

RISK ASSESSMENT OF MULTI-ROUTE EXPOSURE TO ORGANOPHOSPHATE PESTICIDE
OF VEGETABLE GROWERS (A CASE STUDY AT BANG RIENG SUB-DISTRICT,
KHUAN NIENG DISTRICT, SONGKHLA PROVINCE)

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การศึกษานี้ได้ศึกษาเส้นทางการรับสัมผัสสารกำจัดศัตรูพืชกลุ่มออร์กาโนฟอสเฟตและประเมินความ
 เสี่ยงต่อสุขภาพจากการได้รับสัมผัสของเกษตรกรในพื้นที่เกษตรกรรมบางเหริ่ง โดยทำการเก็บตัวอย่างเพื่อ
 วิเคราะห์ในช่วงฤดูแล้งและฤดูฝน เพื่อตรวจวัดปริมาณสารกำจัดศัตรูพืชกลุ่มออร์กาโนฟอสเฟตตกค้าง ได้แก่
 คลอร์ไพริฟอส ไดโครโตฟอส และ โพรพิโนฟอส ในน้ำ ดิน อากาศ และ บริเวณพื้นที่ผิวสัมผัสร่างกายของ
 เกษตรกร ได้แก่ มือ และ ลำตัวรวมทั้งทำการวิเคราะห์ปริมาณสารเมตาบอไลต์ของสารกลุ่มออร์กาโนฟอสเฟตใน
 ปัสสาวะของกลุ่มเกษตรกรปลูกผักจำนวน 33 คน และ กลุ่มอ้างอิง 17 คน ผลการศึกษาพบว่า ค่าเฉลี่ยความเข้มข้น
 ของสารกำจัดศัตรูพืชตกค้างกลุ่มออร์กาโนฟอสเฟตในน้ำ อากาศ ดิน มือ และ ลำตัว ของเกษตรกร อยู่ในช่วง 0.11-
 0.217 มก.ก./ลิตร, 0.024-0.070 มก./ลบ.ม., 0.004-0.881 มก./กก., 0.024-0.086 มก./มือสองข้าง, 0.558-2.112
 มก.ก./ตร.ซม. ตามลำดับ นอกจากนี้ค่าความเข้มข้นเฉลี่ยของสารเมตาบอไลต์กลุ่มออร์กาโนฟอสเฟต ในปัสสาวะ
 ของเกษตรกรปลูกผักสูงกว่ากลุ่มอ้างอิงอย่างมีนัยสำคัญทั้งสองฤดู การศึกษายังชี้ประเด็นสำคัญให้เห็นเส้นทางการ
 การรับสัมผัสสารกำจัดศัตรูพืชกลุ่มออร์กาโนฟอสเฟตของอาชีพเกษตรกรปลูกผัก ได้แก่ ทางการดื่มน้ำ การสูดดม
 และการสัมผัสทางผิวหนัง โดยเฉพาะการสัมผัสบริเวณมือและผิวหนังที่ร่างกาย ซึ่งได้รับสารกำจัดศัตรูพืช
 โดยตรง รวมทั้งการสัมผัสสารกำจัดศัตรูพืชที่ตกค้างในดิน และน้ำ การรับสัมผัสสารระยะยาวของสารกำจัด
 ศัตรูพืชกลุ่มนี้ ซึ่งจัดเป็นสารที่ไม่ก่อให้เกิดมะเร็ง แต่อาจจะก่อให้เกิดผลกระทบต่อสุขภาพชนิดเรื้อรังได้ เนื่องจากค่า
 ดัชนีบ่งชี้อันตราย Hazard Index (HI) ทางเส้นทางการสัมผัสได้แก่ การสูดดม มือสัมผัส และผิวหนังที่ร่างกาย มี
 ค่าเกินกว่าค่าที่ยอมรับได้ ($HI > 1$) ในฤดูแล้งเท่ากับ 38 6 และ 88 เท่า ตามลำดับ และในฤดูฝน เท่ากับ 36 11 และ
 62 เท่า ตามลำดับ อย่างไรก็ตามยังพบว่าการใช้น้ำเพื่อการอุปโภคและบริโภค และการสัมผัสดิน ของเกษตรกร
 อาจจะไม่ก่อให้เกิดความเสี่ยงต่อการรับสัมผัสสารกำจัดแมลงกลุ่มนี้ สำหรับผลกระทบต่อสุขภาพชนิดเฉียบพลัน
 นั้น เกษตรกรอาจจะมีความเสี่ยงต่อการได้รับสัมผัสสารคลอร์ไพริฟอส และไดโครโตฟอส จากการสูดดม ใน
 ระหว่าง การเตรียม การผสม และการฉีดพ่นสารกำจัดแมลง และ พบว่าการสัมผัสสารไดโครโตฟอส อาจจะ
 ก่อให้เกิดความเสี่ยงสูงสุด เนื่องจากมีค่าดัชนีบ่งชี้อันตรายสูงสุด ดังนั้นการศึกษานี้ เสนอให้หน่วยงานรัฐบาล
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ASST. PROF. PONGTHEP SUTHERAVUT, DR. PHIL. 128pp.

This study investigated the multi-route exposure of organophosphate pesticides (OPPs) and evaluated health risk to vegetable growers living in the Bang Rieng agricultural community. Samples were collected in wet- and dry- season, then the residues of organophosphate pesticides i.e. chlorpyrifos, dicofos and profenofos contaminated in water, soil, air, and on the vegetable growers contact area i.e. hand and their bodies were analyzed. OPPs metabolite residues were also quantified from urine samples collected from 33 vegetable growers and 17 reference people living outside farm. The results showed that OPPs mean concentrations in water, air, soil, vegetable grower's hands and their bodies were in the range of 0.011-0.217 $\mu\text{g/L}$, 0.024-0.070 mg/m^3 , 0.004-0.881 mg/kg , 0.024-0.086 mg/two hands , 0.588-2.112 $\mu\text{g/cm}^2$, respectively. Besides, the average concentration of urinary OPPs metabolite in the vegetable growers was significantly higher than the reference in both seasons. The results indicated that the occupational exposure pathways of the vegetable growers were (1) water ingestion, (2) air inhalation, (3) dermal contact of OPPs by hand and body directly and OPPs residues in water and soil. Long-term exposure of these non-carcinogenic pesticides in the vegetable growers may result in chronic adverse health effect in which the Hazard Index (HI) of the exposure pathways for inhalation, hand contact, and body contact were greater than acceptable level ($\text{HI} > 1$). The HI of the pathways in the dry season were 38, 6, and 88 times, respectively and 36, 11, and 62 times, respectively in the wet season. Water use for the vegetable growers, i.e., drinking and bathing, and soil contact may not be at risk. For acute adverse effects, the vegetable growers may be at risk via the inhalation pathway of chlorpyrifos and dicofos during their applications through pesticide mixing, loading, and spraying. The dicofos with the highest risk estimation (highest HI) is the most dangerous pesticides. This study suggested that the authorities and community should have the appropriate strategies concerning about risk reduction and risk management.

Field of Study: Environmental Management Student's Signature:
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Co-advisor's Signature:
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ABBREVIATIONS

ABS	= Absorption factor
ACGIH	= American Conference of Government Industrial Hygiene
Ach	= Acetylcholine enzyme
ADD	= Average daily dose
A	= Averaging time
BW	= Body weight
C	= Concentration
CF	= Contact frequency
CR	= Contact rate
DAP	= Dialkyl phosphate
DEP	= Diethylphosphate
DETPD	= Diethylthiophosphate
DMP	= Dimethylphos
DMTP	= Diethylthiophosphate
Dpot	= Potential Dose
Dint	= Internal Dose
ED	= Exposure duration
EF	= Exposure frequency
GC-FPD	= GAS chromatography- flame photometric detector
HI	= Hazard Index
HQ	= Hazard Quotient
IPCS	= International Program on Chemistry
IR	= Intake rate
IRIS	= Integrated Risk Information System
LEL	= Lowest effects level
LOAEL	= Lowest observed-adverse-effects level
LOD	= Limit of detection
MOE	= Margin of Exposure
Mw	= Molecular Weight
NOAEL	= No-observable-adverse-effects level
NOEL	= No-observable-effects level
OPPs	= Organophosphate Pesticides
RfD	= Reference dose
US EPA	= United State Environmental Protection Agency
WHO	= World Health Organization
EXTOXNET	= Extension Toxicology Network
US EPA	= United State Environmental Protection Agency

CHAPTER I

INTRODUCTION

1.1 Theoretical Background

Thailand exports a large amount of agricultural products to the world market every year. About 55.7 % of Thai population is working in the agricultural sector with their incomes generated by selling farm products (Agricultural Extension Department, 2007). To minimize crop damage and to increase land productivity yield, the use of pesticides has been more and more essential. Pesticides import has increased considerably from approximately 4,000 tons in 1962 to 37,039 tons in 2001 (Siriwong, 2006). The burden of pesticides, as applied for crop protection, may affect environmental quality and human health (Purdue University Cooperative Extension Service, 2006; Siriwong, 2006).

Pesticides which are easy to buy and highly effective for pest control has attracted farmers to apply them at large quantity. In Thailand, since the ban of organochlorine pesticides, the most widely used pesticide has become organophosphate pesticides (OPPs). OPPs are very effective in eradication of insects and have short life time. But they are harmful to people. At certain dose, they can inhibit the function of nervous system enzyme, especially acetylcholinesterase. Severity of its poison varies with exposed dose and duration. Their adverse effects emerge as pulmonary edema, cyanosis, muscle spasm, muscle weakness, blurred vision, respiratory difficulty and eventually death due to the respiratory failure (Toxnet, 2006).

Generally farmers work in areas contaminated with pesticides applied. These pesticides can enter their bodies through many routes of exposure penetration through skin (dermal exposure), inhalation (respiratory exposure) and ingestion (oral exposure), according to National Association of State of Agricultural Foundation (2008). Because of their wide usage, frequent exposure to OPPs can cause adverse effect among farmers. Therefore, health risk posed by exposure to OPPs requires a careful assessment to protect the farmer. Conventional approaches to exposure and risk assessment, however, has their limitations that lead to underestimated risk:

(1) Exposure via different routes is usually treated as separated event (EPA, 1992a). Therefore, the exposures that occur through different routes at the same duration of time are not considered.

(2) Exposure of different chemicals is often treated as individual events and their cumulative toxicity effect of different chemicals is not addressed.

To address this weakness, the assessment can be based on a new method developed by the U.S. Environmental Protection Agency (EPA), cumulative Risk Assessment, the assessment of risk resulting from all routes of exposure to several substances sharing a common mechanism of toxicity (EPA, 2000b).

In Thailand, however, the use of conventional practice of exposure and risk assessment is still common while the cumulative risk assessment method has never been attempted. This study will employ the cumulative risk assessment method to

estimate risk from three widely used OPPs (chlorpyrifos, dicotofos and profenofos) for the vegetable growers in Bang Rieng sub-district.

Bang Rieng sub-district is a large agricultural sub-district in Songkhla Province. The Bang Rieng community can be divided into two regions based on the patterns of agricultural practices: intensive and integrated pest management. Intensive agriculture refers to a commercial agriculture system that relies on a large market. As part of intensive practices, farmers mainly use pesticides for pest control. IPM agricultural, on the other hand, focuses on reducing pesticide use through alternative techniques such as biological control, crop rotation, or netted crop growing. This study focuses on the intensive agricultural area due to intensive pesticide use in Thailand. The intensive agricultural region within the Bang Rieng community consists of approximately 891 rai (143 km²) of vegetable farm area, including 92 households (information obtained from the GIS survey by the Faculty of Natural Resources, Prince of Songkhla University, 2004). The vegetable farmers are living in, or around, the vegetable farms. Non-agricultural areas (reference areas) are rubber plantation areas, 7-8 km away from the farm area, within the same sub-district. The reference areas consist of 1,056 rai (169 km²) for rubber plantations including 96 households (Office of Bang Rieng sub-district, 2004) (Figure 1.1).

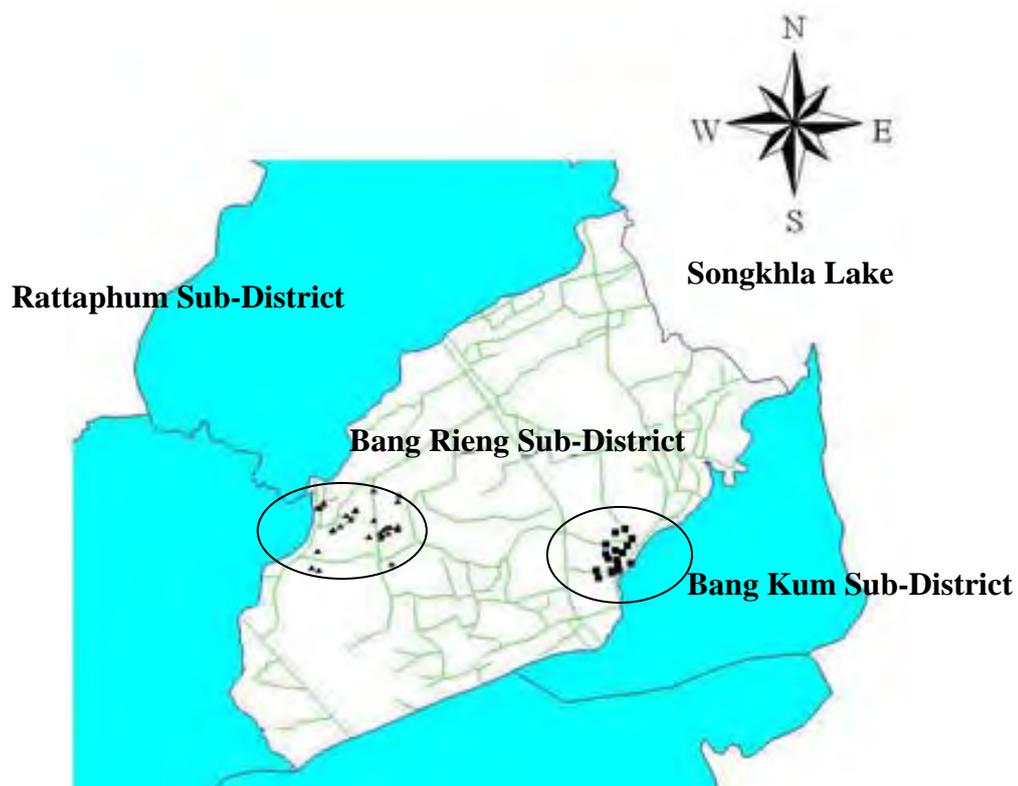


Figure 1.1 Locations of Farm Area (▲) and Reference Area (●) of Bang Rieng Community.

