DETERMINATION OF SELECTED ORGANOCHLORINE PESTICIDES IN FARMERS' BIOLOGICAL SAMPLES USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY AND THEIR KNOWLEDGE, ATTITUDE AND PRACTICE TOWARDS PESTICIDES USE

by

JULIANA BINTI MOHD NOOR

Thesis submitted in fulfillment of the requirements
for the degree of Master of Science

March, 2011

ACKNOWLEDGEMENTS

I begin in the name of Allah, Most Beneficent and Most Merciful. I thank Allah S.W.T. for the ability to complete my master research. I would like to express my deepest appreciation and gratitude to my supervisor, Prof Madya Razak Hj. Lajis for his valuable advice and assistance through comments, opinions, guidance and very helpful and critical reading of my manuscript. Without that, it was impossible for me to finish my thesis. I am very grateful to him. I would also like to express my sincere gratitude and appreciation to Science Officer Mr Nor Hasani Hashim from Chemistry School, Science Officer at National Poison Centre, Mrs. Che Nin Man, Mrs. Norjuliana Mohd Noor and all the staff at Toxicological Laboratory for their suggestion and generous help throughout my study especially during the analytical stage of my research.

I also want to thank Department of Agriculture Bumbung Lima, Kepala Batas, Penang especially Mrs Zakiah and Mr Ridzuan for the help in sample collection for my research. To Institute of Postgradutes Studies for supporting my research and providing me a Graduate Assistant scheme for two years.

My heartiest gratitude to my parents and my siblings for their love and support. I am also grateful indebted to all my relatives, colleagues and friends for their encouragement and support. May Allah bless all of you.

TABLES OF CONTENTS

CHAPTER 3 – MATERIALS AND METHODS

CHAPTER 5 – DISCUSSION AND CONCLUSION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

α – alpha

β – beta

γ – gamma

δ – delta

p,p’ – para, para

DDE – dichlorodiphenyldichloroethylene

DDD – dichlorodiphenyldichloroethane

DDT –dichlorodiphenyl trichloroethane

DOE – Department of Environmental

EPA – Environmental Protection Agency

FOTE – Friends of the environment

GC-MS – gas chromatography – mass spectrometry

HCH – hexachlorohexane

LLE – liquid-liquid extraction

MMA – Malaysian Medical Associations

ng/g – nanogram per gram

N – normal

OCP – organochlorine pesticide

PCB – polychlorinated biphenyls

POP – persistent organic pollutant

US EPA – United States Environmental Protection Agency

WHO – World Health Organization

WHA – World Health Assembly

WWF – World Wide Fund For Nature

LIST OF APPENDICES

PENENTUAN RACUN MAKHLUK PEROSAK ORGANOKLORIN TERPILIH DALAM SAMPEL BIOLOGI PETANI MENGGUNAKAN KROMATOGRAFI GAS – SPEKTROMETER JISIM DAN PENGETAHUAN, SIKAP DAN AMALAN MEREKA TERHADAP PENGGUNAAN RACUN MAKHLUK PEROSAK

ABSTRAK

Kajian ini dilakukan di kawasan pertanian di Pinang Tunggal, Kepala Batas, Pulau Pinang. Tujuan utama kajian ini ialah untuk menentukan paras racun makhluk perosak organoklorin terpilih dalam sampel-sampel biologi petani terutama rambut dan urin dengan menggunakan Kromatografi Gas - Spektrometri Jisim. Seiring dengan itu, ia turut dilakukan bagi menilai pengetahuan, tanggapan dan amalan petani terhadap penggunaan racun makhluk perosak. Organoklorin terpilih dalam kajian ini ialah HCHs (α-, β-, γ- dan δ-hch), DDTs (p ,p'-ddt, p ,p'-ddd dan p,p'-dde), aldrin, dieldrin, endosulfan sulfate, heptaklor, heptaklor epoksid dan metoksiklor. Sampel rambut dipilih kerana diketahui ia sebagai penunjuk pendedahan jangka masa panjang yang baik terhadap pendedahan bahan kimia manakala urin biasanya digunakan untuk menentukan pendedahan jangka masa pendek. Pembangunan dan pengesahan kaedah telah disahkan dan beberapa parameter telah dianalisis. Parameter yang diperhatikan adalah masa dan kelajuan untuk penyebatian, kelajuan dan masa untuk pengemparan, suhu untuk penghancuran rambut dan pelarut untuk pengekstrakan. R^2 berada dalam julat yang diterima, pekali-pekali variasi adalah kurang daripada 20% dan pemerolehan semula berada dalam lingkungan 70 - 120%. 33 % sampel rambut (n=60) dan 21% contoh urin (n=60) daripada responden telah dikesan mengandungi kepekatan tertentu beberapa racun perosak terpilih itu. β-HCH adalah racun perosak organoklorin yang paling banyak dikesan dalam rambut manakala Dieldrin paling banyak dikesan dalam urin.

