ANALYSIS OF PESTICIDE RESIDUES IN THE VEGETABLES BY USING GAS CHROMATOGRAPHY – ELECTRON CAPTURE DETECTOR

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ABSTRACT

Over the last few decades, the Malaysian agriculture industry has contributed to the growth and major contributors to national income and export earnings. It is become basis of economic growth and main contributor in national economy prior to the 1970s. However, in order to increase the food production such as vegetables and fruits, pesticides is widely used in agriculture industry to prevent, destroying or mitigating any pest that can cause harm to plant. Unfortunately, the pesticide residue level in vegetables is dangerous and can cause harm to human health if excessive consumption of pesticides in vegetables is highly taken. Commonly, people tend to wash the vegetables only by using tap water before cook or eaten raw without knowing kevel of food safety before these commodities been consumed. Thus, the objective of this thesis are to determine and compare the concentration of pesticide residue level in selected vegetables after being washed by using distilled water and vegetables detergent and to determine the food safety of these commodities by comparing the pesticides concentration result with Malaysian Maximum Residue Limits standard that has been listed out by Ministry of Health under Food Regulation 1985. In this study, presence of *chlorpyrifos* pesticides is detected in cabbage and eggplant vegetables. Both vegetable samples are washed and soaked with distilled water and vegetables detergent (*Pureen Liquid Cleanser*) before sample preparation is made and analyzed by using Gas Chromatogrpahy-Electron Capture Detector method. From the result, it has showed the presence of *chlorpyrifos* pesticide in both vegetable samples and concentration of *chlorpyrifos* pesticides residue is lower when washed and soaked with vegetables detergent compare when washed and soaked with distilled water. It proved that vegetable detergent is an effective way to remove or kill the pesticide residue that left in these vegetable. Result from this study then is compare with Maximum Residue Limits to determine the level of food safety of this type of commodities and from the comparison, concentration of pesticides residue in vegetable could not be consider a serious public health problem. However, continuous monitoring and tighter regulation of pesticide residue in vegetables is recommended.

ABSTRAK

Sejak beberapa dekad yang lalu, industri pertanian di Malaysia telah menyumbang kepada pertumbuhan dan penyumbang utama kepada pendapatan negara dan pendapatan eksport sebelum tahun 1970-an. Dalam usaha untuk meningkatkan pengeluaran makanan seperti sayur-sayuran dan buah-buahan, racun perosak digunakan secara meluas dalam industri pertanian untuk mencegah, memusnahkan atau mengurangkan mana-mana perosak yang boleh menyebabkan kemudaratan kepada tumbuhan. Malangnya, tahap sisa racun perosak dalam sayur-sayuran adalah berbahaya dan boleh menyebabkan kemudaratan kepada kesihatan manusia jika penggunaan racun perosak yang berlebihan dalam sayur-sayuran diamalkan. Objektif projek ini adalah untuk membandingkan kepekatan tahap sisa racun perosak dalam sayur-sayuran dipilih selepas dicuci dengan menggunakan air suling dan sabun khas sayur-sayuran dan untuk menentukan keselamatan komoditi ini dengan membandingkan hasil kepekatan racun perosak dengan standard *Maximum Residue Limit*. Kepekatan tahap sisa racun perosak dianalisis dengan menggunakan Gas Chromatography-Electron Capture Detector (GC-ECD). Dalam kajian ini, kehadiran racun perosak chlorpyrifos dikesan dalam kubis dan sayur-sayuran terung. Kedua-dua sampel sayuran dibasuh dan direndam dengan air suling dan sayur-sayuran detergen (*Pureen Liquid Cleanser*) sebelum penyediaan sampel dibuat dan dianalisis dengan menggunakan kaedah GC-ECD. Hasil kajian telah menunjukkan kehadiran racun perosak *chlorpyrifos* dalam kedua-dua sampel sayur-sayuran dan kepekatan chlorpyrifos racun sisa adalah lebih rendah apabila dibasuh dan direndam dengan sabun khas sayur-sayuran membandingkan apabila dibasuh dan direndam dengan air suling. Keputusan daripada kajian ini kemudian bandingkan dengan *Maximum Residue Limit* untuk menentukan tahap keselamatan jenis makanan ini dan telah menujukkan bahawa kepekatan sisa racun perosak dalam sayur-sayuran ini tidak akan membwa kepada masalah kesihatan yang serius. Walau bagaimanapun, pemantauan berterusan dan peraturan yang lebih ketat sisa racun perosak dalam sayur-sayuran adalah disyorkan