Much of the research in Thailand concerns on dermal or inhalation or ingestion route. In addition, Bang Rieng agricultural area has been for studied exposure assessment of the pesticides on inhalation route only (Jirachaiyabhas, 2004). No research has been conducted to studying all pathways together. Moreover, no research has used biomarker (urine metabolite) with exposure pathway. This study will focuses on demal, inhalation and ingestion exposure and biomarker in urine to examine the relationship between potential risk and potential farmers exposure to organophosphate pesticides.

1.2 Objective

The main objective of this study is to estimate organophosphate pesticide exposure hrough pathway of inhalation, ingestion and dermal contract. The specific objectives include:

1.2.1 To identify factors concerning the use of pesticide by vegetable growers.

1.2.2 To estimate organophosphate pesticides exposure by measuring concentration of urinary metabolites.

1.2.3 To evaluate the potential risk associated with the vegetable growers' exposure to OPPs.

1.2.4 To devise the model for studying vegetable growers exposure to pesticides in Thailand.

1.3 Hypothesis

Vegetable growers are at risk of OP pesticide exposure from inhalation, ingestion and dermal pathways.

1.4 Scope of the Study

This study took place at Bang Rieng agricultural community, Khuan Nieng District, Songkhla Province. It was designed to determine organophosphate pesticide exposure of vegetable growers working in this community. The farmer exposure was studied using both; direct and indirect method. The indirect method, the pesticide exposure questionnaire, was used to interview the farmers, whereas in the direct method was analyzed pesticides concentration which expose the farmers via dermal, inhalation and oral pathway. The samples were collected in dry and wet seasons. Air and soil samples with contaminated pesticides in working area were collected. Water consumed and use for bathing by farmers was collected. OPPs on farmer's body skin, hand and dialkyl phosphates (DAPs) of farmer's urine samples as biomarker were collected. The OPPs in this study was focused on chlorpyrifos, profenophos and dicotophos which have been widely used in Bang Rieng Sub-district. The data from direct and indirect methods were evaluated to be database for risk estimation. Risk estimation will be performed to assessing the potential risk associated with farmer's exposure to OPPs.

CHAPTER II

LITERATURE REVIEW

2.1 Organophosphate Pesticide

Organophosphate pesticides (OPPs) were developed during the early 19th century. Since the removal of organochlorine pesticides from use, OPPs have been the most widely used pesticides available today. More than forty of them are registered for use and all run the risk of acute and sub acute toxicity. OPPs are used in agriculture, in house, in garden, and in veterinary practice (EPA, 1999).

OPPs are classified in group of non-persistent pesticides. By their nature, OPPs do not persist in the environment; most decompose within several weeks with exposure to sunlight and water. In addition, these pesticides are not bioaccumulated, therefore they are typically metabolized and excreted from the body in few days. However, these non-persistent pesticides are structurally diverse and have varied mechanism to action (Barr and Needham, 2002)

2.1.1 Organophosphate Pesticide Groups

OPPs shared a common chemical structure of OPPs is shown in figure 2.1, but they are differed greatly in the detail of their structure, in their physical and pharmacological properties, and consequently in the use to which they have been put or for which they have been proposed. The majority of OPPs, the alkyl group (R1, R2) are represented by either methyl or ethyl groups, whereas, the chemical structure of X moiety defines the “leaving group”, the majority of the structural difference between individual OPPs (Figure 2.1). OPPs are often used the phosphate moiety in the “thio” form (P=S) where metabolic oxidative desulphuration is necessary to produce an OPPs with anticholinesterase activity, the “oxon” form (P=O).

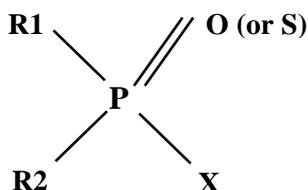


Figure 2.1 Common Structure of Organophosphate Pesticide

All the compounds may be placed in four main categories, depending on the character of the X constituent (Gallo and Lawlyk, 1991), as flows:

(1) Categories I; X is contained a quaternary nitrogen such as ecothiopate isodide.

(2) Categories II; X is F: Fluorophosphate groups have only a few compounds such as dimefox and diisopropyl fluorophosphates.

(3) Categories III; X is CN, OCN, SCN or Halogen other than F such as tabun, parathion.

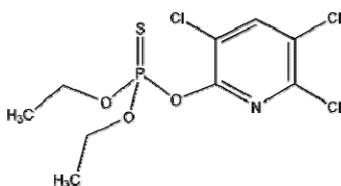
(4) Categories IV; It may be subdivided into at least eight groups on the basis of their R1 and R2 constituents. Several of this group differed either quantitatively or qualitatively in toxicity, and in some instance the basis for the difference was known. The eight groups and an example of each are as follows:

- (4.1) Dimethoxy compounds such as dicrotophos, dimethoate, malathion
- (4.2) Diethoxy compounds such as chlorpyrifos, diazinon, parathion
- (4.3) Other dialkoxy compounds such as propaphos
- (4.4) Diamino compounds: schradan
- (4.5) Chlorinated and other substituted dialkoxy compounds such as haloxon
- (4.6) Trithioalkyl compounds: merphos, S,S,S-tributyl phosphorotrithioate
- (4.7) Triphenyl and substituted triphenyl compounds such as o- and p-cresyl saligenin phosphate
- (4.8) Mixed substitute compounds such as leptophos, methamidifos

2.1.2 Organophosphate Pesticide Properties

The information for OPPs pesticide as described below base on information from Extension Toxicology Network (EXTOXNET, 1996), Pesticide Action Net Work (PAN, 2000) and United State Environmental Protection Agency (US EPA, 1999).

(1) Chlorpyrifos



Chemical structure: $C_9H_{11}Cl_3NO_3PS$

Molecular weight: 350.6

CAS registry NO.2921-88-2

The scientific name for chlorpyrifos is *O,O*-diethyl *O*-3,5,6 -trichloro-2-pyridyl phosphorothioate. Technical-grade of chlorpyrifos is composed of not less than 82 %. The trade names used for chlorpyrifos is composed of Chlozan, Dorsban, Eraser, Govern, Lorsban, Nufos, Pilot, Saurus, Warhank, Whirlwind and Yuma.

Technical chlorpyrifos is a white crystalline solid with a melting point of 41.5 to 42.5 °C. Chlorpyrifos is stable in neutral and acidic aqueous solution; however stability decrease with increase pH. Chlorpyrifos is practically insoluble in water, but is soluble in most organic solvents (i.e., acetone, xylene and methylene chloride). Chlorpyrifos is not particularly volatile based on its low vapor pressure of 1.87×10^{-5} mmHg at 20 °C (Merck Index, 11th edition). Its maximum attainable vapor concentration is 25 ppb at 22 °C.

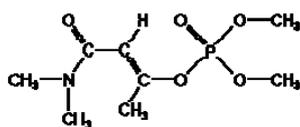
Fate in Human and Animals:

In the human, chlorpyrifos and its metabolites are eliminated relatively rapidly following a single dose. Its half-life in the blood after a single oral appears to be about one day. Following oral intake of chlorpyrifos by rats, 90 % was removed in the urine. Metabolic reaction of the chlorpyrifos that occurs in the human body is diethylthiophosphate, diethylphosphate and trichloro-2-pyridinol.

Environmental fate:

Chlorpyrifos adsorbs strongly to soil particles and it is not readily soluble in water. It is not mobile in sandy loam and loamy sand soils. Chlorpyrifos is less persistent in the soil with a higher pH. Adsorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis and soil microbes. The persistence in soil varies depending on soil type, and environmental condition. The typical aerobic soil metabolism half life ($T_{1/2}$) ranges from 11 to 180 days, with mean 28.7 days. Much longer half life of 175 to 1576 days has been reported for termiticide application rate. The soil/water coefficient (K_c) values range from 360 to 31000, indicating it is not very mobile in soil.

(2) Dicrotophos



Chemical structure: $C_8H_{16}NO_5P$

Molecular weight: 237.21

CAS registry NO. 141-66-2

The scientific name for dicrotophos is 3-dimethoxyphosphinoyloxy-*N,N*-dimethylisocrotonamide. The trade names used for dicrotophos is composed of Birdrin, Carbicron, Diapadrin, Dicron, Ektafos and DDV. Dicrotophos is a mixture of the *E*- and *Z*-isomers in which the *E*- isomer is pesticidally active. Technical dicrotophos is a yellow to dark amber liquid at room temperature with boiling point of 111-112 °C at 0.022 mmHg (399 °C at 760 mm Hg), a density of 1.19 – 1.22 g/mL at 20 °C, a vapour pressure 2.2×10^{-5} mmHg or 2.9 Pa at 20 °C. Dicrotophos is

miscible (mixable in all proportion) with water, acetone, alcohol, acetonitrile, chloroform, methylene chloride and xylene. Dicrotophos is only slightly soluble in kerosene and diesel fuel.

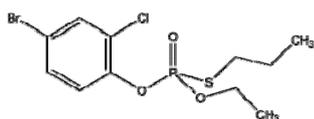
Fate in human and Animal

Dicrotophos is metabolized in part to monocrotophos. Hydrolysis of the vinyl phosphate bond of dicrotophos or its oxidative metabolite to produce dimethyl phosphate is the predominant detoxifying reaction in human. In mammals, including rats, mice, dogs, rabbits, and goats, dicrotophos undergoes hydrolysis to dimethyl phosphate. The residues of dicrotophos are excreted almost entirely within 24 hours, as indicated by a rapid decrease in not-hydrolysed metabolites in urine or milk.

Environmental Fate

The major routes of dissipation of dicrotophos in the environment are microbial degradation in soil and movement into surface and ground water. Dicrotophos degradation is not induced by light exposure. Laboratory studies showed that dicrotophos was stable to photolysis in aqueous solutions (pH = 7) and soil surface (sandy loam soil, pH = 5.7). The half-lives of dicrotophos in the aqueous and soil at pH 5, 7, and 9 are 117, 72, and 28 days, respectively. Dicrotophos and its degradation products do not persist in the environment. In soil, dicrotophos is rapidly degraded under aerobic and anaerobic conditions. The half-life of dicrotophos in sandy loam soil is 2.7 days and 7 days under aerobic and anaerobic condition respectively.

(3) Profenofos



Chemical Formula: $C_{11}H_{15}BrClO_3PS$

Molecular Weight: 373.65

CAS Registry No.: 41198-08-7

The scientific name for profenofos is *O*-4-bromo-2-chlorophenyl *O*-ethyl *S*-propyl phosphorothioate. The trade names used for profenofos include Curacron, Mardo and Kelstrel. Technical profenofos is a pale yellow liquid with a boiling point 100 °C (1.8 Pa) and a density of 1.46 g/cm³ at 20 °C. Pure profenofos is an amber-colored oily liquid with a boiling point of 110 °C (0.001 mmHg). Profenofos has limited solubility in water (20 ppm) but is completely soluble in organic solvent (ethanol, acetone, toluene, *n*-octanol, and *n*-hexane) at 25 °C (Griffin, 1999). Profenofos is stable under neutral and slightly acidic condition, and it is unstable under alkaline condition.

Environmental Fate

Available environmental fate studies show that pH-dependent hydrolysis is the major route of dissipation for profenofos while aerobic and anaerobic metabolisms become important after the initial hydrolysis. Profenofos dissipates in neutral to alkaline soil with a half-life of several days. One of the major degradable, 4-bromo-2-chlorophenol, is persistent in the environment while the fate of another degrade, *O*-ethyl-*S*-propyl-phosphotioate, is not well known. Profenofos hydrolyzes in neutral and alkaline solution, with half-lives of 104-108 days, 24-62 days at pH 7 and 7-8 hours at pH 9. Profenofos metabolizes rapidly in alkaline aerobic and anaerobic condition. In an alkaline (pH 7.8) soil, profenofos degraded with half-life of 2 days under aerobic condition and 3 days under anaerobic condition. Photolysis is not a major pathway in degradation of profenofos.

2.1.3 Effect of Organophosphate Pesticides

OPPs poison insects and mammal primarily by phosphorylation of the acetylcholinesterase enzyme (AChE) at nerve endings. The result is a loss of available AChE so that the effector organ becomes overstimulated by the excess acetylcholine (ACh, the impulse-transmitting substance) in the nerve ending. The enzyme is critical to normal control of nerve impulse transmission from nerve fibers to smooth and skeleton muscle cells, glandular cells, and autonomic ganglia, as well as within the central nervous system (CNS). Some critical proportion of the tissue enzyme mass must be inactivated by phosphorylation before symptoms and signs of poisoning become manifest.

At sufficient dosage, loss of enzyme function allows accumulation of ACh peripherally at cholinergic neuroeffector junction (muscarinic effects), skeletal, nerve-muscle junction, and automatic ganglia (nicotinic effect), as well as centrally. At cholinergic nerve junctions with smooth muscle and gland cells, high Ach concentration cause muscle contraction and secretion, respectively. At skeletal muscle junctions, excess Ach may be excitatory (cause muscle twitching), but may also weaken or paralyze the cell by depolarizing the end-plate. In the CNS, high ACh concentrations cause sensory and behavior disturbances, incoordination, depressed motor function, and respiratory depression. Increased pulmonary secretions coupled with respiratory failure are the usual cause of death from organophosphate poisoning. Recovery depends ultimately on generation of new enzyme in all critical tissues.

Symptoms of acute organophosphate poisoning develop during and after exposure, within minutes to hours, depending on the method of contact. Exposure by inhalation results in the fastest appearance of toxic symptom, followed by the gastrointestinal route and finally the dermal route. All signs and symptoms are chlonergic in nature and affect muscarinic, nicotinic, and central nervous system receptors. The critical symptoms in management are the respiratory symptoms. Sufficient muscular fasciculations and weakness are often observed as to require respiratory support; respiratory arrest can occur suddenly. Likewise, bronchorrhhea and bronchospasm may often impede efforts at adequate oxygenation of the patient.

Bronchospasm and bronchorrhea can occur, producing tightness in the chest, wheezing, producing cough, and pulmonary edema. A life threatening severity of poisoning is signified by loss of consciousness, incontinence, convulsions, and respiratory depression. The primary cause of death is respiratory failure, and secondary cardiovascular component. The classic cardiovascular sign is bradycardia which can progress to sinus arrest. However, this may be superseded by tachycardia and hypertension from nicotinic (sympathetic ganglia) stimulation. Toxic myocardopathy has been a prominent feature of some severe organophosphate poisoning.

Some of the most commonly report early symptoms include headache, nausea, dizziness, and hypersecretion, the later of which manifested by sweating, salivation, lacrimation, and rhinorrhea. Muscle twitching, weakness, tremor, incoordination, vomiting, abdominal cramps, and diarrhea all signal worsening of the poison state. Miosis is often a helpful diagnostic sign and the patient may report blurred and/or dark vision. Anxiety and restlessness are prominent, as are a few reports of choreaform movements. Psychiatric symptoms including depression, memory loss, and confusion have been reported. Toxic psychosis, manifested as confusion or bizarre behavior, has been misdiagnosed as alcohol intoxication (EPA, 1999).

