UNIVERSITI PUTRA MALAYSIA

SIMULTANEOUS QUANTIFICATION OF PESTICIDES IN PADDY SOIL AND WATER USING UHPLC-MS/MS AND ASSOCIATED DERMAL HEALTH RISK ASSESSMENT

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Pesticides are agrochemicals that, despite having many benefits, pose underlying effects on environment and human. Contamination of pesticides in the environment leads to their exposure to human especially via dermal contact. Farmers are the most susceptible population as they work directly with the pesticides. Regular monitoring is required to observe pesticide residues in the environment. However, low concentration of the pesticide residues in complex matrices hinders the process. The objectives of this study were to study the work practice and the self-reported health symptoms of the farmers, and to simultaneously quantify thirteen commonly used pesticides in paddy soil and water using two optimised and validated methods with ultra-high performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS). First, the socio-demographic, work practice and self-reported health symptoms of the farmers were investigated. Then, the extraction method of pesticides in both matrices were optimised based on several previously published methods. The percent of recovery of the methods were compared and further optimised to improve the percent of recovery for all target analytes. Next, the optimised methods were validated by determining recovery, method detection limit (MDL), method quantification limit (MQL), and matrix effect of all analytes. The developed methods were then applied to quantify the target analytes in paddy soil and water samples from Tanjung Karang, Selangor. The concentration of each analyte were employed to assess dermal health risk of paddy farmers. Based on the result, the farmers are predominantly Malay male with average years or working of 27 years. Most of them shower and change clothes after and almost 50% wore PPE during farming activities. Headache and skin rash are two of the most frequently reported health symptoms among the farmers. The optimised UHPLC-MS/MS showed good linearity at calibration points ranging from the IQL to 500 ng mL^{-1}, and the correlation coefficients (R^2)

for all of the target analytes were higher than 0.999. The developed method for soil samples was optimised and modified based on the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) procedure, followed by a dispersive solid phase extraction (dSPE) clean-up technique. Whereas the developed method for water samples was based on glass fibre and nylon filtration, followed by the solid phase extraction (SPE). The percent of recovery of the target analytes in soil and water were ranged from 74% to 111% and 77% to 117% respectively. The MDL of the target analytes were ranged from 0.03 to 0.4 ng g^{-1} in soil, and 0.1 to 10 ng L^{-1} in water. Meanwhile, MQL in soil and water were ranged from 0.08 to 1 ng g^{-1} and 0.5 to 25 ng L^{-1} respectively. The matrix effects were ranged from 67% to 126% and 71% to 136% in soil and water samples respectively. The result of the simultaneous quantification showed that chlorantraniliprole was the highest mean concentration of pesticides in paddy soil (15.82 ng mL^{-1}) and paddy water (6.56 ng mL^{-1}) samples. Fipronil showed the highest dermal hazard quotient (HQ) calculated in paddy soil and water which were 1.10×10^{-2} and 5.26×10^{-4} respectively. There was no significant non-carcinogenic dermal health risk due to occupational exposure of target pesticides in paddy soil and water to farmers. Meanwhile, the dermal lifetime cancer risk (LCR_{dermal}) for pymetrozine in paddy soil indicates negligible risk, while LCR_{dermal} of pymetrozine in paddy water indicates potential risk ($\geq 1.0 \times 10^{-6}$) to farmers via dermal route. The two improved analytical methods for pesticides analysis in soil and water can be employed in the analysis of pesticide residue environmental and agricultural matrices, consequently contributing in the monitoring pesticide usage in agricultural fields.

