



UNIVERSITI PUTRA MALAYSIA

***OCCURRENCE OF PESTICIDES IN TENGI RIVER AND PESTICIDES
REMOVAL EFFICIENCY IN SUNGAI SIREH DRINKING WATER
TREATMENT PLANT AND THE HEALTH RISK TO CONSUMERS***

NURULIZANI BINTI ELFIKRIE

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FPSK4 2017 55**

ACKNOWLEDGEMENTS

I am grateful to a number of people who helped me to conduct this research and supported me during the study. I am appreciating my supervisor Dr. Ho Yu Bin for her kindness, guidance and advices from the beginning until the end of my project. Apart from that, I would like to express my sincere thanks to all lecturers and stuffs of Department of Environmental and Occupational Health, Universiti Putra Malaysia who had contributed directly in making this study success. I also would like to thank the Salak Tinggi Veterinary Public Health Laboratory, Department of Veterinary Services, Malaysia for the use of their UHPLC-MS/MS. My deepest appreciation also goes to the respondents of Tanjung Karang for their participation and cooperation to make this study possible and successful. Several of my friends, especially my team mates who helped me in completing this study and gave me motivation to complete my research. Finally, I am grateful to my parent who has given me non-conditional support until I finished my study.



ABSTRACT

OCCURRENCE OF PESTICIDES IN TENGI RIVER AND PESTICIDES REMOVAL EFFICIENCY IN SUNGAI SIREH DRINKING WATER TREATMENT PLANT AND THE HEALTH RISK TO CONSUMERS

NURULIZANI BINTI ELFIKRIE

Introduction: Tanjung Karang is the third largest paddy farming area in Malaysia. The population in Tanjung Karang were exposed to pesticide contaminated drinking water via daily ingestion of treated water from Sungai Sireh drinking water treatment plant. This may cause adverse health effects to the water consumer. **Objective:** To determine the occurrence pesticides in Tengi River and pesticides removal efficiency in Sungai Sireh drinking treatment plant and the health risk to consumers. **Methodology:** The study was conducted in Tanjung Karang. 10 water samples from Tengi River and 6 water samples from Sungai Sireh drinking water treatment plant were collected. The in-situ water quality parameters such as temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and turbidity were measured. Before injected to the Ultra-High Performance Liquid Chromatography Tandem Mass Spectrometry (UHPLC-MS/MS), the water samples were extracted using solid phase extraction (SPE). 510 respondents were interviewed using questionnaires to obtain information for non-carcinogenic and carcinogenic health risk assessments. **Results and Discussion:** Propiconazole showed the highest mean concentration (4493.1 ng/L) and pymetrozine showed the lowest mean concentration (1.3 ng/L) in Tengi River. The pesticides removal efficiency in Sungai Sireh drinking water treatment plant was 77% (imidacloprid), 90% (tebuconazole) and 86% (trifloxystrobin and buprofezin), respectively. The Hazard Quotient (HQ) for all selected pesticides were less than 1. **Conclusion:** Pesticides was detected in the Tengi River and Sungai Sireh drinking water treatment plant. Removal of efficiency of pesticides in Sungai Sireh drinking water treatment plant need to be improved as some of the pesticides were not completely removed. HI and HQ indicates the respondents were unlikely to be affected by adverse non-cancer effect for consuming the treated water from the Sungai Sireh drinking water treatment plant.

Keywords: Pesticides, river water, agriculture, in-situ water quality parameters, health risk assessments

ABSTRAK

KEJADIAN RACUN MAKHLUK PEROSAK DALAM SUNGAI TENGI DAN KECEKAPAN PENYINGKIRAN RACUN MAKHLUK PEROSAK DALAM LOJI RAWATAN AIR SUNGAI SIREH DAN RISIKO KESIHATAN TERHADAP PENGGUNA

NURULIZANI BINTI ELFIKRIE

Pengenalan: Tanjung Karang merupakan kawasan penanaman padi yang ketiga terbesar di Malaysia. Penduduk di Tanjung Karang terdedah kepada air minuman yang tercemar dengan racun perosak melalui pengambilan harian air terawat dari loji rawatan air Sungai Sireh. Ini boleh menyebabkan kesan buruk kepada kesihatan pengguna air. **Objektif:** Untuk mengenal pasti kejadian racun perosak di Sungai Tengi dan kecekapan penyingkiran racun makhluk perosak di dalam loji rawatan air Sungai Sireh dan risikonya kepada pengguna. **Metodologi:** Kajian ini telah dijalankan di Tanjung Karang. 10 sampel air dari Sungai Tengi dan 6 sampel air dari loji rawatan air Sungai Sireh. Parameter in-situ seperti suhu, pH, konduktiviti, oksigen terlarut dan kekeruhan telah dikur. Sampel air diekstrak menggunakan pengekstrakan fasa pepejal (SPE) sebelum disuntik ke dalam *Ultra-High Performance Liquid Chromatography Tandem Mass Spectrometry* (UHPLC-MS/MS). 510 responden telah ditemubual dengan menggunakan soal selidik untuk mendapatkan maklumat bagi penilaian risiko kesihatan karsinogen dan bukan karsinogen. **Keputusan dan Perbincangan:** Propiconazole menunjukkan kepekatan yang paling tinggi (4493.1 ng/L) dan pymetrozine menunjukkan kepekatan yang paling rendah (1.3 ng/L) dalam Sungai Tengi. Kecekapan penyingkiran racun perosak dalam loji rawatan air minuman Sungai Sireh adalah 77% (imidacloprid), 90% (tebuconazole) dan 86% (trifloxystrobin dan buprofezin). *Hazard Quotient* (HQ) untuk semua racun perosak yang terpilih kurang daripada 1. **Kesimpulan:** Racun perosak dikesan di loji rawatan air minuman Sungai Sireh dan sungai Tengi. Kecekapan penyingkiran racun perosak di dalam loji rawatan air minuman Sungai Sireh perlu diperbaiki kerana beberapa racun perosak tidak dapat disingkarkan sepenuhnya. *Hazard Quotient* (HQ) dan *Hazard Index* (HI) menunjukkan responden tidak terjejas oleh kesan buruk kerana meminum air yang dirawat dari loji rawatan air Sungai Sireh.

Kata kunci: Racun perosak, air sungai, pertanian, parameter in-situ kualiti air, penilaian risiko kesihatan

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LIST OF ABBREVIATIONS

ADD	Average Daily Dose
AT	Average Time
BW	Body Weight
DO	Dissolved Oxygen
DOE	Department of Environment
DWTP	Drinking Water Treatment Plant
EC	Electrical Conductivity
ED	Exposure Duration
EF	Exposure Frequency
EPA	Environmental Protection Agency
HCL	Hydrochloric Acid
HI	Hazard Index
HQ	Hazard Quotient
IR	Ingestion Rate
IS	Internal Standard
LCR	Lifetime Cancer Risk
MOH	Ministry of Health
POP	Persistent Organic Pollutant
RfD	Reference Dose
RRF	Relative Response Factors
SF	Slope Factor
SPSS	Statistical Package for the Social Sciences
UHPLC-MS/MS	Ultra-High Performance Liquid Chromatography Tandem Mass Spectrometry

USEPA **United State Environmental Protection Agency**
WHO **World Health Organization**



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CHAPTER 1

INTRODUCTION

1.1 Background

According to Environmental Protection Agency (EPA) (2016), pesticides is any substance or mixture intended for destroying, preventing, repelling or mitigating any pest that harmful to cultivated plants or animals. It is also has been used as a plant regulator, defoliant or desiccant and also a nitrogen stabilizer. Using of pesticides is highly in agriculture field and there is a lot of pesticides have been used by the farmers such as herbicides, insecticides, fungicides, fumigants, nematicides, rodenticides and plant growth regulators.

Pesticides are important in agriculture field as the problems of agriculture pest have been increasing from time to time. However, the use of pesticides is not only giving benefit but also caused many problems including human health. The previous study has reported that most of the agricultural pesticides have detrimental effects on human health. It can be immediate and long-term effect. The health effect is including rashes, headaches, nausea, vomiting, disorientation, shock, respiratory failure, coma and also death. Not only that, pesticides can effect in the form of cancer, neurologic and reproductive problems (Arcury, Quandt, & Russell, 2002).

Exposure of pesticide can be in many ways and varying dosage (Jeyaratnam, 1990). Pesticide exposure can be via ingestion, dermal and inhalation where in term of population, exposure of pesticides seems often via ingestion. This is might due to the contamination of environment which then lead to the accidentally ingest the pesticide. For example, the contaminated water or river can affect the aquaculture life such as fish which being ingest by human thus give a health effect due to pesticide poisoning.

In Malaysia, after palm oil and rubber, paddy is the third most planted crop (Department of Agriculture, 2014). Tanjung Karang in Kuala Selangor is one of the famous rice granary area which is the fourth largest area of rice cultivation land in Malaysia (Rasit et al., 2016). The source of water supply are from Tenggi River that not only supply for paddy farming but also the main supply for drinking water to the residents in Tanjung Karang. However, the use of pesticides in the agricultural activity may affect the river and drinking water quality and subsequently cause harmful effect to the consumers.

In Malaysia, Pesticides Act 1974 has been gazetted regarding the use of pesticides. This act is to control the chemicals in pesticides and their use where the active substance in the pesticide has to undergo assessment on environmental and health evaluation.

1.2 Problem Statement

Pesticides have been used widely not only for vector control but also in agricultural activities. However, the use of pesticides can impact not only vector and other pest but also able to harm human health. According to Arora, Mukherjee and Trivedi (2008), the use of pesticides able to affect the quality of environmental resources including surface water. Pesticide which is used in agricultural activities might flow to river and increase concentration of pesticide in water.

Anasco, Koyama and Uno (2010) reported the pesticide residues in coastal water in southern Japan which affected by rice paddy effluent temporarily stored in a wastewater reservoir. In the study, Mefenacet, Fenobucarb and Iprobenfos was detected at concentration of 4.2 $\mu\text{g/L}$, 0.27 $\mu\text{g/L}$ and 0.19 $\mu\text{g/L}$ respectively. Phong et al. (2010) also reported on Mefenacet in a paddy catchment in Kose River, Japan. In the study, Mefenacet was detected at concentration of 9.42 $\mu\text{g/L}$, 9.85 $\mu\text{g/L}$ and 13.10 $\mu\text{g/L}$ in the water samples in Kose River. Whereas in Kedah, Malaysia, Ab Latiff, Abu Bakar and Md Isa (2010) had reported on the presence of difenoconazole in surface water surrounding the rice production area at a concentration of 2.2164 ppm.

Sawah Sempadan is one of the paddy farming area in Tanjung Karang, Selangor. In order to maintain the rice production, the farmers used a lot of pesticides including pesticides that has been subsidized by government. Plus, the farmers also used pesticides that bought by their own. As the pesticides were subsidies by government, farmers tend to use a lot of pesticides excessively for their crop. This details

information of target compound such as their name, type, class, CAS number, molecular formula, molecular structure, molecular weight, log K_{ow} and their cancer classification are summarized in Table 1.1.



Table 1.1: Compounds under study (ISO common name, class, type, CAS-No, molecular formula, molecular structure, and molecular weight, Log K_{ow} and cancer classification)

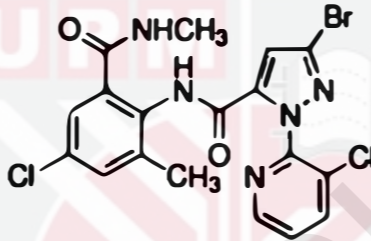
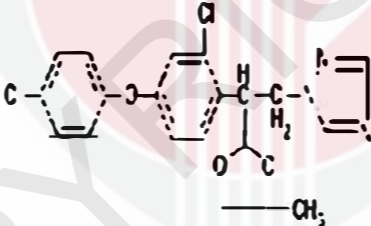
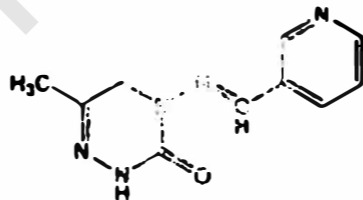
ISO Common Name, Type, Class, CAS Number	Molecular formula	Molecular structure	Molecular weight	Log K _{ow}	Cancer Classification
Chlorantraniliprole, Insecticide ¹ , Anthranilic diamide ¹ , 500008-45-7 ¹	C ₁₈ H ₁₄ BrCl ₂ N ₅ O ₂		483.15 ¹	2.76 ¹	Not Likely to be Carcinogenic to Humans ⁴
Difenoconazole, Fungicides ² , Triazole ² , 119446-68-3 ²	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃		406.3 ²	4.2 @ 25 °C ²	Group C. Possible Human Carcinogen ⁴
Pymetrozine, Insecticide ³ , Pyridine azomethines ³ , 123312-89-0 ³	C ₁₀ H ₁₁ N ₅ O		217.23 ³	-0.18 ³	Likely to Be Carcinogenic to Humans ⁴

Table 1.1: Compounds under study (ISO common name, class, type, CAS-No, molecular formula, molecular structure, and molecular weight, Log K_{ow} and cancer classification) (continued.)

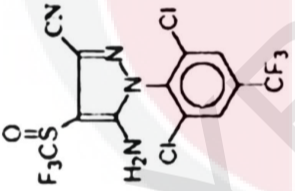
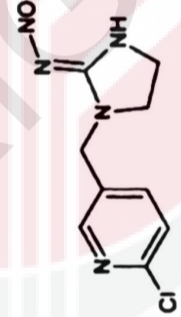
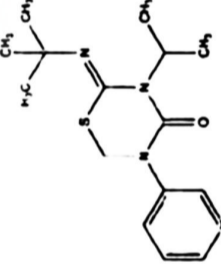
ISO Common Name, Type, Class, CAS Number	Molecular formula	Molecular structure	Molecular weight	Log K _{ow}	Cancer Classification
Fipronil, Insecticide ⁴ , Pyrazole ⁴ , 120068-37-3 ⁴	C ₁₂ H ₄ C ₁₂ F ₆ N ₄ O ₂		437.15 ⁴	4.0 ⁴	Group C. Possible Human Carcinogen ⁴
Imidacloprid, Insecticide ⁴ , Chloronicotinyl nitroguanidine ⁴ , 138261-41-3 ⁴	C ₉ H ₁₀ C ₁ N ₅ O ₂		255.7 ⁴	3.7 @ 25°C ⁴	Group E. Evidence of Non-Carcinogenicity for Humans ⁴
Buprofezin, Insecticide ⁴ , Chitin synthesis inhibitor ⁴ , 69327-76-0 ⁴	C ₁₆ H ₂₃ N ₃ O ₂		305 ⁴	4.3 ⁴	Suggestive Evidence of Carcinogenicity, but Not Sufficient to Assess Human Carcinogenic Potential ⁴

Table 1.1: Compounds under study (ISO common name, class, type, CAS-No, molecular formula, molecular structure, and molecular weight, Log K_{ow} and cancer classification) (continued.)

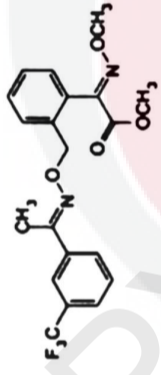
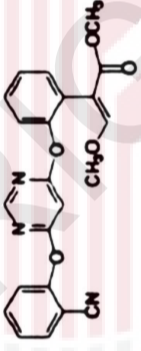
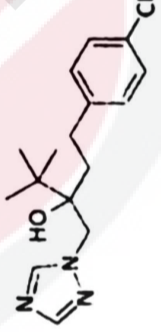
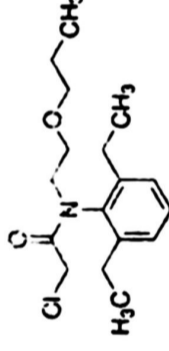
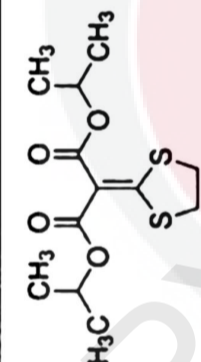
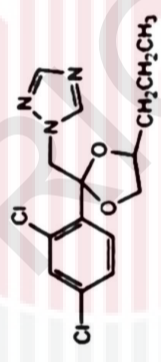
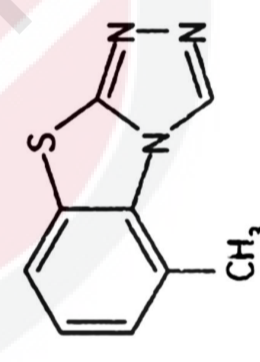
ISO Common Name, Type, Class, CAS Number	Molecular formula	Molecular structure	Molecular weight	Log K _{ow}	Cancer Classification
Trifloxystrobin, Fungicide ⁴ , Beta-methoxyacryl ester ⁴ , 141517-21-7 ⁴	C ₂₀ H ₁₉ F ₃ N ₂ O ₄		408.4 ⁴	4.5 @ 2.5°C ⁴	Not Likely to Be Carcinogenic to Humans ⁴
Azoxystrobin, Fungicide ⁴ , Methoxyacrylate ⁴ , 131860-33-8 ⁴	C ₂₂ H ₁₇ N ₃ O ₅		403.4 ⁴	2.5 @ 20°C ⁴	Not Likely to Be Carcinogenic to Humans ⁴
Tebuconazole, Fungicide ⁴ , Azole ⁴ , 107534-96-3 ⁴	C ₁₆ H ₂₂ C ₁ N ₃ O		307.8 ⁴	3.7 ⁴	Group C. Possible Human Carcinogen ⁴
Pretilachlor, Herbicide ⁴ , Amide ⁴ , 51218-49-6 ⁴	C ₁₇ H ₂₆ C ₁ N ₃ O ₂		311.89 ⁴	4.08 ⁴	NA ⁵

Table 1.1: Compounds under study (ISO common name, class, type, CAS-No, molecular formula, molecular structure, and molecular weight, Log K_{ow} and cancer classification) (continued.)

ISO Common Name, Type, Class, CAS Number	Molecular formula	Molecular structure	Molecular weight	Log K _{ow}	Cancer Classification
Isoprothiolane, Fungicide ⁴ , Phosphorothiolate ⁴ , 50512-35-1 ¹¹	C ₁₂ H ₁₈ O ₄ S ₂		290.4 ⁴	3.3 ⁴	NA ⁵
Propiconazole, Fungicide ⁴ , Triazole ⁴ , 60207-90-1 ⁴	C ₁₅ H ₁₇ N ₃ O ₂		342.23 ⁴	3.72 ⁴	Group C. Possible Human Carcinogen ⁴
Tricyclazole, Fungicide ⁴ , Azole ⁴ , 41814-78-2 ⁴	C ₉ H ₇ N ₃ S		189.24 ⁴	1.4 ⁴	Not Likely to Be Carcinogenic to Humans ⁴

¹USEPA (2008). Pesticide Fact Sheet: Chlorantraniliprole.

²USEPA (1994). Pesticide Fact Sheet Difenoconazole.

³USEPA (2000). Pesticide Fact Sheet: Pymetrozine.

⁴National Center for Biotechnology Information. PubChem Compound Database; CID=3352, <https://pubchem.ncbi.nlm.nih.gov/compound/3352> (accessed May 10, 2017).

⁴USEPA, 2016. Chemicals Evaluated for Carcinogenic Potential (Annual Cancer Report 2016). http://npic.orst.edu/chemicals_evaluated.pdf (accessed April 2017).

⁵Data were not available

The paddy farming area in Sawah Sempadan is near the Tengi River. Thus, the use of pesticides especially in paddy farming in Sawah Sempadan possibly pollute the Tengi River. The river water is used as the main water supply for paddy farming. Besides, it is also the source of drinking water to the population in Tanjung Karang via *Sungai Sireh* drinking water treatment plant (DWTP). Therefore, the pesticides that pollute the Tengi River subsequently may affect the health of Tanjung Karang's population because they consume the water from *Sungai Sireh* drinking water treatment plant.

Exposure to pesticides can be through many routes including water (Kim, Kabir, & Jahan, 2016). According to Damalas and Koutroubus (2016), when pesticides enter to human body, they can be distributed via the bloodstream and may be excreted via urine, skin and exhaled air. Pesticides has been always related with several of diseases such as cancers, leukemia and asthma which these outcome is vulnerable to certain people including children, pregnant women and aging population (Kim et al., 2016). A study in Ethiopia was reported that the pesticides that have been found in drinking water sources may affect the health of consumer although the estimated daily intakes were below than acute reference dose which is safe. However, due to the cumulative effect of pesticides, there may adverse the human health through chronic exposure (Mekonen et al., 2016). The toxicity of pesticides is depending on the dosage and also the type of the pesticides itself.