2.1.4 Urinary Organophosphate Metabolites

Urine is the most readily available body fluid, it does not require an invasive procedure such as venipuncture to obtain blood and biopsy to obtain fat and other tissue. Many organophosphates degrade to dialkylphosphate (DAP) metabolites that are excreting in the urine. DAP are rapidly excreted and represent recent exposure, within the post two and three days at most. They are useful for monitoring and exposure since they are detectable in urine at level too low to cause cholinesterase depression and symptoms of poisoning. So Urinary DAP metabolites are important biomarkers of OPPs exposure in biological monitoring.

OP pesticides are usually metabolized to the more reactive oxon form which may bind to cholinesterase or be hydrolyzed to a dialkylphosphate and a hydroxylated organic moiety specific to the pesticide. As a result of binding to cholinesterase, the organic portion of the molecule is released. The cholinesterase-bond phosphate group may be by the loss of the *O,O* dialkyl groups, or may be hydrolyzed to regenerate the active enzyme. These metabolite and hydrolysis product are excreted in the urine within 24-48 hours of absorption.

Six dialkylphosphate (DAP) metabolites are the most commonly measured metabolite of OPPs, include dimethylphosphate (DMP), diethylphosphate (DEP), dimethylthiophosphate(DMTP),diethylthiophosphate (DETP), dimethyldithiophosphate (DMDTP), and dietyldithiophosphate (DEDTP) as present in figure 2.2. Each of the six urinary dialkylphosphate metabolites can be produced from the metabolism of more than one OPPs. In addition to reflect parent pesticide exposure, the level of the metabolites in person's urine may reflect exposure to the metabolite itself, if it was present in the person's environment (CDC, 2003).

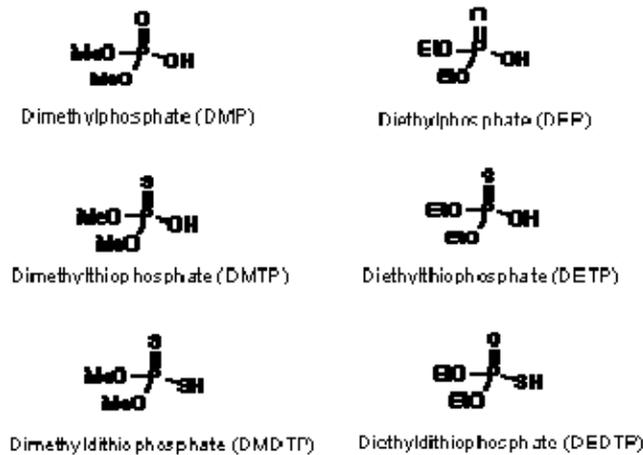


Figure 2.2 Chemical structure of six urinary dialkylphosphate metabolites

2.2 Farmers' Health Risk

Farmers are the biggest users of pesticides and one of the most highly exposed groups to pesticides. They can be exposed through mixing, loading and applying pesticides and from working in treated fields. Agricultural workers can get pesticides into their bodies by various routes including skin (dermal exposure), nose (inhalation exposure), and mouth (oral exposure) (NASDAF, 2008; Rutgers, 1996)

(1) Dermal Exposure

The majority of agricultural pesticide poisoning and injury incident happen through skin exposure. Skin exposure can also occur when a careless application result in pesticide drifting onto people who are working nearby or if agricultural workers are directly sprayed or mixed. The skin can be also exposed to pesticide residues through contact treat soil. Even contact with irrigation water may result in pesticide exposure if pesticides are applied through an irrigation system or residues from the soil and plants get into irrigation water. Pesticide residues can be transferred from dirty hands to other parts of the body if agriculture workers do not wash their hands thoroughly before eating, drinking, smoking, or using the bathroom.

(2) Inhalation Exposure

Pesticide in form of dust, spray mist, or fumes can be sucked into your lungs as you inhale. This route of entry is important during mixing of wettable powders, dust, or granules. You can also be poisoned when fumigating or spraying without the proper respirator. Even inhalation of dilute pesticides can result in poisoning.

(3) Oral Exposure

Pesticides may enter the body through the mouth. They may be taken by mistake while eating or smoking on the job or when improperly stored in food containers.

Pesticide Poisoning Database on Thai Farmer exposure

The heavy use of pesticides in Thailand causes agricultural workers' illness. The number of pesticide poisoning cases rose from 3,498 cases in 1995 to 4,398 cases in 2003 (Thai Epidemiology Division, 2004). According to the epidemiology report in 1995, the types of pesticides found that organophosphate was the major pesticide problem (51.14%), followed by herbicides (18.47%), carbamate (13.75%) and others (11.47%) respectively. The causes of pesticide poisoning to farm workers found that 95.7% of the farmers didn't use proper protective equipment, 57.8% did not follow pesticide instructions, 32.6% ate food and drank water between spraying, 21.0% sprayed pesticides all day long, and 20.6% harvested their vegetables before the specified dates (Siripuchaka, Sitaraphake and Pinitwedchakarn, 1998).

The project was introduced by WHO/IPCS/HQ, whilst the Royal Thai Government contributed local management in year 2000. Poisoning cases were reported using IPCS Pesticide Exposure Record. The collective data show that agricultural workers 37 cases suffer from pesticides. Dermal and Respiration routes of exposure are dominant (14 cases); followed by respiratory and dermal routes; i.e. 12 cases and 8 cases respectively (Table 2.1) (Poblab and Silkavute, 2001).

Table 2.1 The agriculture workers exposed to pesticide via any routes

Exposure Route	No. of cases
Ocular	1
Dermal	8
Respiration	12
Dermal & Oral	1
Dermal & Respiration	14
Dermal & Ocular & Respiration	1
Total	37

2.3 Environmental Health Risk Assessment

Environmental health risk assessment has been defined as the "systematic scientific characterization of potential adverse health effects resulting from human exposure to hazard agents or situations". Since the 1980s, most health, environmental, and even technological risk assessments have been largely consistent with the basic health risk assessment paradigm put forth by the National Academy of Sciences' National Research Council (National Research Council; NRC, 1983). The paradigm

describes a four-step process for analyzing data, drawing inferences from all available related information and then summarizing the implication in a risk characterization that others, including risk managers and the public, can easily follow and understand. For each step, the relevant and scientifically reliable information is evaluated. In addition, the related uncertainties and science policy choice are described. The four steps described by NRC are (1) hazard identification, (2) dose-response assessment, (3) exposure assessment, and (4) risk characterization (Wu and Farland, 2007).

(1) Hazard Identification

Hazard identification is to confirm that the chemical is capable of causing adverse effect in humans (IPCS, 2000). The method common use to identify hazard is the weight-of-the-evidence: a qualitative scientific evaluation of a substance for a specific purpose. The method for the evaluation includes chemical and physical properties of the substance, routes and pattern of exposure to substance; and the metabolic, pharmacokinetic, and toxicological data of the substance. Based on this evidence, conclusions are then made regarding the capability of particular substance to cause a particular health effect.

(2) Dose Response Assessment

Dose response assessment is the relationship between the magnitude of dose of the substance and the occurrence of the health effect. Typically, the relationship is presented as a plot between dose and the probability of the occurrence of a selected toxic endpoint (e.g. percent of mortality), or the probability that the end point will occur (e.g. probability of having cancer). Human studies are preferred sources of information for developing dose-response relationship. However, they may not be available and determination of the relationship may be based on studies done on animals. In such cases, extrapolation of data from animal to human is required.

(3) Exposure Assessment

Exposure assessment is the process of determining the extent to which humans, animals, or other life forms are exposed to hazardous agents. Exposure could be measured in terms of concentration of the agent or of duration or frequency of the agent's presence in the environment.

(4) Risk Characterization

Risk characterization is the description of the nature and magnitude of the risk to human health, other life forms, or the environment, including attendant uncertainty. It involves combining the results of the analysis of effects and the exposure assessment.

2.4 Exposure Assessment

The condition of a chemical contacting the outer boundary of a human is exposure. Most of the time, the chemical is contained in air, water, soil, a product, or a transport or carrier medium; the chemical concentration at the point of contact is the exposure concentration. Exposure over a period of time can be represented by a time-

dependent profile of the exposure concentration. A certain essential definition is introduced below (US EPA, 1992a).

Exposure: Contact of a chemical, physical, or biological agent with the outer boundary of an organism. Exposure is quantified as the concentration of the agent in the medium in contact integrated over the time duration of that contact.

Outer boundary: the visible exterior of a person, e.g. nose, mouth, skin and eyes.

Exchange boundary or absorption barrier: the boundary of the body that allows differential diffusion of various substances, e.g. skin, lung, tissue, and gastrointestinal tract wall.

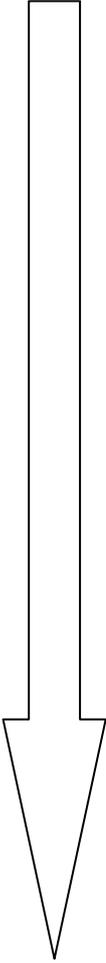
Exposure route: The way a chemical or pollutant enters an organism after contact, e.g., by ingestion, inhalation, and dermal absorption.

Exposure pathway: the course that a chemical or pollutant takes from the source to the organism exposed.

Dose: the amount of a substance available for interaction with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism.

Table 2.2 is summarized exposure and dose of the flow of an agent from the outer boundary to the receptor organ. The scheme in Table 2.2 starts with the contact of a chemical with the outer boundary, which established an exposure. The outer boundary of inhalation route is the nose; and the outer boundary of ingestion route is the mouth; and the boundary of dermal route is the skin. The amount of the chemical after crossing the outer boundary is called a potential dose. Inhalation dose, oral dose, and dermal dose are common names for route-specific potential dose. The amount of a chemical at the absorption barrier (skin, lung, gastrointestinal tract) available for absorption is called applied dose. It is equal to or less than the potential dose depending on the availability factor—a proportion indicating the availability of the chemical to interact with metabolic processes of an organism. The uptake processes take place at exchange boundary and involve absorption of the chemical through the skin or lung or gastrointestinal tract. The amount of chemical absorbed is called an absorbed dose. The amount of chemical transported to an individual organ and the amount that reaches it called a delivered dose and a biological effect dose, respectively. The biological effective dose, or the amount that actually reaches organs such as cells, tissue, or membrane where adverse effects occur (EPA, 1992a).

Table 2.2: Exposure and dose scheme (EPA, 1992a; Karuchit, 2001)

Flow Direction chemical into the body	Type of exposure dose, and boundary	Description
	Exposure	Contact of an agent with the outer boundary of an organism (in this study: human receptor)
	Outer boundary	The visible exterior of the person-the skin and the opening into the body such as mouth and nose.
	Potential dose (also called administered dose)	For inhalation and ingestion route, potential dose is the amount of a chemical that crosses the outer boundary: the amount of chemical in materials ingested (dietary and non-dietary) or in the air breathed. For dermal route, it is the amount of chemical in the bulk material applied to the skin. Route-specific potential dose is called inhalation dose, oral dose, or dermal dose.
	Applied dose	The amount of substance in contact with the exchange boundaries of an organism (skin, lung, gastrointestinal tract) and available for absorption. This is the product of potential dose times bioavailability factor (0-1). Bioavailability is the state of being capable of being absorbed and available to interact with the metabolic process of an organism.
	Internal dose (Absorbed dose)	The amount of substance penetrating across the absorption barriers of organism
	Delivered dose	The amount of a chemical transported to an individual organ (cell, tissue, membrane)

2.4.1 Calculate Potential Dose for Intake Process (via Intake and Inhalation)

(1) Potential Dose Estimation

The general equation for the potential dose (Equation 1) for intake processes, e.g., inhalation and ingestion is simply the integration of the chemical intake rate (concentration of the chemical in the medium(C) multiplied by the intake rate (IR) of the medium) overtime (US. EPA, 1992b).

$$D_{pot} = C \times IR \times ED \qquad \qquad \qquad Eq. 1$$

Where;

C [$\mu\text{g/L}$] = pesticide concentration

IR [L/day] = intake rate

ED[day] = Expose duration

(2) Average Daily Dose Estimation

For a number of non-cancer effects, risk assessment considers the period of time over which exposure occurs, and often, if there are no excursions in exposure that would lead to acute effects, average exposures or doses over the period of exposure is sufficient for the assessment. These averages are often in the form of average daily doses (ADDs). ADDs (Equation 2) are essentially potential dose (D_{pot}) over body weight and averaging time (US.EPA, 1992b).

$$\text{ADDs} = C \times \text{IR} \times \text{ED} / \text{BW} \times \text{AT} \quad \text{Eq. 2}$$

Where;

BW(kg) = body weight

AT(day) = the averaging time

2.4.2 Calculating Internal Dose for Uptake Processes (via the dermal route)

For absorption processes, there are two methods generally in use for calculating internal dose.

The first, commonly used for dermal absorption from a liquid where at least partial immersion occurs, is derived from the equation for internal dose, D_{int} which is analogous to equation 1 except the chemical uptake rate ($C \times K_p \times SA$) replaces the chemical intake rate ($C \times \text{IR}$). Thus the internal dose was described in equation 3. This is the method to use when calculating internal for swimmer or bathing water.

(1) Internal Dose Estimation (D_{int})

$$D_{\text{int}} = C \times K_p \times SA \times \text{ED} \quad \text{Eq. 3}$$

Where:

D_{int} [$\mu\text{g/day}$] = the internal dose

C [$\mu\text{g/L}$] = pesticide concentration

K_p [cm/hr] = the permeability coefficient

SA[cm^2] = the average surface area exposed

(2) Average Daily (Internal) Dose (ADD_{int}) Estimation

$$\text{ADD}_{\text{int}} = [C \times K_p \times SA \times \text{ED}] / [\text{BW} \times \text{AT}] \quad \text{Eq. 4}$$

Where:

ADD_{int} [mg/kg.day] = average daily dose

The second method of calculating internal dose use empirical observations or estimates of the rate that a chemical is absorbed when a dose is potential dose or applied. It is useful when a small or known amount of chemical (such as pesticide) contacts the skin. The potential dose of chemical to the skin, D_{pot} can often be calculated from knowing the concentration (C) and the amount of carrier medium applied (M_{medium}), either as a whole or on a unit surface area basis. For example, potential dose contact with soil can be calculated using the following equation:

(1) Potential Dose Estimation

$$D_{pot} = C \times F_{adh} \times SA \times ED \quad Eq. 5$$

Where:

D_{pot} [$\mu\text{g}/\text{day}$] = potential dose

F_{adh} [mg/cm^2] = the adherence factor for soil (the amount of soil applied to and adhering to the skin on a unit surface area per unit time).