Keywords: Agricultural; Environmental; Rice; Pesticides; QuEChERS; dSPE; SPE; dermal; health risk; personal protection equipment; ultra-high performance liquid chromatography coupled with tandem mass spectrometry

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KUANTIFIKASI SERENTAK RACUN MAKHLUK PEROSAK MENGGUNAKAN UHPLC-MS / MS DALAM TANAH DAN AIR DAN RISIKO KESIHATAN DERMA DALAM KALANGAN PETANI

Oleh

SITI ZULFA ZAIDON

Mei 2019

Pengerusi: Ho Yu Bin, PhD
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Walaupun racun makhluk perosak merupakan agrokimia yang mempunyai banyak faedah, ia juga mempunyai kesan negatif terhadap alam sekitar dan manusia. Pencemaran racun perosak dalam alam sekitar membawa kepada pendedahan racun perosak terhadap manusia terutamanya melalui laluan derma. Petani adalah populasi yang paling mudah terdedah kepada bahan agrokimia ini kerana mereka bekerja secara langsung dengan racun perosak. Sehubungan itu, pemantauan yang kerap diperlukan untuk memerhati residu racun perosak dalam alam sekitar. Walau bagaimanapun, kepekatan residu racun perosak yang rendah dalam matrik kompleks menyukarkan proses pemantauan. Objektif kajian ini adalah untuk mengkaji amalan kerja dan simptom kesihatan dalam kalangan petani, dan menentukan kepekatan tiga belas racun makhluk peroak yang sering digunakan dalam tanah dan air sawah menggunakan kromatografi cecair berprestasi ultra tinggi dengan spektrometri massa tandem (UHPLC-MS/MS). Latar belakang sosiodemografi, amalan kerja dan simptom kesihatan dalam kalangan petani disiasat. Kaedah pengekstrakan racun perosak dalam kedua-dua matrik dioptimumkan dengan menguji kebolehgunaan kaedah yang pernah diterbitkan ke atas analit sasaran. Kemudian, peratus pemulihan untuk semua analit sasaran dalam kaedah-kaedah tersebut telah dibandingkan. Seterusnya, kaedah yang dioptimumkan telah disahkan dengan menentukan peratus pemulihan, had pengesanan kaedah (MDL), had kuantifikasi kaedah (MQL), dan kesan matrik untuk kesemua analit. Kaedah yang dibangunkan kemudiannya digunakan untuk menentukan kepekatan analit sasaran dalam sampel tanah dan air sawah dari Tanjung Karang, Selangor. Kepekatan kesemua analit telah digunakan dalam penilaian risiko kesihatan kulit (HRA) racun perosak terhadap petani. Berdasarkan keputusan, secara dominan, petani terdiri daripada lelaki Melayu dan mempunyai purata tahun bekerja selama 27 tahun. Majoriti petani mandi dan menukar pakaian selepas bekerja, serta hampir 50% menggunakan PPE semasa bekerja. Pening dan ruam kulit merupakan antara simptom kesihatan yang kerap dilaporkan dalam kalangan petani. Instrumen UHPLC-MS/MS yang telah dioptimum menunjukkan kelineran yang baik pada titik penentukuran antara had kuantifikasi instrumen (IQL) hingga 500 ng mL^{-1}, dan koefisien korelasi (R^2) untuk semua analit sasaran adalah lebih tinggi daripada 0.999. Kaedah yang dibangunkan di dalam tanah telah dioptimumkan dan diubah suai berdasarkan prosedur Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS), diikuti dengan teknik pembersihan pengekstrakan fasa pepejal dispersi (dSPE). Manakala, kaedah yang dibangunkan dalam sampel air diasaskan pada penapisan serat kaca dan nilon, diikuti dengan pengekstrakan fasa pepejal (SPE). Peratus pemulihan untuk kesemua analit sasaran dalam tanah dan air masing-masing berkisar daripada 74% hingga 111% dan 77% hingga 117%. Had pengesanan kaedah (MDL) bagi analit sasaran adalah daripada 0.03 ng g^{-1} hingga 0.4 ng g^{-1} dalam tanah, dan daripada 0.1 hingga 10 ng L^{-1} dalam air. Sementara itu, MQL dalam tanah dan air masing-masing adalah daripada 0.08 hingga 1 ng g^{-1} dan 0.5 hingga 25 ng L^{-1}. Kesan matrik adalah daripada 67% hingga 126% dalam sampel tanah, dan 71% hingga 136% dalam sampel air. Keputusan kuantifikasi serentak racun makhluk perosak dalam tanah dan air sawah menunjukkan chlorantraniliprole mempunyai purata kepekatan racun perosak tertinggi dalam sampel tanah (15.82 ng mL^{-1}) dan air (6.56 ng mL^{-1}) padi. Fipronil menunjukkan hazard quotient (HQ) derma yang tertinggi dalam tanah dan air (1.10×10^{-2} dan 5.26×10^{-4}). Walau bagaimanapun, tidak terdapat risiko kesihatan bukan karsinogenik yang ketara disebabakan oleh pendedahan pekerjaan terhadap racun perosak sasaran dalam tanah dan air padi. Sementara itu, risiko kanser seumur hidup derma (LCR_{dermal}) untuk pymetrozine dalam tanah menunjukkan risiko kanser yang boleh diabaikan, manakala LCR_{dermal} dalam air menunjukkan risiko berpotensi ($LCR_{dermal} \geq 1.0 \times 10^{-6}$) kepada pesawah. Kedua-dua kaedah analisis yang diperbaik untuk analisis racun perosak dalam tanah dan air boleh digunakan dalam analisis sisa racun perosak dalam matriks alam sekitar dan pertanian, seterusnya menyumbang dalam pemantauan penggunaan racun perosak dalam bidang pertanian.