Kepekatan organoklorin lebih tinggi dikesan dalam rambut berbanding yang dikesan dalam urin. Beberapa racun perosak dalam kajian tidak dikesan langsung. 122 responden telah menyertai satu kajian kendiri terhadap pengetahuan, sikap dan amalan mereka terhadap penggunaan racun makhluk perosak. Berdasarkan penemuan, kebanyakan petani didapati mempunyai pengetahuan yang tinggi terhadap penggunaan racun perosak. Peratusan yang tinggi (67-91%) dalam kalangan petani menunjukkan sikap dan amalan yang baik berdasarkan jawapan-jawapan mereka terhadap soalan-soalan yang berkaitan kebersihan individu, bagaimana racun perosak harus disimpan, bekas racun perosak sama ada boleh digunakan semula atau tidak dan pelupusan bekas racun perosak. Lebih daripada 80% responden mempraktikkan cara yang sesuai dan selamat dalam pengendalian dan penyemburan racun perosak. Tahap pengetahuan adalah tinggi terhadap penggunaan racun perosak. Sangat sedikit rungutan kesan kronik terhadap kesihatan telah dibuat. Kajian ini telah berjaya membangunkan satu kaedah untuk penaksiran secara serentak racun perosak organoklorin terpilih. Kaedah ini adalah mudah, menjimatkan kos dan kurang tenaga kerja. Beberapa program pendidikan dan langkah keselamatan yang telah dijalankan oleh pihak berkuasa kelihatan telah memberi impak yang baik terhadap petani.

DETERMINATION OF SELECTED ORGANOCHLORINE PESTICIDES IN FARMERS' BIOLOGICAL SAMPLES USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY AND THEIR KNOWLEDGE, ATTITUDE AND PRACTICE TOWARDS PESTICIDES USE

ABSTRACT

This study was conducted in agricultural areas in Pinang Tunggal, Kepala Batas, Penang. The main objective of the study was to determine the level of selected organochlorine pesticides in farmers' biological samples particularly in hair and urine samples by using Gas Chromatography – Mass Spectrometry (GC-MS). Concomitantly, it was also carried out to assess the farmers` knowledge, attitude and practice towards pesticide use. Organochlorine pesticides selected in this study were HCHs (α-, β-, γ- and δ-hch), DDTs (p,p'-ddt, p,p'-ddd and p,p'-dde), aldrin, dieldrin, endosulfan sulfate, heptachlor, heptachlor epoxide and methoxychlor. Hair sample was chosen as it is known to be a good long term indicator for chemical exposure while urine is normally used to determine short term exposure. Method development and validation using GC-MS were established and several parameters were analyzed. Parameters observed were speed and time for agitation, speed and time for centrifugation, temperature for hair digestion and type of solvent for extraction. R^2 was in accepted range, coefficients of variation were less than 20% and recoveries were in the range of 70% to 120%. A total 33 % of the hair samples (n=60) and 21% of the urine samples (n=60) from the respondents were detected to contain certain concentrations of the pesticides. β-HCH was the most organochlorine pesticide detected in hair, while Dieldrin was mostly found in urine. On weigh to weigh basis, higher concentration of organochlorine pesticides (OCPs) were detected in hair as compared to those found in urine. Others pesticides

under study were not detected at all. They were 122 respondents participated in a self-administered survey on their knowledge, attitude and practice towards pesticides use. Based on the finding, most of the farmers seemed to have high knowledge towards pesticides use. High percentage (67 – 91%) of farmers appeared to possess reasonably good attitude in pesticide use based on their answers on the questions related to individual hygiene, how pesticides should be kept, whether pesticides containers can be re-used or not, and disposal of pesticides containers. More than 80% of respondents practiced the appropriate and safe way in handling and spraying pesticides. High level of knowledge towards pesticide use was noted. Very few claims of chronic effects on health were made. This study has successfully developed an assay for simultaneous quantification of selected organochlorine pesticides. This method is simple, cost effective and non-laborious. Some educational programs and safety precautions carried out by the authority seemed to give good impacts towards farmers.

CHAPTER 1

INTRODUCTION

1.1 Background

Pesticides have been used extensively in agriculture as the most common way of controlling pests world-wide. All over the world, there is a growing concern about the known and unknown consequences of the effects of pesticides on the environment and human health. In some developed and developing countries there has been a strong public pressure to reduce the use of pesticides. Problems with pesticide use seem to be more serious and delicate in developing countries particularly in countries where surveillance and control measures are still lacking or undeveloped.

There have been many studies carried out in farmers with the goal of determining the health effects of pesticide exposure (McCauley et al., 2006). The World Health Organisation and the United Nation Environment Programme estimate that each year, 3 million workers in agricultural sectors in the developing world experience severe poisoning from pesticides, about 18,000 of whom died. According to one study, as many as 25 million workers in developing countries may suffer mild pesticide poisoning yearly (Jeyaratnam, 1990). With the increasing manipulation of pesticides, the numbers could be higher. In term of pesticide use, organophosphate pesticides have increased in use, because they are less damaging to the environment and they are less persistent than

organochlorine pesticides (Jaga and Dharmani, 2003). These are associated with acute health problems for workers who directly handle the chemicals. These symptoms include abdominal pain, dizziness, headaches, nausea, vomiting, as well as skin and eye problems (Ecobichon, 1996). According to researchers from the National Institutes of Health (NIH), USA licensed pesticide applicators that used chlorinated pesticides for more than 100 days in their lifetime were at greater risk of diabetes. In a paper appearing in the American Journal of Epidemiology May 2008 issue, researchers said that the associations between specific pesticides and incident of diabetes ranged from 20 percent to 200 percent increase in risk. New cases of diabetes were reported by 3.4 percent of those in the lowest pesticide use category compared with 4.6 percent of those in the highest category. Risks were greater when users of specific pesticides were compared with applicators who never applied that chemical (Montgomery et al., 2008).