(2) Internal dose Estimation

$$D_{int} = D_{pot} \times AF \quad Eq. 6$$

Where:

D_{int} [$\mu\text{g}/\text{day}$] = internal dose

AF [no unit] = absorption factor (%)

(3) Average Daily Dose Estimation

$$ADD_{int} = [C \times F_{adh} \times SA \times ED \times AF] / [BW \times AT] \quad Eq. 7$$

Where:

BW (kg) = body weight

AT (day) = the averaging time

2.4.3 Calculating Internal Dose for Intake Processes (via respiratory and oral routes).

Chemical in air, food, or drinking water normally enter the body through intake processes, then are subsequently absorbed through internal uptake processes in the lung or gastrointestinal tract. Sometimes it is necessary to estimate resulting internal doses, D_{int} after intake. In addition, if enough is known about the pharmacokinetics of the chemical to make addition of doses across routes a meaningful exercise, the dose must be added as internal dose, not applied dose, potential dose, or exposure.

(1) Internal Dose Estimation (D_{int})

$$D_{int} = D_{pot} \times AF = C \times IR \times ED \times AF \quad Eq. 8$$

Where:

C [$\mu\text{g/L}$] = pesticide concentration

IR [L/day] = intake rate

ED [day] = Expose duration

AF [no unit] = absorption factor (%)

(2) Average Daily Dose Estimation (ADD_{int})

$$\text{ADD}_{\text{int}} = \text{ADD}_{\text{pot}} \times \text{AF} = [\text{C} \times \text{IR} \times \text{ED} \times \text{AF}] / [\text{BW} \times \text{AT}] \quad \text{Eq. 9}$$

Where;

BW(kg) = body weight

AT(day) = the averaging time

AF [no unit] = absorption factor (%)

Table 2.3 provides a summary of the exposure and dose term as discussion above, along with examples of units commonly used.

Table 2.3 Generic Exposure and Dose Unit (US.EPA, 1992b)

Term	Generic Unit	Inhalation Units	Ingestion Units	Dermal Units
Exposure	Concentration ×time	$\mu\text{g}/\text{m}^3\text{air} \times \text{hrs of contact}$	$\text{mg}/\text{Lwater} \times \text{min of contact}$	$\text{mg}/\text{kg soil} \times \text{hrs of contact}$
Potential dose	mass of the chemical mass of chemical/time mass chem./(time ×body weight)	$\mu\text{g}/\text{m}^3 \times \text{m}^3/\text{min} \times \text{min exposed}$ = mg chemical in air breath (also dose rate:mg/day)	$\text{mg}/\text{kg} \times \text{kg}/\text{day} \times \text{day exposed}$ = mg chemical ingested in water (also dose rate:mg/day)	$\text{mg}/\text{kg soil} \times \text{kg soil on skin}$ = mg chemical in soil applied to skin (also dose rate:mg/day)
Applied dose	as above ×% chem. touch lung = mg chem	$\text{ug chem}/\text{m}^3\text{air} \times \text{m}^3\text{air touch lung}$ ×% chem. touch lung = mg chem touch lung absorption barrier	$\text{ug chem}/\text{kg water} \times \text{kg water consume}/\text{d}$ ×%of chemical touch G.I. tract =mg chem. touch G.I.tract absorption barrier	$\text{ug chem}/\text{kg soil} \times \text{kg soil touch skin}$ ×%of chem.touch skin = mg chem touch skin
Internal dose	as above	mg chem. absorbed via G.I. tract	mg chem. absorbed via lung	mg chemical absorbed through skin

2.5 Risk Characterization

Risk characterization is the final step to assess human health risks from pesticides. It combines and uses appropriate method to analyze the essential information from hazard identification, dose response assessment, and exposure assessment. The chlorpyrifos, dicofol and profenofos are non carcinogen pesticides. The criterion that is most widely used in risk characterization of non-carcinogens is the reference dose (RfD). RfD is defined as the daily oral dose of chemical that is unlikely to cause adverse effect given a lifetime exposure (EPA, 1986a; EPA, 1999b). An evaluation of non-carcinogenic toxicity of individual risk can be computed by using the hazard quotient (HQ) ratio; which is a comparison of the exposure dose, or average daily dose (ADDs), to the reference dose (RfD). This value indicates the degree to which exposure is greater or less than the RfD. When the ratio is equal to or greater than 1 when exposure exceeds the RfD, the exposed population may be at risk.

$$\text{Hazard Quotient (HQ)} = \text{Exposure} / \text{RfD} \qquad \text{Eq. 10}$$

Where: unit of exposure and reference dose is mg/kg/day

2.6 Cumulative Risk Assessment

Cumulative risk assessment based on concept and method developed by U.S. EPA. This method present solution of the two of the major weakness of conventional risk assessment: lack of simultaneous and comprehensive consider of exposures via difference routes and different substance. The EPA has been developed a series of guidance document for cumulative that can assess the accumulation of a common toxic effect from all routes of exposure to multiple substances sharing a common mechanism of toxicity. Certain important concepts are included in the following term (US.EPA, 2000b; US. EPA, 1999b):

Cumulative dose: the amount of multiple substances that share a common mechanism of toxicity available for interaction with biological targets from multiple routes of exposure.

Cumulative risk: the likelihood for the accumulation of a common toxic effect resulting from all routes of exposure to several substances sharing a common mechanism of toxicity.

Cumulative toxic effect: the net change in magnitude of a common toxic effect resulting from exposure to multiple substances that causes the common toxic effect from a common mechanism, relative to the magnitude of the common toxic effect cause by exposure to any of the substances individually.

Common toxic effect: refers to same toxic effect cause by different substance in or at the same anatomical or physiological site or locus (e.g. the same organ or tissue).

Common mechanism group (CMG): refers to substances that cause a common toxic effect by the same sequence of major biochemical events.

Cumulative Assessment Group (CAG): a subset of the CMG that are selected for inclusion in the cumulative risk assessment.

There are several methods for cumulative risk assessment (EPA, 1999a; EPA, 2000b) include: Margin of Exposure (MOE) method, Aggregate Risk Index (ARI) method, Hazard Index (HI) method, Relative Potency Factor (RPF) method, and Toxicity Factor (TF) method. The HI method is selected as the most suitable method for this study. It has an ability to accommodate different uncertainty factors associated with each substances and route; and its results are relatively easy to interpret.

HI is a commonly known risk metric used for assessing risk from difference exposure routes (EPA, 1999a). The particular method presented here is based on the concept of aggregate risk and cumulative risk (EPA, 1999a). First, the hazardous Quotient (HQ) is defined as the following ratio:

$$HQ_{r,p} = \frac{D_{r,p}}{RfD_{r,p}}$$

$D_{r,p}$ is the measured or estimated dose of the subject; the subscripts r and p denotes the route and chemical, respectively. The sum of $HQ_{r,p}$ is a HI. Generally, a value of HI less than or equal to one is of little concern, but a value of HI greater than one suggests a risk of concern. HI is expressed as below:

$$HI = \sum_r \sum_p HQ_{r,p}$$

2.7 Biological Monitoring

Biological monitoring (i.e. biomonitoring) is a tool used for measuring pesticide exposure level which enters the body. It can assess human exposures to both environmental and workplace. In case where exposure fluctuates in time, and or the skin is a significant route of absorption, biological monitoring has proved for obtaining the absorbed dose information. In general, biological monitoring use measurements in blood, urine, saliva, breast milk, or meconium as biological media by estimating the amount of pesticide as its metabolite or its reaction product that is absorbed into the body.

2.7.1 Biomarker

The term "biomarker" is used in a broad sense to include almost any measurement reflecting an interaction between a biological system and an environmental agent, which may be chemical, physical or biological. The biomarkers are identified in three classes (IPCS, 2000).

(1) biomarker of exposure: an exogenous substance or its metabolite or the product of an interaction between a xenobiotic agent and some target molecule or cell that is measured in a compartment within an organism.

(2) biomarker of effect: a measurable biochemical, physiological, behavioral or other alteration within an organism that, depending upon the magnitude, can be recognized as associated with an established or possible health impairment or disease.

(3) biomarker of susceptibility: an indicator of an inherent or acquired ability of an organism to respond to the challenge of exposure to a specific xenobiotic substance.

2.7.2 Uses of Biomarkers

Biomarkers may be used to assess the exposure (absorbed amount or internal dose) and effect(s) of chemicals and susceptibility of individuals, and they may be applied whether exposure has been from dietary, environmental or occupational sources. Biomarkers may be used to elucidate cause-effect and dose-effect relationships in health risk assessment, in clinical diagnosis and for monitoring purposes. Biomarkers of exposure can be used to confirm and assess the exposure of individuals or populations to a particular substance from any source including life-style activities. In an occupational context, biomarkers will provide a supplementary means for reviewing the adequacy of protective measures, including work practices and working conditions.

2.7.3 Urinary Metabolize

Current biological monitoring methods for Organophosphates (OPs) focus two approaches. One is related to the inhibition of the enzyme activity of blood cholinesterases (plasma cholinesterase and red blood cell acetylcholinesterase) by OPPs. The second approach has been to measure a set of six possible urinary metabolites of OPs (alkyl phosphates), which would allow detection of absorption of the vast majority of OPPs that have been recently in use. Table 2.4 show the comparison of biological monitoring technique for OPPs (Manson, 2000).

Table 2.4 The comparison of biological monitoring technique for OPPs

	Blood cholinesterases	Urine alkyl phosphates
Availability	widely available test- but analytical precision important for correct interpretation	not widely available; relatively difficult assay using expensive equipment

Table 2.4 The comparison of biological monitoring technique for OPPs (Con't)

	Blood cholinesterases	Urine alkyl phosphates
Interpretation	interpretable in terms of anticholinergic effects, but has needed a baseline value which can be problematic for incidents- need to wait 60 days	Currently interpretable as a relative measure of exposure only. Can be compared with limited reference range from "unexposed" individuals
Time of sampling	within 3-5 days of single exposure	within 1 day of single exposure, but depends on route of exposure.
Sample collection	Invasive- need medical/nursing input	easy to collect without specialist help.
Scope	influenced by all anticholinergics, but not good for carbamates	detects about 85% of all OP structures
Current improvements 1	Specific activity measurements for plasma assay can remove need for baseline	Better definition of "unexposed" reference range, including possible influence of diet residues at low levels
current improvements 2		Better understanding of relationship between absorbed dose and urine levels of chlorpyrifos, propetamphos and malathion

Urine is a widely used matrix for biological monitoring especially for nonpersistent pesticide. Non persistent compounds are rapidly metabolized, and their metabolized are excrete with urine (Bar and Needham, 2005). The presence of a contaminant or its metabolite in urine generally represents recent exposure. Another advantage of using urine in biological monitoring is its ease of collection for spot and grab (untimed) urine samples but not for 24-hr urine voids, because 24 hr collection can be cumbersome, often resulting in improper or incomplete collection. Therefore, spot urine samples, are generally used for biomonitoring. The major disadvantage of spot urine samples includes the variability in the volume of urine and the concentrations of endogenous and exogenous chemicals from void to void. To reduce the variability of spot sample the first morning void urine has been generally selected to be a sample because it was found to be the best predictor of average daily metabolite concentration (Kissel *et al.*, 2005), and simply to collect from farmers. For farmer applicator one day after a OPs application each farmer was provided with one polyethylene urine collection bottle and instructed to collect an urine sample from the first morning void (Yucra *et al.*, 2006). Biomarker in urine is typically corrected for creatinine. High creatinine values suggested that the individual is dehydrated, while very low creatinine level suggested kidney function anomalies or other factor that may produce dilute urine. The method of creatinine adjustment involves dividing the analyte concentration (micrograms analyze per liter urine) by the creatinine concentration (gram creatinine per liter urine). Analyte result is then

reported as weight of analyte per gram of creatinine (micrograms analyze per gram creatinine). Alternative method of normalizing urine samples for hydration and dilution such as specific gravity can be done, but they are not commonly accepted (Freeman, 2007). The typical of persistent and non-persistent pesticide in human is illustrated in figure 2.3.

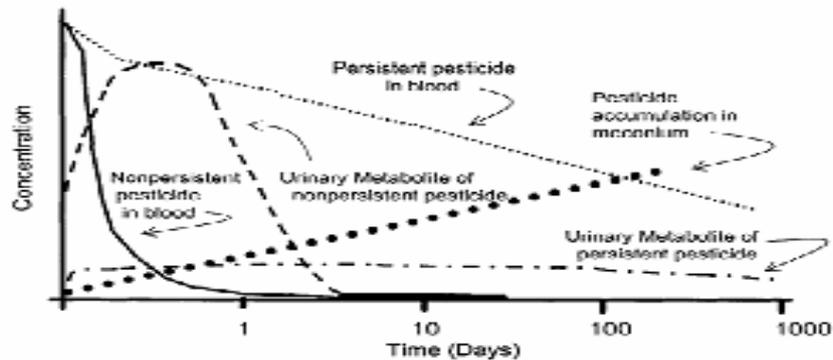


Figure 2.3 Typical fate and lifetime of persistent and non persistent pesticides in human blood, urine and fetal meconium.
Source: Barr and Needham (2002)

2.8 Farmers' Pesticide Exposure Studies

There are some researches have studied of farmers' pesticide exposure in occupation and environment.

Chaimuti (2001) studied on "knowledge, attitude and behavior of farmer on the pesticide application at Bang Rieng sub-district, Thailand. She collected the questionnaires from 224 vegetable growers and interviewed 112 farmers. The study showed that farmers in Bang Rieng sub-district had good knowledge in pesticide application. But their pesticides usage behavior were the main causes of adverse effect from pesticide exposure in the farmers for example, using the high concentration and toxicity pesticide, violating the pesticide instruction and using or not using appropriate personal protective devices. In addition, the farmers didn't concern on the pesticide residues in the soil and water sources and were lack of method to dispose pesticide containers.

Sakultheingtong *et al.* (2001) studied contaminated of pesticide in groundwater. They collected 44 water samples from artesian wells in northeast part of Thailand. They found organophosphate, organochlorine, carbamate, pyrethoid, 2,4-D, paraquat, butachlor and triazines pesticides in water samples. For Organophosphate pesticides, profenofos, was found ranging from 0.02 – 1.5 $\mu\text{g/L}$.

NRDC (2006) reported in the period 1991-1995, the U.S. Geological Survey (USGS) sampled from 5000 streams and wells and found at least one pesticide in every stream and in at least half of the wells sampled. The triazine herbicides (atrazine and simazine), 2,4-D, and several organophosphates including chlorpyrifos and diazinon were the most commonly detected of the 85 pesticides assayed.

Jirachaiyabhas *et al.* (2002) studied OPPs (chlorpyrifos and methyl parathion) in ambient air breathed by farmer during spraying OPPs in Bang Rieng sub-district, Thailand. The result indicated that traditional farmers were exposed to higher levels of the pesticides, with an average concentration of 0.19 mg/m^3 , compared with 0.037 mg/m^3 for Integrated Pest Management (IPM) farmers. It was estimated that a farmer of Bang Rieng sub-district would be exposed to 81- 12,261 mg of the OPPs via inhalation throughout his or her lifetime. Moreover, traditional farmers absorbed more of pesticide via inhalation than did IPM farmers.