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ECD	Electron Capture Detector
EPA	Environmental Protection Agency
FAMA	Federal Agricultural Marketing Authority
FAO	Food and Agriculture Organizations
FIDs	Flame Ionisation Detector
FPD	Flame Photometric Detector
GC	Gas Chromatography
IRS	Indoor Residual Spraying
MRLs	Maximum Residue Limits
NPD	Nitrogen Phosphorus Detector
SCOT	Support-Coated Open Tubular
USGS	U.S. Geological Survey
WCOT	Wall-Coated Open Tubular
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

This chapter provides the general ideas on the subjects that were studied which included objective, problem statement, significant study, scope and also expected result.

1.1 BACKGROUND OF STUDY

Vegetables are one of the essential constituents of the human healthy diet. The healthy food recommends eating vegetables for several reasons including vitamins, cancer prevention, and low calories. Therefore, in order to improve food production, pesticide is widely used in agriculture firm to prevent or destroy agriculture pest. This is supported by Colume at al. (2001), the uses of pesticides are necessary and play an important role in agriculture sector to eliminate pest and control plant disease in order to increase the production of vegetables throughout the world.

Unfortunately, extensive use of pesticides may pose potential health risks to humans if harmful residue appears in foods. According to Sanchez et al. (2011), pesticides that applied to crops can be toxic and can thus be harmful to human health. Because of their high demand for farm produce and low perception of the toxic effects of pesticides residue in vegetables, some farmers do not wait long enough for the residue to wash off after spraying before harvesting the crops. Thus, high content of pesticides might be still trap in the commodities and this will become a problem since consumers does not aware of this situation. Study done by Chen et al. (2011) has pointed out that without proper handling of the use of pesticide, it will resulted in contamination of the environment and caused long term effect to the human health.

Thus, it can show that the increase use of pesticides in agriculture sector has resulted in the occurrence of residue in food commodities. Unfortunately, without any preventive action to avoid this scenario, high intake of pesticide residue in vegetables might become a major problem to consumer. Excessive consumption of pesticides residue in food commodities can result in both acute and chronic health effects such as lung damage, chemical burns, and infant methemoglobinemia which is because of the presence of nitrate in groundwater (Dennis, 1993).

Due to the matter, public concern over pesticides residue has risen over the past decade to the point where it has become a significant food safety issue. This can be prove when increasing demand of food safety has excite research regarding the risk when consume food that contaminated by pesticides, heavy metals and toxin as reported by Mansour et al. (2009)

In order to solve this matter, maximum residue levels (MRL) has been established and set by many countries that stated the upper legal concentration that allowed or permitted for a pesticides residue in or on food. This is supported by Chen et al. (2011) that highlight, MRLs encourage food safety by restricting the concentration of a residue permitted on a food commodity and by limiting the type of commodity on which it is allowed.

Due to this reason, monitoring residues of pesticides in vegetables is vital and nowadays become a priority in pesticides research. According to Colume et al. (2001), to avoid possible risks to human health, the pesticides residues that left in the vegetables need to be monitored in order to get an extensive evaluation of vegetables quality.

Therefore, as the MRLs are becoming more and more strict, it is necessary to improve the laboratory result on the pesticides residue level in food consumption. Hence, this study was aimed to determine and compare the pesticide residue level in the vegetables after it has being washed by using tap water and vegetable detergent and monitored by using Gas Chromatography-Electron Detector method. Thus, present of chlorpyrifos pesticides in eggplants and cabbage would be analysed.