World Health Organization estimates almost 300,000 accidental deaths occur in a year as a consequence of pesticide poisoning. A bigger portion of this figure mainly happened in developing country. In 1996, the International Labour Office, Geneva reported that 14% of all known occupational injuries and 10% of all fatal injuries were caused by pesticides. It is estimated that about 60-70% of all cases of acute unintentional pesticide poisoning are due to occupational exposure. The risks are greater in developing countries.

In view of the hazardous effects of pesticides, several International Regulation on Pesticide Use that relate to pesticides and pesticide control have been initiated. The examples are The Basel Convention, The Stockholm Convention and The Rotterdam Convention. The Basel Convention is an international treaty that was designed to reduce

the movements of hazardous waste between nations, and specifically to prevent transfer of hazardous waste from developed to less developed countries (LDCs). It does not, however, address the movement of radioactive waste. The Basel Convention is one of the most important instruments in the transformation to a clean production-based economy – a prerequisite for sustainable development. The Convention is also intended to minimize the amount and toxicity of wastes generated, to ensure their environmentally sound management as closely as possible to the source of generation, and to assist LDCs in environmentally sound management of the hazardous and other wastes they generate (Duvvuri, 2009).

The Rotterdam Convention is a multilateral agreement to promote shared responsibilities in relation to importation of hazardous chemicals. It became legally binding on its parties in 2004. The convention promotes open exchange of information and calls on exporters of hazardous chemicals to use proper labeling, include directions on safe handling, and inform purchasers of any known restrictions or bans. Aldrin, DDT, Dieldrin, Lindane and Heptachlor are an example of substances covered under this convention.

Stockholm Convention on Persistent Organic Pollutants is an international legally binding agreement on persistent organic pollutants (POPs). In 1995, the Governing Council of the United Nations Environment Programme (UNEP) called for global action to be taken on POPs, which it defined as “chemical substances that persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment”. Following this, the Intergovernmental Forum on Chemical Safety (IFCS) and the International Programme for Chemical Safety

(IPCS) prepared an assessment of the 12 worst offenders that known as the *dirty dozen*. The dirty dozen lists include eight organochlorine pesticides: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex and toxaphene; two industrial chemicals: hexachlorobenzene (HCB) and the polychlorinated biphenyl (PCB) group; and two groups of industrial by-products: dioxins and furans. Co-signatories agree to outlaw nine of the dirty dozen chemicals, limit the use of DDT to malaria control, and limit the production of dioxins and furans. Parties to the convention have agreed to a process by which persistent toxic compounds can be reviewed and added to the convention if they meet certain criteria for persistence and transboundary threat. In spite of some critics that the treaty is responsible for the continuing death related to malaria, in reality the treaty specifically permits the public health use of DDT for the control of mosquitoes (the malaria vector). From a developing country perspective, a lack of data and information about the sources, releases, and environmental levels of POPs, and specific compounds involve indicates a strong need for research (U.S.EPA, 2002).

1.2 Problem Statement

Some pesticides especially organochlorine types of compounds were already banned but studies have shown that they could still be detected in the environmental and human biological samples. Knowledge in proper handling and use of pesticides are essential particularly for those workers who are always exposed to pesticides. Numerous programs and activities have been conducted by the concerned authorities in disseminating the information about proper handling and hazardous effects of pesticides. Lack of information or lack of attitude of workers may contribute to the greater number of untoward incidences of pesticide exposure.

So this study is carried out to determine:-

a) whether some selective organochlorine pesticides can still be detected from biological samples of the farmers who assumingly should be exposed to pesticides.

b) the level of knowledge that the farmers have gathered or accumulated while working with these hazardous compounds.

1.3 Significance of Pesticides Monitoring In Farmers' Biological Samples.

Various groups of pesticides are one of the most important environmental problems posed by rice cultivation because of their overuse and misuse (WWF, 2005). Pesticides disrupt healthy ecological processes. Equally important, pesticide poisoning is a health issue for both farmers and plantation workers (WWF, 2005). Modern rice production tends to use insecticides, herbicides, molluscicides, and to a small extent fungicides in order to cope up with the rising food demand and its economic importance. In the major rice-producing countries of Asia, more agrochemicals are used on rice than on all other crops combined. As examples, in the Philippines, 47% of all insecticides and 82% of all herbicides were used on rice (WWF, 2005).

In the late 1980s and early 1990s, pesticides that had been banned in other countries such as Malaysia, Vietnam and Taiwan were still being used in Thailand and the Philippines. Examples as chlordane, DDT, HCH (hexachlorohexane, better known as lindane), hexachlorobenzene, methyl parathion, mercury compounds, and PCP (pentachlorophenol). In the Philippines, 4 pesticides which are monocrotophos, methyl

parathion, azinphos-methyl, and endosulfan constituted 70% of the pesticides used in rice cultivation in the early 1990s (WWF, 2005).