1.3 Research Justification

Agricultural activities have been arising along with the use of pesticides. Without realised, pesticides can affect not only pest but also environment and human health. To date, there are limited of studies reporting the water contamination due to the pesticides selected in this study. A study by Tanabe and Kawata (2009) reported the daily variation of pesticides in surface water of a small river flowing through paddy area was 1.2 µg/L (isoprothiolane) and 13 µg/L (flutolanil), respectively. Chau et al. (2015) also reported the concentration of isoprothiolane was 2.32 µg/L in drinking water sources in the Mekong Delta, Vietnam.

Plus, in Malaysia, the occurrence of pesticides in drinking water treatment plant is not yet explore. Ang et al. (2015) in Malaysia reported that the traditional conventional drinking water treatment plant was unable to remove pollutants such as pesticides from water resources. Ormad et al. (2008) in Spain reported that the existing conventional treatment in drinking water treatment plant was found to be more efficient by combining with an activated carbon absorption process up to 90% to degrade pesticides. Therefore, it is essential to study the occurrence and distribution of pesticide concentration in Tenggi River and drinking water treatment plant and their associated health risk to provide some baseline information in Malaysia.

Throughout this study, the carcinogenic and non-carcinogenic health risk to the consumers was determined using health risk assessment. Prolonged and repeated

exposure to the pesticide via ingestion of drinking water can give adverse effect to the consumer (Kim, Kabir, & Jahan, 2016).

1.4 Conceptual Framework

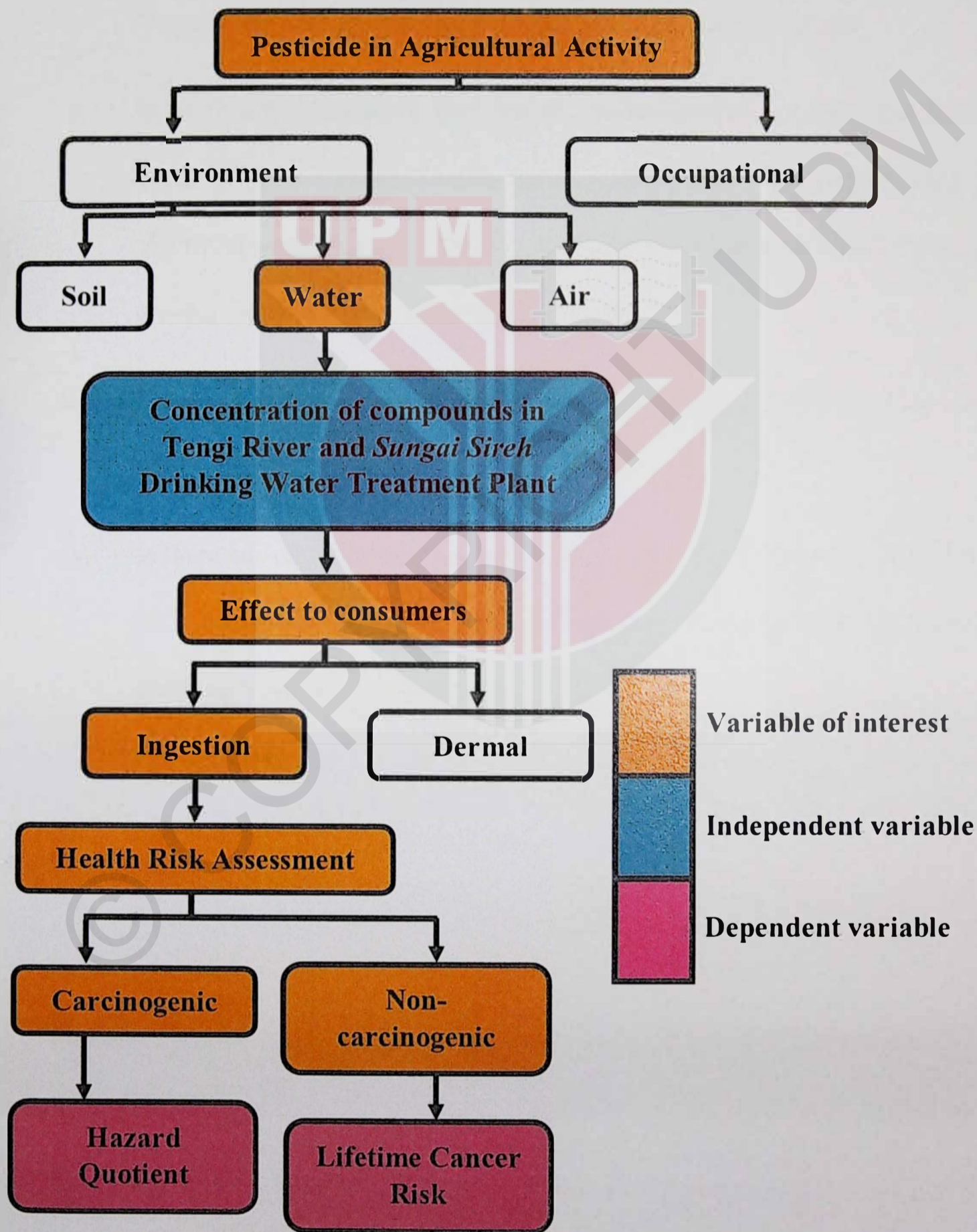


Figure 1.1: Conceptual Framework

1.5 Research Question

Questions arise from this research are as follow:

- i. What is the concentration of pesticide in water samples collected from Tengi River and *Sungai Sireh* drinking water treatment plant?
- ii. Is there any correlation between the concentrations of the pesticides in water samples with the in-situ water quality parameters (temperature, pH electrical conductivity, dissolved oxygen and turbidity) in Tengi River and *Sungai Sireh* drinking water treatment plant?
- iii. What is the pesticides removal efficiency in *Sungai Sireh* drinking water treatment plant?
- iv. Is there any carcinogenic and non-carcinogenic health risk to the population in Tanjung Karang due to the consumption of water from *Sungai Sireh* drinking water treatment plant?

1.6 Hypothesis

There is significant relationship between the concentrations of pesticides in water samples with the in-situ water quality parameters in Tengi River and *Sungai Sireh* drinking water treatment plant.

1.7 Objectives

To determine the occurrence pesticides in Tenggi River and pesticides removal efficiency in Sungai Sireh drinking water treatment plant and the health risk to consumers.

The specific objectives are as follows:

1. To determine the concentration of pesticides in water samples collected from Tenggi River and *Sungai Sireh* drinking water treatment plant.
2. To determine the correlation between the concentrations of pesticides in water samples with the in-situ water quality parameters (temperature, pH electrical conductivity, dissolved oxygen and turbidity) in Tenggi River and *Sungai Sireh* drinking
3. To determine the pesticides removal efficiency in *Sungai Sireh* drinking water treatment plant water treatment plant.
4. To assess the carcinogenic and non-carcinogenic health risk of Tanjung Karang population due to the consumption of water from *Sungai Sireh* drinking water treatment plant.

1.8 Definition of Terms

Pesticide contamination

Pesticide from the agriculture activities may contaminated the river where in this study thirteen targeted compounds of pesticides were selected and were analysed through ultra high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS).

Ultra-High Performance Liquid Chromatography (UHPLC)

The UHPLC-MS/MS was used to analyse pesticide compound in the water samples using electro spray ionization in positive method with optimized operating conditions.

Health Risk Assessment

In this study, the risk assessment through dietary intake was calculated based on the pesticides exposure through water consumption. The non-carcinogenic and carcinogenic effects were assessed using hazard quotient (HQ) and lifetime cancer risk (LCR) to estimate the health risk of those who were exposed to pesticides in contaminated water through ingestion.

CHAPTER 2

LITERATURE REVIEW

2.1 Pesticides

Pesticides have been used to kill pests such as insects, rodents, fungi and weeds. It often used destroy vector of disease including mosquitoes. It has been classified into herbicides, insecticides, fungicides, fumigants, nematocides, rodenticides and plant growth regulators. In agriculture, pesticide usually used to kill the pest that damage crops. The use of pesticides has been growing rapidly. Pesticides not only dispersed in the environment but also to other which cause serious effect and their residues can contaminate soils and water; thus effect health via ingestion (Carvalho, 2006).

There are two types of pesticides which is persistent and non-persistent pesticides. Persistent pesticides such as Organophosphate pesticides are able to remain in human body and environment for such a long period while the non-persistent pesticides may metabolized in the human body or degrade in environment. The use of pesticides may increase the production of food; however, it seems that this can cause more damage to environment and degrade food and water quality (Carvalho, 2006) thus effecting the human health.

The presence of pesticide residues has been reported in many studies. One of the study in Bangladesh revealed that the detected concentrations of cypermethrin, chlorpyrifos and diazoxon residues in paddy field water were 0.695, 0.06 and 0.039 $\mu\text{g/L}$, respectively (Bhattacharjee et al., 2012). The pesticide residues mixed with the Kaligonga River and contaminated the surface water where low level of pesticides residue detected in the river water. Even the concentration of pesticide residues in river water were found below than maximum residue limit value in drinking water (0.1 $\mu\text{g/L}$) yet the health risk of consumption remain unknown.

A preliminary study by Latif, Abu Bakar and Md Isa (2010), reported difenoconazole residues in the network of surface water surrounding the rice production area in Tajar, Kedah. The concentrations of difenoconazole in paddy field and Mengkuang River before the application of pesticides were 0.0118 mg/L and 0.0068 mg/L, respectively. After pesticide application, the concentrations of difenoconazole were increased to 8.7834 mg/L and 0.9583 mg/L, respectively. Chau et al. (2015) surveyed the use of different drinking water sources and their pollution with pesticides in Vietnam. In the study, 7.2% of the concentration of difenoconazole in drinking water sources exceeded 0.1 $\mu\text{g/L}$.

Besides, a study conducted in China by Li et al. (2011a) revealed the concentrations of pymetrozine in water of rice field after two hours , four hours, half day, one day and three days of pymetrozine application was 0.305 mg/L, 0.156 mg/L, 0.105 mg/L, 0.028 mg/L and 0.012 mg/L, respectively. After seven days of

application, the pymetrozine was undetectable in water. However, undetectable concentration may not reflect the water was completely free from pymetrozine.

Zhang, Chai and Wu (2012) in China found the presence of chlorantraniliprole in rice water field at concentration 0.028 mg/L, 0.020 mg/L, 0.004 mg/L, 0.00025 mg/L and 0.0001 mg/L after two hours, eight hours, one, three and seven days after application of pesticides, respectively. Different from pymetrozine, chlorantraniliprole was detected even after 14 days of application.

On the other hand, another study conducted in eggplant farms in Philippines recorded that the chlorantraniliprole was not found in the irrigation water from the farms. Most of the farmers in the eggplant farms used pesticides that has chlorantraniliprole as the active ingredients and also other pesticides; yet, no chlorantraniliprole has been detected in the study. One of the reason provided by the researchers is because chlorantraniliprole is a chemical that has low solubility in water which degraded the pesticide faster. (Lu, 2011).

Pesticides undeniably can cause harm to the environment and also human health via direct and indirect exposure. The presence of the residue is depending on how long the pesticides used and how frequent it was. Plus, the half-life of the pesticides also play important roles on their harmful effect. Even though no concentration of pesticides detected, it does not mean there is no pesticide pollution in the area.

2.2 Tenggi River

In Tanjung Karang, the existing irrigation system comprised of the main conveyance system and distribution canal at the farm level. The main conveyance includes a diversion of Headwork on the Bernam River, Feeder Canal connecting Bernam River to Tenggi River and Main Canal. From Bernam River Headworks, the feeder canal conveys the water to the Tenggi River which runs for 14.5 km through Tanjung Karang Swamp area. Then, the improved Tenggi River runs further 24.5 km to Tenggi River Headworks and Main Canal. From the Main Canal, it runs 3.3 km to the south to irrigate Sawah Sempadan area and 34.6 km to the north to irrigate the remaining area. Overall, the total length of the Main Canal is 37.9 km. The Tenggi River Headworks is used to maintain water in main canal to the required full supply level (Department of Irrigation and Drainage, 2016). The Tenggi River is also the main supply of water for the *Sungai Sireh* drinking water treatment plant which supplies water to Tanjung Karang area.

Figure 2.1 shows that Tenggi River has two tributaries. One is used for paddy farming irrigation and drinking water treatment plant; and another one for fishery activity and for irrigation of remaining paddy water in the farming area. The main canal is used to irrigate to Sawah Sempadan paddy field and after harvest season, the remaining water in the farming area will be discharged to three outlet sluices which connected with Tenggi River. The river water will be supplied once paddy farming season begin via the main inlet sluice. The outlet sluices will opened after the harvest season and in case of heavy rain to adjust water level. The three outlet sluices are used

to discharge irrigation water from paddy farming; discharge irrigation water for paddy farming and permanent crop; and permanent crop only. Opening of these outlet sluices may cause the water contaminated with pesticides as the water is discharged from paddy area and other farming area. In addition, the contamination may occur during the rainy season as the probability of overflow is high. Besides, the condition of the sluice itself is poor as it has been used for a long time.

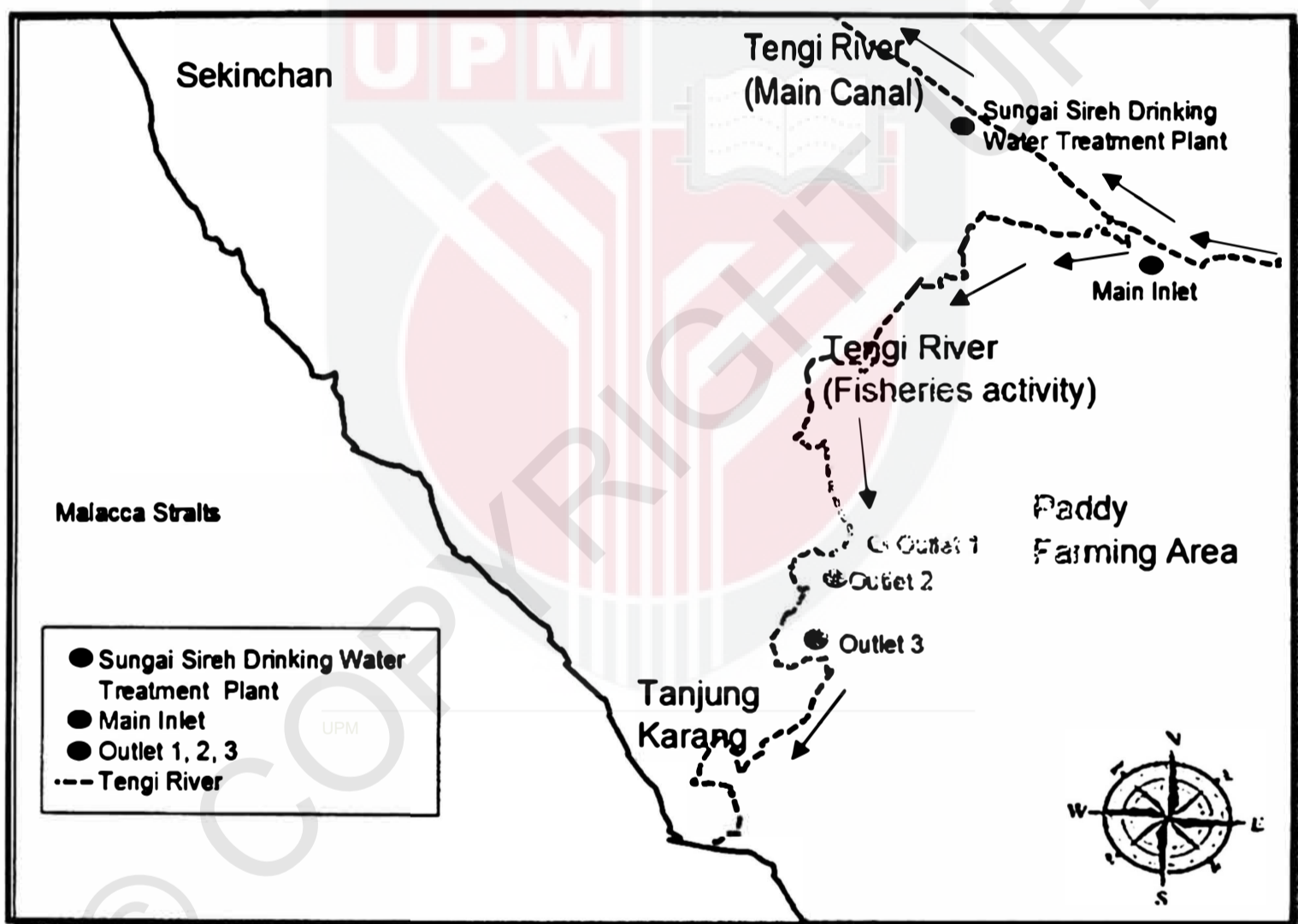


Figure 2.1: Map of Tenggi River and location of *Sungai Sireh* drinking water treatment plant; main inlet sluice; and outlet sluices

2.3 Sungai Sireh Drinking Water Treatment Plant

Sungai Sireh Drinking Water Treatment Plant is located at Parit 1, *Sungai Sireh*, Tanjung Karang as depicted in Figure 2.1. It has been operated since 1988. The water treatment plant supplies six million gallons of clean water to population of Tanjung Karang and Sekinchan. Since 1 April 2007, it has been operated under the Puncak Niaga (M) Sdn. Bhd. The water treatment process are started with the Tenggi River where the river water will flow through intake process for the screening process. In the screening process, two types of filters are involved which are coarse and fine filter. These filters are used to remove and prevent coarse and fine particles from the water.

Then, the water will flow to the raw water tank via through gravity. Aluminium sulphate and Superfloc C591 will be added to the raw water where it form coagulation and produce flocs. When flocculation process occurred, those flocs will coagulate and become denser. Water then being pump to the mixing process via submersible pump. Hydrated lime is added during this process in order to obtain suitable pH which is between 4.80 until 5. To simplify the sedimentation process, polymer AH912 is added before entering the sedimentation tank.

During the sedimentation process the flocs will become a sludge blanket to avoid and trap flocs from going up to the surface. Again, the water will be filtered via gravity to remove any trap particles in the surface followed by chlorination, pH and fluoridation process in filtration gallery. For chlorination, chlorine gas is added to disinfect and to remove bad smell and taste in the clean water until the chlorine level

achieve between 2.00 mg/L to 2.50 mg/L. While the pH is between 6.5 until 9.0. As for fluoridation, Sodium Silicofluoride is added to prevent tooth decay especially for children within the level from 0.40 mg/L to 0.60 mg/L. After that, clean water is stored in the clean water tank and pump house where the clean water will be distributed to the population of Tanjung Karang and Sekinchan.