California EPA (2001) studied on exposure of chlorpyrifos as a toxic air contaminant which currently had a wide range of agricultural and non agricultural use for control for a variety of foliar, soil, and household pests. This document was assessment of public exposure to ambient concentrations of airborne, chlorpyrifos in the community. The estimation absorbed dose of chlorpyrifos from a single-day exposure to off-site concentrations of chlorpyrifos from an agricultural application ranged from $11.7 \text{ } \mu\text{g/kg/day}$ for a six-year-old child to $3.01 \text{ } \mu\text{g/kg/day}$ for an adult female. Ambient air concentrations, while were measured in urban areas during a peak of pesticide use season resulted in a daily exposure of $0.27 \text{ } \mu\text{g/kg/day}$ for a six-year-old child to $0.07 \text{ } \mu\text{g/kg/day}$ for adult female. Annual exposure to chlorpyrifos in ambient air ranged from $0.03 \text{ } \mu\text{g/kg/day}$ for the child to $0.01 \text{ } \mu\text{g/kg/day}$ for the adult female.

Geer *et al.* (2001) studied on comparative analysis of passive dosimetry and biomonitoring for assessing chlorpyrifos exposure in pesticide workers. Eighty workers across four job classes were include: mixer/loader (M/L, n=24), applicator (A, n=9), re-entry scout (RS, n=10) and mixer/loader/applicator (M/L/A, n=37). The inhalation, dermal exposure and chlorpyrifos urine metabolite was investigated in this study. Inhalation exposure was evaluated by personal capturing both gas and particle phase chlorpyrifos in the workers' breathing zone. Dermal exposure was assessed using whole body dosimetry (WBD) including hand wash sample. Chlorpyrifos urine metabolite was measured 3,5,6 trichloro-2- pyridinol (3,5,6 TCP). Result showed that doses were highly variable and differenced by job class ($P < 0.05$) with median total (inhalation and dermal combined) exposed-derived absorbed dose (EDAD_{tot}) of 129, 88, 85 and 45 $\mu\text{g/application}$ for A, M/L/A, M/L and RS. Dose derived from the measurement of 3,5,6-trichloro-2-pyridinol (3,5,6 TCP) in urine were similar in magnitude but differed in rank with median values of 275, 189, 122 and 97 $\mu\text{g/application}$ for A, M/L/A, M/L and RS.

Cattani *et al.* (2001) studied potential dermal and inhalation exposure to chlorpyrifos in Australian pesticide workers. Chlorpyrifos inhalation, dermal exposure and working practices of 28 pesticide applicators in Western Australia were assessed during a series of single property applications of a 0.5% ($n=2$) or 1% ($n=26$) concentration of active ingredient in water solution. Deposition on new cotton gloves worn beneath applicators' usual protective gloves was 2.4 (range $0.12\text{--}86.1$) mg h^{-1} . Median deposition of chlorpyrifos onto a new cotton overall worn over other clothing (24 sections removed, corrected for body proportions) was 11.1 (range $0.2\text{--}41.9$) mg h^{-1} . Deposition onto seven patches taped to the applicators' skin was 0.04 (range $0.01\text{--}4.7$) mg h^{-1} . Inhalation concentration was 5.7 (range $0.7\text{--}219$) $\mu\text{g m}^{-3}$ time weighted average. In one group of 17 applicators' applying to existing properties,

breathing zone air concentration correlated ($P < 0.05$) with ambient air temperature (15–38°C). The questionnaire results (29 respondents) indicated applicators' practices led to increased exposure, in particular concerning poor usage and condition of protective equipment and a high frequency of splashes and spills onto the body. Prevention of deposition on clothing, in particular on the lower body is suggested, as well as improved working practices.

NRDC (2006) reported pesticides used on family farms end up in increased concentrations inside the home, compared with homes in non-agricultural areas, as the following studies show: A study of dust exposures among farm children was carried out in an apple, pear, and cherry-growing area of Washington State. A total of 26 farming families, 22 farmworker families, and 11 non-agricultural families participated. All had at least one child between the ages of one and six. Soil from outdoor play areas was sampled, as was household dust from indoor play areas. These samples were analyzed for the presence and concentration of four organophosphate insecticides: azinphos-methyl, phosmet, chlorpyrifos, and ethyl parathion. Residues found in household dust and soil was almost exclusively due to agricultural use, rather than home use of these products. One or more of the four target pesticides was found in 58 percent of the soil samples outside agricultural homes and in only 18 percent of soil samples near comparison homes. At least one of the pesticides was found in 100 percent of the house dust samples from farmworker and farmer homes, and all four of the targeted pesticides were found in 62 percent of farm homes. In comparison, in non-agricultural homes, only 9 percent of dust samples contained all four pesticides. Median indoor pesticide concentrations in house dust were generally 17 to 100 times higher than outdoor soil levels, although both were significantly higher in farm homes. Furthermore, maximum detected concentrations were generally 10 to 100 times greater than the median concentration detected, and the range of detected concentrations was generally much broader in farm homes.

The finding some studies in personal monitoring (urine metabolite) were related to pesticide exposure is described below.

Petchuay *et al.* (2006) studied biological monitoring of organophosphate pesticides in preschool children in a Bang Rieng agricultural community in Thailand. The OPPs (chlorpyrifos, dicofol, methyl parathion and profenofos) exposure of preschool children in a Thailand agricultural community and reference children living outside the farm area in the same sub district were determined. Levels of dialkylphosphate (DAP) metabolites were measured in first-morning-void urine samples. During the dry season (April-May), the farm children excreted significantly higher levels of all DAP metabolites than the reference children did (Mann-Whitney U test, $p < 0.05$; Wilcoxon signed-rank test, $p < 0.05$). During the wet season (September-October), DAP metabolite the levels were similar in the two groups. Reference children showed no significant difference related to season. Pesticide spraying during the dry season is a likely cause of the farm children's organophosphate exposures.

Heudorf *et al.* (2006) studied reference value of metabolite of pyrethroid and organophosphorous insecticides in urine for human biomonitoring in environmental medicine. They studied the level of metabolites of organophosphorous acids in urine of about 1200 children and adult, as well as data on levels of pyrethroid metabolites

in urine of about 2100 children and adults. The reference values for metabolites of organophosphorous acids are as follows: DMP 135 µg/L, DMTP 160 µg/L and DEP 16 µg/L and for metabolite of pyrethroid: cis-C12CA 1 µg/L, trans-C12CA 2 µg/L and 3-PBA 2 µg/L. As the volume-related concentration of organophosphate and pyrethoid metabolites show no significant age-dependence, the reference values derived are not age-stratified.

Yucra *et al.* (2006) determined the concentration of dialkylphosphate (DAP) in urine pesticide applicator. The organophosphates that farmer used in this study comprise of pyroxyphos, coumaphos, fenthion, diazinon, dicrotophos, profenofos, disulfoton, azinphos methyl, malathion, trichlorphon, monocrotophos, methyl parathion and methamidophos. The study showed that 76% of applicators had at least one urinary dialkylphosphate metabolite above the limit of detection. The geometric mean (GM) and the geometric standard deviation (GSD) of DMP and DEP were 5.73 µg/g cr. (GSD 2.51), and 6.08 µg/g cr. (GSD 3.63), respectively. The percentage of applicator with detectable DMP, DMDTP, and DMTP in urine was 72.72 %, 3.03%, and 15.15% respectively, while the corresponding figures for DEP, DETP and DEDTP were 48.48%, 36.36% and 15.15 %, respectively. There was no significant association between the use of protection practices and the absence of urine OPs metabolite suggesting inadequate protection practices.

Curl *et al.* (2002) studied on evaluation of take-home organophosphorus pesticide exposure among agricultural workers and their children. They analyzed organophosphorus pesticide exposure in 218 farm worker households in agricultural communities in Washington State to investigate the take-home pathway of pesticide exposure and to establish baseline exposure levels for a community intervention project. House dust samples (n = 156) were collected from within the homes, and vehicle dust samples (n = 190) were collected from the vehicles used by the farm workers to commute to and from work. Urine samples were obtained from a farm worker (n = 213) and a young child (n = 211) in each household. Dust samples were analyzed for six pesticides, and urine samples were analyzed for five dialkylphosphate (DAP) metabolites. Azinphosmethyl was detected in higher concentrations ($p < 0.0001$) than the other pesticides: geometric mean concentrations of azinphosmethyl were 0.53 µg/g in house dust and 0.75 µg/g in vehicle dust. Dimethyl DAP metabolite concentrations were higher than diethyl DAP metabolite concentrations in both child and adult urine ($p < 0.0001$). Geometric mean dimethyl DAP concentrations were 0.13 µmol/L in adult urine and 0.09 µmol/L in child urine. Creatinine-adjusted geometric mean dimethyl DAP concentrations were 0.09 µmol/g in adult urine and 0.14 µmol/g in child urine. Azinphosmethyl concentrations in house dust and vehicle dust from the same household were significantly associated ($r^2 = 0.41$, $p < 0.0001$). Dimethyl DAP levels in child and adult urine from the same household were also significantly associated ($r^2 = 0.18$, $p < 0.0001$), and this association remained when the values were creatinine adjusted. The results of this work support the hypothesis that the take-home exposure pathway contributes to residential pesticide contamination in agricultural homes where young children are present.

CHAPTER III

METHODOLOGY

3.1 Study Design

This study was approved by the Ethical Review Committee for Research Involving Human Subjects and/or Use of Animals in Research, Health Science Group of Faculties, Colleges and Institutes, Chulalongkorn University, Thailand under document No. 097/2006. All participants signed a consent form prior to participation in this study.

This study is a cross-sectional study. The study is assessed the pesticide exposure in Bang Rieng agricultural community, Kuan Nieng District, Songkhla Province, Thailand. The purpose of the study is to determine organophosphate pesticide exposure to vegetable grower living in Bang Rieng community. Sample was collected in dry season (April-June 2006) and wet season (September - October 2006).

Thirty-three vegetable growers were selected as the study group. Vegetable growers were selected based on organophosphate pesticide use. Information on pesticide use was obtained from a 2004 population database on vegetable farmers. Some vegetable growers also volunteered. The reference, or control, groups were made up of seventeen non-vegetable growers that most of them worked on rubber plantation gardens.

3.2 Interview questionnaire study

Thirty-three vegetable growers and seventeen non vegetable growers were interviewed by pesticide exposure questionnaire. The questionnaire was adapted from U.S. EPA. (1996) and WHO (2001). The questionnaire comprises of three parts as follow:

Part 1: General Information; This is to ask about general information and personal background of the farmers such as ages, gender, education background, residence location, pesticide applying information.

Part 2: Health Information; to assess farmer's health problems which may be cause from exposure to OPPs, including signs and symptoms.

Part 3: Pesticide Exposure Assessment; it contains with 26 items for assess farmer's behaviors and their activities related with pesticide exposure. Each item consists with ranking score for evaluation of each behavior's content.

The details of questionnaire are shown in appendix A.

3.3 Pesticide Concentration in the Environmental Monitoring

3.3.1 Groundwater (Artesian Well) Sampling

In total 100 water samples were collected; 50 were collected during the dry season (April-June 2006) and 50 during the wet season (September - October 2006). Each season, 33 water samples were collected from artesian wells in agricultural areas and 17 water samples were collected from artesian wells in non-agricultural areas (reference areas).

Water samples were collected using 2.5 L amber glass bottles with screw-top, Teflon-lined covers. The bottles were prewashed with a non-phosphate detergent and then rinsed with distilled water and methanol. Samples were collected from taps supplied by artesian wells. Prior to each sample collection, the tap was kept open for 5 minutes to wash out any contaminants in the pipes and to rinse out the bottles. Water samples were maintained below 4°C during transportation and storage, and were analyzed within 7 days, following sample collection methods (Lawrence, 1996). Water samples were then analyzed for chlorpyrifos, dicofol, and profenofos.

A solid phase extraction (SPE) method was used to extract the water samples. We used 500 mg CarboGraph SPE packing, a homogenous, non-porous graphite carbon black with a surface area of 100 m²/g and a particle size range of 38–125 µm. Prior to sample extraction, the SPE cartridge was activated by passing 5 mL of dichloromethane: methanol (80:20), 2 mL of methanol, and 5 mL of an acidic water, (pH 2.0) through the cartridge. After activation of the SPE cartridge, a 1 L water sample was passed through the cartridge at a flow rate of approximately 20–100 mL/min. The SPE cartridge was then washed with 5 mL of deionized water and dried for 5 minutes to remove interstitial water. The sorbed OPP compounds in the SPE cartridge were eluted with 1 mL of methanol and 5 mL of dichloromethane: methanol (80:20). The elute was evaporated with nitrogen gas and reconstituted with 20 µL of toluene for analysis using gas chromatography (Alltech, 2001; Jha and Wydoski, 2003)

An Agilent 6890 Gas Chromatograph (GC) equipped with a flame photometric detector was used for quantification. OP compounds were completely separated using a Zebron 1701 fused silica capillary column (30 m x 0.32 mm I.D. x 0.25 µm film thickness) coated with 14% cyanopropyl phenyl and 86% dimethyl polysiloxane. We injected 1.0 µL of analyte into the GC on splitless mode with a 0.75 min vent delay. The injector temperature was maintained at 250°C. The initial oven temperature was set at 80°C for 2 min and then increased at a rate of 15°C/min until it reached 180°C, where it remained for 2 min. The temperature was then increased at a rate of 6°C/min. until it reached 260°C, where it remained for 2 min using this temperature program, the retention times of chlorpyrifos, dicofol, and profenofos were 16.917, 13.924, and 20.255 min, respectively.

3.3.2 Air Sampling

The sampling method for measuring the pesticide concentration in air followed NIOSH manual of analytical methods, number 5600: Organophosphate Pesticides, Issue 1:15 August 1994, fourth edition (NIOSH, 1994). The method is summarized as follows:

Air samples were collected by using personal sampling pump with sorbent tube (OVS-2 tube: 13 mm quartz filter; XAD-2 140/270 mg). The personal sampling pump was set and calibrated the flow rate at 1L/min. The sorbent tube was put in the vegetable growers' breathing zone and personal pump was put on wrist with the belt. The personal pump was used to evacuate the air through solid sorbent tube. The required air sampling volume is 30-120 liters or use sampling time 30-120 min. The pesticide in air was sampled during vegetable growers mixing, loading and spraying pesticide. After the sampling process was finished, the sorbent tube was removed from the sampling device and seal with plastic caps and pack securely for shipment.

The plastic cap and polytetrafluoroethylene (PTFE) retainer ring of sorbent tube was removed. The quartz filter and front XAD-2 section was transfer to a 4 mL and the short polyurethane foam plug along with back-up XAD-2 section was transfer to another 4-mL vial. The desorbing solvent (2mL of acetone/toluene solution: 1/9) was added to each vial and let stand for 30 min. Then the sample was extracted in ultrasonic bath for 30 min and concentrated by nitrogen gas purged and reconstituted with 500 μ L of desorbing solvent for gas chromatography with flame photo detector (GC/FPD) analysis.