A report prepared for the Institute of Agricultural Economics in Hanover, Germany, estimates that nearly 40,000 farmers in Thailand suffer from various degrees of pesticide poisoning every year and caused a lot of money for health problems (WWF, 2005). This report also highlighted the studies done in Thailand that showed the existence of pesticide residues in more than 90% samples of soil, river sediment, fish, and shellfish.

Many other studies have clearly demonstrated that farmers and plantation workers have been the most vulnerable groups who are exposed directly to the pesticides. In view of this development, this study is conducted to determine the level of the selected organochlorine pesticides in the hair and urine samples of farmers and also to see their levels of knowledge, attitude and practice of pesticides use.

1.4 Outcome to Be Measured

Three (3) main outcomes of the study:-

a) Simple assay to determine the organochlorine pesticides in the biological samples (hair and urine)

b) Detection of the level of selected organochlorine pesticides in farmers' urine and hair samples

c) Knowledge and attitude about pesticide used among farmers

1.5 Scope of present work

The study was carried out in a number of stages. The first stage was to get approval from the Department of Agriculture, Seberang Perai District, Penang. A sampling site that involved farmers from Pinang Tunggal District was selected for this study. This site was chosen because it is an agricultural area where pesticides are believed to be commonly used by farmers. Farmers were briefed about the study and were randomly selected according to the list given by the Department of Agriculture.

Respondents were later asked to complete a self-administered questionnaire which had been validated prior to the study. Hair and urine samples were collected upon their consent. Hair and urine were collected around December 2007 until January 2008. The samples were analyzed for the presence of selected organochlorine pesticides under study.

1.6 Objectives of the Present Study

The main objectives of this study are:

a) to develop and validate suitable methods for the analysis of selected organochlorine pesticides in farmers' biological samples (hair and urine).
b) to determine the level of selected organochlorine pesticides in farmers' biological samples.
c) to observe and relate the farmers' knowledge, attitude and practice towards pesticide use.
d) to detect any significant health effect that occurs in farmers who are exposed to pesticides.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Poisoning and over exposure have always been the main health concern when dealing with pesticides. They are manifested in the form of illness or injuries resulting from exposure to a single or mixture of pesticides. The illness or injury can be acute, sub-acute, sub-chronic or chronic depending on the exposure whether it is immediate, short-term or long-term. Generally pesticides are designed to be harmful to pests. Hence when not used properly, pesticides can also cause harm to humans, animals, or the environment (Florida Health, 2007).

In 1962, Rachel Carson through her book, 'The Silent Spring' discussed the potential dangers of pesticides to wildlife and humans. "Silent Spring" brought about the first major wave of public concern over the chronic effects of pesticides. Pesticides exist in many forms. Some formulations could be of non-persistence in nature while a few others may stay longer in the environment. The organochlorine pesticides for example, are extremely persistent and they accumulate in fatty tissues. DDT, Aldrin and Dieldrin are some examples of the persistence organochlorine pesticides. The effects are manifested in various forms of illnesses once they enter the body. Generally pesticides will enter the body via various routes of exposure such as through ingestion, inhalation,

or contact with the skin, eyes or mucous membranes (Florida Health, 2007). Other chemicals, with unintentional hormone-like activity also include pesticides such as DDT, vinclozolin, endosulfan, toxaphene, dieldrin, and DBCP, and industrial chemicals and byproducts such as polychlorinated biphenyls (PCBs), dioxins, and phenols. They are suspected to cause disruption of the endocrine system hence are known as endocrine disruptors.

With such devastating effects, some of the pesticides namely the organochlorine pesticides (OCPs), they have been banned in developed country for agricultural purposes, but there are still some of the cheapest and effective chemicals such as DDT and BHC that continue to be used in many agricultural sectors (Maruf, 2001). With such strong economic reasons, most farmers find it difficult to avoid using pesticides in their farms.

The contribution of pesticides to health and the economy is closely related. They contribute directly to health through control of certain vector-borne diseases. They also contribute directly to the economy through increasing production of food and the production of many materials during storage (Abd Majid, 2007). One of the main contributions of pesticides to the control of human diseases is in the control of diseases spread by arthropods and the other vectors. Outbreaks of malaria, louse-borne thypus, plague and urban yellow fever are four of the most important epidemic diseases in history that are controlled by an organochlorine, DDT.

2.2 Background of the study

According to the World Health Organization (WHO), some 37,000 cases of cancer occur annually due to exposure to pesticides. Various reports in recent WHO journals also revealed that 25 million agricultural workers in developing countries suffered an episode of pesticide poisoning each year (Sangaralingam, 2005).

Most estimates concerning the extent of acute pesticide poisoning have been based on data from hospital admissions which would include only the more serious cases. The latest estimate by a WHO task group indicates that there may be 1 million serious unintentional poisonings each year and in addition 2 million people hospitalized for suicide attempts with pesticides. These situations reflect only a fraction of the real problem. On the basis of a survey of self-reported minor poisoning carried out in the Asian region, it is estimated that there could be as many as 25 million agricultural workers in the developing world suffering an episode of poisoning each year (Jeyaratnam, 1990).