1.2 PROBLEM STATEMENT

Vegetable has been known as an important protective food and highly beneficial for the maintenance of health and prevention of disease. In order to increase the production of the vegetable, pesticides is used to prevent or destroy the agriculture pest. Unfortunately, the pesticide residue level in vegetables is dangerous and can cause harm to human health if excessive consumption of pesticides in vegetables is highly taken. Studies done by Dennis, (1993) stated in his journal that health problems such as lung damage, chemical burns and infant methemoglobinemia can be encounter by public who does indirectly consume pesticides in their food intake.

As human being, it has been a habit to wash the vegetables only by using tap water before cook or eaten raw without know the level of pesticides left trap in the vegetable. It show that, public awareness towards the safety in food is less as they does not realize the adverse effect of this pesticides to the human being. Thus, Maximum residue limits (MRLs) has been set by many countries in order to determine the level of pesticides that can be consider safe to eat by the public. Gas Choromatography – Electron Capture Detector is one of the method that use widely in the world to analyze the level of pesticides residue that trap inside the vegetables.

Therefore, this study is specially designed to find the level of pesticides in vegetables sample by using Gas chromatography – electron capture detector (GC-ECD). Two types of vegetables which are cabbage and eggplant will be used as a sample and both sample will be wash by using tap water and vegetable detergent before being analyzed in GC-ECD. In addition, the outcome of the study will increase the awareness in food safety and also government can increase the law enforcement in agriculture field by restricting the amount of pesticides used in the vegetables.

1.3 OBJECTIVE OF STUDY

The objectives of the research project are:

1.3.1 To compare the concentration of chlorpyrifos pesticide residue level in selected vegetables sample after being wash by using distilled water and vegetables detergent.

1.3.2 To determine the safety of food consume after being wash by using distilled water and vegetables detergent by comparing the concentration of chlorpyrifos pesticide residue level with Maximum Residue Limits.

1.4 SCOPE OF STUDY

This study is focus generally on the laboratory experiment for the analyzing the content of pesticides trap inside the vegetables by using Gas Chromatography- electron capture detector method.

One type of pesticides which is cholorypyrifos pesticides that used in agriculture field will be analyzed inside only two sample of vegetables which are cabbage and eggplant. These vegetables samples were purchased with vegetables supplier that growth their own vegetables farm at Gambang, Pahang area. .Both samples then will be wash by using tap water and Pureen Liquid Cleanser or known as vegetables detergent that can be purchased in Kuanran, Pahang area. After sample preparation, the sample will be analyze by the GC-ECD method. Lastly, result of the analysis was compared with Maximum Residue Limits (MRLs).

1.5 SIGNIFICANCE OF STUDY

This study is important to determine the level of chlorpyrifos pesticides residue level in cabbage and eggplant vegetables and comparing the level of pesticide after being wash with two different types of parameter which are tap water and vegetables detergent.

Nowadays, public usually wash their food by using tap water before it was eating raw or cook without concern about the cleanliness of their food. The content of pesticides might be still trap inside the vegetables and the problem arises when the level of pesticide inside the commodity is unknown. Thus, this study is aim to compare the new alternative with the old one to reduce the pesticides residue level in vegetables. This can be achieve by comparing the result of pesticides level in both samples after being wash by using distilled water and vegetables detergent. Result from the study then compare with Maximum Residue Limit to determine the food safety of these commodities.

Moreover, from this study, public awareness toward the hazardous content in vegetables might be increase and the government also can take action to restrict the amount of pesticides used in vegetables fields by providing information on level of pesticides in vegetables. Besides that, by monitoring the food contaminant in vegetables will contributes to improve the food safety and facilitate evaluation of possible health hazards causes by the pesticides content (Sameeh et al., 2008).

CHAPTER 2

LITERATURE REVIEW

The purpose of this chapter is to provide the review of past literature on level of pesticides in vegetables which includes its characteristics, regulatory standard, and its procedure. A review of other relevant studies which is includes method of pesticides analysis also included in this chapter.