Kata kunci: Pertanian; Alam Sekitar; Beras; Racun perosak; QuEChERS; dSPE; SPE; kulit; risiko kesihatan; cecair berprestasi ultra tinggi dengan spektrometri massa tandem; peralatan perlindungan diri

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ABSd	Dermal absorption fraction
AF	Adherence factor
Ais	Area of internal standard in sample extract
AOAC	Association of Analytical Communities
AOEL	Acceptable Operator Exposure Level
AP	Available phosphorus
AT	Averaging time
BOD	Biochemical oxygen demand
BW	Body weight
CE	Collision energy
CEC	Cation exchange capacity
Cex	Concentration of the target analyte in sample extract
CF	Conversion factor
CH	Ceramic homogenizer
Cis	Concentration of internal standard in
COD	Chemical oxygen demand
Cs	Concentration of the target analyte in solid sample
Cw	Concentration target analyte in water sample
DAD	Dermal absorbed dose
DAevent	Absorbed dose per event
DO	Dissolved oxygen
dSPE	Dispersive solid phase extraction
EC	Electrical conductivity
ED	Exposure duration
EF	Exposure frequency
EFSA	European Food Safety Authority
EMEA	Europe, Middle East and Africa
ERAS	Espek Research and Advisory Services
ESI	Electrospray ionisation
ET	Exposure time
EU	European Union
EV	Event frequency
FA	Fraction absorbed
GFF	Glass fibre filter
HAc	Acetic acid
HI	Hazard index
HLB	Hydrophobic-lipophilic balance

HQ	Hazard quotient
HRA	Health risk assessment
ICH	International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use
IDL	Instrumental detection limit
IDL	Instrumental detection limit
IQL	Instrumental quantification limit
IQL	instrumental quantification limit
IS	Internal standard
Ka	Dermal absorption coefficient
Kp	Dermal permeability coefficient
LCR_{dermal}	Dermal lifetime cancer risk
LOD	Limit of detection
Log Kow	Octanol/water partition coefficient of the non-ionized species
LOQ	Limit of quantification
MDL	Method detection limit (MDL) and
ME	Matrix effect
MeCN	acetonitrile
MeOH	Methanol
MgSO4	Magnesium sulphate
MQL	Method quantification limit
MRM	Multiple reaction monitoring
MW	Molecular weight
NaAc	Sodium acetate
NaCl	Sodium chloride
NS	Native standard
PPE	Personal protection equipment
PSA	Primary secondary amine
QuEChERS	Quick, Easy, Cheap, Efficient, Rugged and Safe
R^2	Coefficient of determination
RfD	Reference dose
RISDA	Rubber Industry Smallholders Development Authority
RR	Relative risk
RRF	Relative response factor
RSD	Relative standard deviation
SA	Surface area
SFABS	Absorbed cancer slope factor
SIRIM	Standard and Industrial Research Institute of Malaysia
SPE	Solid phase extraction
TDS	Total dissolve solids

tevent	Event duration
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
UHPLC-MS/MS	Ultra-high performance liquid chromatography tandem mass spectrometry
USEPA	United states of environmental protection agency
Vex	Volume of extract
Vs	Sample volume
Ʈevent	Lag time per event