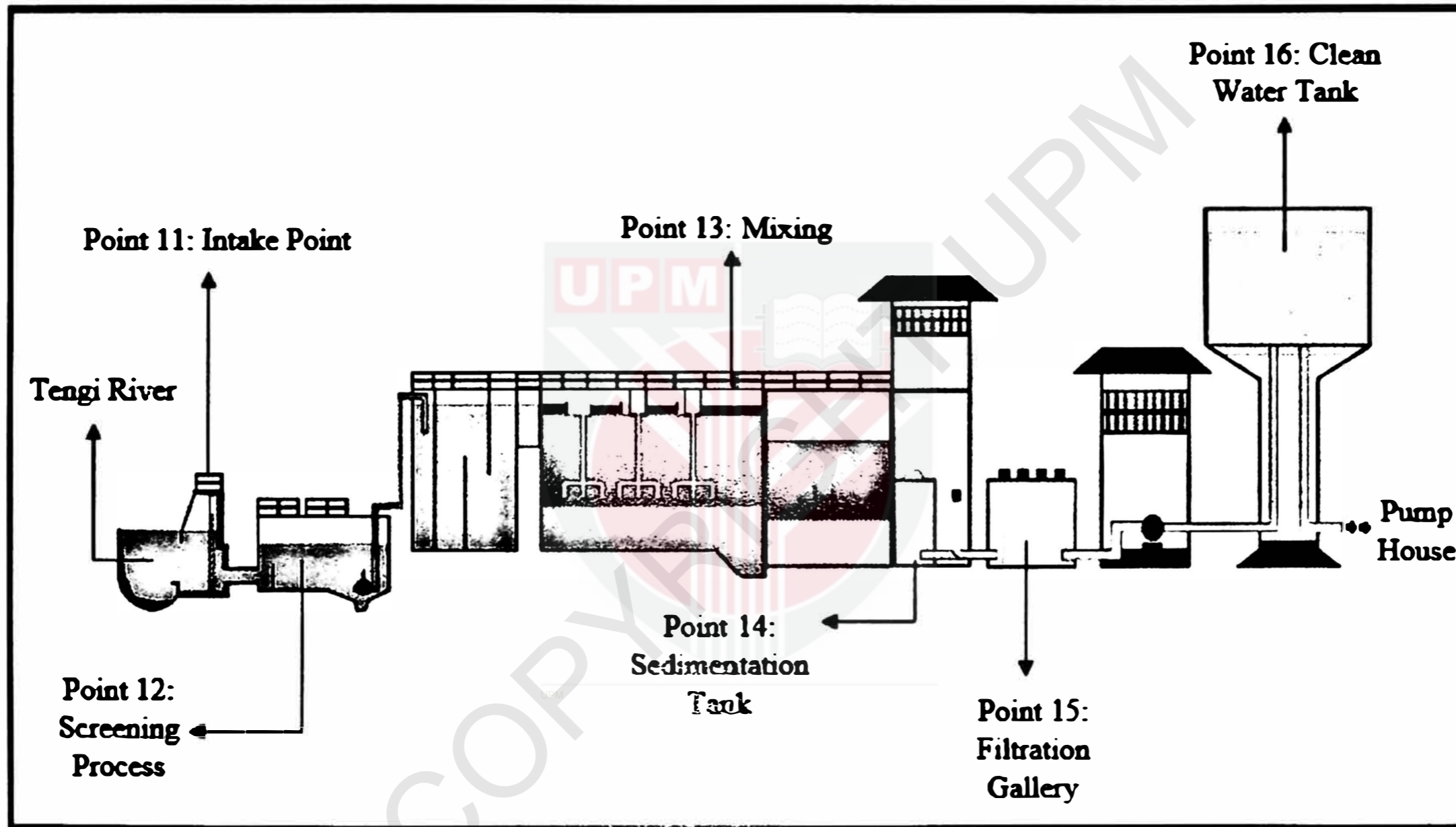


Figure 2.2: Process flow of water treatment plant and the sampling points in *Sungai Sireh* drinking water treatment plant

2.4 Fate of Pesticides

Patterns and distribution of pesticides is varying in the environment. The pesticides that has been applied especially during agriculture activities may affect the whole site not only crop plants but also soil, water, air thus human health. In water, pesticide may leak from the irrigation of plant into the groundwater while in surface water; it can go into aquatic organism like fish and may sediment into other organism (WHO, 1990) which can cause the increasing of pesticides concentration in water and water pollution. Each of the active ingredients in the pesticides have their own half-life. A few studies was done in regard of the half-life of certain active ingredient in pesticides. The half-life was depend on many factors including the physical characteristics of the active ingredients itself.

For example, chlorantraniliprole able to contaminate water via runoff especially after application for a long time. However, by avoiding application within 48 hours of rainfall occur may reduce the runoff. If the insecticide apply directly to water, it may be hazardous to aquatic organisms (EPA, 2008). Chlorantraniliprole has low solubility in water with 1.023 mg/L (EPA, 2008; Lu, 2011). Therefore, the degradation of chlorantraniliprole in water system is classified as moderate fast. This was supported by a kinetic study of chlorantraniliprole in water where after 28 days of application of these insecticides, the concentration of the chlorantraniliprole is non-detected. The degradation rate of chlorantraniliprole in water was the fastest with the half-lives 0.85 days (Zhang et al., 2012).

Difenoconazole, once it has been applied showed an increase concentration in water and immediately decrease after a few days of application. Similar with chlorantraniliprole where the degradation of difenoconazole in water correspond with the rainfall factor. A study on the dissipation of difenoconazole in paddy water in three provinces in China was conducted. These provinces include Guangxi, Hubei and Zhejiang. Throughout the study, it was identified that the half-lives of difenoconazole in water were 2.59, 1.77 and 1.39 days in Guangxi, Hubei and Zhejiang, respectively (Wang, Wu, & Zhang, 2012).

Besides, pymetrozine where it is classified under family of Pyridine Azomethines. It is used as insecticides. The mechanism of pymetrozine in insects may involve neuroregulation to prevent insect from the plant tissues via it stylus (EPA, 2000). From previous study, pymetrozine has a half-lives of 0.7 days which slightly faster than in rice straw and also soil (Li et al., 2011a); but, the presence of pymetrozine should be emphasize as it is classified as “likely” carcinogenic according to EPA. Although, these pesticides has low degradation rate and short half-lives, the existence of these pesticide in the environment should not being taken lightly. Prolonged consumption or contact with contaminated water may cause harmful effect to environmental and also human health.

2.5 Health Effect

Due to the widely used of pesticides to control weeds and insect infestation in agriculture fields, there are increasing concern about environmental risk that associates through exposure of pesticides including residues in drinking water. Pesticides hazard can be ranged from acute which is short-term adverse effect including skin and eye irritation, headaches, dizziness and nausea to chronic impact which is the adverse effect due to prolong or repeated exposure including cancer, respiratory disease and neurotoxicity (Kim et al., 2016).

However, the risk of pesticide exposure is difficult to assess due to the involvement of other factors such as period and level of exposure and type of pesticides. Kim, et al. (2016) also stated that there are certain people who are prone to get the health impact from the pesticides exposure including children, pregnant women and aging population. There is another study which review the chronic health impact from pesticides exposure where in the study, the researcher found that there is significant relationship between exposure to pesticides and developments of cancers, Non-Hodgkin Lymphoma and leukemia (Bassil et al., 2007).

Some of the pesticides has been classified as carcinogenic and some are non-carcinogenic. Based on the scientific evidence of carcinogenicity, chemicals in the environment assessed by Environmental Protection Agency (EPA) are classified in five groups. Group A is human carcinogenic which is when evidence from epidemiologic studies was sufficient; group B is probable human carcinogen which

used when evidence is limited and evidence via animal studies was sufficient; group C is possible human carcinogen where the evidence of carcinogenicity in animals were limited and the human data were absence; and group D is not classifiable as to human carcinogenicity where the evidence of carcinogenicity neither human nor animal were inadequate or no data available (Fallis, 2013).

2.6 Regulation

In 2001, the Stockholm Convention on Persistent Organic Pollutant (POP) was adopted in order to protect human health and environment from chemicals that persist for a long time in the environment and may accumulate in human body; thus, give effect to human and also environment. Pesticides are one of the POP where some of pesticides are persist in environment and also affect human health.

In Malaysia, a law regarding the control of pesticides used was gazetted under Pesticides Act 1974. In this act, it provides the control of importation and manufacturer of pesticides where it is including the provision to register the pesticide used (Act 149 Laws of Malaysia, 2015).

CHAPTER 3

METHODOLOGY

3.1 Chemicals and Standard

Reference standards of chlorantraniliprole (99.5%), difenoconazole (98.7%), and pymetrozine (99.0%) were purchased from Dr. Ehrenstorfer (Germany). The internal standard (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). 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

A cross sectional study was conducted. The concentrations of pesticide were quantified before assessing the health risk of the population in Tanjung Karang.

3.3 Study Location

The study was conducted at Tengi River and *Sungai Sireh* drinking water treatment plant, Tanjung Karang, Selangor as in depicted in Figure 3.1. The water samples was collected on 27 February 2017 from 10.00 a.m to 12.00 p.m. at *Sungai Sireh* drinking water treatment plant and on 5 March 2017 from 10.00 a.m to 2.00 p.m.

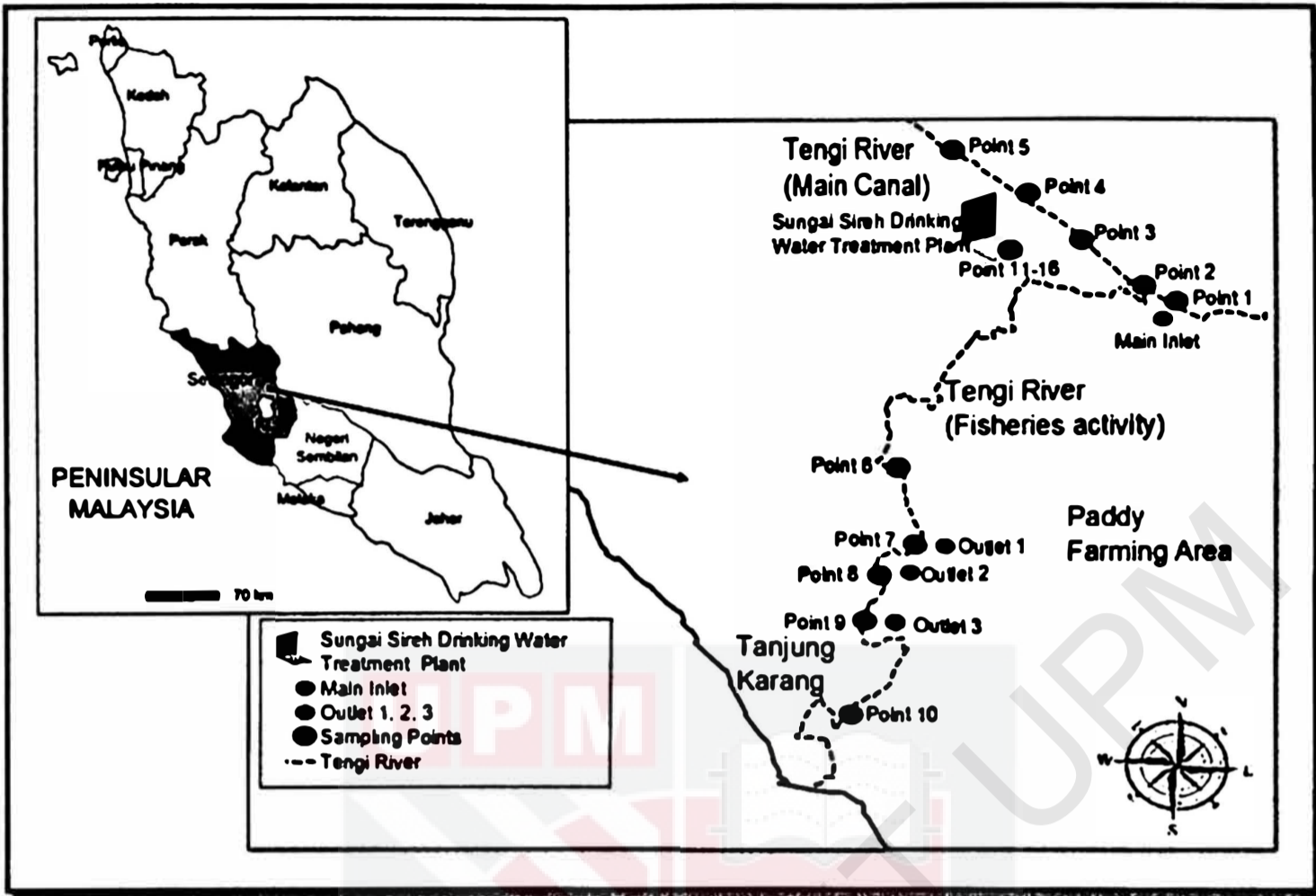


Figure 3.1: Location of Tengi River and *Sungai Sireh* drinking water treatment plant and sampling points

3.4 Sampling Technique

3.4.1 Water Sample

Purposive sampling was applied because the sampling points were based on the activity surrounded by the Tenggi River and also *Sungai Sireh* drinking water treatment plant. The water samples were collected from 10 sampling points in Tenggi River and 6 points from *Sungai Sireh* Drinking Water Treatment Plant as shown in Figure 2.2. For each point, composite samples were collected as shown in Figure 3.2. The composite samples were mixed and kept in 1L amber glass bottles. The bottles then were labelled, wrapped with aluminium foil and stored in ice box at 0-4°C. These steps were repeated triplicate.

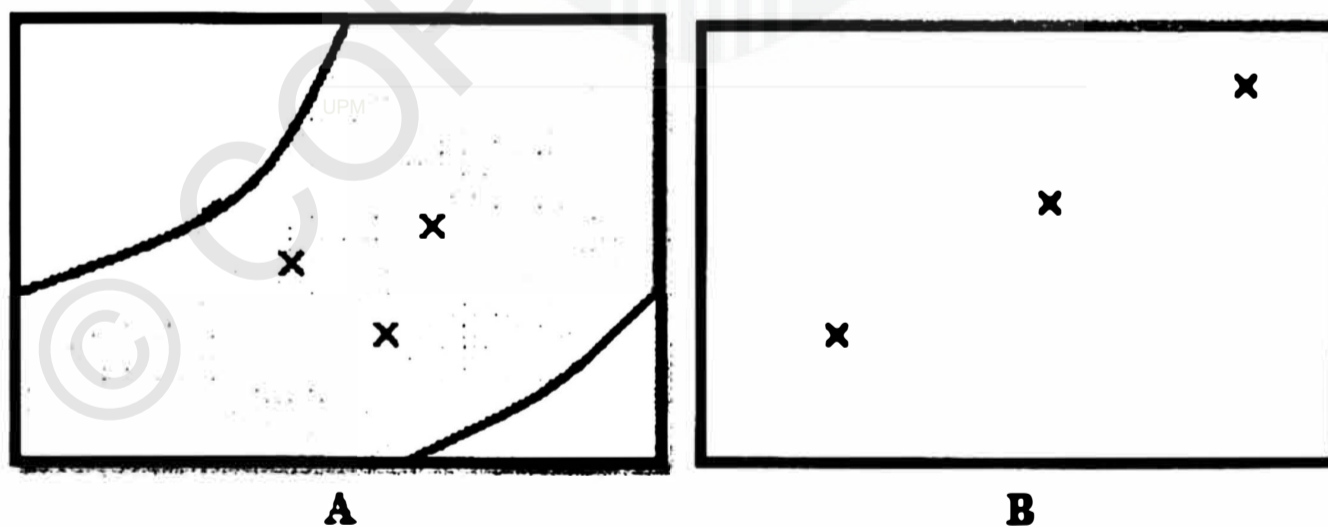


Figure 3.2: Composite sampling for sampling point at Tenggi River (A) and *Sungai Sireh* drinking water treatment plant (B)

3.4.2 Sample Population

Ten percent of total population in Kampung Sawah Sempadan was as respondents as the local data showed that the total population was more than 10,000 people in Tanjung Karang. The total population of Tanjung Karang was 14692 where the data was obtained from the Head of Sub-district (Penghulu) Tanjung Karang. Table 3.1 shows the details of the population in Tanjung Karang.

Table 3.1: Tanjung Karang total population

No.	Village/ Blocks	Total
1	Kampung Sawah Sempadan	4595
2	Kampung Tengi Kanan	2434
3	Kampung Seri Tiram	2808
4	Kampung Tok Adam	4355
	Total	14692

The sample size of respondents for community survey in Kampung Sawah Sempadan was calculated according to Eq. 3.1.

$$\text{Sample size population} = 10\% \times \text{Total population} \quad \text{Eq. 3.1}$$

$$\text{Sample size} = 10\% \times 4595$$

$$\text{Sample size} = 459.5 \text{ respondents}$$

For any missing data during the data collection process, value was rounded up to 10%, which:

$$\text{Sample size} = 459.5 \times 10\%$$

$$\text{Sample size} = 505.45 \approx 510 \text{ respondents}$$

3.5 Selection of Targeted Compound

The target pesticides were selected based on the interview with the farmers. The top thirteen pesticides were selected as the target compounds in this study. Table 3.2 summarized the frequency of the usage of pesticides active ingredients.

Table 3.2: List of pesticides and their frequency of usage of the pesticides active ingredients by farmers (n=152) in Kampung Sawah Sempadan, Tanjung Karang

Pesticides 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	29	24
Azoxystrobin	27	23
Fipronil	22	18
Tricyclazole	21	18
Imidacloprid	17	14
Buprofezin	13	11

3.6 Extraction and Preparation

3.6.1 Water Sample Preservation

In this study, 1 L of water samples was collected from the Tengi River, Tanjung Karang using the amber glass bottles. The sample was then stored in the dark at temperature of 4°C and was preserved and extracted before the analysis.

80 mg of sodium thiosulphate was used to dechlorinate the water samples after the collection. The samples were preserved in order to ensure no significant happened in the composition of water before the analysis. Next, the samples were filtered through 0.45- μm nylon membrane filter to remove particles that may interfere with the analysis. Prior to solid phase extraction, 30- μL of 1 mg/L internal standard was added to 60 mL of the filtered samples and then, the samples were diluted with 60 mL of ultrapure water to decrease their organic matter content, viscosity and minimize matrix effects.

3.6.2 Solid Phase Extraction

This extraction was modified according to De Geronimo et al., (2014). The OASIS HLB 60 mg Solid Phase Extraction cartridges were conditioned with 5 mL of methanol followed by 5 mL of ultrapure water. Then, 120 mL of diluted samples were loaded using a vacuum system. After that, the cartridges were washed with 3 mL of ultrapure water. The cartridges were dried for 20 minutes under vacuum to remove water. Next, the cartridges were eluted with 4 mL of methanol. After that, the extract were evaporated with a gentle flow of nitrogen gas (40°C) and reconstituted with 0.6 mL of methanol-water (50:50, v/v). Analysis were performed by injecting 2 µL of the final extract into the UHPLC-MS/MS system.

3.7 Study Instrument

3.7.1 Questionnaire

The study instrument was questionnaire which was comprised of two sections namely Section A (personal information of the respondents) and section B (water intake). The questionnaires were distributed from 16 January until 19 January 2017.

The information that was obtained then was incorporated into the equation to calculate the ingestion risk by the population around Tenggi River. The details sample of questionnaire can be referred in Appendix 1.

3.7.2 In-Situ Water Quality Parameters

The in-situ water quality parameter were measured including pH of the water, temperature, electrical conductivity, dissolved oxygen and turbidity. These parameters were measured immediately by using the respective instrument.

Turbidity was measured using HACH 2100P Turbidimeter, USA. pH was measured using Milwaukee Portable pH meter, USA while dissolved oxygen using Eutech Instrument Cyberscan DO110 Dissolved Oxygen Portable meter (Thermo Fisher Scientific Inc, USA). Next, electrical conductivity and temperature was

measured using Waterproof Portable Meter (CyberScan Series 600, USA). The water portable meter able to measure the parameters simultaneously at a single time.

All parameters were measured and recorded on site to ensure that the data was accurate and precise at the time of collection. The data was then compared with the standards which are National Water Quality Standard.

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

The UHPLC-MS/MS (Agilent, USA) method conditions are as follows: chromatographic separations was performed on an Eclipse Plus C18 column (2.1mm×50mm I.D., 1.8 μ particle size) (Agilent, USA). The mobile phase was as follows: ultrapure water with 0.1% formic acid and 5mM ammonium formate, and B, methanol 0.1% formic acid and 5mM 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 20min 94%, 6% B. The flow rate will be 0.5ml min⁻¹ and the total runtime was 20 min. The column temperature was set at 40°C and the injection volume was 2.0 μ l. All pesticides were detected using electro spray ionization (ESI) in positive ion mode. The optimised operating conditions were as follows: capillary voltage, 3500 V; gas temperature, 220°C; gas flow, 11L/min and nebulizer was 30 psi. The optimised ESI and MS/MS parameters, comprising of precursor ions, products ions, collision energy (C.E.) and fragmentation voltage are shown in Table 3.3. The optimized ESI and MS/MS parameters were subsequently used for the 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 3.3: MRM conditions

Target Compound	Precursor ion, m/z	Product, m/z (Collision energy, V)	Fragmentation, V
Chlorantraniliprole	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
Azoxystrobin	404.10	372.10 (8), 329.10 (32)	380
Buprofezin	306.20	116.10 (10), 106.10 (28)	380
Fipronil	435.00	330.00 (12), 250 (28)	380
Imidacloprid	256.10	209.00 (13), 209.00 (13)	380
Isoprothiolane	291.10	231.00 (8), 188.80 (20)	380
Pretilachlor	312.17	252.10 (17), 176.10 (29)	380
Propiconazole	342.10	159.00 (32), 69.10 (16)	380
Pymetrozine	218.11	78.00 (52), 51.00 (60)	380
Tebuconazole	308.10	124.90 (47), 70.00 (40)	380
Tricyclazole	190.00	163.10 (24), 163.20 (28)	380
Trifloxystrobin	409.10	186.00 (12), 145.00 (52)	380
Internal standard	Precursor ion, m/z	Product, m/z (Collision energy, V)	Fragmentation, V
Imidacloprid-d4	260.10	212.90 (21)	380

3.7.4 Measurement of Pesticides Removal Efficiency in *Sungai Sireh* Drinking Water Treatment Plant

Average percent removal by each water-treatment process was calculated for pesticides as in Eq. 3.2.

$$= \frac{\text{concentration of pesticide in the raw water} - \text{concentration of pesticide under treatment } X}{\text{Concentration of pesticide in the raw water}} \times 100\% \quad \text{Eq. 3.2}$$

Where,

X = Process in drinking water treatment plant (screening, mixing, sedimentation, filtration, clean water)

3.8 Statistical Analysis

The Statistical Package for the Social Sciences (SPSS) version 22 was used to perform the statistical analysis. Pearson correlation (parametric) or Spearman correlation (non-parametric) was used to determine the correlation between the concentrations of pesticides in water samples with the in-situ water quality parameters.