Figure 3.1 Personal Pump and sorbent (OVS-2) tube

3.3.3 Soil Sampling

Soil samples were collected during the dry season and the wet season from Bang Rieng Sub-District, Khuan Nieng District, Songkhla Province. Thirty-three soil samples were collected from vegetable farm areas and seventeen soil samples were collected from non-vegetable farm areas (reference area) during the dry and wet season (Figure 1). The soil in vegetable farm was sampled after applying pesticide

and before tillage. Soil was sampled in a systematic pattern to attempt to ensure complete field coverage and potentially increase the accurate of soil test. The top soil (depth 0 – 2 inches) was evacuated as soil sampling. The sampling unit was about 0.32 – 1.6 hectare (2-10 rai) in which 20 samples was collected. All of samples were mixed homogeneously to produce 1 sample (Chavengsi, 2001). Put soil in aluminum foil and transport on dry ice, and stored at - 20 °C.

Sample Preparation

Samples were thawed to room temperature and sieved through a 500 -µm stainless mesh to remove large nonsoil debris. Wet sample were dried in a desiccators for 5-16 hr. All sample contained less than 10 % moisture at the time of extraction. Five grams soil samples were pre-wet with 400 µl distilled water and refrigerate at 4 °C for 15-18 hr. We added 50 ml acetone and sonicated the soil for 10 minute in an ultrasonic processor. The clear supernatants were separated and evaporated to dryness under gentle nitrogen (N₂) steam. The dried sample was reconstituted with 100 µL of hexane (Simcox *et al.*, 1995).

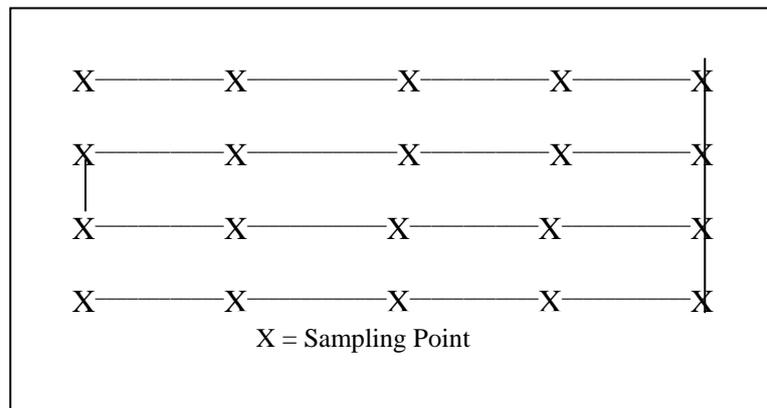


Figure 3.2 Soil sample-taking schema for each point selected in areas (0.32 – 1.6 hectare) sprayed with organophosphate pesticides.

Sample Analysis

The sample was analysed by GC-FPD. The analysed method used as same condition as method for analyzing water.

The optimal condition of organophosphate measurement was presented in Appendix B.

3.4 Pesticide Concentration on Personal Monitoring

3.4.1 Hand Wipe Sampling

The OPPS on farmers' hand was collected by wiping farmers' hand after applying pesticide by cotton gauze pads and sampling method following Geno P.W., *et al.* (1996). Two moistened gauze pads with 10 ml of isopropanol were used to wipe each hand of farmer. Both hands would be wiped. All wipe samples was transferred to

zip-lock plastic bag and frozen until analysis. The gauze pads were extracted by adding 30 mL of ethyl acetate and shaking on a mechanical shaker for 30 minutes. The clear supernants were separated and was injected to GC.

3.4.2 Body Skin Sampling

The method for study the pesticide absorbed on skin is followed HSE Methods for the Determination of Hazardous Substances Number 94. An estimate of dermal exposure made by using 10 x 10 cm cotton gauze swabs, set in seven positions on the worker's inner and outer clothing. Position 1 is on the hat as close a practicable to the top of the head. Position 2 is over sternum, on outside of normal clothing. Position 3 is on sternum, on inside of normal clothing. Position 4 is upper surface of right forearm held with elbow bent at right angle across body, midway between elbow and wrist, on outside of normal clothing. Position 5 is front of left leg, mid – thigh on outside of normal clothing. Position 6 is front of left leg, above ankle, on outside of normal clothing. Position 7 is on the back between shoulder blades, on outside of normal clothing. At the end of the sampling period, the 7 patches are removed from the clothing and placed in seal plastic back. Desorbed each swab in sealed glass bottles containing desorbing solution and analyzed with GC.

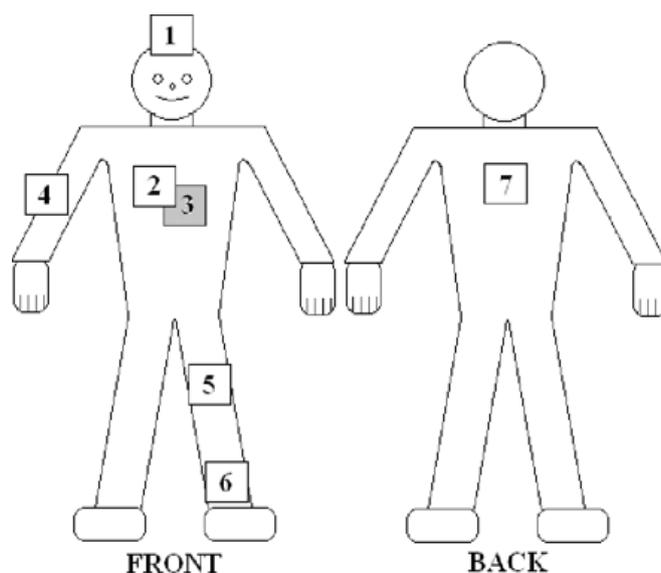


Figure 3.3 Position of the seven sampling patches used in the WHO sampling protocol.

Source: Johnson, Rimmer, Garrod, Helps and Mawdsley (2004)

3.5 Biological Monitoring

3.5.1 Urine sampling and analysis

For farmer applicator one day after a OPPs application, each farmer was provided with one polyethylene urine collection bottle and instructed to collect a urine sample from the first morning voice. The urine sample was transfer to 15 ml plastic tube with screw cap and put in zip-lock plastic bag and kept in refrigerator.

Then researcher picked up urine sample and maintained below 4°C in ice box during transportation and store at -40 °C in deep freeze refrigerator in laboratory before analyzing. All urine samples were analyzed for OP metabolite and creatinine. The urinary DAP metabolites in urine using lyophilization technique, derivatization with pentafluorobenzyl bromide (PFBBr) and analysis by gas chromatography with flame photometric detector (GC-FPD)(Oglobline *et al.*,2006; Bravo *et al.*, 2004).

(1) Reagents and Chemicals

Acetonitrile was obtained from Labscan Asia Co. Ltd.; Anhydrous potassium carbonate was obtained from Merck, Germany and pentafluorobenzylbromide (PFBBr) was obtained from Aldrich, USA. The DAP metabolite that use as standard reagent comprise of DMP, DEP, DMTP, DETP and DEDTP. DMP was purchased from Aldrich Chemical Co, Germany; DEP was ordered from ACROS Organics, NJ, USA. DMTP, DETP, and DEDTP were obtained from Aldrich, USA. Dibutylphosphate (DBP) used as the internal standard purchase from Fluka Chemie, Switzerland.

(2) Instrument

An Agilent 6890 Gas Chromatograph (GC) equipped with a flame photometric detector was used for quantification. DAP in urine metabolize were completely separated using a HP 5 capillary column (30 m x 0.32 mm I.D. x 0.25 µm film thickness) coated with 5% Phenyl Methyl Siloxane). We injected 2.0 µL of analyte into the GC on splitless mode with a 0.75 min vent delay. The injector temperature was maintained at 250°C. The initial oven temperature was set at 80°C for 2 min and then increased at a rate of 17°C/min until it reached 210°C, where it remained for 3 min, the retention times of DMP, DEP, DMTP, DETP and DEDTP were 5.791, 6.423, 6.914, 7.605 and 8.132 min respectively.

(3) Sample Preparation

Five milliliter (5 mL) of urine sample in a screw-top vial was spike with 100µg/L DBP and then freeze at -40 °C. After the sample was frozen, it was taken to freeze – dry (lyophilization) technique by the Dura-Top freeze dryer about 7-8 hours until sample was dried. Then 2 mL of acetonitrile was added to urine tubes and put anhydrous 30 mg potassium carbonate and filled 25µL of PFBBr. The sample was mixed and heated at 60 °C for 3 hours in water bath. The supernatant was transfer to clean vial and evaporated until dry with a gentle nitrogen stream and reconstituted with 200 µL of toluene for analysis using GC-FPD.

The optimal condition of organophosphate measurement and optimal condition of dialkylphosphate measurement was present in appendix B.

3.6 Data and Statistical Analysis

Statistical analysis: using the SPSS for Windows (version 16).

Central tendency; mean, median and percentage for describing the general information of the study population.

3.6.1 Predict Exposure Modeling

Multiple linear regression analysis was applied to evaluate the association of pesticide levels in environmental and personal media, with urinary DAP metabolite level (dependent variable). The regression models were conducted using stepwise procedures. Variable with $p < 0.05$ were retained in the model; the best fitting model was selected

The models have the same general form as follows:

$$\text{Concentration} = C + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_n X_n$$

In which the dependent variable concentration is the total urinary DAP metabolite concentration, β_i is the regression coefficients, and the X_i independent variable; the constant C present the background exposure level in model.

3.6.2 Average Daily Dose Calculation

The average daily dose (ADD) is used to estimate the exposure for non-carcinogenic effects which calculated by the route-specific mathematical algorithms based on the following generation equation

$$\text{ADD} = C \times \text{IR} \times \text{AF} \times \text{EF} / \text{BW} \times \text{AT} \quad \text{eq 3.1}$$

ADD = Average Daily Dose

C = Contaminant concentration

IR = Intake rate

AF = Bioavailability factor

EF = Exposure factor

BW = Body weight

AT = Averaging time

3.6.3 Biological Based Pesticide Dose Estimation

The absorbed OP pesticide dose (biologically based pesticide dose estimates) from urinary metabolite concentrations were estimated with a deterministic steady state model (Fenske *et al.*, 2000).

The first step: Total molar quantities ($\mu\text{mol/L}$) for each OP pesticide of interest were calculate by converted metabolite concentrations to their molar equivalents and summed to produce a single dialkyl phosphate for each OPP, as according to the following formula.

$$\text{For: Dicrotophos: [Dimethyl DAP]} = [\text{DMP}]/126 \quad \text{eq 3.2}$$

$$\text{Chlorpyrifos: [Diethyl DAP]} = [\text{DEP}]/154 + [\text{DETP}]/170 \quad \text{eq 3.3}$$

Where: the metabolite concentrations are in units of micrograms per liter ($\mu\text{g/L}$)

The molecular weight of each metabolite is in units of grams per mole (g/mol)

The second step: The total molar concentrations were multiplied by the adjusted volume of the 24 hr urine sample and molecular weight (MW) of parent pesticide, and are divided by the vegetable growers' body weight; as according to the following formula (Duggan *et al*, 2003).

$$\text{Dose } (\mu\text{g/kg/day}) = \frac{[\text{Diethyl DAP}] \text{ or } [\text{Dimethyl DAP}] \times \text{volume}}{\times \text{MW pesticide} \times 1/\text{Body weight}} \quad \text{eq 3.4}$$

Where: urine volume = 1.2 L/day for adult (men average 1.4 L, and woman average 1.0 L per day)

Molecular Weight of OPPs = 237 for dicrotophos, 351 for chlopyrifos, and 373 for profenofos

Body Weight = 65 kg.

3.6.4 Non – Carcinogen Risk Estimation

The risk estimation expressed based on the hazard index (HI). The non carcinogenic effects were calculated according to the following relationship (US EPA., 1999a);

$$\text{Hazard Quotient (HQ)} = \text{Exposure/RfD}$$

Where: Exposure = chemical exposure level, or intake (mg/kg/day)

RfD = reference dose (mg/kg/day)

Then, the hazard index is given by:

$$\text{Total hazard index (HI)} = \sum (\text{HQ})$$

Where: HI less than or equal 1, acceptable level (no concern)

HI higher than 1, adverse non –carcinogenic effect concern

The figure of field study and sample analysis was shown in appendix C.

CHAPTER IV

RESULT AND DISCUSSION

4.1 Pesticide Exposure Questionnaire Information

4.1.1 General Information

The general information from the pesticide exposure questionnaires were obtained from 50 persons consisting of 33 vegetable growers and 17 non-vegetable growers as reference. The general information such as age, gender, education background, time for applying pesticides and duration of farming is illustrated in Table 4.1.

The result showed that the highest frequency of age and education background between vegetable growers and reference group almost the same. Most of them were in range age 26-45 years and most of them graduated from primary school grade 6. Most of the vegetable growers had their house located in their farms or around their farm area whereas the reference group lived outside the farm area. The average time for applying pesticide in their farms for a month was asked. According to the results, 38% of the samples applied two to five times a month and 16 % of the samples applied five to ten times a month whereas all of reference group had not been applied pesticides. Most of the farmers worked in their vegetable farms for 8 hours and had annually worked and cultivated their farms for 300 days or approximately 10 months. It could be said that they worked in their farm throughout the year, except only in heavy rainy season during November to December. But the reference group did not work in the vegetable farm. This information indicated that the vegetable growers who work in farm could be exposed to pesticide more than the reference group working outside farm.