CHAPTER 1

INTRODUCTION

1.1 Background

Agriculture sector has become the bread and butter for most of Malay communities in Malaysia over several generations in the past. Over time, this sector has mushroomed into one of the most important sectors in Malaysia. This is due to the surge of improved technologies and high demands which encourage more people to explore the sector and persuade farmers to develop more reliable technique to ensure the quality and productivity of their crops. One of the most essential crops is paddy which is highly sowed in Peninsular Malaysia such as Kedah, Perak, Selangor, and Negeri Sembilan and also in the East of Malaysia, Sabah and Sarawak. Its production has increased from 2.51×10^{6} metric ton (2010) to 2.64×10^{6} metric ton (2014) (MOA, 2017). It provides the staple food not only for Malaysia but also for other South East Asia countries such as Thailand, Philippines, Cambodia, and Vietnam (Toriman et al., 2014).

Since the cultivation requires direct irrigation where the crops are planted, this contributes to the large exposure to pests such as fungi and bacteria. Case in point, *Curvularia lunata* which causes black kernel, and *Erwinia chrysanthemi* which is responsible for a condition called footrot. Other notable diseases infecting the paddy crops include downy mildew, brown spot, and bacterial blight. This leads to various methods to overcome this problem. In modern paddy plantation, the rice yielded are modified to be highly resistant to pests. Besides that, the usage of biological control such as catfish culture in the irrigation system is highly used by the farmers to manage the pests. However, the use of chemicals such as pesticides is very useful due to its fast and accurate action.
Pesticides are chemical or biological substance that created to obliterate pests by attracting and eradicating them through a series of chemical reactions. There are active ingredients in these substances that modulate this effect. For instance, naphthalene that works through sublimation, Malathion which is highly used in Aedes eradication, and imidacloprid which works against sucking insects. These pesticides can strike in form of liquid, wettable powder, aerosol, emulsifiable concentrate, and many others. They are mainly used to protect plants from pests in agriculture field. Globally, there are about 2.36 billion kg of pesticides used every year. In the United States alone, approximately 0.5 billion kg of pesticides are used and about 80% of it is employed by the agriculture sector (Grube et al., 2011). Based on the data by FAO (2016), the total use of pesticides such as herbicides, fungicides and insecticides amount to approximately 4.1×10^{-6} t/y worldwide and 4.9×10^{-4} t/y in Malaysia in 2016. Nonetheless, there is no denying that the active usage of these substances causes major concerns among the communities.

Pesticides able to contaminate the surrounding soil, water or air by mitigating from the application point through various processes such as leaching, run-off or volatilization (Vryzas, 2018). According to Demoliner et al. (2010), a pesticide has the highest potential to move to and contaminate water if it meets the following criteria: water solubility> 30 mgL^{-1}, K_{OC} (organic carbon partition coefficient) < 300 mLg^{-1}, K_d (distribution adsorption constant) < 5 mL g^{-1} and soil half-life >3 weeks. The residues of the active analytes of the pesticides in the environmental matrix provide cidal effects on other organisms that act as biological control. Some of the commonly detected pesticides in paddy field are organochlorines (Sharip et al., 2017), organophosphates (Thummajitsakul et al., 2015) and multi-class pesticides such as pymetrozine (Li et al., 2011) and hexaconazole (Ju et al., 2017).