3.9 Quality Control

3.9.1 Cleaning of Glassware

All glassware were undergo acid wash before used to ensure that they are free of any contaminants based on US EPA method 1694 (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, they were rinsed with methanol again, followed by acetone, and then dichloromethane. After washing, all glassware were going to dry at 60°C and cap with solvet rinsed aluminium foil to prevent any accumulation of dust or other contaminants.

3.9.2 Calibration of UHPLC-MS/MS Performance

The instrument was calibrated with each analytes at a five-point calibration curve. The labelled internal standard (ISs) corresponding to the analytes were added to each calibration point at a concentration of 50 ng/mL to generate relative response factors (RRF). Calibration curve were obtained by injecting the standards of difenoconazole, chlorantranilprole and pymetrozine ranged from 0.1 ng/L to 500 ng/L.

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 et al., 2009). The percentage of recovery were 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 Eq. 3.3 according to Ho et al. (2012), where C_{qc} is the concentration of analytes in the blank sample.

$$\text{Recovery (\%)} = \frac{C_p - C_{qc}}{C_a - C_{qc}} \times 100 \quad \text{Eq. 3.3}$$

3.9.4 Procedural Blank

In order to avoid any interference or contamination, a procedural blank sample was analysed same as the samples from the extraction until the instrumental analysis for every batch of samples. The blank was ultrapure water.

3.10 Health Risk Assessment

The risks for ingestion exposure to pesticide residues in *Sungai Sireh* drinking water treatment plant were quantified. The risk characterizations for carcinogenic and

non-carcinogenic health risk were considered separately by using two different formulae.

3.10.1 Non-Carcinogenic Risk

The non-carcinogenic risk was calculated using hazard quotient (HQ) which was a ratio of exposure dose to the compounds-specific reference dose (RfD). The HQ was used to determine the non-carcinogenic risks when HQ less than one there will be as no significant risk of non-carcinogenic effects whereas HQ more than one there will be significant non-carcinogenic risk as HQ increases. The RfD values for the targeted compound are shown in Table 3.4 based on USEPA (2010; 2011; 2012; 2013).

Table 3.4: The Chronic reference dose for each target compounds

<u>Analytes</u>	<u>cRfD (mg/kg/day)</u>
Azoxystrobin	0.18 ^a
Buprofezin	0.033 ^a
Propiconazole	0.0125 ^a
Tebuconazole	0.029 ^a
Trifloxystrobin	0.05 ^a
Chlorantraniliprole	1.58 ^a
Difenoconazole	0.01 ^a
Imidacloprid	0.057 ^a
Fipronil	0.0002 ^a
Isoprothiolane	N/A
Pretilachlor	N/A
Tricyclazole	N/A

^aIntegrated Risk Information System (IRIS), USEPA

N/A: Data are not available

The ingestion HQ was defined based on USEPA (2004) (Eq. 3.4):

$$HQ = \frac{ADD}{RfD} \quad \text{Eq. 3.4}$$

ADD is defined by Eq. 3.5 based on USEPA (2004):

$$\text{ADD} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad \text{Eq. 3.5}$$

Table 3.5 summarized all value of the parameters stated in the equation above.

Table 3.5: Value of parameters state above

	Parameter	Value	Reference
ADD	Average Daily Dose by ingestion.	Based on calculation	Calculation
RfD	Reference Dose	Refer table 3.4	USEPA 2010
C (mg/L)	Concentration of Pesticides	Based on calculation.	Calculation
IR (L/day)	Ingestion Rate	Age below 6	1.56
		Primary school	1.51
		Secondary school	1.71
		Adults	2.21
		Elderly	2.01
EF (day/years)	Exposure Frequency	365	Questionnaire
ED (years)	Exposure Duration	Age below 6	4.08
		Primary school	9.38
		Secondary school	14.17
		Adults	24.06
		Elderly	27.38
BW (kg)	Body Weight	Age below 6	13.88
		Primary school	27.54
		Secondary school	50.04
		Adults	70.32
		Elderly	68.20

Table 3.5: Value of parameters state above (continued).

	Parameter	Value	Reference
AT (days)	Average Time	Age below 6	1489.2
		Primary school	3423.7
		Secondary school	5172.1
		Adults	8781.9
		Elderly	9993.7

3.10.2 Carcinogenic Risk

Ingestion cancer risk was estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen. The Eq. 3.3 was used to calculate cancer risk associated with ingestion exposure by USEPA (2004):

$$LCR = ADD \times SF \quad \text{Eq. 3.6}$$

Where:

LCR = Lifetime cancer risk

ADD = Average daily dose (mg/kg/day)

SF = Slope factor of the residues (mg/kg/day)

The carcinogenic risk is acceptable if the lifetime cancer risk within 10^{-6} to 10^{-4} (Rodriguez & Proteau, 2005).

CHAPTER 4

RESULT AND DISCUSSION

4.1 Quality Control

The extraction recovery examined for concentration at 100 ng/mL and the result showed that the percentage of recovery were ranged from 37.2 % to 84.5 %.

4.2 Information on Questionnaire

The questionnaire consist of two parts which is Part A (respondent particulars) and Part B (water intake of respondents).

4.2.1 Socio-Demographic Background of Respondents

510 of Tanjung Karang's populations were involved in this study. The socio-demographic information of respondents are summarized in Table 4.1.

Table 4.1: Socio-demographic information of respondents (n=510)

	Variable	Mean (SD)	Minimum	Maximum
Age (years)	6 and below	4.17 (1.64)	2	6
	7 to 12	9.24 (1.2)	7	12
	13 to 18	15.94 (1.73)	13	18
	19 to 60	40.59 (12.44)	19	60
	60 and above	69.77 (5.54)	61	84
Weight (kg)	6 and below	13.88 (4.05)	9	25
	7 to 12	27.54 (8.06)	15	50
	13 to 18	50.04 (13.93)	25	100
	19 to 60	70.32 (15.64)	34	130
	60 and above	68.20 (15.73)	37	140

Table 4.1: Socio-demographic information of respondents (n=510) (continued.)

Variable	Category	Frequency	Percentage
Gender	Male	334	65.5
	Female	176	34.5
Race	Malay	500	98.0
	Chinese	6	1.2
	Indian	4	0.8

The respondents were ranged into five categories which are kindergarten (age 6 and below), primary school (age 7 to 12), secondary school (age 13 to 18), adult (age 19 to 60) and elderly (age 60 and above) with a mean of 4.17, 9.24, 15.94, 40.59 and 69.77 respectively.

Out of 510 respondents, 334 respondents were male and 176 respondents were female and consisted of 500 Malay respondents, 6 Chinese respondents and 4 Indian respondents.

4.2.2 Exposure of Respondents based on Water Intake

In order to assess the health risk, information on the water intake was obtained from the questionnaire. The information of the water intake of respondents were showed in Table 4.2.

Table 4.2: Information of respondent's exposure to pesticides (n=510)

Parameters		Average
Ingestion rate (L/days)	6 and below	1.56
	7 to 12	1.51
	13 to 18	1.71
	19 to 60	2.21
	60 and above	2.01
Exposure frequency (days/ year)	6 and below	365
	7 to 12	365
	13 to 18	365
	19 to 60	365
	60 and above	365
Exposure duration (years)	6 and below	4.08
	7 to 12	9.38
	13 to 18	14.17
	19 to 60	24.06
	60 and above	27.38
Average time (days)	6 and below	1489.20
	7 to 12	3423.70
	13 to 18	5172.05
	19 to 60	8781.90
	60 and above	9993.70

The ingestion rate is the amount of water which contain the contaminant (pesticide compounds) ingested by the respondents for a specific period of time. Exposure frequency is the frequency of exposure in days per year while exposure duration refer to the amount of time the respondent exposed to the pesticides in years. Average time is the exposure duration multiply by 365 days/year.

4.3 Concentration of Pesticides in Water Samples Collected from Tenggi River and Sungai Sireh Drinking Water Treatment Plant and the Removal Efficiency in each Treatment Process

The concentration of pesticides in Tenggi River is tabulated in Table 4.3. Eleven out of thirteen compounds were detected in water samples in Tenggi River.

Among the 13 compounds, the maximum mean concentration was propiconazole (4493.1 ng/L) and the minimum mean concentration was pymetrozine (1.3 ng/L). Multiple pesticides were detected in the water samples due to the cultivation period of paddy in the study location area was different for all paddy plot and the type of pesticides used were also different.

The maximum concentration of propiconazole in this study were higher than in other studies. Battaglin (2011) reported that the maximum concentration of propiconazole in the selected US streams was 1.15 µg/L. However, another study by Kammerbauer and Moncada (1998) reported selected agricultural production systems in the Choluteca River Basin of Honduras showed the highest maximum concentration of propiconazole at 1.5 mg/L with detection rates of 6%.

In this study, point 10 was polluted with most of the pesticides at this point was located after the irrigation of outlet 3. The highest mean concentration in point 10 was pymetrozine (260.81 ng/L) and the lowest mean concentration was azoxystrobin (4.92 ng/L). All outlet sluices released the pesticides from the paddy farming area and also

from other agricultural area such as oil palm plantation. Therefore, most of the pesticides were detected at this point.

From this study, 2 out of 13 pesticides, pesticides were not detected in all river water samples which were fipronil and pretilachlor. According to the farmers, these two pesticides are in the same class will not be used at the same time. Instead of fipronil, farmers preferred imidacloprid. Pretilachlor was not detected as herbicide was applied during the early cultivation phase to kill weeds (Azmi, M., Karim, S.M.R. and Ismail, 2005).

Imdacloprid and tebuconazole were the most frequently detected pesticides in the water samples in Tenggi River. During the sampling, the paddy farming was in middle phase of cultivation. According to the interview with the farmers, insecticides oftenly used at the middle phase of cultivation. Therefore, the use of insecticide such as imidacloprid was higher. Insecticide was frequently detected because the insecticide should be applied at every 15 days interval after the cultivation (Ali et al., 2017). Tebuconazole is fungicide. Based on Battaglin (2011), fungicide are used for protective measure and often applied before infections take place.

Table 4.3: Target compound concentrations in Tenggi River (ng/L) (n=3)

Target compound	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8	Point 9	Point 10
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Pymetrozine	ND	ND	ND	4.8 ± 2.4	2.7 ± 0.6	ND	1.3 ± 0.3	4.6 ± 0.8	7.9 ± 6.0	260.8 ± 284.4
Imidacloprid	19.5 ± 8.9	4.6 ± 2.5	8.5 ± 2.0	9.8 ± 5.7	7.2 ± 4.4	15.3 ± 11.9	20.6 ± 14.2	23.2 ± 5.9	57.7 ± 37.5	38.8 ± 21.4
Tricyclazole	ND	ND	ND	ND	ND	4.44 ± 0.42	ND	8.72 ± 1.13	14.90 ± 1.07	20.92 ± 10.88
Chlorantraniliprole	24.9 ± 6.0	ND	ND	ND	ND	56.9 ± 63.5	ND	ND	19.2 ± 2.8	25.4 ± 16.0
Azoxystrobin	ND	ND	ND	ND	ND	10.9 ± 14.1	ND	ND	ND	4.9 ± 0.5
Isoprothiolane	ND	ND	ND	ND	ND	34.9 ± 60.3	ND	5.1 ± 2.5	16.2 ± 2.3	32.7 ± 18.0
Fipronil	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tebuconazole	17.4 ± 4.5	5.1 ± 1.6	4.0 ± 1.7	6.9 ± 4.6	5.5 ± 4.4	512.1 ± 1496.8	17.7 ± 3.2	23.2 ± 7.4	43.3 ± 8.1	48.5 ± 27.7
Propiconazole	22.5 ± 8.0	28.2 ± 8.3	23.5 ± 7.3	48.9 ± 18.1	23.7 ± 13.0	4493.1 ± 10938.4	ND	17.6 ± 8.0	34.3 ± 9.3	49.1 ± 41.8
Difenoconazole	48.7 ± 12.6	ND	ND	ND	ND	1620.3 ± 4172.8	14.5 ± 3.5	16.8 ± 3.7	52.6 ± 10.5	67.1 ± 50.9
Pretilachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trifloxystrobin	33.3 ± 9.9	ND	ND	ND	ND	607.8 ± 1534.6	9.3 ± 2.7	13.8 ± 3.3	47.7 ± 9.6	62.9 ± 43.0
Buprofezin	42.2 ± 11.3	ND	ND	4.2 ± 2.2	6.8 ± 2.3	729.1 ± 1846.3	15.7 ± 4.0	19.6 ± 3.6	53.7 ± 7.0	64.5 ± 40.1

ND – Not Detected

Table 4.4 illustrates the concentration of pesticides found in *Sungai Sireh* Drinking Water Treatment Plant and the removal efficiency in each treatment process. Nine pesticides were detected in the water samples in *Sungai Sireh* drinking water treatment plant intake point which were pymetrozine, imidacloprid, tricyclazole, chlorantraniliprole, azoxystrobin, tebuconazole, propiconazole, trifloxystrobin and buprofezin. Whereas four pesticides included isoprothiolane, fipronil, difenoconazole and pretilachlor were not detected in the water samples from *Sungai Sireh* drinking water treatment plant intake point.

From this study, the combine water treatment processes were considered effective as it remove or reduce most of the pesticides. The most persistent pesticides were imidacloprid, tebuconazole, trifloxystrobin and buprofezin. This is because these pesticides was detected at clean water with the removal efficiency 77% (imidacloprid), 90% (tebuconazole) and 86% (trifloxystrobin and buprofezin).

The detection frequency and concentration of compounds in the water were highly depending on their relative $\log K_{ow}$ and water solubility (Stackelberg et al., 2007). Imidacloprid ($\log K_{ow}= 3.7$), tebuconazole ($\log K_{ow}=3.7$), trifloxystrobin ($\log K_{ow}=4.5$) and buprofezin ($\log K_{ow} =4.30$) have high $\log K_{ow}$. According to Stackelberg et al. (2007), the occurrence of organic compounds such as pesticides in finished water may indicate that the drinking water is a source of human exposure and evidence of incomplete of degradation or removal of compounds through the existing water treatment process.

Table 4.4: Concentrations of target compounds in *Sungai Sireh* drinking water treatment plant (ng/L) (n=3).

Target compound	Drinking Water Treatment Process										
	Intake point	Screening		Mixing		Sedimentation		Filtration		Clean Water	
	Mean ±SD (ng/L)	Mean ±SD (ng/L)	Efficiency removal (%)	Mean ±SD (ng/L)	Efficiency removal (%)	Mean ±SD (ng/L)	Efficiency removal (%)	Mean ±SD (ng/L)	Efficiency removal (%)	Mean ± SD (ng/L)	Efficiency removal (%)
Pymetrozine	4.2 ± 0.6	3.0 ± 1.4	29	2.8 ± 1.2	33	2.3 ± 1.5	45	2.1 ± 0.1	50	ND	100
Imidacloprid	115.3 ± 15.7	105.4 ± 29.5	9	177.7± 58.5	-54	116.1 ± 23.5	-1	88.7 ± 39.9	23	26.3 ± 11.2	77
Tricyclazole	12.2 ± 2.4	7.2 ± 4.7	41	10.2 ± 1.6	16	6.0 ± 3.7	51	5.4 ± 1.8	56	ND	100
Chlorantraniliprol e	54.7 ± 10.1	31.57 ± 4.5	42	29.0 ± 3.6	47	27.9 ± 5.5	49	25.4 ± 3.0	54	ND	100
Azoxystrobin	17.9 ± 7.3	7.0 ± 1.8	61	7.0 ± 1.1	61	6.7 ± 4.0	63	6.5 ± 2.1	64	ND	100
Isoprothiolane	ND	ND	-	ND	-	ND	-	ND	-	ND	-
Fipronil	ND	ND	-	-ND	-	ND	-	ND	-	ND	-
Tebuconazole	42.3 ± 10.7	24.4 ± 9.2	42	20.8 ± 6.0	51	18.8 ± 3.6	55	14.5 ± 9.2	66	4.2 ± 5.2	90
Propiconazole	265.1 ± 75.4	169.0 ± 28.3	36	161.5± 45.3	39	158.6 ± 25.4	40	115.1 ± 62.5	57	37.7 ± 31.3	86
Difenoconazole	ND	ND	-	ND	-	ND	-	ND	-	ND	-
Pretilachlor	ND	ND	-	ND	-	ND	-	ND	-	ND	-
Trifloxystrobin	52.6 ± 18.5	47.3 ± 7.8	10	45.6 ± 12.6	13	38.5 ± 6.4	27	21.0 ± 2.1	60	ND	100
Buprofezin	392.8 ± 147.6	234.7 ± 20.8	40	272.9± 39.2	31	227.6 ± 47.5	42	191.7 ± 81.5	51	56.6 ± 29.7	86

ND – Not Detected

4.4 In-Situ Water Quality Parameters

During the samples collection, the in-situ water quality parameters such as temperature, pH, electrical conductivity, dissolved oxygen and turbidity were measured at the sampling location. The results are tabulated in Table 4.5 and Table 4.6, respectively.

Table 4.5 In-situ water quality parameters of water samples in Tengi River and comparison with standards

	Temperature (°C)	pH	Electrical conductivity (µS/cm)	Dissolved oxygen (mg/L)	Turbidity (NTU)
Mean	27.80	6.03	171.11	4.80	105.87
SD	0.77	0.47	196.98	1.19	19.44
Minimum	26.10	5.27	33.06	3.08	77.20
Maximum	28.70	6.63	542.90	6.36	129.00
Standards*	Not available	5 - 9	6000	< 3	Not available

*In-situ water quality standard in irrigation water (Class IV) by Department of Environmental (DOE)

Table 4.6 In-situ water quality parameters of water samples in Sungai Sireh DWTP (clean water) and comparison with standards

	Temperature (°C)	pH	Electrical conductivity (µS/cm)	Dissolved oxygen (mg/L)	Turbidity (NTU)
Mean	26.83	7.14	85.46	6.04	0.89
SD	0.38	0.21	0.79	0.20	0.41
Minimum	26.40	6.9	84.56	5.81	0.42
Maximum	27.10	7.29	86.02	6.16	1.16
Standards*	Not available	6.5-9.0	Not available	Not available	5

*Drinking water quality standard by Ministry of Health (MOH)

In-situ water quality parameter is important for evaluating temporal variations of river pollution. This is due to natural or anthropogenic input of point and non-point sources (Ouyang et al., 2006).

The mean temperature of the water samples in Tenggi River and *Sungai Sireh* DWTP was 27.80 and 26.83°C as the sampling was conducted during cloudy and rainy weather of January to February. Therefore, the atmospheric temperature affect the temperature of the water. The mean turbidity of water samples Tenggi River and *Sungai Sireh* DWTP was 105.87 and 0.89 NTU. Low turbidity in *Sungai Sireh* DWTP was due to the water was went through different treatment processes. The turbidity of DWTP was below MOH acceptable range.

pH of the water samples was 6.03 (Tenggi River) and 7.14 (*Sungai Sireh* DWTP). Too high or too low pH can affect the pesticides concentration (Fishel & Ferrell, 2010). These water samples were within the DOE and MOH acceptable range. Electrical conductivity (EC) is a parameter refer to ability of water to conduct an electric current and it occurrence reflect the mineral and salt content of water (The Environmental Protection Agency, 2001). Mean EC of water samples for Tenggi River and *Sungai Sireh* DWTP was 171.11 $\mu\text{S}/\text{cm}$ and 85.46 $\mu\text{S}/\text{cm}$. Both samples were below the DOE limit. Dissolved oxygen (DO) refer to the activity takes place in water (The Environmental Protection Agency, 2001). The DO reading was 4.80mg/L and 6.04 mg/L in Tenggi River and *Sungai Sireh* DWTP. Dissolved oxygen of Tenggi River was exceed the acceptable range.

4.5 Correlation between the Concentration of Pesticides in Water Samples with the In-Situ Water Quality Parameters in Tengi River and *Sungai Sireh* Drinking Water Treatment Plant

By using non-parametric spearman correlation, the correlation of pesticides concentration and in-situ water quality parameters were conducted. Appendix 7 shows the result of the correlation test.