Malaysia is one of the developing countries which depend on agriculture produces as one sector of its economic importance. Rice, oil palm, fruits and vegetables are examples of these main products. In order to increase the productivity of these sectors, pesticides are widely used to protect the crops from insects and pests, hence increase productivity. They are widely used in all countries due to their proven effect in vector control and their effectiveness in agriculture (Isa, 2007). Pesticides use in agriculture, forestry, industry, public health and households make them one of the most common types of chemicals coming into contact with all groups of population. In many instances, it could lead to poisoning which could be due to acute or chronic exposure.

The unwanted effects due to such exposure could be monitored, checked and avoided if certain precautionary measures are instituted. One of them is by monitoring the health status of the people who are exposed to pesticides. Levels of pesticides residues could be measured in appropriate biological samples to determine the extent of exposure. Good knowledge, attitude and hygienic practices may also help in alleviating the problem of excessive exposure to pesticides.

Acute and chronic effects of occupational exposure to pesticides have been well documented. These exposures have been partly explained because of unsafe work practice and habits of pesticide handling especially among farmers in developing countries. Occupational exposure to pesticides could occur at the following handling of pesticides such as purchase, transportation, storage, retrieval, mixing, loading, spraying, disposal of used container, and care of pesticide sprayer. Exposure could also occur from misuse of protective equipment and clothing, unsafe work habit such as drinking, eating, and smoking while working and lack of personal hygiene. Besides that, enforcement of occupational health and safety legislation, custom and tradition, climatic, socioeconomic, demographic and other local factors have substantial effects on the extent of occupational exposure to pesticides (Nordin et al., 2001).

2.3 Pesticides

Pesticide is described as any substance or mixture of substances purposely for preventing, destroying, repelling, or mitigating any pests (US EPA, 2009). Pesticides are toxic chemicals and are designed to kill living organisms. Sometimes they can have adverse effects on users or others who may come into contact with pesticides, either in

the short or the longer term. The word “pests” refer to the living organisms that occur where they are not wanted or that cause damage to crops or humans or other animals. Examples include insects, mice and other animals, unwanted plants (weeds), fungi, microorganisms such as bacteria and viruses.

Pesticides are categorized by their method of dispersal or mode of action, such as an ovicide, which kills the eggs of pests. Although insect growth regulators are not specifically kill pests, but they are also considered as pesticides because they modify the insect’s growth in such a way as to stop its damages effects. Other categories are insecticides, herbicides, rodenticides, fungicides etc.

Since pesticides may be not entirely specific for their target organisms, their presence in the environment may endanger other living species, including human being. Knowledge of exposure levels is a first step in the risk-evaluation process, and can be acquired by measuring the dose that enters the body. This is usually done by monitoring the biological samples. In cases of exposure**,** the skin is a significant route of absorption, biological monitoring has proven to be reliable for obtaining information on absorbed dose (Aprea, 2002).

2.3 Pesticides Issues

The Third World uses 80% of the world’s pesticide and World Health Organization (WHO) estimates that all of the 220,000 annual pesticide related deaths occur in the Third World (Xavier et. al, 2004). The concerns begin since Rachel Carson’s publication, “Silent Spring” year 1962 which described the effects of organochlorine pesticides such as DDT on bird populations. It was the first public

statement of concern that pesticides could affect the environment. There was also real concern about the possible effects of hazardous pesticides causing severe health and environmental problems in developing countries. A United Nation Food and Agriculture Organization survey in 1995 compared the effect of ten years of effort to reduce the impact of pesticide use in developing countries. It revealed no change on health issues and a deterioration of the environment.

In 1992, a WHO-sponsored World Declaration on the Control of Malaria and a Global Strategy for Malaria Control had been signed and endorsed by governments. Prior to this time, DDT was considered as the insecticide of choice and it was thought that there were no acute toxic health impacts to applicators or any significant risks to humans. However, the new Global Strategy recognized the need for an integrated approach that involved early diagnosis and prompt treatment, selective and sustainable preventive measures, including vector control, prevention, early detection, and containment of epidemics (WHO, 1993). However, because new and safer insecticides such as synthetic pyrethroids were available, the experts indicated that "DDT no longer merits being considered the only insecticide of choice" (WHO, 1995). There has been a growing concern globally in highlighting the hazards of OCP exposures and their impact on bio-diversity and human health, particularly those involving hormone-disrupting chemicals since year 1993.

In 1997, reflecting growing interest at various international forums in the reduction and elimination of POPs, the World Health Assembly adopted a resolution to reduce reliance on insecticides for control of vector-borne disease by promoting Integrated Pest Management and ensuring that DDT was used only within programs that

take an integrated approach.

In 2002, the Stockholm Convention was held to discuss the persistent organic pollutants (POPs) issues which persist in environment and cause hazardous effects to human and wildlife. It is a global treaty to protect human health and the environment from POPs. This convention focuses on eliminating or reducing the releases of 12 POPs, the so-called 'Dirty Dozen' (UNIDO, 2006). Because of long-standing concerns about their high toxicity, these compounds are among the most widely studied synthetic chemicals (WWF, 1999).