There are various analytical instruments used in pesticides determination. Many studies opted to use gas chromatography. These instrument coupled with various type of detectors such as flame photometric detector (GC-FPD) (Chai et al., 2012), electron-captured (GC-ECD) (Chai & Tan, 2009), or coupled with mass spectrometry based on the analyte physical properties and for their economical and time-saving features, liquid chromatography - tandem mass spectrometry (LC-MS/MS) has been proven as one of the most reliable instruments for pesticide analysis because of its high sensitivity and selectivity to quantify analyte residues in complex matrices (Fenoll et al., 2009; Montagner et al., 2014)

High performance liquid chromatography (HPLC) is a technique of quantification that is derived from the conventional technique of liquid chromatography (LC). The major difference between these techniques is, HPLC uses atmospheric pressure to force the liquid solvent eluting the components also known as the mobile phase through a column filled with adsorbent materials or the stationery phase. The separation of these various components depends on their interaction with the coating of the adsorbent material. Every components interacts differently with the adsorbent material causing them to have different flow rates through the column. Living up to its name, HPLC works more efficiently compared to the conventional LC. It is capable of separating much wider range of components such as analytes that have high polarity, thermally labile, or possessing high molecular mass, all of which are difficult to analysed using LC.

A high pressure liquid chromatography (HPLC) is one of the most common separation technique used in chemical analysis. It uses high pressure to pump the mobile phase throughout the LC system. The retention time of each compound depends on their affinity to the stationery phase; the stronger the bond between the target analyte with the column particles, the longer the retention time (Saul, 2018). Ultra-high pressure liquid chromatography (UHPLC) was first introduced in 2004. It uses column with shorter length and smaller particles. This shorten the analysis time and increase the instrument sensitivity. Due to this, higher pressure (up to 8700 psi) (Fountain, 2011) is required compared to HPLC. The Ultra-high pressure liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) is a technique that combines UHPLC and mass spectrometry. Mass spectrometry is a technique in which spectra of sample molecule is produced and used to modulate the elemental and chemical structure. Modulation of UHPLC-MS/MS ultimately combines the physical separation ability of UHPLC and the sensitive detection ability of mass spectrometry, thus provides high sensitivity and selectivity in conducting simultaneous quantification of a sample. The combination of solid phase extraction (SPE) and LC-MS/MS has been reported to contribute in the development of multi-residue methods for the determination of trace amounts of dozens of pesticides simultaneously in different aquatic matrices (Lazartigues et al., 2011). Besides that, Montagner et al. (2014) also reported that SPE-HPLC-MS/MS combination shows lower limit of detection (LOD) compared to other method of extraction such as sonication, solid phase microextraction, and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method.

Thirteen analytes of the common used pesticides are identified upon interviewing numbers of farmers. 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. From the list of brands, their active ingredients were recorded. Table 1.1 represents physicochemical properties of the 13 analytes.

Table 1.1: Physico-chemical properties of the analytes studied.

Analyte	Type	Class	Vapour pressure (mPa)[b]	Henry's law constant	log K_{ow}	Water solubility (mg L^{-1})[b]	Koc (mL g^{-1})	K_d
Azoxystrobin	fungicide	strobin	1.10×10^{-7}	7.30×10^{-09}	2.50	6.7	589	8.93
Buprofezin	insect growth regulator	thiadiazin	1.25	2.80×10^{-02}	4.93	0.46	5363	103
Chlorantraniliprole	insecticide	anthranilic diamide	6.30×10^{-12}	3.20×10^{-09}	2.86	0.88	362	3.18
Difenoconazole	fungicide	azole	3.30×10^{-5}	9.00×10^{-7}	4.4	15	n/a	n/a
Fipronil	insecticide	pyrazole	3.70×10^{-5}	3.70×10^{-5}	4.0	3.78	n/a	n/a
Imadacloprid	insecticide	neonicotinoid	9.00×10^{-7}	$1.70 \times 10\text{-}^{10}$	0.57*	610	n/a	n/a
Isoprothiolane	fungicide	dithiolane	1.88×10^{1}	1.00×10^{-1}	2.88*	54	1352	n/a
Pretilachlor	herbicide	chloroacetanilide	1.33×10^{-1}	8.10×10^{-04}	4.08	500	n/a	n/a
Propiconazole	fungicide	azole	5.60×10^{-2}	9.20×10^{-5}	3.72	150	1086	33.7
Pymetrozine	insecticide	triazine	4.20×10^{-03}	3.00×10^{-6}	-0.18*	270	n/a	n/a
Tebuconazole	fungicide	azole	1.70×10^{-3}	1.00×10^{-05}	3.70	36	n/a	n/a
Tricyclazole	fungicide	azole	2.70×10^{2}	5.86×10^{-7}	1.7*	596	169	n/a
Trifloxystrobin	fungicide	strobin	3.40×10^{-3}	2.30×10^{-3}	4.5	0.61	n/a	n/a

