 or less
Ib	Highly hazardous	Toxic	Red		5 -50	20 - 200	10 – 100	40 -400
II	Moderately hazardous	Harmful	Yellow		50 -500	200 - 2000	100 - 1000	400 – 4000
III	Slightly hazardous	Caution	Blue	-	>500	>2000	>1000	>4000
U	Unlikely to present hazard in normal use	-	Green	-	>2000	>3000	-	-

2.2.2 Staple Crops

Generally, there are around 50 000 plants planted worldwide. Out of 50 000, only three plants were considered staple crops which are rice, maize and wheat. According to United Nations Food and Agriculture Organization (FAO), staple crops are food that are eaten regularly and is a standard diet in certain population in the world. Staple food provides 60 percent of food energy intake to human diet (FAO, 2015).

Paddy (*Oryza sativa L.)* is a staple crop worldwide and became king of cereals for more than fifty percent of the population (Abdullah et al., 1997). As reported by Prasanna-Kumar et al. (2013) paddy is major staple food in India, South East Asia, East Asia, Latin America and Africa and meet dietary requirements of 70% of the community in these countries. In order to maintain and enhance the paddy production, a huge range of pesticides are needed to kill pests like insects, pathogens, fungal bacterial and weeds (Abdullah et al., 1997). As reported by Zaim et al. (2012), approximately about 672 000 hectares areas was covered by planted paddy throughout Malaysia and around 3.660 metric tonnes per hectares of national paddy production was recorded annually.

Apart from rice, maize is another leading cereal grain which is essential worldwide. More than 750 million metric tons of maize was produced in 2008, with United States being the world leading supplier followed by European Union, China, Brazil, Mexico and India (USDA/FAS, 2008). Due to the high demand, pesticides were used in huge quantities to control diseases and pests (Akoto et al., 2013). As mentioned by Dinham (2003), around 87% of farmers used pesticides to control their maize cultivation from pests and diseases.

2.2.3 Pesticides Use in Agriculture

In Malaysia, agriculture can be categorized into two distinct sectors which are smallholder's sub-sectors and co-existence of planting farming. Agriculture sector was contributed to the Malaysian economic growth by the high export earning every year. Statically, around 300 000 farmers in Malaysia depend on paddy farming as their source of livelihood and main income (Zaim et al., 2012). However, uses of pesticides are the primary concern in agriculture sector. Pesticides are widely used in modern commercial agriculture nowadays (Ismail et al., 2012). Pesticides are widely used in the agriculture sector to minimize or eliminate yield losses caused by pests (Damalas and Eleftherohorinos, 2011). Pesticides can boost yield and can be categorized as labour saving, economic, as well as becoming a tool for pest management. It will indirectly increase the quality of production and enhance income (Oerke and Dehne, 2004, Cooper and Dobson, 2007).

In addition, pesticides are abundantly used in vegetables and fruit because of their high resistance to prevent disease and insect attacks (Zawiyah et al., 2007). The use of pesticides was introduced to the farmers in developing countries in order to increase income to the farm households, providing food, as well as for plantation growth productivity. Webster et al. (1999) mentioned that without pesticides, consumption in farming areas would lead to great economic losses. Pesticide is one of the excellent mediums for increasing the production of crops. However, it gives unfavourable impacts to the aquatic life and food chain (Gilliom, 2007).In addition, pesticides are sprayed to the crops or applied to the soil, it is automatically released to the surrounding environment and hence causing contamination. The pesticides will also contaminate surface water via run-off or drift through drainage in farmland soil (Belmonte-Vega et al., 2005).

2.2.3.1 Pesticide Use in Paddy Plantation

Paddy is planted in humid temperatures with temperate climates and has become one of the staple foods in the world. Paddy is planted in large scale to meet the daily food needs of the population (Raihanah et al., 2015). To enhance productivity of paddy plantation, irrigation system has been implemented in certain countries especially for tropics and subtropics regions with two or more paddy plantation produced in the same year (Witt et al., 2000). Besides, to ensure the consistency of paddy growth, about one-third of paddy productions are generated by using pesticides (Raihanah et al., 2015).