2.1 MALAYSIA AGRICULTURE INDUSTRY

Over the last few decades, the Malaysian agriculture industry has contributed to the growth and major contributors to national income and export earnings. It's become basis of economic growth and main contributor in national economy prior to the 1970s. The agriculture sector initially derived from the increase in the production of livestock, fisheries and other miscellaneous crops. The agriculture industry more valuable cash crops owing to the increase in earnings from major commodities such as palm oil, rubber and food commodities.

In Malaysia, a large part of the mountainous steep lands is kept under forest for agriculture purpose. According to study done by, Midmore et al.(1996), in peninsular Malaysia, nearly 104 ha of steep mountainous land in the Cameron Highlands (CH) have been developed for temperate vegetables include cabbage, tomato and leafy vegetables as well as for tea, floriculture, and fruits. Midmore et al., added in his journal that other highland areas in Malaysia which have been developed for agricultural purposes can be found in east Malaysia, where cocoa and pepper are planted on steep lands. Another land use type in steep areas is shifting cultivation, also mainly found in east Malaysia (Sarawak) and amounting to about 2.7 × 106 ha, of which 0.1 × 10 6 ha are cleared

annually for the cultivation of hill rice and other food crops. The other east Malaysian state, Sabah, is dominated by a landscape of hilly and steep land which accounts for over 60% of its total area. In Kundasang, primary jungle is being replaced through clearing operations and vegetable production on steep land is gaining popularity.

2.1.1 Vegetable Statistics In Malaysia

Lots of study has been done to determine the vegetable statistic in agriculture industry. For example, in the study of Soil erosion and environmental impact on vegetable production in the Cameron Highland, Malaysia, Midmore et al., (1996) has state that Federal Agricultural Marketing Authority (FAMA) has estimates the vegetable consumption based on consumption surveys and found that consumption of vegetables increased from ll8 g per capita day^{-1} in 1982 to 153 g per capita day^{-1} in 1985. However, the most recent FAO figures for availability of vegetables indicate a per capita daily supply of just over 100 g (FAO, 1991), as well as in domestic production and trade in 1985-1990 which indicate that vegetable availability falls significantly short of the 200 g per capita day^{-1} considered necessary to meet daily micro-nutrient requirements .

2.2 PESTICIDES IN AGRICULTURE INDUSTRY

The Malaysian agriculture industry has been recognized for its contribution towards economic growth and rapid development, but it has also increase the public awareness toward the food safety due to the usage of pesticides in the industry. In order to increase the food production such as vegetables and fruits, pesticides is widely used in agriculture industry to prevent, destroying or mitigating any pest that can cause harm to plant. This statement also supported by Colume et al.,(1999) and Clarke et al., (1997), pesticides are widely used to help farmers in agriculture farm to control the pest and plant diseases that can decrease the crop loss.

Agriculture pest such as bacteria, fungi, weeds, insects and other potentially harmful pests can affect plant health by consumption of plant tissues. Eventually, plant disease such as wilting, stunting, leaf yellowing and drop, leaf spots, and death of plants might

reduce the food production. Thus, pesticides is designed as a chemical that apply in vegetables or other agriculture products that can kills or discourages production of agriculture pest. According to the study by Ng et al. (2005), pesticide are used to control insects, weeds, spoilage bacteria and fungi and other pests that can harm the production of vegetables.

Figure 2.1: Spraying pesticides to increase yields in agriculture sector

2.2.1 Benefits of pesticides

Tremendous benefits have been derived from the use of p in forestry, public health and the domestic sphere and agriculture sector especially in Indian and China country which economy is largely dependent. Increases in productivity have been due to several factors including use of fertilizer, better varieties and use of machinery. Pesticides have been an integral part of the process by reducing losses from the weeds, disease and insect pests that can markedly increase the amount of harvestable produce.

2.2.1.1 Increase in Food Production

In agriculture industry, pesticide is practically used to reduce agriculture losses, resulting in improved yield production and greater availability of food. For example, the effect of killing caterpillars that feeding on the crops such as cabbage to live on will increase the yields of cabbage and eventually will give better quality of cabbage. According to Pimentel (1997), there is a four-fold return on investment in pest control and in his other research, he has pointed out that, in USA and India which are the former country of famine has quadrupled grain production since 1951 result from the pesticide use in agriculture sector.