The correlation coefficient (r) is to measure the degree or strength between relationships of two variables. Zero correlation coefficient indicates that no association exist between the variables while the closer the coefficient correlation to ± 1 indicates the stronger the association between the two variables (Taylor, 1990).

According to the Spearman correlation test on pesticides and in-situ water quality parameters, there was no significant correlation between the temperature with other in-situ water quality parameters and pesticides.

However, there was significant positive correlation between (i) electrical conductivity and isoprothiolane and difenoconazole, (ii) dissolved oxygen (DO) and imdacloprid, (iii) imidacloprid and tricyclazole, (iv) imiacloprid and tricyclazole, chlorantraniliprole and azoxystrobin, (v) tricyclazole and isoprothiolane, tebuconazole, trifloxystrobin and buprofezin, (vi) chlorantraniliprole and azoxystrobin, tebuconazole, propiconazole, trifloxystrobin and buprofezin, (vii)

azoxystrobin and propiconazole, trifloxystrobin and buprofezin, (viii) isoprothiolane and tebuconazole, difenoconazole and trifloxystrobin, (ix) tebuconazole and difenoconazole, trifloxystrobin and buprofezin, (x) propiconazole and trifloxystrobin and buprofezin, (xi) difenoconazole and trifloxystrobin, (xii) trifloxystrobin and buprofezin ($p < 0.01$). There was also significant negative correlation between (i) pH and dissolved oxygen (DO), (ii) pH and azoxystrobin and (iii) pH and tebuconazole ($p < 0.01$).

4.6 Health Risk Assessment

Pesticides contamination are important as they may cause harmful effect to the environment and human. Some of the pesticides may accumulate in the body and become more concentrated and cause toxic effect if the concentration reaches high enough level (World Health Organization, 1990).

In terms of risk assessment, focused was on the chronic exposure to the target compounds via ingestion of drinking water from *Sungai Sireh* Drinking Water Treatment Plant. The chronic exposure of 510 respondents of Tanjung Karang populations were calculated based on the information given as summarized in Table 4.2.

The health risk assessment focused on four compounds (imidacloprid, tebuconazole, propiconazole and buprofezin) as these compounds were the only

compounds detected in the last stage of treatment plant which was the clean water. The HQ and HI for non-carcinogenic health risks are summarized in Table 4.7. Among the target compounds, buprofezin had the highest HQ with 3.3×10^{-4} among primary school children and tebuconazole had lowest HQ with 8.0×10^{-6} among primary school children.

All HQ values of these four target compounds were less than 1 which indicate that there is no significant health risk due to ingestion of drinking water via *Sungai Sireh* drinking water treatment plant. Zheng et al. (2016) reported the risk quotient of the river water for human consumption Jiulong River and estuary in South China including imidacloprid, propiconazole, tebuconazole and buprofezin were less than 0.01 which suggesting that the pesticides posed low risk to human health. To date, there is no publication on the non-carcinogenic health risk due to ingestion of pesticides in drinking water. However, Lozowicka (2015) reported the health risk for consuming apples with propiconazole and tebuconazole was 0.15% and 0.04%.

All HI value for this study was less than 1 which indicate that the risk to pesticides related disease was low. Among these four pesticides, kindergarten children recorded the highest HI value which was 5.9×10^{-4} while primary school children showed the lowest HI value with 8.0×10^{-6} . A study by Lozowicka (2015) reported that the HI for children and toddlers have the highest exposure. This is because children consume more per kg bodyweight compared to adult. Lifetime cancer risk (LCR) for these four pesticides was not calculated because these pesticides were not classified as likely to be carcinogenic.

Table 4.7: Hazard Quotient (HQ) and Hazard Index (HI) values for non-carcinogenic health risk

Compound	Non-carcinogenic health risk									
	Kindergarten (age < 6)		Primary school (age 7 – 12)		Secondary school (age 13 – 18)		Adult (age 19 – 60)		Elder (age > 61)	
	HQ	HI	HQ	HI	HQ	HI	HQ	HI	HQ	HI
Imidacloprid	5.2×10^{-5}		2.5×10^{-5}		1.6×10^{-5}		1.5×10^{-5}		1.4×10^{-5}	
Tebuconazole	1.6×10^{-5}		8.0×10^{-6}		5.0×10^{-6}		4.6×10^{-6}		4.3×10^{-6}	
Propiconazole	3.3×10^{-4}		1.6×10^{-4}		9.9×10^{-5}		9.1×10^{-5}		8.5×10^{-5}	
Buprofezin	1.9×10^{-4}		9.4×10^{-5}		5.9×10^{-5}		5.4×10^{-5}		5.1×10^{-5}	
		5.9×10^{-4}		2.9×10^{-4}		1.8×10^{-4}		1.6×10^{-4}		1.5×10^{-4}

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This study showed that the selected pesticides were detected in Tengi River and *Sungai Sireh* drinking water treatment plant. Most the pesticides detected in *Sungai Sireh* drinking water treatment plant was efficiently remove except for imidacloprid, buprofezin, tebuconazole and propiconazole. The pesticides removal efficiency in *Sungai Sireh* drinking water treatment should be improved to reduce the risk of exposure for the residents in Tanjung Karang and Sekinchan.

The in-situ water quality parameter (temperature, pH, turbidity, electrical conductivity (EC) and dissolved oxygen (DO) in *Sungai Sireh* drinking water treatment plant were within the permissible limit of DOE. However, the dissolved oxygen for in Tengi River was the only parameter that exceeded the permissible range.

Hazard quotient showed that the respondents were unlikely to be effected by adverse non-cancer effect for consuming the drinking water from the drinking water treatment plant. The hazard index were less than one which indicate that the cumulative risk of exposure to the mixture of pesticides was considered as acceptable.

Since there was pesticide contamination, consistent water quality monitoring on pesticides was recommended to conduct in *Sungai Sireh* drinking water treatment plant. Besides, by adding some water treatment processes such as activated carbon can increase the efficiency of the pesticides removal in drinking water treatment plant.

There is limitation in this study. The application of pesticides were different depending on the paddy farming season which varied the concentration of pesticides in the environment. Thus, it was difficult to estimate the pesticides trend of usage in the study area.

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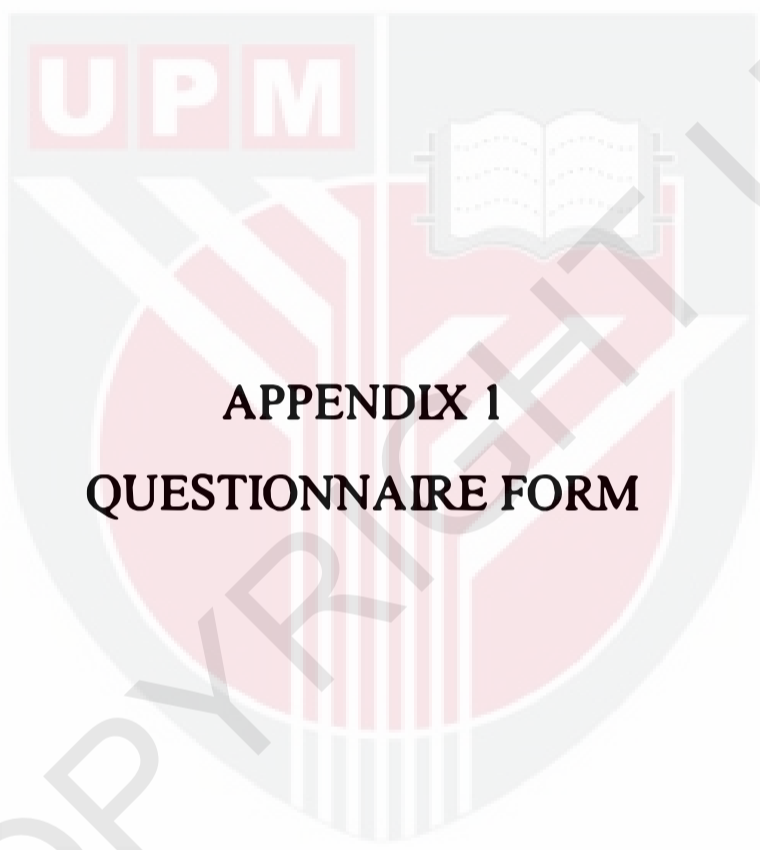
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APPENDIX 1
QUESTIONNAIRE FORM

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**JABATAN KESIHATAN PERSEKITARAN DAN PEKERJAAN
FAKULTI PERUBATAN DAN SAINS KESIHATAN
UNIVERSITI PUTRA MALAYSIA**

Kajian soal selidik:

**KEJADIAN DAN PENGAGIHAN RACUN DALAM SUNGAI TENGI DAN LOJI
RAWATAN AIR MINUMAN SUNGAI SIREH DAN RISIKO KESIHATAN DI
KALANGAN PENDUDUK BERDEKATAN SUNGAI TENGI.**

ARAHAN SOALAN:

1. Borang soal-selidik ini mengandungi **Dua (2)** bahagian iaitu:
Bahagian A: Maklumat responden
Bahagian B: Soalan berkaitan pengambilan air minum
2. Anda diminta menjawab semua soalan yang ada dalam buku soalan ini.

PART A: RESPONDENT PARTICULARS

PART A: MAKLUMAT RESPONDEN

1. Age / Umur: Year / Tahun

2. Gender / Jantina :

Male / *Lelaki*

Female / *Perempuan*

3. Race:

Malay / *Melayu*

Chinese / *Cina*

Indian / *India*

Others / *Lain-lain*:

4. Weight / *Berat*: kg

5. Height / *Tinggi*: m

6. Do you smoking / *Adakah anda merokok?*

Yes / *Ya*

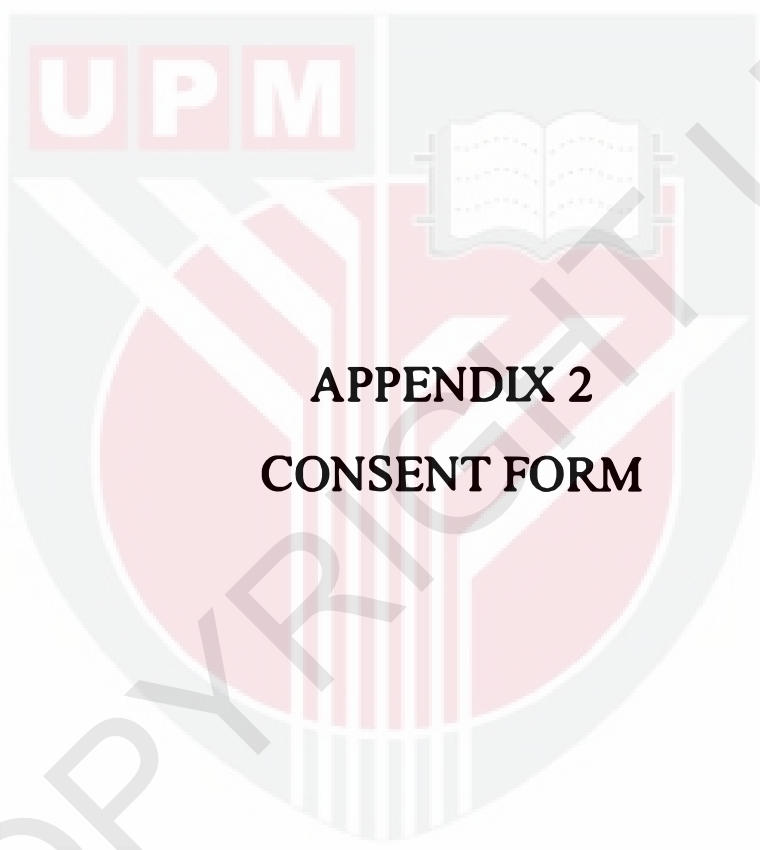
No / *Tidak*

7. Occupation / *Pekerjaan*:

PART B: WATER INTAKE / PART B: PENGAMBILAN AIR

1. How frequent do you consume water in a week / *Berapa kerapkah anda minum air dalam seminggu?*
..... times/week / *kali/minggu*
2. How many liter per day are you consuming water / *Berapakah liter air yang anda minum dalam sehari?*
..... liter/day / *liter/hari*
3. What are the available sources of your drinking water / *Apakah sumber-sumber air minum yang ada bagi anda?*
 - (a) River water / *Air Sungai*
 - (b) Tap water / *Air Paip*
 - (c) Private water well / *Air perigi persendirian*
 - (d) Public water well / *Air perigi awam*
 - (e) Bottled water / *Air botol*
 - (f) Recycled water / *Air yang dikitar semula*
 - (g) Others / *Lain-lain:*
4. What is the main source of your drinking water / *Apakah sumber air minum utama anda?*
 - (a) River water / *Air Sungai*
 - (b) Tap water / *Air Paip*
 - (c) Private water well / *Air perigi persendirian*
 - (d) Public water well / *Air perigi awam*
 - (e) Bottled water / *Air botol*
 - (f) Recycled water / *Air yang dikitar semula*
 - (g) Others / *Lain-lain:*

If your answer is tap water, please answer question 5 / *Jika anda memilih air paip, sila jawab soalan 5.*
5. How long have you consume tap water as the source of drinking water in this area / *Berapa lamakah anda menggunakan air paip sebagai sumber air minum di kawasan ini?*
..... Year / *Tahun*
6. Do you treat your water before consumption / *Adakah anda merawat air anda sebelum penggunaan anda?*
 - (a) Yes / *Ya*
 - (b) No / *Tidak*
7. If yes, how do you treat your water / *Jika ya, bagaimanakah anda merawat air anda?*
 - (a) Filter / *Tapis*
 - (b) Boil / *Masak*
 - (c) Others / *Lain-lain:*



APPENDIX 2
CONSENT FORM

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**JAWATANKUASA ETIKA UNIVERSITI UNTUK
PENYELIDIKAN MELIBATKAN MANUSIA (JKEUPM)
UNIVERSITI PUTRA MALAYSIA, 43400 UPM SERDANG,
SELANGOR, MALAYSIA**

BORANG B1: PENERANGAN DAN PERSETUJUAN RESPONDEN

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

1.TAJUK KAJIAN

Kejadian dan pengagihan racun dalam Sungai Tenggi dan loji rawatan air minuman Sungai Sireh dan risiko kesihatan di kalangan penduduk berdekatan Sungai Tenggi.

2. PENGENALAN

Sungai Tenggi merupakan sumber air minuman utama di Tanjung Karang. Ia juga digunakan untuk pengairan ke sawah padi. Namun, penggunaan racun perosak yang meningkat di dalam sektor pertanian terutama sawah padi boleh memberi kesan kepada Sungai Tenggi dan seterusnya memberi kesan kesihatan kepada penduduk sekitar Tanjung Karang.

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 MENYERTAI KAJIAN INI?

Kanak-kanak kerana had umur yang diperlukan dalam kajian ini ialah 18 hingga 59 tahun.

5. APAKAH FAEDAH MENYERTAI KAJIAN INI?

a) KEPADA ANDA SEBAGAI PESERTA?

Responden yang menyertai kajian ini dapat mengetahui maklumat risiko pendedahan peribadi masing-masing kepada racun perosak dan kesan pendedahan ini kepada kesihatan, samaada membawa masalah kesihatan seperti masalah pernafasan atau kanser.

b) KEPADA PENYELIDIK?

Penyelidik akan dapat mengumpul maklumat mengenai kehadiran racun perosak dalam air di kawasan Sungai Tenggi dan loji pembersihan air minum Sungai Sireh dan seterusnya mengkaji kesan kehadiran racun perosak dalam air ini kepada kesihatan populasi yang terdedah kepada air 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 :

0199996451

**NURULIZANI BINTI ELFIKRIE
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

UPM

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

Research title Occurrence And Distribution Of Pesticide In Tenggi River And Sungai Sirih Drinking Water Treatment Plant And The Health Risk Associated Among Population Nearest Tenggi River

Study Site Selangor

JKEUPM Ref No. FPSK(EXP16-OSH)U055

Researcher Nurulizani Binti Elfikrie

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 (English) Version 1 dated 18/10/2016
3. Respondent Information Sheet & Consent (Malay) Version 1 dated 18/10/2016
4. Proposal (English), Version 2 dated 8/12/2016
5. Questionnaire (English), Version 1 dated 18/10/2016
6. Questionnaire (Malay), Version 1 dated 18/10/2016
7. Curriculum Vitae of:
 - a. Dr. Ho Yu Bin

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

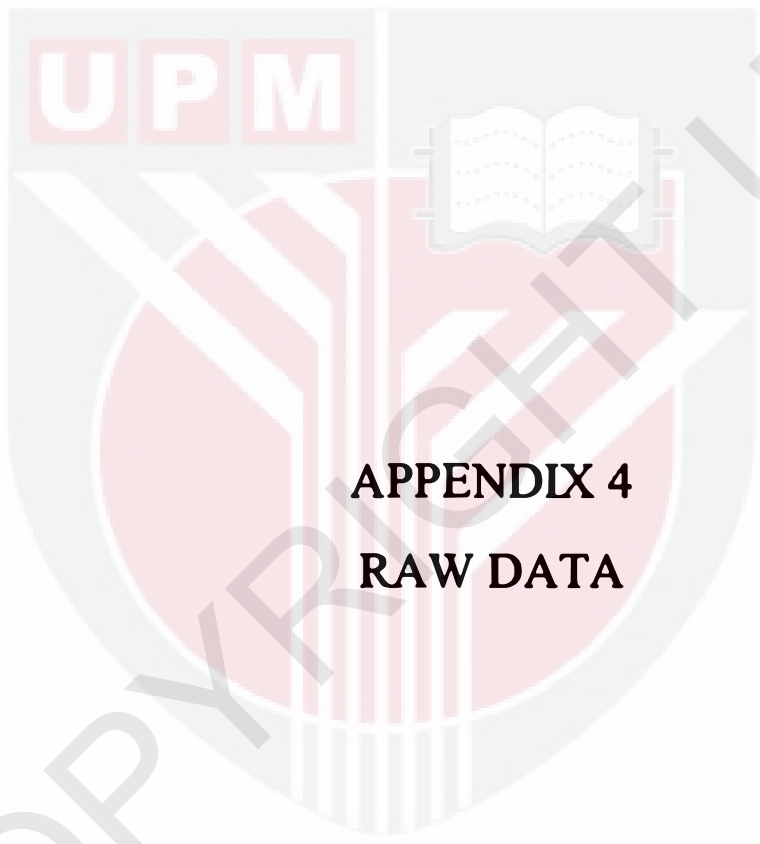
Decision by JKEUPM:

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

Please note that the approval is valid until 23 December 2017

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: In-situ Water Quality Parameter (Sungai Sireh Drinking Water Treatment Plant)

Point		Weather	In-situ Water Quality Parameters				
			Temperature (C°)	pH	Electrical Conductivity (µS)	Dissolved Oxygen (mg/L)	Turbidity (NTU)
1	a	Rainy	28.1	5.15	38.50	8.33	245
	b		28.6	5.06	41.62	8.33	249
	c		28.1	4.99	41.69	8.28	251
2	a		25.8	5.64	34.91	8.09	269
	b		26.9	5.39	35.72	8.09	269
	c		27.2	5.14	35.47	8.09	270
3	a		26.6	5.75	50.68	6.04	266
	b		27.0	5.75	50.61	6.47	270
	c		26.8	5.74	50.25	6.08	275
4	a		26.3	5.52	46.51	5.90	3.57
	b		27.1	5.50	45.95	5.91	3.55
	c		27.1	5.50	46.11	5.87	3.64
5	a		25.9	5.62	47.79	5.68	1.72
	b		26.3	5.59	47.57	5.68	1.72
	c		26.5	5.58	47.51	6.07	1.65
6	a		26.4	6.90	86.02	6.16	1.16
	b		27.1	7.24	85.80	5.81	1.1
	c		27.0	7.29	84.56	6.15	0.42

Table 2: In-Situ Water Quality Parameter (Tengi River-Main canal)

Points		GPS	Weather	In-situ Water Quality Parameters				
				Temperature (C°)	pH	Electrical Conductivity (µS)	Dissolved Oxygen (mg/L)	Turbidity (NTU)
1	a	Lat: 3.47996, Long: 101,22282	Cloudy	26.6	6.63	35.55	3.62	115
	b			26.4	6.55	42.90	3.64	117
	c			27.0	6.37	56.71	3.73	115
2	a	Lat: 3.482556, Long: 101.2181		27.1	6.34	35.59	3.08	120
	b			27.3	6.31	35.49	3.08	118
	c			27.3	6.27	39.41	3.74	119
3	a	Lat: 3.491413, Long: 101.208432		26.1	6.57	33.33	4.03	126
	b			26.4	6.53	34.05	3.42	124
	c			26.8	6.51	40.82	3.71	121
4	a	Lat: 3.498062, Long: 101.199126		28.2	6.47	33.06	4.08	128
	b			27.8	6.46	35.31	3.87	129
	c			27.8	6.44	37.28	3.91	128
5	a	Lat: 3.491413, Long: 101.208432	28.5	6.46	35.39	3.99	127	
	b		28.6	6.43	37.57	3.85	128	
	c		28.6	6.42	35.23	3.71	127	