2.5 Exposure and general effects of pesticides to human

In the last 50 years more than 75,000 chemicals have been developed and introduced into the environment. In this century, several hundred billion pounds of pesticides have been produced and released into the global environment. Nearly 5 billion pounds of DDT alone have been applied both indoors and out since it was introduced in 1939 and DDT is only one of the nearly 600 pesticides currently registered for use in the world (WWF, 1998).

Human especially farmers can be exposed to the pesticides through diet and application of pesticides in agricultural sector.

Table 2.1: The general effects of pesticides (Murphy, 1997)

General toxicity categories		
CATEGORY	SYSTEM AFFECTED	COMMON SYMPTOMS
Respiratory	Nose, trachea, lungs	Irritation, coughing, choking, tight chest
Gastrointestinal	Stomach, intestines	Nausea, vomiting, diarrhea
Renal	Kidney	Backpain, urinating more or less than usual
Neurological	Brain, spinal cord	Headache, dizziness, behaviour confusion, depression, coma convulsions
Haematological	Blood	Anaemia (tiredness, weakness)
Dermatological	Skin, eyes	Raches, itching, redness, swelling
Reproductive	Ovaries, testes, fetus	Infertility, miscarriage

Some general effects of pesticides can be divided into several categories as seen in the Table 2.1. Many reports suggest numerous consequences of pesticide exposure which include an increasing incidence of breast cancer in women and decreased sperm counts and increased incidence of testicular cancer in men. They also caused adverse wildlife effects which include birth defects, reproductive failures, and sexual abnormalities. These have stimulated research into both the chemical and molecular actions of the pesticides particularly in the clinical and epidemiological effects of such

pesticides presents in the environment. The growing body of evidence on the hormone-like effects of many synthetic chemicals, including pesticides, in fish, wildlife and humans, has led to the endocrine disruption screening programs relating to persistent organic pollutants (Jacobs, 2001).

2.6 Pesticides exposure among farmers

Farmers in the developing countries depend on the use of chemical pesticides to get rid of their pest problems. In this process, a large quantity of these toxic chemicals remain in the environment and cause human health hazards, and the symptoms may vary from headache to cancers. Pesticides are a major source of occupational injury and illness to which farmers are exposed. Such health effects are dependent upon the nature of the substance, the dose received, the route of exposure such as inhalation, ingestion or skin absorption and individual acceptability. The chronic effect usually occurs following repeated low dose exposure over an extended period of time. Exposure to pesticides normally occurs while preparing the spray solutions, loading in the spray tank and while applying the pesticide (MMA, 2000).

Jeyaratnam (1990) carried out a survey on acute pesticides poisoning among agricultural workers in Indonesia, Malaysia, Sri Lanka and Thailand. The ranged of pesticides uses among agricultural workers in Indonesia to Malaysia was found to be 29.8 % to 91.9 %. About 10 to 20 % of the pesticide users suffered episodes of pesticides poisoning during their working life.

Acute pesticide intoxications are a high priority of concern in developing countries. These intoxications are not “third world diseases” because this problem exists in all countries, although at a different level.

2.7 Persistent Organic Pollutants (POPs)

One of the well-known groups of pesticides that always come under scrutiny is the persistent organic pesticide group. Due to its chemical nature, characteristic and properties, members of this group are often referred as persistent organic pollutants (POPs). Short-term exposure to high concentration can be fatal or result in serious illness. Lower chronic levels have been implicated in a wide array of health and environmental problems (WWF, 1999). POP pollution has touched every region in the world. Most developed and developing nations have given much attention to POPs and strong action has been taken to curb problems due to POPs’ contamination. Reproductive, developmental, behavioral, neurological, endocrine, and immune adverse health effects on people have been linked to POPs. Chronic exposure to certain POPs in low doses can affect reproductive and immune system deficits (EPA, 2009).

2.7.1 Definition

Persistent organic pollutants (POPs) are carbon-based chemical compound and mixtures that share several characteristics which include high toxicity, persistence, a special affinity for fat and a propensity to evaporate and travel long distances (WWF, 1999). POPs are halogenated organic compounds that resist photochemical, biological and chemical degradation.

POPs are highly stable organic compounds used as pesticides or in industry. They are also byproduct generated from some combustions and industrial processes. The characteristics that make POPs chemicals unique also make them an urgent global environmental health problem. Because of their physical properties, these chemicals persist in the environment for many years, concentrate in fatty tissues and bioaccumulate as they move up the food chain, travel long distances in global air and water currents. They generally move from tropical and temperate regions to concentrate in the northern latitudes and have been linked with serious health effects in humans and other living organisms, even at very low exposures (Schafer and Kegley, 2002).

2.7.2 Types of POPs

POPs include a range of substances that include intentionally produced chemicals currently or once used in agriculture, disease control, manufacturing, or industrial processes. PCBs have been useful in a variety of industrial applications (e.g., in electrical transformers and large capacitors, as hydraulic and heat exchange fluids, and as additives to paints and lubricants) and DDT, which is still used to control mosquitoes that carry malaria in some parts of the world. Unintentionally produced chemicals, such as dioxins, that result from some industrial processes and from combustion (for example, municipal and medical waste incineration and backyard burning of trash) (U.S.EPA, 2002). POPs include aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex and toxaphene, two industrial chemicals include hexachlorobenzene (HCB). By-products of industrial processes and combustion are dioxins, furans, HCB and polychlorinated biphenyls (PCBs) (FOTE, 2006) which also known as Dirty Dozens.