Source: PPDB; *PubChem; [a]at 25°C; [b]at 20°C; log K_{ow} : Octanol-water partition coefficient at pH 7; Koc: Soil organic carbon-water partitioning coefficient; K_d: Distribution coefficient

1.2 Problem Statement

Pesticides are widely used in agriculture sector to maintain the quality and appearance of the crops. Nevertheless, there are few apprehensions arise regarding the contamination of the pesticide residues such as there is insufficient information on permissible limit of pesticides usage in agricultural activity. As a result, pesticides may be used excessively. Regular monitoring of the pesticides in environmental samples is required to optimise pesticide usage and limit its exposure to human and the environment. In order to fulfil the monitoring requirement, method of analysis pesticide residues in soil and water is required.

Analysis of multi residue of pesticides is still challenging despite having countless developed methods since the 1970s (Dejonckheere et al., 1975; Ferri et al., 1989; Mayer and Greenberg, 1981; Shotwell et al., 1976; Singh, 1989; Zurmuhl, 1990). They are unable to quantify pesticide residues in complex matrices because they occur in low concentration (Masiá et al., 2014). There are various available methods for pesticides determination in environmental samples with high limit of detection (LOD) or limit of quantification (LOQ) (Demoliner et al., 2010; Fenoll et al., 2009; Montagner et al., 2014; Thuyet et al., 2010) . In addition, there are insufficient studies that focused on classes of pesticides such as anthranilic diamide (Caldas et al., 2011; Djue Tea et al., 2018; Zhang et al., 2012) triazine (Li et al., 2011) and dithiolane (Toan et al., 2013). Most of the existing methods were targeting the common pesticides such as organophosphates and organochlorines (Ahmadi et al., 2015; Hassan et al., 2010; Yaxi Liu et al., 2016; Nodeh et al., 2017; Salemi et al., 2013; Saraji et al., 2016). Thus it is important to persist the development of sensitive and rapid method for pesticide residues analysis in environmental matrices especially for the less-covered-but-extensively-used pesticides. Besides that, to the best of the authors' knowledge, there has yet a method that is able to simultaneously quantify thirteen target analytes in paddy soil and water.

The use of personal protective equipment (PPE) and level of personal hygiene practiced by the farmers can minimize the pesticides effects. However, lack of understanding on their importance and unwillingness to use PPE can increase the rate of pesticide absorption and chance of pesticides poisoning (Sharifzadeh et al., 2017). Figure 1.1 shows that some of the paddy farmers in Kampung Sawah Sempadan, Tanjung Karang neglected the use of PPE during spraying or farming activities.

The exposure of pesticides via different routes such as dermal, ingestion, and inhalation cause various health effects that range from mild effects such as skin and eye irritation, nausea and headache (Miswon et al., 2016) to severe effects such as asthma, reproductive system malfunction and even cancer (Hossain et al., 2010; Koutros et al., 2015). Health risk assessment is one of the tools that function as preliminary study to categorise a pesticide as a risk or not before proceeding to more invasive toxicity studies. However, there were lack of studies on dermal health risk of pesticides especially for those that are frequently used in paddy cultivation.

Figure 1.1: The PPE practice of some of the paddy farmers in Kampung Sawah Sempadan