Table 4.1 General information of study population at Bang Rieng Sub-District

General Information	Vegetable Growers		Reference		Total	
	N	%	n	%	n	%
1. Participant	33	66	17	34	50	100
2. Gender						
-Male	32	64	16	32	48	96
-Female	1	2	1	2	2	4
3. Age						
-Less than 25 yrs.	5	10	2	4	7	14
-Between 26–35 yrs.	10	20	5	10	15	30
-Between 36–45 yrs.	10	20	3	6	13	26
-Between 46–55 yrs.	6	12	5	10	11	22
-More than 56 yrs.	2	4	2	4	4	8

Table 4.1 General information of study population at Bang Rieng Sub-District

General Information	Vegetable Growers		Reference		Total	
	N	%	n	%	n	%
4. Education Background						
-Uneducated	1	2	-	-	1	2
-First Primary School (Grade 1 - 4)	9	18	7	14	16	32
-Second Primary School (Grade 5 - 6)	14	28	9	18	23	46
-Junior High School (Grade 7 - 9)	5	10	1	2	6	12
-Senior High School (Grade 10 – 12)	3	6	-	-	3	6
-Diploma	1	2	-	-	1	2
5. Duration of vegetable farming						
-0 years	-	-	17	34	17	34
-5 years	18	36	-	-	-	36
-5-10 years	14	28	-	-	-	28
6. House Location						
-In the farm area	8	16	-	-	8	16
-Around the farm area	24	48	-	-	24	48
-Out of the farm area	1	2	17	34	18	36
7. Number of vegetable farm area						
- 0 hectare (0 rai)	-	-	17	34	17	34
-Less than 0.8 hectare (5 rais)	25	50	-	-	25	50
-More than 0.8 hectare (5 rais)	8	16	-	-	8	16
8. Average time for applying pesticide for a month						
-0 times	-	-	17	34	17	34
-2-5 times	19	38	-	-	19	38
-5-10 times	8	16	-	-	8	16
-10 -15 times	2	4	-	-	2	4
-15 -20 times	2	4	-	-	2	4
-more than 20 times	1	2	-	-	1	2
9. Daily Working hour in the vegetable farms						
-No work	-	-	17	34	17	34
-Less than 8 hrs.	12	24	-	-	12	24
-8 hrs.	8	16	-	-	8	16
-More than 8 hrs.	12	24	-	-	12	24

Table 4.1 General information of study population at Bang Rieng Sub-District

General Information	Vegetable Growers		Reference		Total	
	N	%	n	%	n	%
10.Number of annual growing period						
-0 days	-	-	17	34	17	34
-Less than 240 days	2	4	-	-	2	4
-270 days	2	4	-	-	2	4
-300 days	24	48	-	-	24	48
-330 days	2	2	-	-	2	2
-360 days	3	6	-	-	3	6

4.1.2 Health Information

From interviewed 33 vegetable growers found that some have only one sign and symptom but some had more than one sign and symptoms. In this study found that the most sign and symptom was found from vegetable grower was headache (12 persons) and muscle weakness (12 persons) follow by blurring vision (9 persons), muscle seizure (7 persons), abdomen cramp (4 persons), difficult breathing (2 persons) and chess pain (1 person), and loss consciousness (1 person) respectively as shown in Figure 4.1.

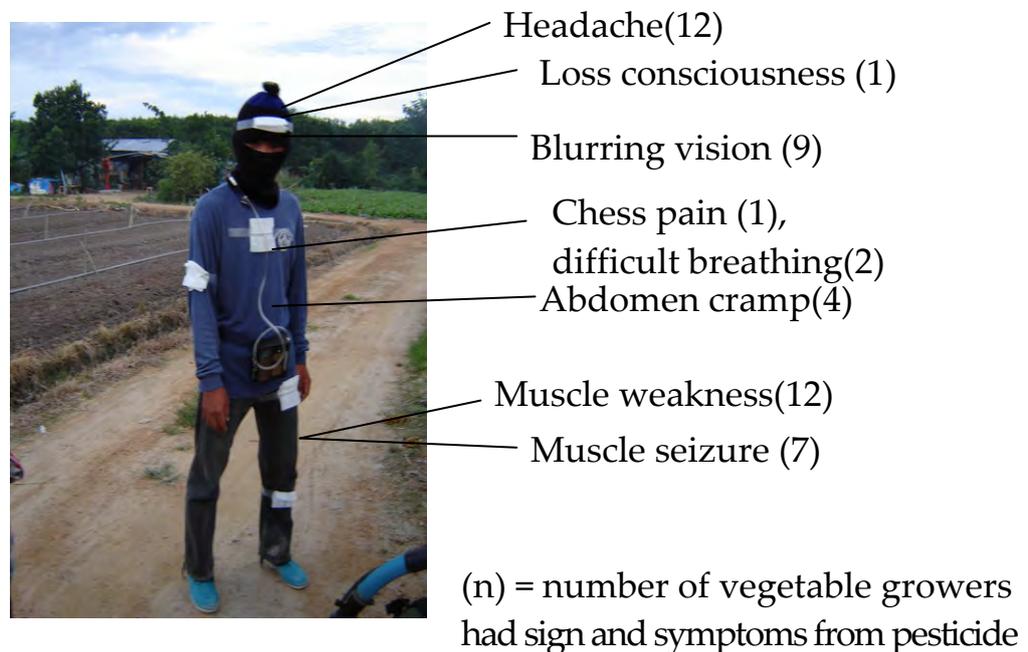


Figure 4.1 Body mapping with sign and symptom of Bang Rieng’s vegetable growers during applying pesticide.

The researcher evaluated health effect of the vegetable growers after applying and being exposed to pesticides by assigning the scores for each effect (depending on its severity and frequency). The maximum and minimum scores of the health effect equaled 35 points and 0 point respectively. The highest score from the interview was 11 point and its details were shown in the Table 4.2.

Table 4.2 Health information of vegetable growers

General Information	Number of Persons	Percentage
Health effect's scores from pesticide exposure	7	21.2
- 0 point	7	21.2
- 1 point	7	21.2
- 2 point	6	18.2
- 3 point	1	3.0
- 5 point	2	6.1
- 6 point	2	6.1
- 7 point	1	3.0
- 11 point		
Total	33	100.0

4.1.3 Pesticide Exposure Assessment Scores

The result of the pesticide exposure questionnaires from the vegetable growers were described in the mode of each item as follows:

Table 4.3 Results and description of question in the pesticide exposure assessment questionnaire of vegetable growers (N = 33)

Question	Number of Answers	Description
1. Where do you mix pesticide?	15	In the farm and near the water source
2. What is the method that you select to apply pesticides?	25	Follow instruction
3. How do you mix the pesticides	31	Bare hand and use stirring stick
4. When you mixing or applying pesticide, which part of body usually contact the pesticide?	29	Hand and arm
5. When do you spray pesticide?	30	Evening, morning

Table 4.3 Results and description of question in the pesticide exposure assessment questionnaire of vegetable growers (N = 33)

Question	Number of Answers	Description
6. What equipment do you use for spraying pesticides?	18	Portable Pump
7. If you spill some of pesticide on your clothes, when do you change clothes?	26	Change after finish spraying
8. If your last pesticide application is ineffective, what will you do with the first pest control?	21	Change the new one
9. After spraying pesticides, when do you usually change into clean clothes?	32	Immediately
10. How do you wash your clothes, which you wore during applying pesticide?	27	Separate from family washed
11. After mixing and applying pesticides, where do you usually wash up or shower?	30	Bathroom at home
12. What is the method in disposing the pesticides container?	17	Dispose on the ground
13. How do you wash the pesticide equipment after used?	27	Sometimes
14. What is the method for washing the pesticide equipment?	23	Rinse all equipment
15. Do you usually repair your own spraying or mixing equipment?	18	Yes
16. Where do you store the pesticides?	18	In the separate storage facility
17. Where is the source of water used?	30	Artesian well
18. Normally, what kind of drinking water do you usually drink?	33	Artesian well (directly)
19. Whether the water source used for consuming is the same source for mixing pesticides?	20	Different source from farming
20. How far is your usage well from the nearest area where pesticides are mixed?	23	Less than 10 m.
21. Where do you have lunch?	17	At home (out of farm area)
22. Do you smoke while working in the farm?	24	No
23. Do you drink while working in the farm?	20	No

From the results it can be concluded that:

The vegetable growers used bare hands and stick to mix pesticide. Their hands would be contaminated with pesticides. The vegetable growers did not dispose

the pesticide container properly and left the container on the ground. The ground water in Bang Rieng Sub-District was contaminated. In addition, the spraying pesticide also went to surface and groundwater. For the water source (surface water and groundwater) for farming and consuming, Bang Rieng community faced the health effects from being exposed to pesticide residue in drinking water. Since local people drank water directly from that water source. The behavior such as eat, drink and smoke in the farm is not safe because they would intake pesticide from hand contaminated with pesticides during their eating, drinking and smoking time.

(1) Pesticide Exposure Scores

For the question of wearing of Personal Protective Devices (PPD) item, the scores were calculated from the PPD wearing in each farmer. The full score meant that farmers did not wear any necessary PPD such as, long pants and long sleeve shirts, rubber boots and gloves, goggles and chemical protective masks therefore those farmers were more exposed to pesticide. On the other hand, if the farmers wore all of the necessary PPD, they would get the fewer score down to zero. These scores were also included to calculate pesticide exposure score.

Table 4.4 Wearing PPD scores

Wear PPD Score	Number of Person	Percentage
3	3	10
4	2	6
5	14	42
6	6	18
7	6	18
8	1	3
9	1	3

After assigning the ordinal (rank) score for each pesticide exposure item, the maximum score from the questionnaire was 66 points and the minimum score was 45 points. However, the highest exposure score was 92 points and the lowest score was 36 points, while the mean scores were 56.3. The numbers of person in each score is shown in the Figure 4.2

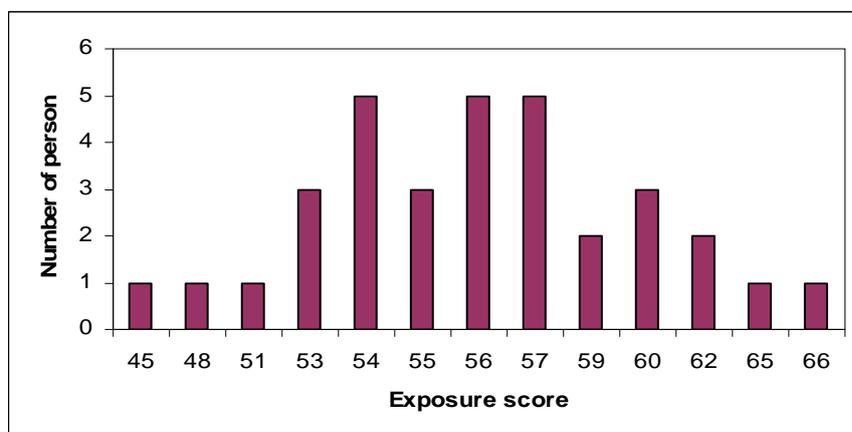


Figure 4.2 Pesticide exposure score of Bang Rieng vegetable growers

The researcher assigned and calculated the pesticide exposure score into 5 levels by categorizing their scores in the following standard. According to Table 4.5 the results showed that 2 of Bang Rieng farmers had moderate low exposure, and 29 farmers had medium exposure, while 2 farmers had moderately high exposure. The levels of pesticide exposure of Bang Rieng farmers were shown as follow.

Table 4.5 Pesticide exposure level of Bang Rieng vegetable growers

Exposure level (exposure score; point)	Number of Person	Percentage
Low of Exposure (22-36)	0	0
Moderate low Exposure (36-50)	2	6
Medium Exposure (50-64)	29	88
Moderately High Exposure (64-78)	2	6
High Exposure (78-92)	0	0
Total	33	100

4.1.4 Reference Group Information

For the reference group, the researcher interviewed the health problem including sign and symptom same question as using to interview vegetable growers. The result revealed that the reference person did not have sign and symptom as exposed from pesticides. For pesticide exposure assessment question, we found that all of them did not expose to pesticide.

4.2 Biological Monitoring

4.2.1 Urinary DAP Metabolites

DAP metabolites has retention times of DMP 5.79 min, DEP 6.42 min, DMTP 6.91 min, DEP 7.60 min and DETP 8.13 min. A calibration curve using the external mixed standard of DAP was performed for each compound to be quantified as concentration of 10, 50, 100 and 300 µg/L. In Appendix B, a calibration curve was performed in the ranges of linearity found for each compound. The limit of detection (LODs) of DMP, DEP, DMTP, DETP and DEDTP was 4, 3, 1, 1 and 1 µg/L respectively. The recovery of DMP, DEP, DMTP, DETP and DETP were 60, 68, 107, 99 and 90% respectively.

4.2.2 Biological Monitoring Results

Almost five common DAP metabolites was measured in urine samples of vegetable growers but some of five common DAP metabolite was measured in urine sample of non-vegetable growers (reference). Each DAP metabolite concentration ($\mu\text{g/L}$) is presented in Table 4.6

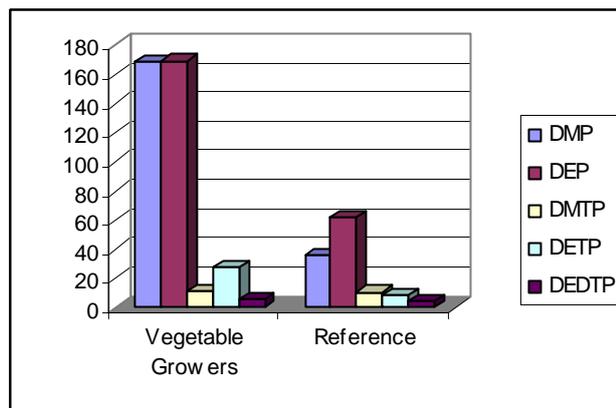
Table 4.6 Concentration of urinary DAP metabolites in urine of vegetable growers and reference in Bang Rieng Sub- District, Khuan Nieng District, Thailand

	Dialkylphosphate ($\mu\text{g/L}$)				
	DMP	DEP	DMTP	DETP	DEDTP
Vegetable Growers	Dry Season				
Mean \pm S.E.	168.64 ^a \pm 30.09	169.43 ^a \pm 15.21	11.55 ^a \pm 1.17	28.02 ^a \pm 6.67	6.22 ^a \pm 1.31
Median	117.07	156.63	8.89	14.98	4.23
Range	<LOD-627.09	37.59-404.51	<LOD-39.18	2.70-175.81	<LOD-30.55
Frequency	91	100	90	100	79
Reference	Dry Season				
Mean \pm S.E.	35.79 ^b \pm 10.48	61.76 ^b \pm 8.41	10.45 ^a \pm 2.30	8.28 ^b \pm 1.22	4.15 ^a \pm 0.84
Median	14.38	51.29	7.49	7.78	6.25
Range	<LOD-136.41	<LOD-110.80	<LOD-39.18	<LOD-19.56	<LOD-8.44
Frequency	82	94	82	82	64
Vegetable Growers	Wet Season				
Mean \pm S.E.	147.39 ^a \pm 29.13	166.46 ^a \pm 20.30	11.68 ^a \pm 1.56	14.42 ^a \pm 2.52	15.27 ^a \pm 7.51
Median	76.64	148.12	8.05	10.75	3.14
Range	26.54-767.71	39.01-515.17	<LOD-58.12	1.17-67.89	<LOD-228.61
Frequency	100	100	94	100	76
Reference	Wet season				
Mean \pm S.E.	28.44 ^b \pm 5.27	85.32 ^b \pm 13.78	10.86 ^a \pm 2.51	8.67 ^b \pm 1.41	5.67 ^a \pm 0.56
Median	27.31	80.36	7.67	7.81	6.30
Range	<LOD-76.20	<LOD-244.17	<LOD-32.93	<LOD-17.82	<LOD-7.13
Frequency	88	94	82	82	88