Similarly outputs and productivity have increased dramatically in most countries, for example wheat yields in the United Kingdom, corn yields in the USA. Study carried out by Cooper and Dobson (2007) has stated the increase of wheat yield production in the United Kingdom rose from 2.5 t/ha in 1948 to 7.5 t/ha in 1997. While, according to Kucharik and Ramankutty (2005), USA showed dramatically increase in corn yield when 30 bushels per acre increase to hundred per acre starting from 1920 to 1980. Due to the use of high yield varieties yield varieties of seeds, advanced irrigation technologies and of course the agricultural chemicals, it result in fourfold of food grain production which is from 50 million tons to 198 million tons in approximately 26 years (Employment Information: Indian Labour Statistics, 1994).

2.2.1.2 Vector Disease Control

Vector-borne diseases are most effectively eliminated by killing the vectors. In general a vector is any agent includes person, animal or microorganism that carries and transmits an infectious pathogen into another living organism. Insecticide is one type of pesticides that seldom use and only the practical way to control the insects that spread diseases such as sleeping sickness, river blindness and a range of serious fevers and disfiguring or debilitating illness and malaria which resulting in an estimates 5000 death people every day (Ross, 2005).

Due to this concern, The World Health Organization (Anon, 2004) has pointed out that nearly 30 years after phasing out the widespread use of indoor spraying with insecticides to control malaria, the World Health Organization (WHO) announced that this intervention will once again play a major role in its efforts to fight the disease. WHO is now recommending the use of indoor residual spraying (IRS) not only in epidemic areas but also in areas with constant and high malaria transmission, including throughout Africa.

2.2.1.3 Preventing or Controlling Organisms That Harm Other Activities or Damage Structures.

Just as effect such as losses, spoilage and damage cause by pests in agriculture and public health, various organisms also give a negative impact on human activities, infrastructure and the materials of everyday life unless controlled. Pesticides play an important, as it seen as one of the methods that can prevent the negative impact occurs by the unwanted organisms.

The transport sector makes extensive use of pesticides, particularly herbicides. Herbicides and insecticides are used to maintain the turf on sports pitches, cricket grounds and golf courses. Besides that, herbicide is widely used in transportation sector to ensure the roads, railways and waterways are kept free of vegetation that might cause a hazard or nuisance (Cooper and Dobson, 2007). For example, if vegetation is allowed to grow too tall on roadsides, it reduces the drivers' view at junctions, and deposits branches or vegetation onto the road that might be an obstruction or make it very slippery. The use of pesticides to manage this vegetation brings secondary benefits of safer transport systems with fewer accidents and less stress for users.

Insecticide is of type of pesticides that can apply to protect buildings and other wooden structures from damage by termites and wood boring insects. Thus, maintenance costs can be decrease and increasing longevity of buildings and their safety. This use also has wider environmental benefits in that timber as it is a renewable resource that can be produced in an environmentally beneficial way as construction material.

2.2.2 Hazards of Pesticides

Although there are benefits to the use of pesticides, some also have drawbacks, such as potential toxicity to humans and other animals. If the credits of pesticides include enhanced economic potential in terms of increased production of food and fiber, and elimination of vector-borne diseases, then their debits have resulted in serious health implications to man and his environment. A study conducted by Sattler et al., (2007) has pointed out that pesticides can pose a risk on the environment and human health. Pesticides that use in agriculture have been found as pollutants in ground and surface water, in soils and the atmosphere.

2.2.2.1 Direct Impact on Humans

There is now overwhelming evidence that some of these chemicals do pose a potential risk to humans and other life forms and unwanted side effects to the environment. The high risk groups exposed to pesticides include production workers, formulators, sprayers, mixers, loaders and agricultural farm workers. During manufacture and formulation, the possibility of hazards may be higher because the processes involved are not risk free. In industrial settings, workers are at increased risk since they handle various toxic chemicals including pesticides, raw materials, toxic solvents and inert carriers.