Table 3: In-situ Water Quality Parameter (Tengi River-outlet)

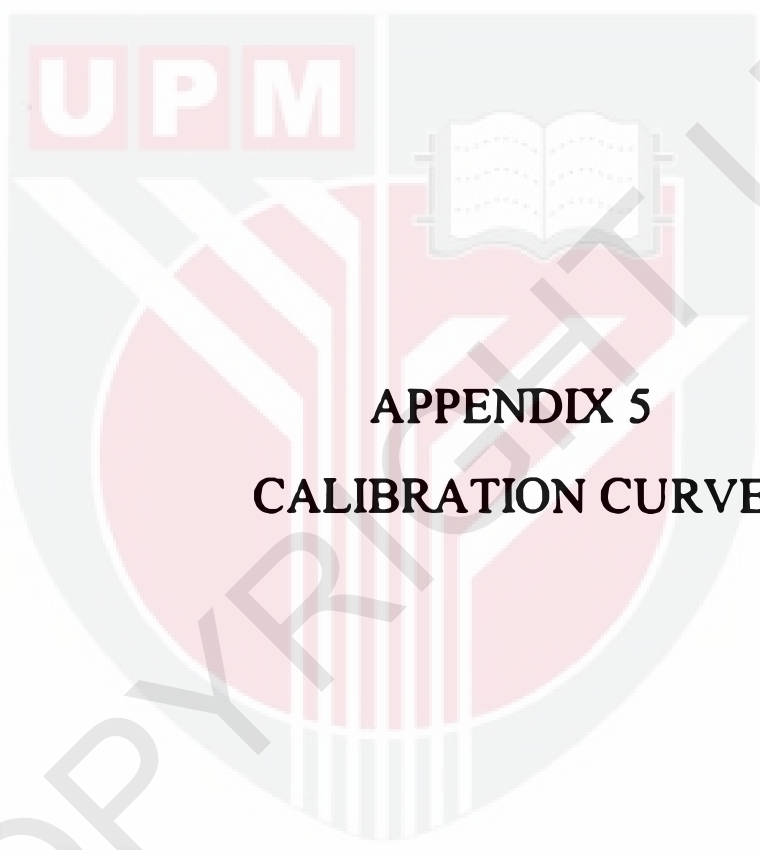
Point			Weather	In-situ Water Quality Parameters				
				Temperature (C°)	pH	Electrical Conductivity (µS)	Dissolved Oxygen (mg/L)	Turbidity (NTU)
B4	A	Lat: 3.422534, Long: 101.174515	Cloudy	27.8	5.27	123.5	6.36	78.3
	B			27.8	5.28	120.0	6.19	77.2
	C			28.6	5.29	123.1	6.16	76.8
K1	A	Lat: 3.45065, Long: 101.181678		28.2	5.96	140.2	6.09	78.1
	B			27.9	5.65	147.2	6.01	78.3
	C			27.9	5.66	141.2	6.00	79.0
K2	A	Lat: 3.439265, Long: 101.184493		27.9	5.69	191.3	6.00	92.4
	B			28.0	5.7	100.3	5.91	95.9
	C			28.2	5.7	217.0	5.96	96.8
K3	A	Lat: 3.435379, Long: 101.177044		28.6	5.79	542.9	5.58	92.2
	B			28.4	5.81	537.7	5.75	92.8
	C			28.4	5.84	534.8	6.02	98.5
AFTER	A	Lat: 3.42253, Long: 101.174515	28.6	5.48	524.7	5.53	99.7	
	B		28.7	5.5	511.0	5.46	98.6	
	C		28.4	5.51	522.0	5.55	98.4	

Table 4: Recovery for each compound

COMPOUND	Recovery (%)
Azoxystrobin	50.25381272
Buprofezin	66.68171799
Chlorantraniliprole	82.13458371
Difenconazole	50.48893226
Fipronil	45.56653607
Imidacloprid	84.46430596
Isoprothiolane	38.82868452
Pretilachlor	68.51815277
Propiconazole	37.20199465
Pymetrozine	62.21433133
Tebuconazole	70.49945725
Tricyclazole	58.52568706
Trifloxystrobin	41.71496507

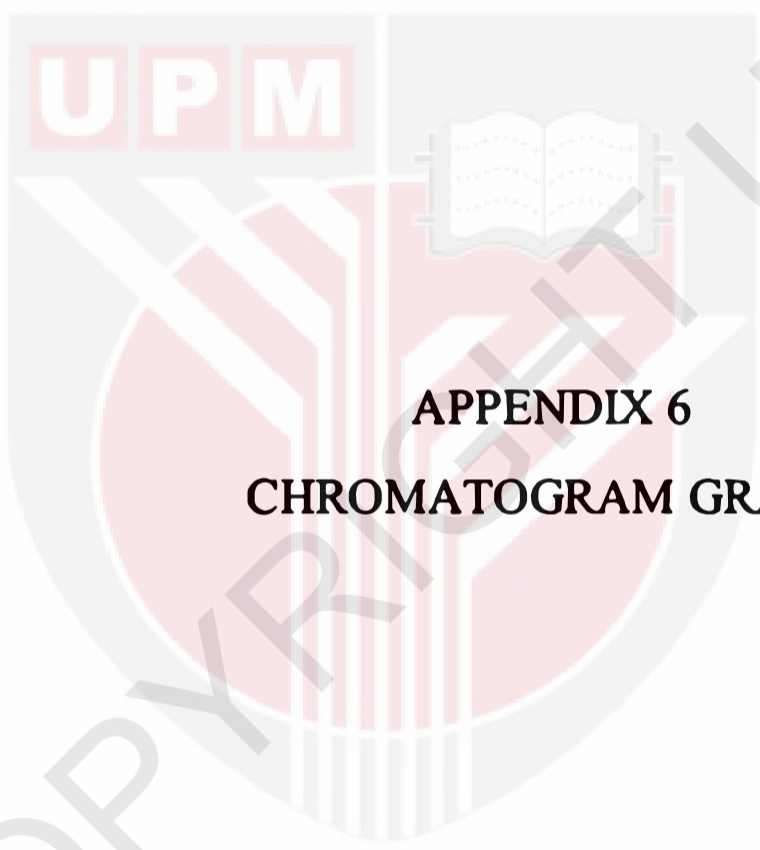
Table 5: Linear range of each compound

COMPOUND	Linear Range (ng/mL)	R2
Azoxystrobin	0.1 - 500	0.9994
Buprofezin	0.1 - 501	0.9998
Chlorantraniliprole	1 - 500	0.999
Difenconazole	1 - 500	0.9988
Fipronil	0.5 - 500	0.9992
Imidacloprid	0.1 - 500	0.9999
Isoprothiolane	0.1 - 501	0.9996
Pretilachlor	1 - 500	0.9997
Propiconazole	0.5 - 500	0.9995
Pymetrozine	0.1 - 500	0.9999
Tebuconazole	0.1 - 500	0.9997
Tricyclazole	0.1 - 500	0.9967
Trifloxystrobin	0.1 - 500	0.9998



APPENDIX 5
CALIBRATION CURVE

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APPENDIX 6
CHROMATOGRAM GRAPH

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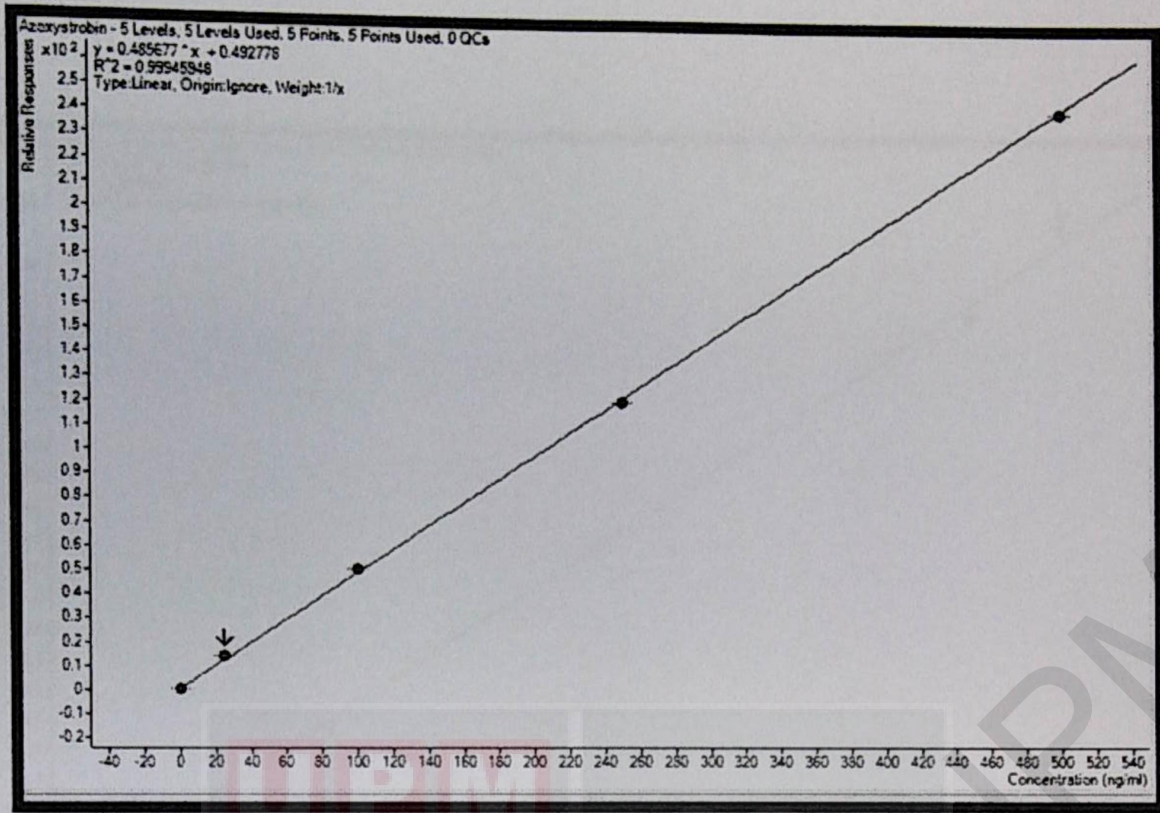