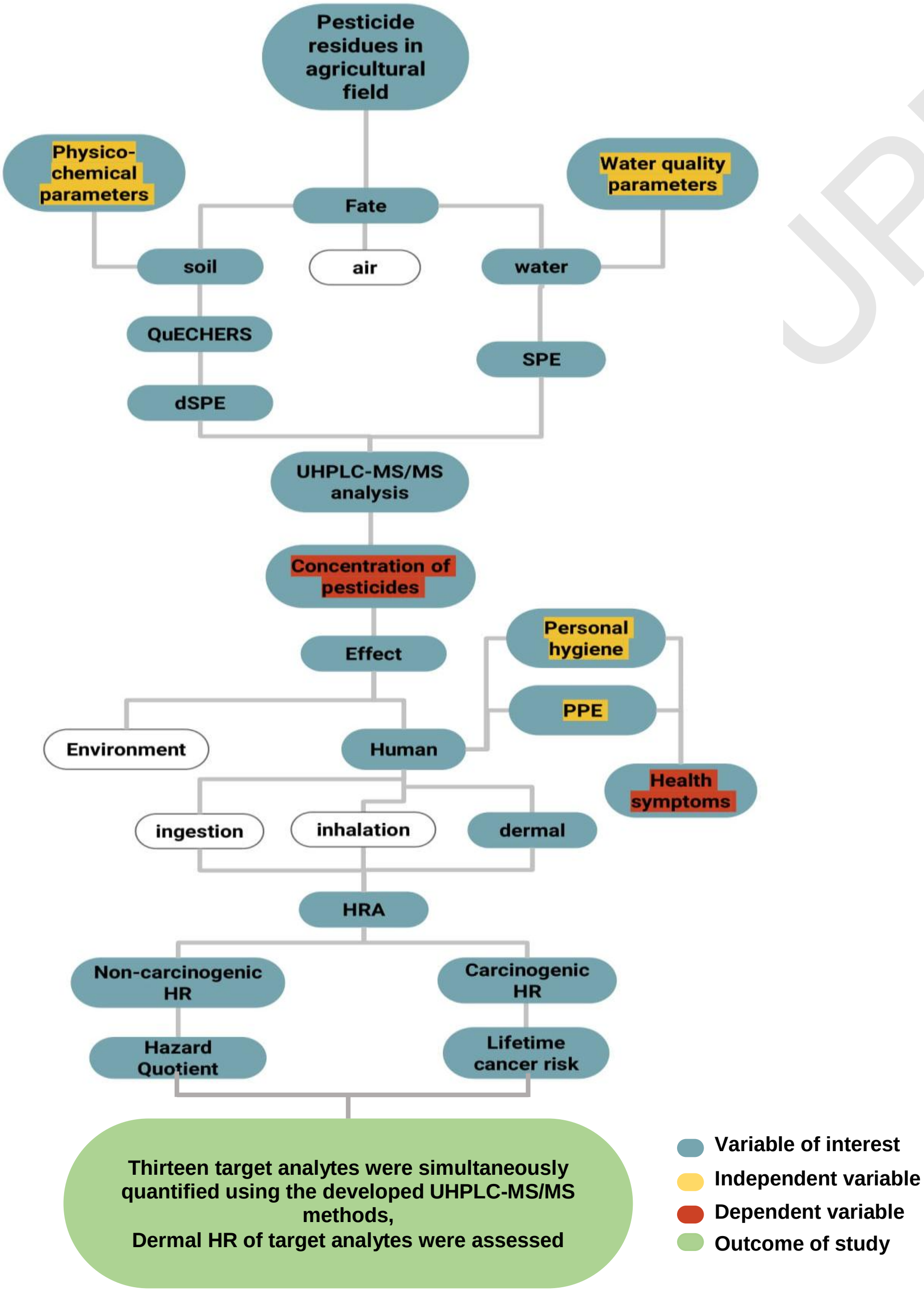
1.3 Research Justification

The widespread use of pesticides indicates that they are very important in increasing the quality and the product of the crops by providing competitive assistance against weeds and also guarding the crops from harmful action of the pests (Delcour et al., 2014). However, despite having many benefits, pesticides are some of the most juvenile, environmentally stable, and mobile substances. Their ability to easily bio accumulate in human body makes them very detrimental when exposed (Fenik et al., 2011). In Malaysia, there is no legislation in the permissible limit of pesticides in environmental matrices. This permits the pesticides handlers to unseeingly use pesticides in order to produce high quality crops that are free from pests, without realising the effects they pose to the environment, and consequently to human health. Thus, regular monitoring of the pesticides in environmental samples is required. The number of research conducted on pesticide occurrence in environment are limited compared to other matrices such as food commodity (Chen et al., 2011; Kujawski et al., 2014; Pelit et al., 2015; Sinha et al., 2012; Sivaperumal et al., 2015; Timofeeva et al., 2017;