2.7.3 Uses and Benefits

Because of their unique physical properties that do not mean that they cannot be used safely and provide real benefits. A main example is DDT, where the only proven problems relate to the high level of accumulation when it was used very widely, in large quantities and in a largely uncontrolled way. In fact, when used at low levels as a residual indoor spray, it remains the most effective and cheapest anti-malarial treatment available (Croplife, 2005).

2.7.4 Health Effects of POPs

Humans are generally exposed to POPs through their food supply. The majority of POPs are known endocrine disruptors and many adversely affect the immune system (Huang et al., 2006). Many such compounds have been shown to have adverse long-term health effects. Organochlorine pesticides (OCPs) and organophosphate pesticides (OPPs) are effective pest control agents and have been widely applied in agriculture all over the world. All these groups of POPs have been shown to be ubiquitous environmental pollutants due to their great chemical stability and lipid solubility (Liu and Pleil, 2002).

2.7.5 Factors Affecting the Absorption of Organochlorine Pesticides

Several factors can affect the absorption of pesticides in human body. According to World Health Organization, people can be exposed to excessive pesticide levels while working via food, soil, water or air or by directly ingesting pesticide products (WHO, 2004).

The toxicity of pesticide in human beings is influenced by various factors such as age, gender and health status of the individual in addition to the intensity and frequency of pesticide used. Comparatively, children are at greater risk than the adults. The human detoxification system plays a vital role in reducing the harmful effects of the pesticides (Xavier et. al. 2004).

Popendorf (2000) had made a comparison among harvesters about factors which might affect the exposure of pesticides residues in his study. The factors included age and sex distribution of work crews, their apparel and work practices as related to foliar contact, and exposure to airborne particulates. Recurring high values of airborne particulates suggest that contaminated dust is the primary vehicle for residue exposure.

Human exposure to OCPs also attributed mainly to food chain. Salem et. al. (2009) stated that consumers of dairy products are exposed to the OCPs residues which accumulated in fat-rich dairy product. The importance of the consumption of eggs, chicken and meat as a source of OCP has been established worldwide (Ahmad et. al., 2009).

2.7.5 Global Regulation and Laws Pertaining to POPs

There are several laws in Malaysia (Ramachandran and Mourin, 2006) which enacted to control other specific aspects of pesticides such as:

1. The Hydrogen Cyanide (Fumigation) Act 1953 which controls the fumigation of premises including ships using either hydrogen cyanide or methyl bromide.

2. The Environmental Quality Act 1974 has the primary objective of controlling the discharge of waste including pesticide from factories into the environment in such volume, composition or manner so as not to cause adverse effects on human health and the environment.

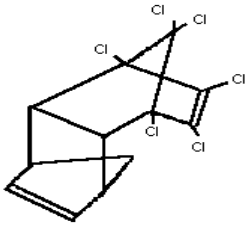
3. The Food Act 1983 of which Schedule 16 of its Food Regulations 1985 prescribe the maximum residue levels of pesticides in food.

4. The Occupational Safety and Health Act 1994 provide the legislative framework to promote, stimulate and encourage high standards of safety and health of workers at work.

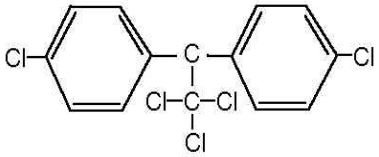
2.8 Organochlorine Pesticides (OCPs)

Organochlorine pesticides are insecticides composed primarily of carbon, hydrogen, and chlorine. They break down slowly and can remain in the environment long after application and in organisms long after exposure. They also build up in fatty tissues, and remain in our bodies for a long time.

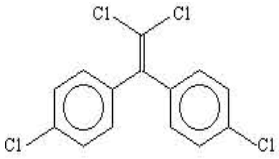
Below are some of the chemical structures for OCPs:



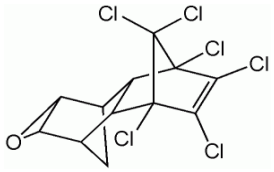
Aldrin

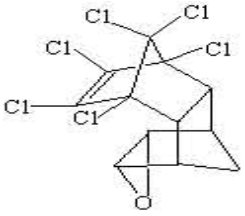


DDT

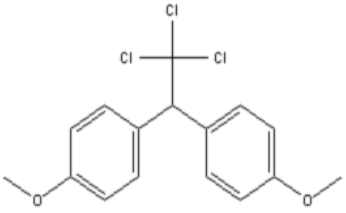


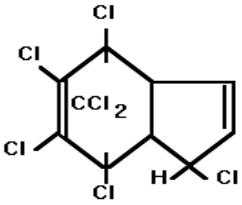
p,p'- dde

Dieldrin 

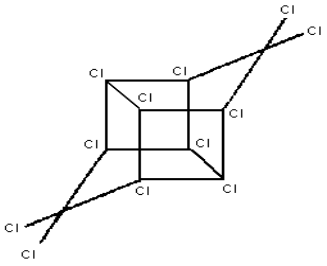


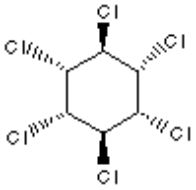
Endrin

Methoxychlor 

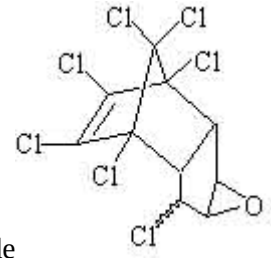


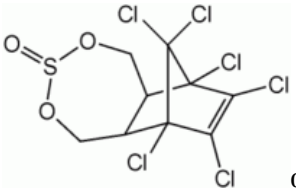
Heptachlor

Mirex 

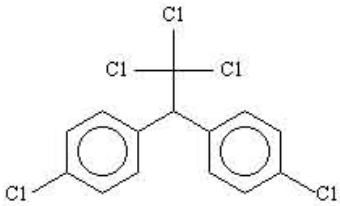


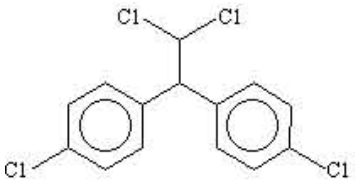
Lindane

Heptachlor Epoxide 



α-endosulfan

p,p-ddt 



p,p-ddd

2.8.1 OCPs characteristics

One common characteristics of OCs is a generally high solubility in lipids or lipophilicity. The highest concentrations of OCs are found in lipids, residues maybe stored in fat depots throughout the organisms.

One of the best known characteristics of organochlorine pesticides is their persistence in the environment. Persistence is based on the half-life both in the physical environment and in the organism. Half-lives can range from month to year. Residues of some organochlorine may persist for decades possibly centuries in the environment but there are many physical factors that influence this including temperature, light, pH and moisture.

Most of the halogenated OCPs have low melting point and a vapor pressure lower than 1000 Pa. These special properties make them semi-volatile and permit OCPs to volatilize from hot region and condense in colder region thus facilitating their range and transport through the atmosphere.

Table 2.2: Physical-chemical properties of organochlorine pesticides (Shen and Wania, 2005).

Pesticides	Half-life (years)	Vapor pressure (mm Hg)	Melting point (^{0}C)
DDT	10-15 years	1.9 x 10^{-7} at 20^0C	109
Dieldrin	5 years	400 µPa at 20^oC	176 - 177
Endrin	12 years	1E-6 (25^oC)	240

Heptachlor	2.7 – 22.9 years	3 x 10-4	95
DDD	> 190 years	1.35×10^{-6}	109.5
Methoxychlor	120 days	Very low	77
γ-hch	400 days	3.3 x 10-5	112.5
Aldrin	20-100 days	2.31 x 10-5	104
DDE	6 years	6.0 x 10-6	89

Almost all the persistent OCPs are lipophilic in nature, which means they are highly lipid soluble and have very low water solubility.

2.8.2 Organochlorine Benefits and Risks

The organochlorine compounds are used on a large scale in agriculture, forestry and public health. In agriculture, they act as insecticides, acaricides, and fumigants to control pests in orchard, vegetable, grain, cotton and tobacco fields and vineyards. Some of them are also used for seed dressing and as rodenticides. In the field of public health they have played an important role in controlling diseases such as malaria. They are still use in many developing countries to control such diseases (Mostafa, 1991).

The greatest benefit from pesticide use has been the millions of human lives saved from yellow fever, encephalitis, malaria and insect borne diseases. Organochlorines also protected food from pest damage (Maruf, 2001).

Some organochlorine pesticides are used on a wide array of crops. Endosulfan for example is use to control pests in vegetables, fruits, cereal and cotton, as well as ornamental shrubs, trees, vines, and ornamental plants. Lindane is another organochlorine with a range of uses. Lindane is used to protect crop seeds from insects, for pest control in forests, on livestock household pets for control of ticks and other pests, and in homes to control another household pest. Lindane is the active ingredient in many medicated shampoos and soaps to control head lice and scabies. It is also used to protect crop seeds from insects, for pest control in forests, on livestock and household pets for control of ticks and other pests, and in homes to control ants and other household pests. The lindane is classifies as a possible human carcinogen and it is particularly dangerous to the nervous and hormone system (Pesticide Fact Sheet, 2000).

A lot of health effects can be associated with organochlorine pesticide exposure including irritation to the eyes, nose, and throat, damage to the central nervous system and kidneys and for some an increased risk of cancer. Since the main ingredients in pesticides can be organic, they can also affect vision and memory. Pesticides are poisonous and dangerous. Although the level used by farmers are believed to be low and less hazardous to human, but residues will build up over the years and cause disease to develop slowly.

Some of the organochlorine are persistent in the environment and can be real hazard to wildlife and many believe a potential hazard to man (Maruf, 2001). DDT, a carcinogenic organochlorine insecticide causes brain and nerve damage and harms both human and wildlife production. Aldrin, dieldrin and endrin are extremely toxic and persistent organochlorine insecticides that have been shown to produce cancer, birth