Figure 1: The calibration curve for Azoxystrobin

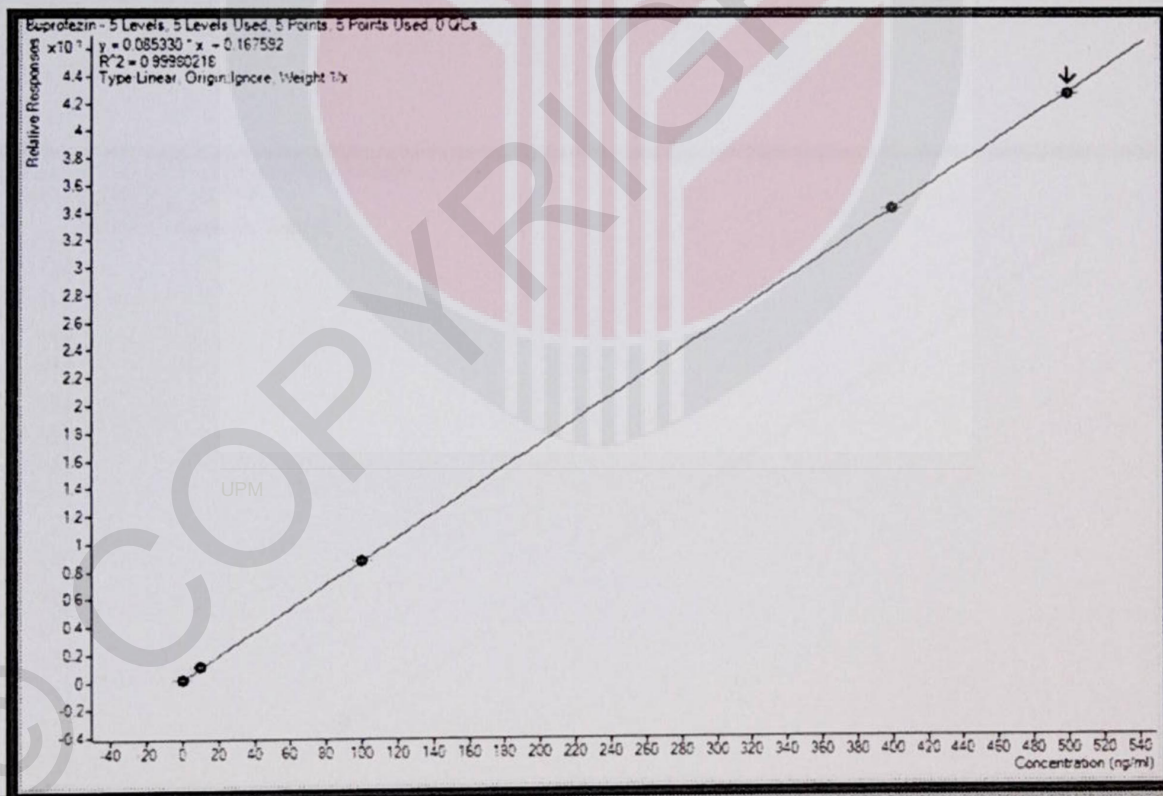


Figure 2: The calibration curve for buprofezin

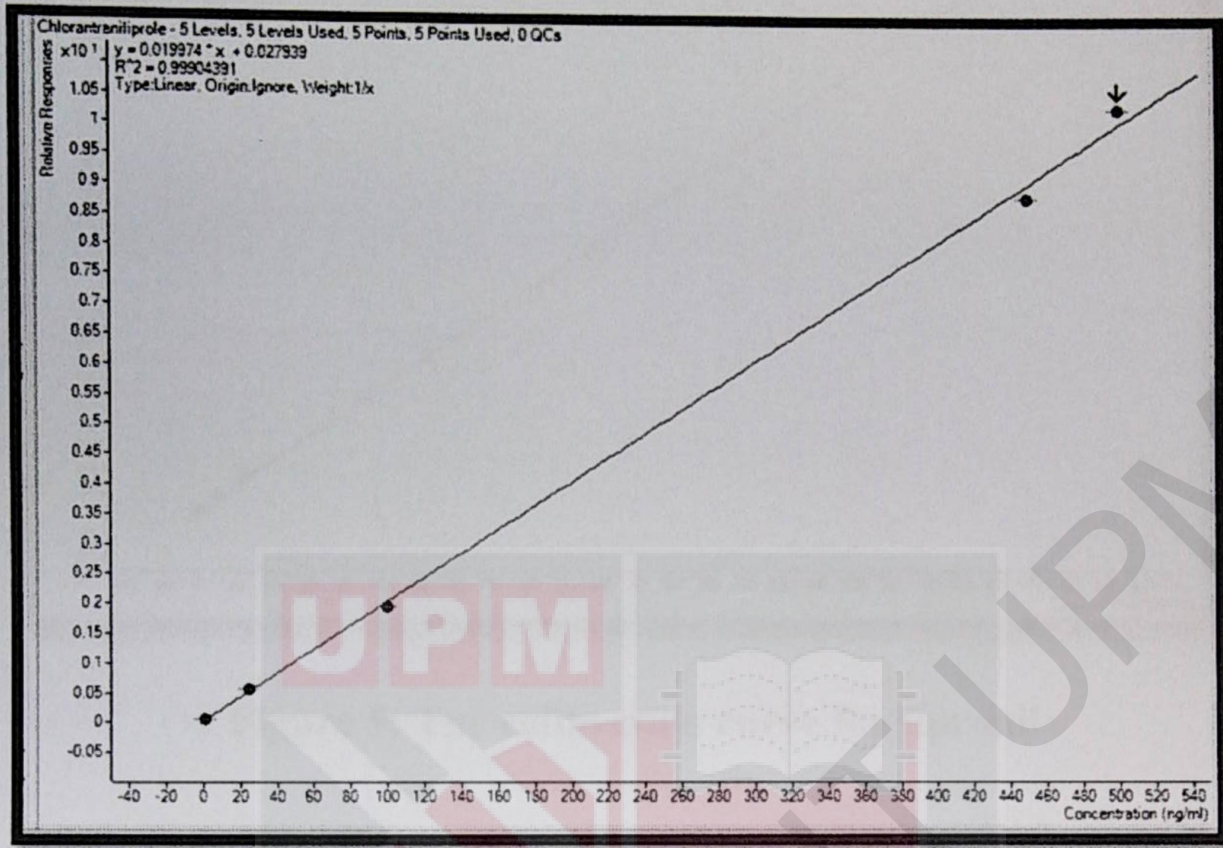


Figure 3: The calibration curve for chlorantraniliprole

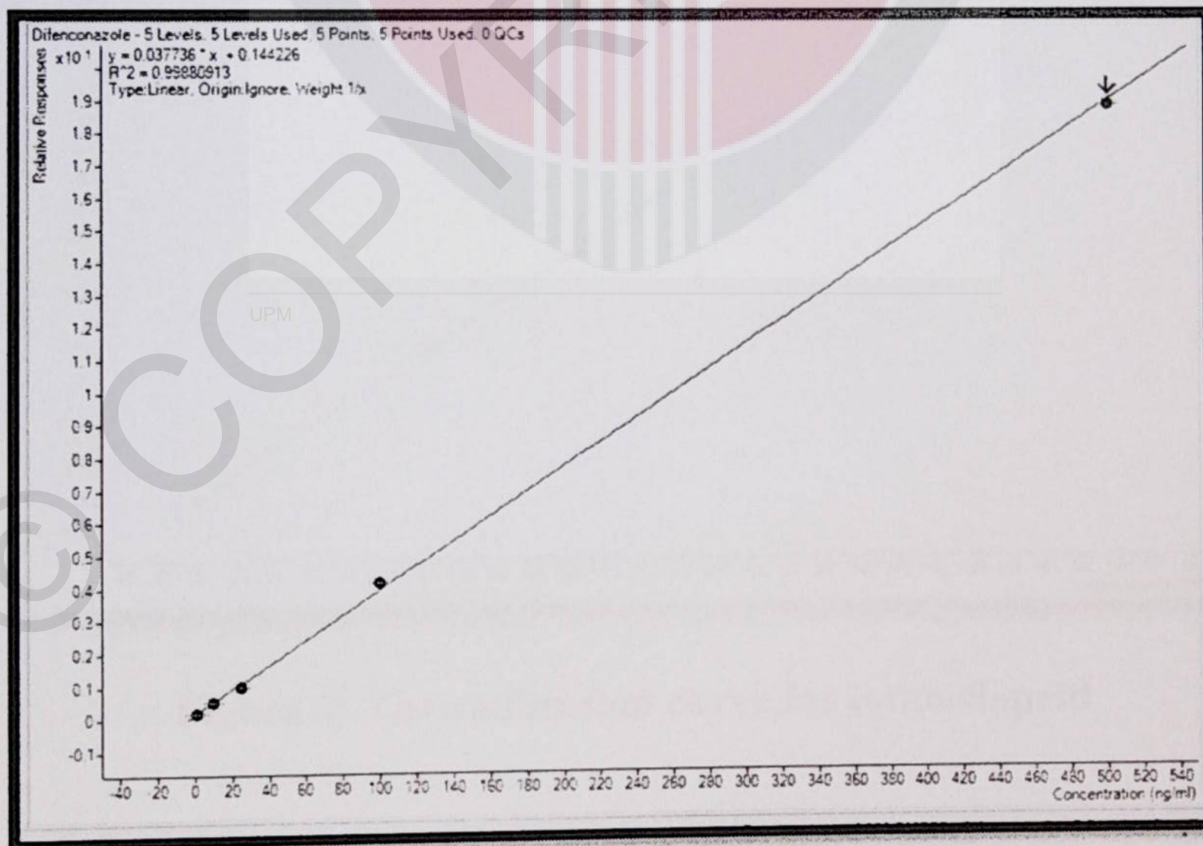


Figure 4: The calibration for difenoconazole

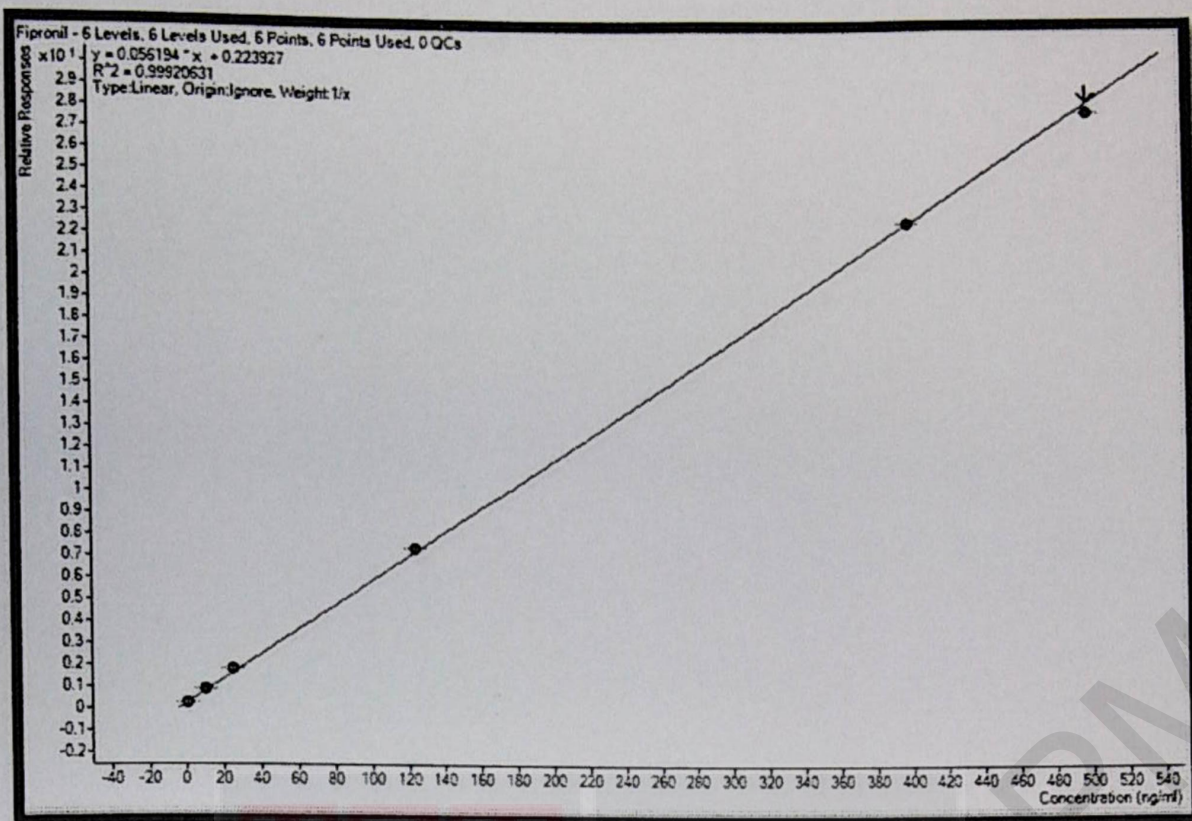


Figure 5: The calibration curve for fipronil

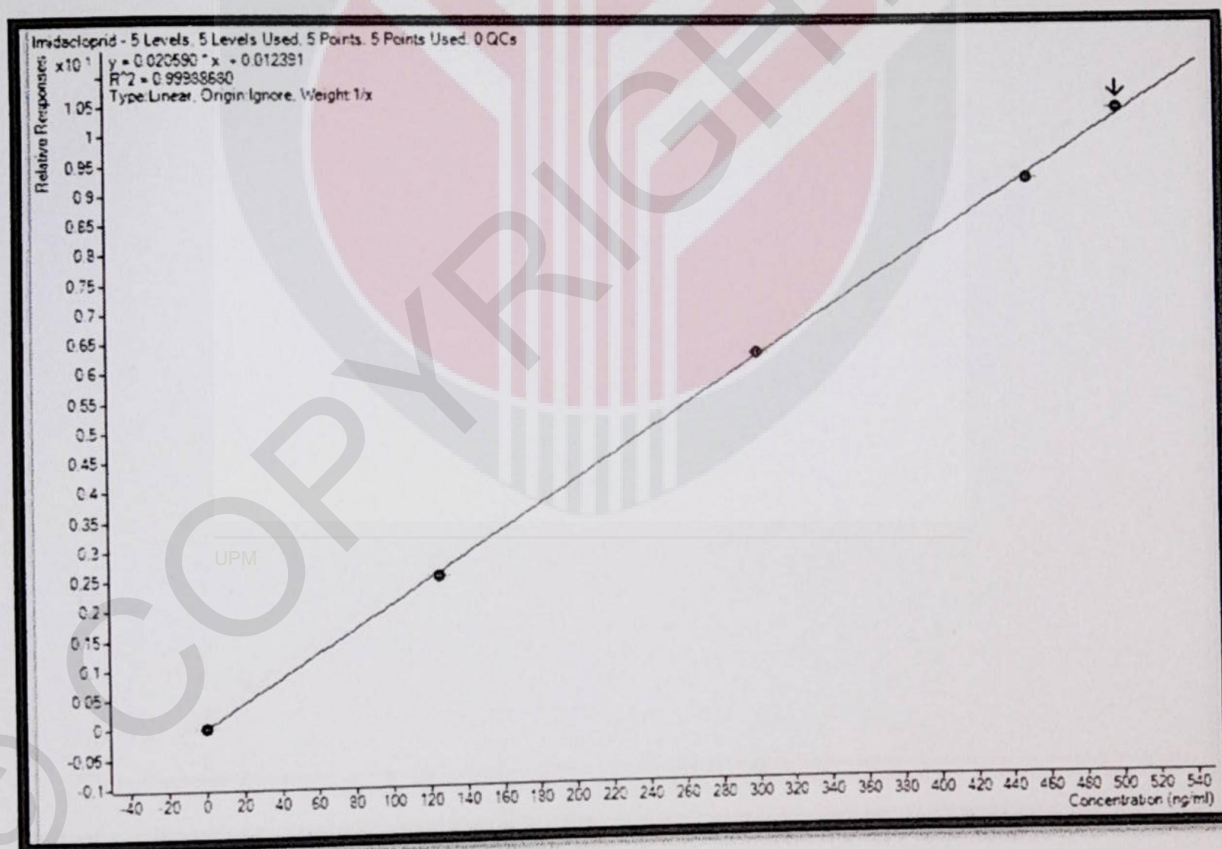


Figure 6: The calibration curve for imidacloprid

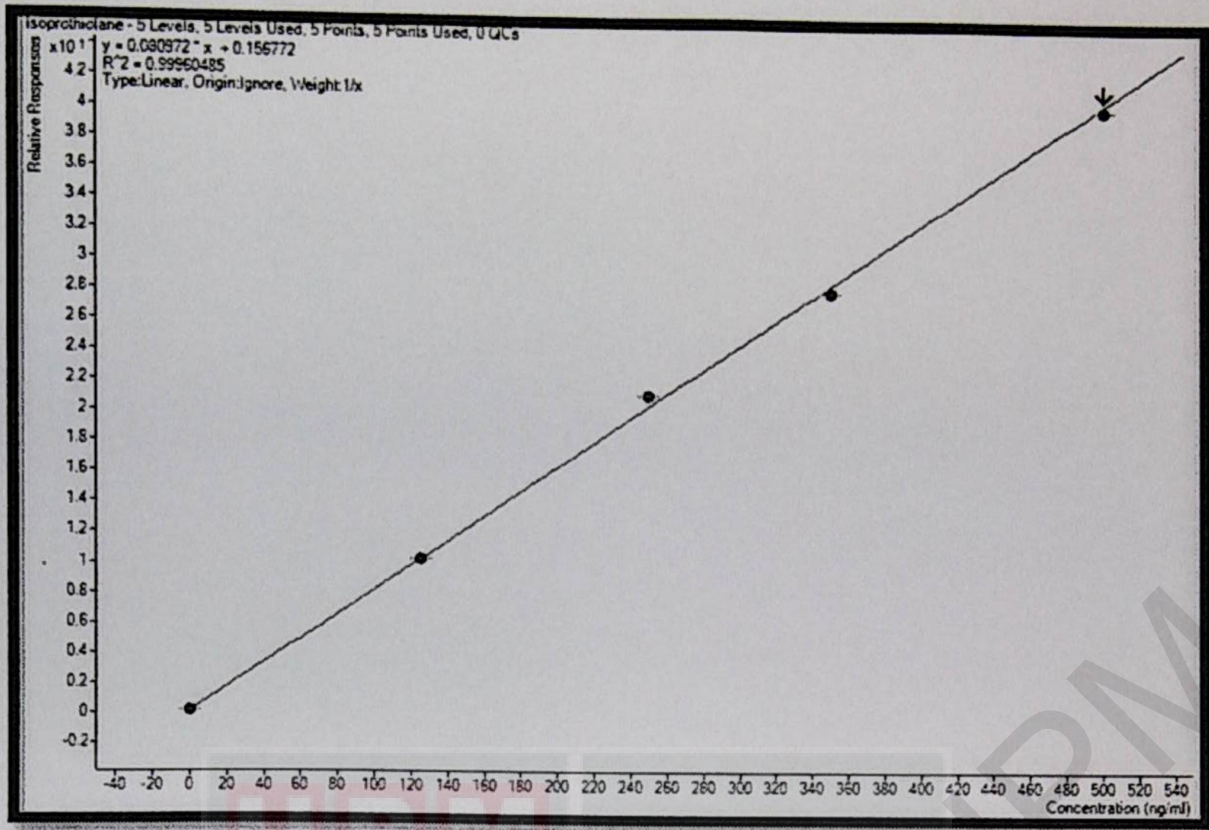


Figure 7: The calibration curve for isoprothiolane

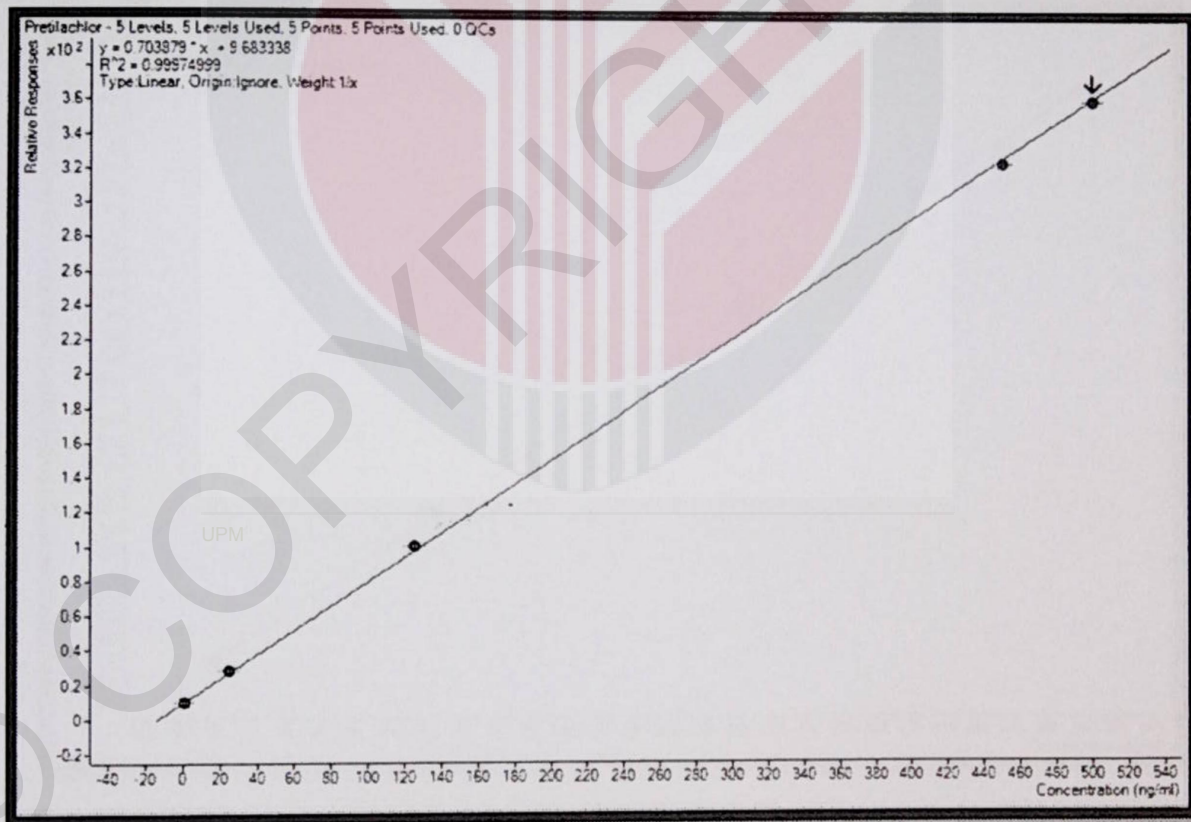


Figure 8: The calibration curve for pretilachlor

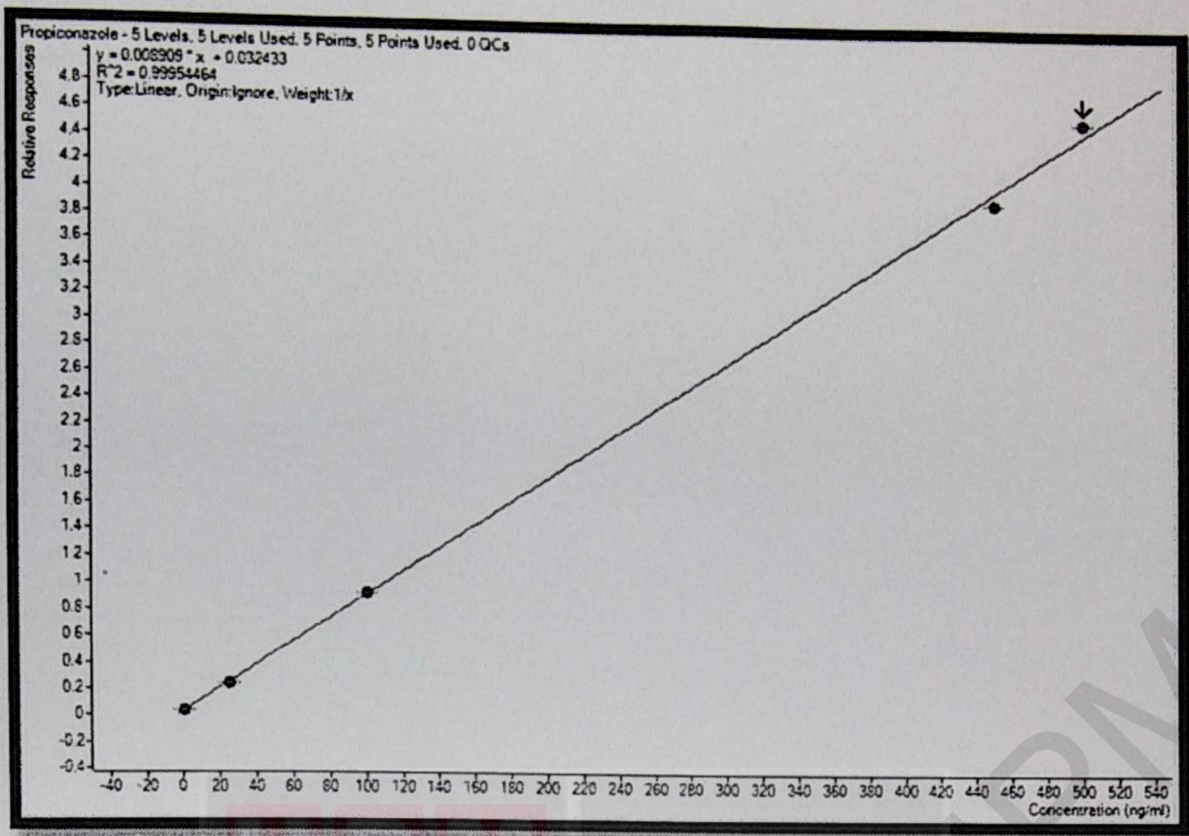


Figure 9: The calibration curve of propiconazole

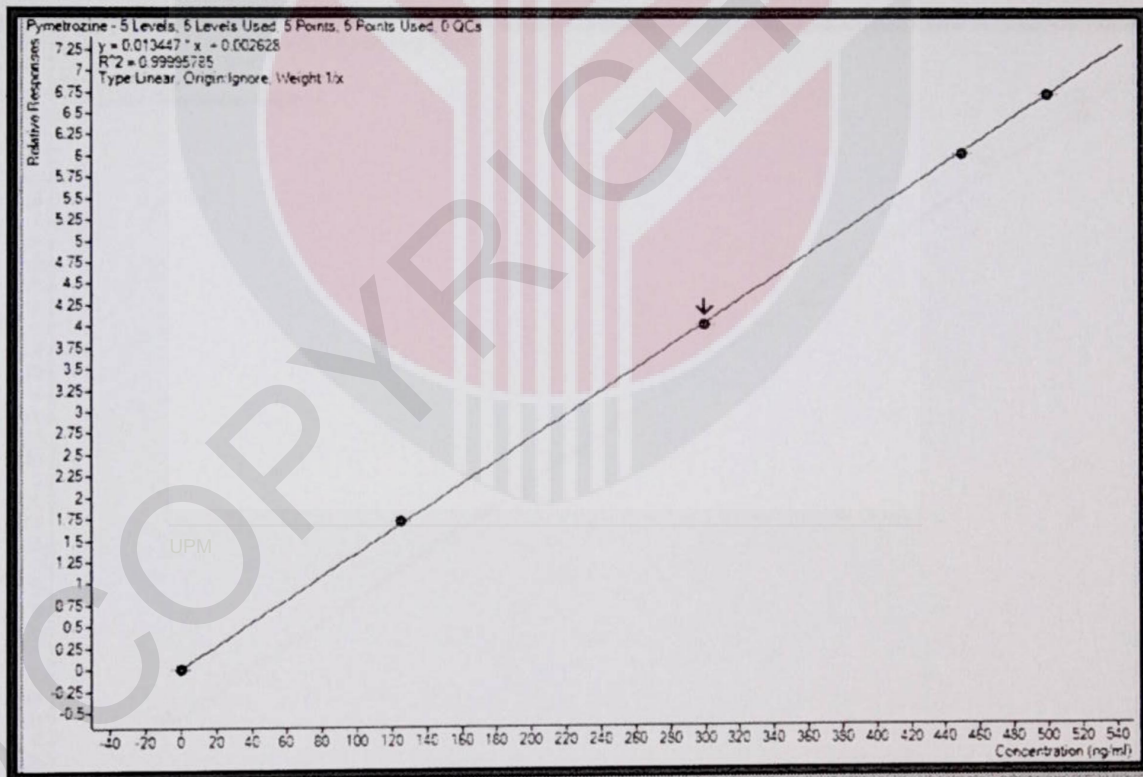


Figure 10: The calibration curve for pymetrozine

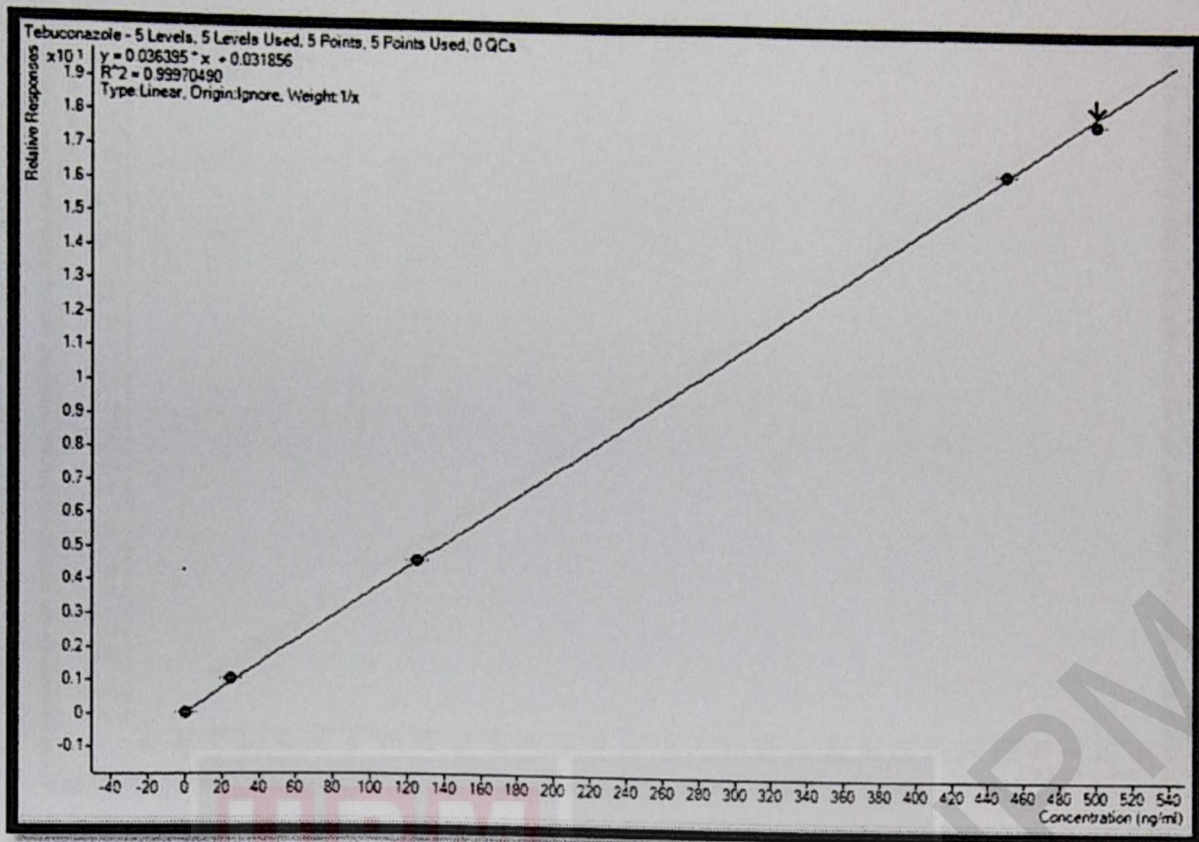


Figure 11: The calibration curve of tebuconazole

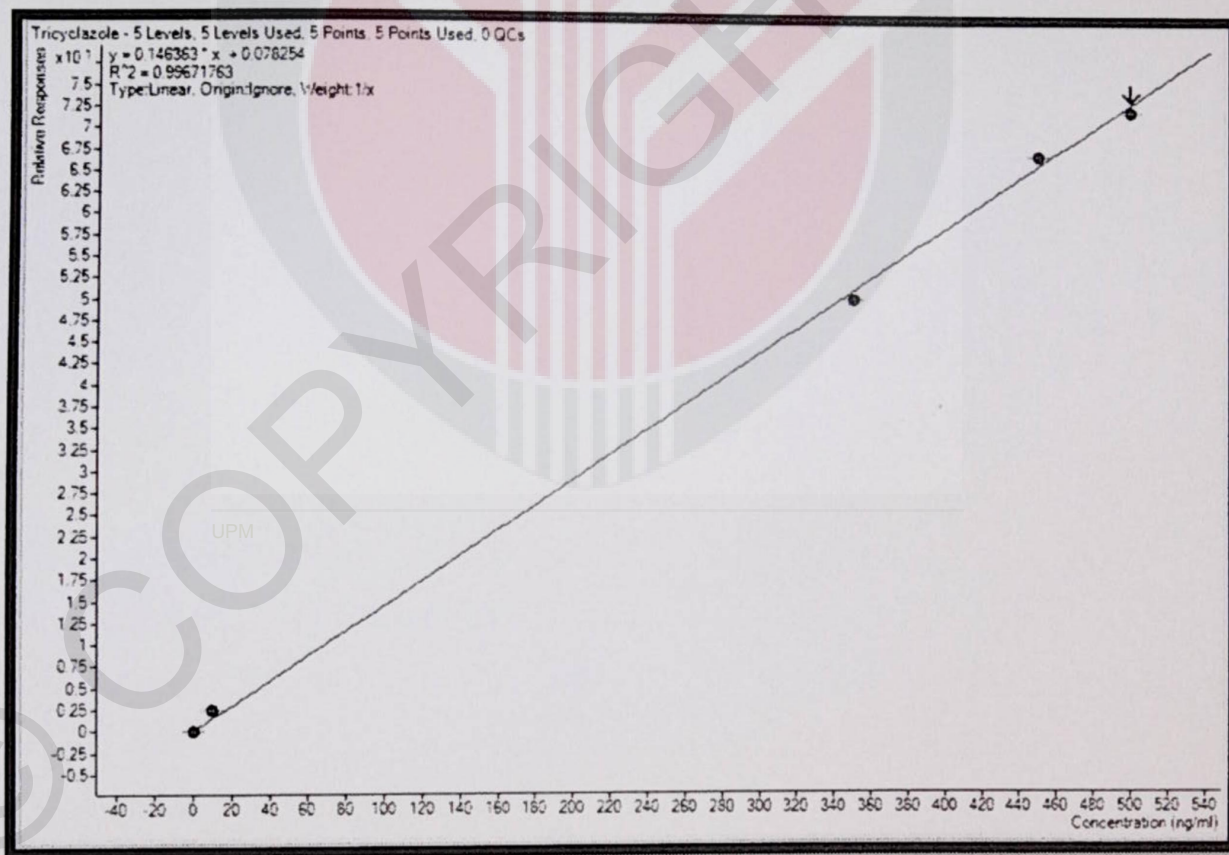


Figure 12: The calibration curve for tricyclazole

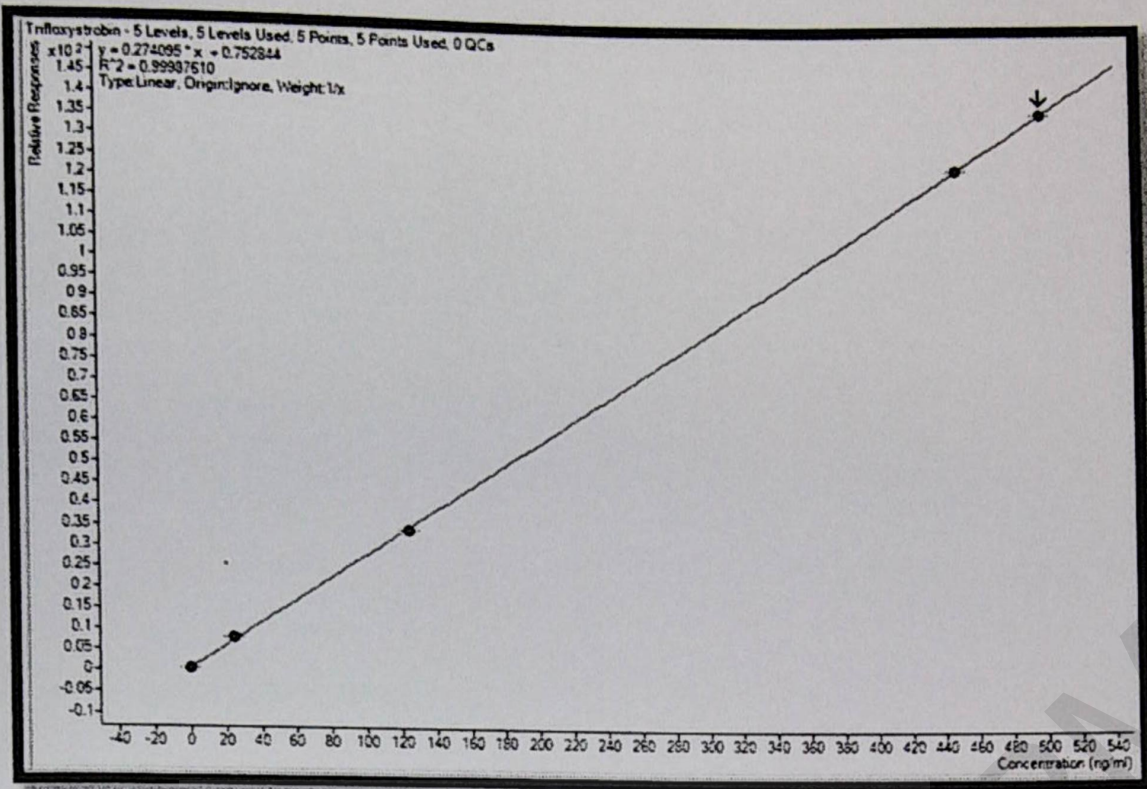


Figure 13: The calibration curve for trifloxystrobin

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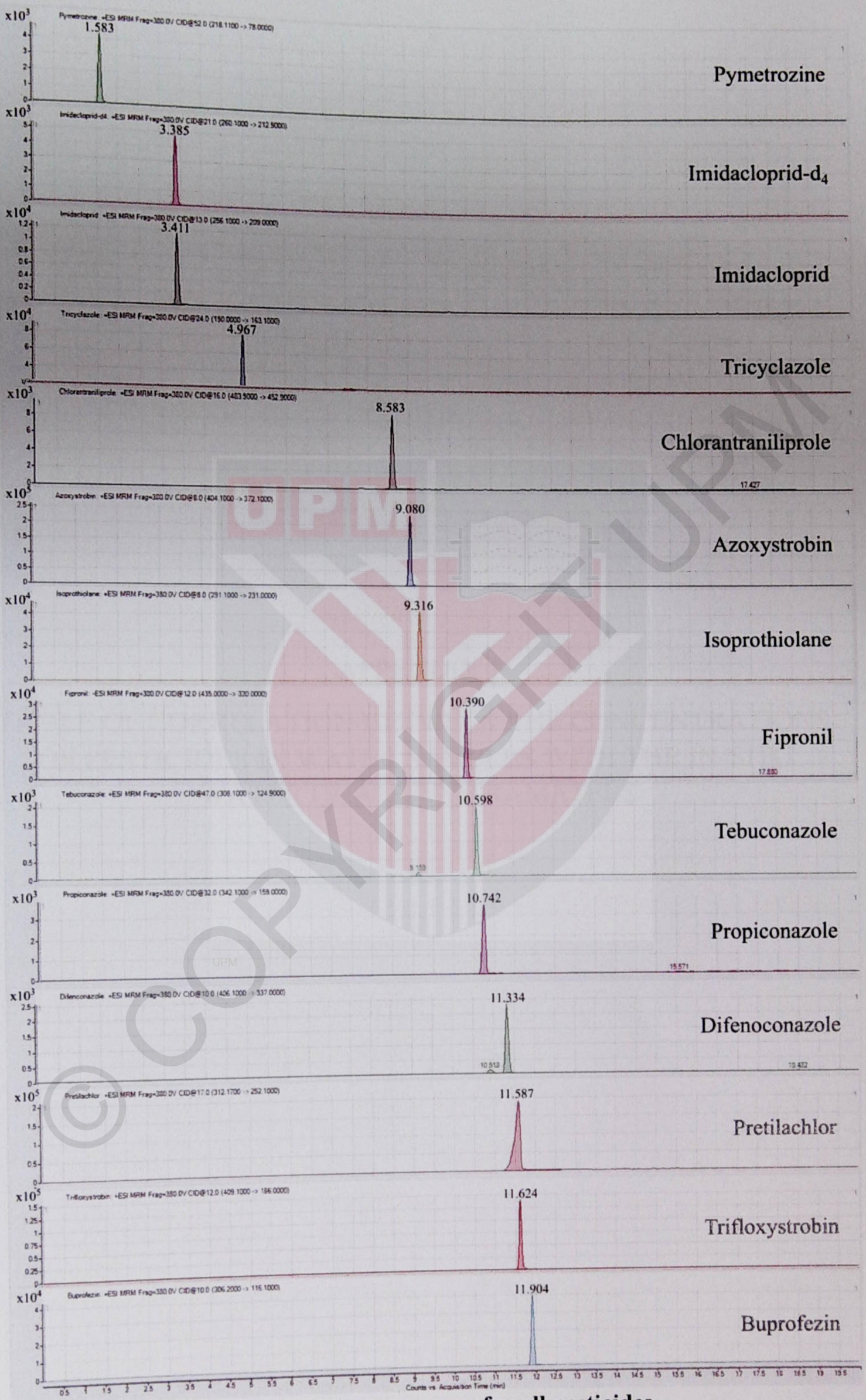


Figure 14: Chromatogram for all pesticides

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APPENDIX 7

**TABLE OF CORRELATION BETWEEN THE CONCENTRATIONS
OF PESTICIDES IN WATER SAMPLES WITH THE IN-SITU
WATER QUALITY PARAMETERS**

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Table 6: Correlation of pesticides concentration and in-situ water quality parameter.

	Temperature	pH	EC	DO	Turbidity	Pymetrozine	Imidacloprid	Tricyclazole	Chlorantraniliprole
Temperature	1								
pH	-0.240	1							
EC	-0.373	-0.215	1						
DO	0.043	-0.641**	0.226	1					
Turbidity	0.009	-0.053	-0.576*	0.003	1				
Pymetrozine	0.199	-0.215	0.152	0.227	-0.081	1			
Imidacloprid	-0.295	-0.541*	0.262	0.729**	-0.088	0.382	1		
Tricyclazole	0.226	-0.531*	-0.547*	0.414	-0.083	0.598*	0.654**	1	
Chlorantraniliprole	-0.126	-0.547*	0.282	0.215	-0.003	0.134	0.648**	0.577*	1
Azoxystrobin	-0.065	-0.655**	0.146	0.344	0.023	0.115	0.658**	0.579*	0.907**