Wu et al., 2015). The available literatures on environmental matrices focus on limited class of pesticides such as organophosphates and organochlorines (Hassan et al., 2010; Nodeh et al., 2017; Saraji et al., 2016). These studies are important to fulfil the requirement of regulating pesticide usage and limit its exposure to human and the environment as they reported on the current profile of pesticides residues. The residues reflect the pesticide usage in the environmental matrices. Nevertheless, there were lack of literatures on commonly used pesticides such as anthranilic diamide, triazine and dithiolane pesticides in environmental matrices and their subsequently method of analysis. Thus, there is a need in filling the gap of knowledge by developing two methods for multi-residue analysis of these analytes in soil and water and consequently applied to paddy field to investigate the concentration of pesticides in Malaysian agricultural field.

The occurrence of pesticides in the environmental matrices can be the source of occupational exposure to the farmers or the farm workers. Occupational dermal exposure can lead to various adverse health effects on the farmers which in turn affects their work ability. Historically, efforts to control exposure to pesticides have focused on ingestion than dermal pathway even though dermal exposure is more common and effective route for pesticide exposure among pesticide applicators and farmers (Anderson and Meade, 2014; Gatto et al., 2016). Dermal health risk assessment was carried out in this study to investigate the risk of pesticides in agricultural field to the farmers via dermal route as a preliminary study to a potential future research on pesticides and human health effects on more extensive level. Personal hygiene practice and use of PPE among farmers were investigated to determine the extent of personal protection applied by the farmers.

1.4 Conceptual framework



SPE: solid phase extraction; QuEChERS: Quick, Easy, Cheap, Efficient, Rugged and Safe; dSPE: dispersive solid phase extraction; PPE: personal protective equipment; HR: health risk

1.5 Research objectives

The general objective in this study is to simultaneously quantify common pesticides in paddy soil and water using developed UHPLC-MS/MS methods and to assess their associated dermal health risk to the farmers.
The specific objectives are:

1. To investigate the socio-demographic background, personal hygiene practice, PPE usage and the self-reported health symptoms among the paddy farmers.
2. To optimise two UHPLC-MS/MS methods for simultaneous quantification of 13 commonly used pesticides (azoxystrobin, buprofezin, chlorantraniliprole, difenoconazole, fipronil, imidacloprid, isoprothiolane, pretilachlor, propiconazole, pymetrozine, tebuconazole, tricyclazole, trifloxystrobin), in paddy soil and paddy water samples.
3. To validate two UHPLC-MS/MS methods for simultaneous quantification of 13 commonly used pesticides in paddy soil and paddy water samples.
4. To investigate the concentration of the commonly used pesticides in paddy soil and water samples.
5. To assess the potential non-carcinogenic and carcinogenic health risk of the paddy farmers due to occupational dermal exposure of pesticides in paddy soil and water.

1.6 Research hypothesis

There is a significant relationship between concentration of pesticides in paddy soil and paddy water collected from Kampung Sawah Sempadan, Tanjung Karang, Selangor.

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She has published five journal articles throughout her study including two research articles in quartile 1 and quartile 2 journals in the field of environmental science and chemistry. Passionate about studies on agrochemicals and their health effects, her study focused on pesticide residues and their associated health risk assessment to the farmers.

LIST OF PUBLICATIONS

Hamsan, H., Ho, Y., Zaidon, S. Z., Hashim, Z., Saari, N., & Karami, A. (2017). Occurrence of commonly used pesticides in personal air samples and their associated health risk among paddy farmers. *Science of The Total Environment*, *603-604*, 381-389. doi: 10.1016/j.scitotenv.2017.06.

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Other publication:

Aziema, N., Samsuddin, A., Zaidon, S. Z., & Ho, Y. Bin. (2016). Determination of Lead in Candies and their Packaging Sold in Malaysia and its Potential Health Risk to Children. Asia Pacific Environmental and Occupational Health Journal, 2(2), 24–30.

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