Additionally, due to long period of time needed to ensure paddy growth, it gives chance for insects, fungi and mites to disrupt the production. Over 70 species of insects were recorded as paddy pests, which are the main constraints on yields and directly cause major output reduction (Nyugen et al., 2007, Zhang et al., 2012). For instance, small brown plant hopper, brown plant hopper and white backed plant hopper are the major pest insects in paddy plantation. Approximately, around 28% of total paddy losses in the world are caused by insect pests, which are four times higher compared to that of the other grain crops in the world (Abdullah et al., 1997). In addition, as much as 10% of worldwide paddy production is reduced by weeds (Oerke, 2006) and another 10 to 15% is due to paddy diseases (Prasanna-Kumar et al., 2013).

In order to overcome these problems, various types of pesticides have been produced annually to increase pesticides' durability and resistance to the target pests with new chemical formulation (Su et al., 2013). Apart from that, more than 90% of the world's end-users use pesticides in paddy plantation (Abdullah et al., 1997). Comprehensive studies are being conducted since 1960 to develop programmes to control pests. In align with this objective, over 30 years ago, insecticides with different active ingredients were created (Cheng, 2009). Furthermore, effective herbicides are highly required to control weed in paddy plantation because under direct seeding, weeds and paddy would normally sprout simultaneously (Jesusa et al., 2012). In the rice-growing sectors in Malaysia, paraquat and 2,4-D are the frequent herbicides used by the farmers to control leaved aquatic weeds in paddy fields (Baharuddin et al., 2011). Besides, fungicide are required as a vital tool to control paddy diseases such as bacteria, fungus, nematode and virus (Prasanna-Kumar et al., 2013). Rodenticide remains as a medium in controlling rodent in paddy agriculture (Singleton et al., 2005).

He et al. (2010) reported that losses caused by insect pests increase drastically from 2.0% up to 31.5% throughout the world each year. It indicates that, insecticides are the best alternative method to control insects which contribute largest losses of paddy yield. Insecticides have been applied previously to ensure quality of paddy plantation and indirectly increase yield production (Zhang et al., 2012). Many studies that have been conducted previously showed that there are several insecticides with different active ingredients are commonly used in paddy plantation such as buprofezin (Wang et al., 2008) , chlorpyrifos (Rozita et al., 2011, Phung et al., 2012a) and lambda cyhalothrin (Bennett et al., 2000) in order to control insect pests.

Buprofezin is one of the active ingredients to control the insect pests. Buprofezin, with IUPAC name 12 – [1,1-dimethylethy1) iminol tetrahydro-3-(1-methylethyl)-5-phenyl-41H-,3,5-thiadiazin-4-one), has a molecular weight of 305.4 g/mol, with moderate persistence in the environment. In terms of hydrolysis in water, buprofezin has half-life of 51 days at pH 5, 378 days at pH 7 and 396 days at pH 9. However, for photolysis in water, buprofezin has half-life of 106 days (summer) and 446 days (winter) at pH 7. While for pH 9, buprofezin has half-life of 140 days (summer) and 589 days (winter) (Velde-Koerts, 2009). Buprofezin is a thiadiazine insecticide regulator and molting inhibitor. Buprofezin has direct larvicidal action against some hemipetra and coleopteran which makes buprofezin an effective active ingredient in controlling harmful pests such as greenhouse whitefly and brown rice planthopper (Valverde-Garcia et al., 1993). Although, buprofezin gives slow response but it lasts longer. It is also toxic to crustaceans and indirectly limits their bodies' use in water (Grafton-Cardwell et al., 2005). Thus, buprofezin is used extensively in plantation especially in paddy plantation, vegetation or staple crop products in worldwide (Armenta et al., 2002).

Besides, active ingredient of chlorpyrifos, a common insecticide is also used in paddy plantations. Chlorpyrifos, IUPAC name (0,0-diethyl-0-(3,5,6-trichloro-2-pyridyl phosphorothioate; CFP) is a broad spectrum organophosphate (OP) insecticide comprising non-systemic cholinesterase (chE) inhibitor which helps in controlling horticulture, agriculture insect pests particularly and control subterranean termites on paddy (Griffin et al., 1999, Deb and Das, 2013). Chlorpyrifos acts by inhibiting acetylcholinesterase, which disrupts nerve function of insects, animals and human. Chlorpyrifos has molecular weight of 350.57 g/mol (Eaton et al., 2008) and has moderate solubility in water bodies. The hydrolysis rates in water vary at