Isoprothiolane	0.344	-0.207	0.740**	-0.054	-0.379	0.396	0.172	0.735**	0.418
Fipronil									
Tebuconazole	0.292	-0.624**	0.603*	0.347	-0.076	0.466	0.521*	0.860**	0.663**
Propiconazole	-0.085	-0.418	0.059	0.262	0.179	0.131	0.579*	0.491	0.829**
Difenoconazole	0.365	-0.169	0.775**	-0.107	-0.402	0.191	0.013	0.491	0.274
Pretilachlor									
Trifloxystrobin	0.123	-0.591	0.549*	0.296	-0.060	0.318	0.615*	0.838**	0.835**
Buprofezin	-0.024	-0.583*	0.399	0.512*	-0.066	0.102	0.777	0.636**	0.897**

**Correlation is significant at the 0.01 level (two-tail)

*Correlation is significant at the 0.05 level (two-tail)

Table 6: Correlation of pesticides concentration and in-situ water quality parameter (continued.).

	Azoxystrobin	Isoprothiolane	Fipronil	Tebuconazole	Propiconazole	Difenoconazole	Pretilachlor	Trifloxystrobin	Buprofezin
Temperature									
Ph									
EC									
DO									
Turbidity									
Salinity									
Pymetrozine									
Imidacloprid									
Tricyclazole									
Chlorantraniliprole									
Azoxystrobin	1								
Isoprothiolane	0.323	1							
Fipronil	-	-	1						
Tebuconazole	0.577*	0.801**		1					
Propiconazole	0.875**	0.297		0.485	1				
Difenoconazole	0.068	0.824**		0.720**	-0.058	1			
Pretilachlor							1		
Trifloxystrobin	0.724**	0.722**		0.937**	0.527**	0.638**		1	
Buprofezin	0.882**	0.412		0.686**	0.830**	0.243		0.810**	1

**Correlation is significant at the 0.01 level (two-tail)

*Correlation is significant at the 0.05 level (two-tail)

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APPENDIX 8

**APPROVAL LETTER FOR WATER SAMPLES COLLECTION IN
SUNGAI SIREH DRINKING WATER TREATMENT PLANT**

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APPENDIX 9

**PICTURES OF WATER SAMPLES COLLECTION AND
EXTRACTION**

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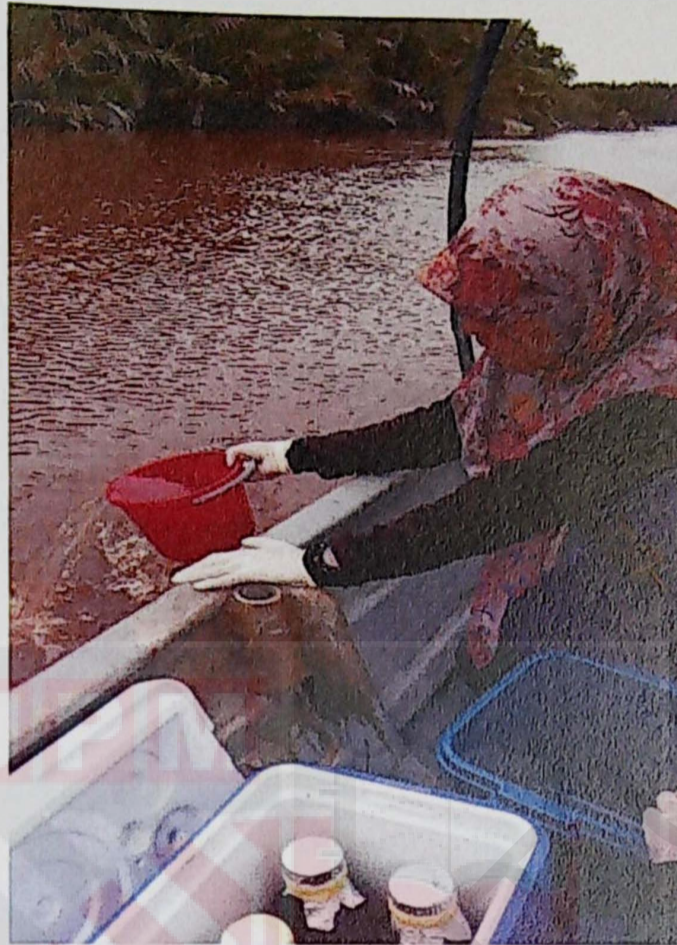


Figure 15: Water sample was collected in the Tenggi River



Figure 16: Water samples was collected by composite sampling

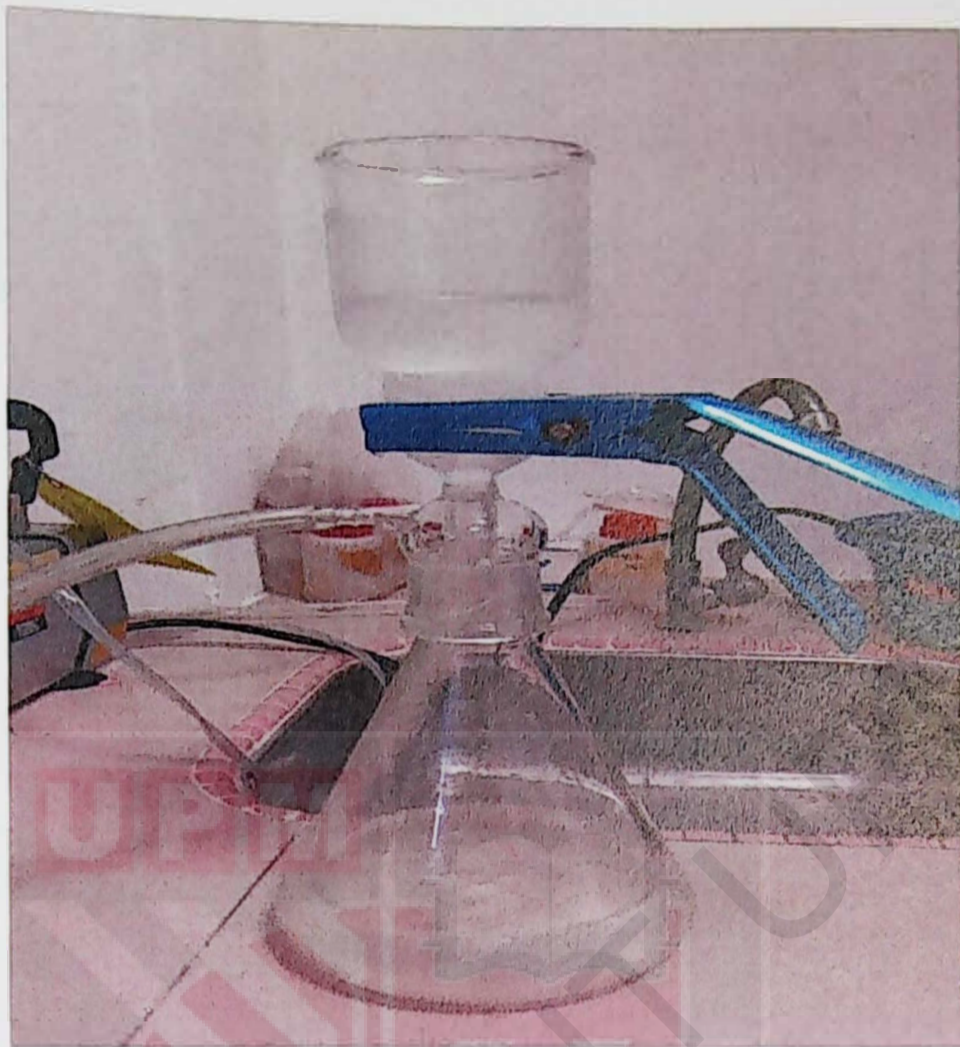


Figure 17: Water sample was filtered



Figure 18: Water sample was extracted using SPE Technique