A study conducted by Safi (1998), has reported that 1 000 000 Palestinian inhabitants living and working, mostly in agriculture expose to formulated pesticides that annually used to protect the major crops, including vegetables, citrus, olives and grapes. Farmers who are engaged in spraying, dusting or handling pesticides are exposed to direct occupational-exposure hazard. In addition, indirect environmental pollution hazards are increasing as a result of pesticide residues being transferred and accumulated across the food chain. According to research done by Safi et al. (1993), the risk of exposure to these residues in the general population is highly increased when these residue are from highly persistent banned pesticides as documented is used.

Incidence of cancer in farmer and agricultural workers who exposed to organochlorine and other pesticides is gradually increased year by year. Previous study done by IIling (1997) reported that, due to the relatively closed system and the frequency of pesticide applications, greenhouse exposure is expected to be of higher risk to the workers. As well as in Mexico, higher rate of cancers were recorded among farmers, and even the general population, due to the continuous exposure to organo chlorine pesticides and other industrial pollutants (Lopez-Carrillo et al., 1996 and Lopez-Carillo et al, 1997).

Children are especially susceptible to the harmful effects of pesticide residues due to their lower body mass, rapid development, and higher rated of consumption of affected products. In children, exposure to certain pesticides from residue in food can cause delayed development, disruption to the reproductive system, endocrine, and immune systems, exposed to certain types of cancer and damage to other organs Bouchard *et al.* (2011). Prenatal exposure to certain pesticides can effect development and behavior.

According to Chen et al. (2011), pesticides have been associated with human health hazards, ranging from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm, and endocrine disruption. This statement is supported by Dennis (1993) that highlights the consumption of pesticides residue in food commodities can result in both acute and chronic health effects such as lung damage, chemical burns, and infant methemoglobinemia which is because of the presence of nitrate in groundwater.

2.2.2.2 Surface Water Contamination

Pesticides can contaminate soil, water, turf, and other vegetation. In addition to killing insects or weeds, pesticides can be toxic to a host of other organisms including birds, fish, beneficial insects, and non-target plants. Pesticides can reach surface water through runoff from treated plants and soil. Contamination of water by pesticides is widespread.

Study done by U.S. Geological Survey (USGS) on major river basins across the country in the early to mis-90s has yielded interesting results. More than 90% of water and fish samples from all streams contained one, or more often, several pesticides. According to Bortleson and Davis, in 1995, pesticides were found in all samples from major rivers with mixed agricultural and urban land use influences and 99 percent of samples of urban streams.

Twenty-three pesticides were detected in waterways in the Puget Sound Basin, including 17 herbicides. According to USGS, more pesticides were detected in urban streams than in agricultural streams .The herbicides 2,4-D, diuron, and prometon, and the insecticides chlorpyrifos and diazinon, all commonly used by urban homeowners and school districts, were among the 21 pesticides detected most often in surface and ground water across the nations.

The USGS also found that concentrations of insecticides in urban streams commonly exceeded guidelines for protection of aquatic life. The herbicide 2,4-D was the most commonly found pesticide, detected in 12 out of 13 streams. The insecticide diazinon, and the weed-killers dichlobenil, diuron, triclopyr, and glyphosate were detected also in Puget Sound basin streams. Both diazinon and diuron were found at levels exceeding concentrations recommended by the National Academy of Sciences for the protection of aquatic life (Bortleson and Davis, 1995)

2.2.2.3 Ground Water Contamination

Groundwater pollution due to pesticides is a worldwide problem. According to the USGS, at least 143 different pesticides and 21 transformation products have been found in ground water, including pesticides from every major chemical class. Over the past two decades, detections have been found in the ground water of more than 43 states (Waskom, 1994). A survey has conducted in India and results in 58% of drinking water samples drawn from various hand pumps and wells around Bhopal area were contaminated with Organo Chlorine pesticides above the EPA standards (Kole and Bagchi, 1995). Some studies by researcher has reported that once ground water is polluted with toxic chemicals, it may take many years for the contamination to dissipate