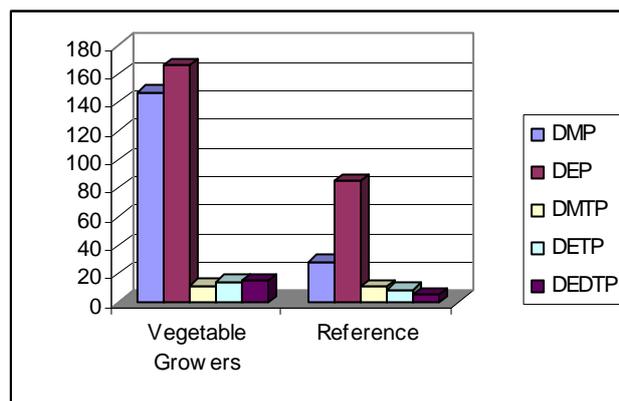
Statistic comparison between vegetable growers and reference in the same season using independent sample t-test, the difference letter (^{a,b}) indicates the significant different at $p \leq 0.05$

Table 4.6 illustrates the mean DAP concentration in urine metabolite ($\mu\text{g/L}$) with the maximum and minimum values. DAP dimethylphosphate (DMP), diethylphosphate (DEP), dimethylthiophosphate(DMTP), diethylthiophosphate(DETP) and diethyldithiophosphate (DEDTP) were found. Mean concentrations of DMP, DEP, and DETP during dry seasons of the vegetable growers (168.64, 169.43, and 28.02 $\mu\text{g/L}$) were significantly greater than the mean levels of the reference groups (35.79, 61.76, and 8.28 $\mu\text{g/L}$) ($p = 0.003$, 0.007 , and 0.004). In addition, mean concentration of DMP, DEP, and DETP during wet seasons of the vegetable growers (147.39, 166.46, and 14.42 $\mu\text{g/L}$) were significantly greater than the mean levels of the reference groups (28.44, 85.32, and 8.67 $\mu\text{g/L}$) ($p = 0.001$, 0.017 , and 0.03). But the dry season, mean dimethylthiophosphate (DMTP) and diethyldithiophosphate (DEDTP) levels of vegetable growers (11.55 and 6.22 $\mu\text{g/L}$) were not significantly greater than the mean levels of reference group (10.45 and 4.15 $\mu\text{g/L}$) ($p = 0.527$ and

0.117). In the wet season also mean dimethylthiophosphate (DMTP) and diethyldithiophosphate (DEDTP) levels of vegetable growers (11.68 and 15.27 $\mu\text{g/L}$) were not significantly greater than the mean levels of reference group (10.86 and 5.67 $\mu\text{g/L}$) ($p = 0.703, 0.051$). It can be concluded that the DMP, DEP and DETP in urine of vegetable growers were higher than reference group in both season because they are originated from OPPs (dicotophos and chlorpyrifos) with contacted to vegetable growers during applying pesticide. The metabolite of dicotophos was DMP and the metabolite of chlorpyrifos was DEP and DETP. We also found some DMP, DEP and DETP in reference group because the reference group might be eaten vegetable contaminated with dicotophos and profenofos. The comparisons of the average concentration of five urinary DAP metabolites between the vegetable growers and reference group are presented in Figure 4.3.



(a)



(b)

Figure 4.3 Concentration of urinary DAP metabolites in vegetable growers and reference group in the dry (a) and wet season (b) at Bang Rieng Sub-District.

As indicated by independent sample t-test the vegetable growers had the same level of DMP, DEP, DMTP and DEDTP metabolites during wet and dry season ($p=0.61, 0.907, 0.062$ and 0.242). Also the reference had no difference of all DAP metabolites in both dry and wet season ($p=0.537, 0.150, 0.904, 0.882$ and 0.146).

4.2.3 Estimate OPPs exposure from urinary alkylphosphate metabolite

Absorbed OPPs dosages can be estimated from the concentration of dialkylphosphate metabolites (DAP). Because the characteristic of DAP metabolites related to their parent OPPs. (Fenske *et al.*, 2000). The parent OPPs in this study comprised of dicotophos, chlorpyrifos and profenofos. The metabolite of dicotophos was produced DMP and the metabolite of chlorpyrifos was produced DEP and, DETP respectively, thus the dose estimation of these parent OPPs was limited to these three common DAP metabolites (DMP, DEP and DETP). In this study, however, profenofos was excluded in the dose estimation because there is no applicable information for its metabolite reported in US EPA's document (US EPA., 2003). The estimation from dialkyl metabolite in urine to total molar quantities ($\mu\text{mol/L}$) of OPPs was using equation 3.2 and 3.3 in Chapter III. Concentrations of dialkylphosphate metabolite and total molar concentration in the urine which provide to estimate OPPs exposure are presented in Table 4.7. Total dimethyl DAP levels for dicotophos was significant difference between the vegetable growers and reference group in both dry and wet season ($p = 0.003, 0.001$). Total diethyl DAP concentration for chlorpyrifos was found to be significant difference between the vegetable growers and reference group in both wet and dry seasons ($p = 0.006, 0.015$).

Table 4.7 Total molar concentration ($\mu\text{mole/L}$) in vegetable growers' and references' urine at Bang Rieng Sub- District, Khuan Nieng District, Thailand

	Dialkylphosphate Metabolites($\mu\text{g/L}$)			Total Molar Concentration ($\mu\text{mole/L}$)	
	DMP	DEP	DETP	Dimethyl ^a	Diethyl ^b
Dry Season					
Vegetable Growers					
Mean	168.64 \pm 30.09	169.43 \pm 15.21	28.02 \pm 6.67	1.34 \pm 0.23	1.26 \pm 0.10
Median	117.07	156.63	14.98	0.93	1.27
Maximum	627.09	404.51	175.81	4.98	2.67
Reference					
Mean \pm S.E.	35.79 \pm 10.48	61.76 \pm 8.41	8.28 \pm 1.22	0.28 \pm 0.08	0.45 \pm 0.06
Median	14.38	51.29	7.78	0.11	0.40
Maximum	136.41	110.80	19.56	1.08	0.79

Table 4.7 Total molar concentration ($\mu\text{mole/L}$) in vegetable growers' and references' urine at Bang Rieng Sub- District, Khuan Nieng District, Thailand

	Dialkylphosphate Metabolites($\mu\text{g/L}$)			Total Molar Concentration ($\mu\text{mole/L}$)	
	DMP	DEP	DETP	Dimethyl ^a	Diethyl ^b
Wet Season					
Vegetable Growers					
Mean \pm S.E.	147.39 \pm 29.13	166.46 \pm 20.30	14.42 \pm 2.52	1.16 \pm 0.23	1.17 \pm 0.14
Median	76.64	148.12	10.75	0.61	1.03
Maximum	767.71	515.17	67.89	6.09	3.39
Reference					
Mean \pm S.E.	28.44 \pm 5.27	85.32 \pm 13.78	8.67 \pm 1.41	0.23 \pm 0.04	0.60 \pm 0.09
Median	27.31	80.3606	7.81	0.22	0.59
Maximum	76.20	244.17	17.82	0.6	1.63

^a Dimethyl molar for dicotophos (DMP metabolite)

^b Diethyl molar for chlorpyrifos (DEP metabolite)

The individual Dimethyl DAP dose (ADD, dicotophos) and Diethyl DAP dose (ADD, chlorpyrifos) for vegetable growers and reference group was calculating by using equation 3.4 are illustrated in Table 4.8. The mean of the estimated average daily doses (ADDs) of dicotophos and chlorpyrifos for the vegetable growers during the dry season were 0.0068 and 0.0096 mg/kg.day which exceed the US. EPA accepted daily intake (ADI). In addition, in the wet season the mean ADDs of dicotophos and chlorpyrifos were exceed ADI. The mean ADD of dicotophos and chlorpyrifos of the reference were little higher than the ADI in both wet and dry seasons. It might be vegetable growers ate vegetable contaminated with pesticide and some from non- pesticide source (Duggan et al, 2003).

This study also indicated the distribution of ADD that exceeded the ADI values for all population. It found that 100% of the ADD of dicotophos and chlorpyrifos of vegetable growers were exceeded ADI values during both wet and dry season. But the ADD of dicotophos of reference group was below the ADI in the dry and wet season 17.6% and 11.7 % respectively. The ADD of chlorpyrifos of reference group was below the ADI 5.8% in both dry and wet season.

This finding support the assumption of the study that the vegetable growers were likely exposed OPPs higher than the reference group. The percentage of vegetable growers who have absorbed OPPs exceeding the US EPA reference dose was higher than those of the reference group in dry and wet season. Nevertheless, potential hazard estimated from the biomarker did not identify the specific exposure pathways because we use oral chronic reference dose (acceptable daily intake) to be comparing with ADD.

This study showed that all ADD level of vegetable growers exceed US EPA for dicotophos and chlorpyrifos respectively in both dry and wet season. Based on biological monitoring, it indicated that biomarkers could play a role in understanding

of the pesticide exposure of vegetable growers. Biomarkers are also important in farmer as their absorbed dose for given external exposure level (Weaver et al., 1998). Biomarker, however, can only provide the information that a person has been exposed to contaminants and can possibly present some quantitative data concerning when an exposure occurred (Lioy, 1995). In addition, the attribution of DAP metabolite measurement to specific pesticide is difficult without detailed knowledge of sources and exposure pathways (Fenske et al. 200a). One or more of the APs could arise from sources other than pesticides. The fraction of the APs derived from non-pesticides source is not known (Duggan et al, 2003).Therefore, there is a need for continued performing of external markers through environmental and personal monitoring.

Table 4.8 Dose estimate (mg/kg/day) for each OPPs base on attribution of dialkylphosphate metabolites

Pesticides (ADI)	Vegetable Growers						Reference					
	Mean	25th	50 th	75th	90th	Max	Mean	25th	50th	75th	90 th	Max
Dry Season												
Dicrotophos(0.0001 ^a)	0.0068	0.0024	0.0047	0.0096	0.0186	0.0244	0.0014	0.0004	0.0005	0.0024	0.0055	0.0055
Chlorpyrifos (0.003 ^a)	0.0096	0.0065	0.0096	0.0118	0.0163	0.0202	0.0034	0.0021	0.0031	0.0054	0.0058	0.0059
Wet Season												
Dicrotophos (0.0001 ^a)	0.0060	0.0023	0.0031	0.0081	0.0141	0.0311	0.0015	0.0005	0.0011	0.0016	0.0024	0.0031
Chlorpyrifos (0.003 ^a)	0.0123	0.0040	0.0077	0.0106	0.0187	0.0256	0.0046	0.0031	0.0044	0.0054	0.0090	0.0124

^a EPA Acceptable Daily Intake (ADI) Value for pesticides

4.3 Environmental and Personal Monitoring

The vegetable growers were exposed to OPPs residues both direct and indirect ways. The OPPs residues were directly contacted to vegetables during mixing, loading and spraying pesticides. For indirect way, they are exposed to OPPs while they are drinking water, bathing, and contacting soil contaminated with OPPs. Three OPPs were used in the vegetable farms comprised of chlorpyrifos, dicotophos and profenofos. The OPPs were collected and analysed from water, working air, farm soil, hand wipe and patch samples. The detection limit and % recovery of samples in each media was shown in appendix D.

4.3.1 Water Samples

Vegetable growers in the Bang Rieng area consume a large amount of water from artesian wells located on the farms. These artesian wells have multi-purpose uses. The water in wells is not only used for drinking, cooking, and bathing, but also for mixing pesticides. Altogether, 100 water samples were collected; 50 were collected during the dry season (April-June 2006) and 50 during the wet season (September - October 2006). In each season, 33 water samples were collected from artesian wells in agricultural areas and 17 water samples were collected from artesian wells in reference areas.

Water samples were found to contain chlorpyrifos, dicotophos, and profenofos. Table 4.9 shows the mean OPPs concentration in water ($\mu\text{g/L}$) with the maximum and minimum values. Concentrations of all three pesticides were significantly higher in agricultural compared to reference areas, in both the wet and dry seasons ($p \leq 0.05$). In the farm area concentrations of all three pesticides in the wet season were higher than the concentration of pesticides in the dry season ($p \leq 0.005$).

Mean chlorpyrifos concentrations in either the wet or dry seasons did not exceed the life time exposure health advisory level of $20 \mu\text{g/L}$, as reported in the U.S. National Drinking Water Standard and Health Criteria (PAN, 2006). Moreover, mean profenofos concentrations in both wet and dry did not exceed the level of $0.3 \mu\text{g/L}$ as recommended by the Australia Drinking Water Guidelines for Pesticides (Halmilton *et al.*, 2007) but 18% of water samples exceeded the criteria. But in the dry and wet season, individual profenofos samples from the agricultural areas contained up to 1.537 and 4.410 times the Australian Drinking Water Guidelines for Pesticides respectively. Dicotophos is a highly toxic pesticide, which has been banned and is not registered for use in developed countries. There is no drinking water standards or guidelines for dicotophos from WHO, EPA, Australia, New Zealand, Japan or other sources to make comparisons.

Table 4.9 Organophosphate pesticides in drinking water ($\mu\text{g/L}$) collected from artesian wells in vegetable farm areas and reference areas at Bang Rieng Sub-District, Khuan Neing District, Thailand

	Guideline/ Advisory ($\mu\text{g/L}$)	Dry Season		Wet Season	
		Farm	Reference	Farm	Reference
Chlorpyrifos					
Mean	20*	0.035	0.003	0.069	0.003
Range		0.001-0.111	<LOD-0.011	<LOD-0.511	<LOD-0.011
Dicrotophos					
Mean	-	0.011	<LOD	0.132	<LOD
Range		<LOD-0.067	<LOD	<LOD-1.738	<LOD
Profenofos					
Mean	0.3**	0.039	0.001	0.217	0.001
Range		<LOD-0.461	<LOD-0.008	0.004-1.323	<LOD-0.008

*Using the U.S. National Drinking Water standard and Health Criteria 20 $\mu\text{g/L}$

**Using the Australia Drinking water standard and Criteria 0.3 $\mu\text{g/L}$

4.3.2 Air Samples

Vegetable growers in the Bang Rieng area inhale a large amount of OPPs during loading, mixing and spraying OPPs without the proper respirator. Vegetable growers might have health effect from breathing contaminated air. Altogether, 99 air samples were collected; 50 were collected during the dry season (April-June 2006) and 49 during the wet season (September - October 2006). During the dry season, 33 air samples were collected in working farm areas and 17 air samples were collected from reference areas. During the wet season, 32 air samples were collected from farm area and 17 air samples were collected from reference area.

Air samples were found to contain chlorpyrifos, dicrotophos, and profenofos. Table 4.10 shows the mean OPPs concentration in air (mg/m^3) with the maximum and minimum values. The concentrations of chlorpyrifos, dicrotophos, and profenofos were significantly higher in the agricultural areas compared to the reference areas, in both the wet and dry seasons ($p \leq 0.05$). In the farm area concentrations of all three pesticides in air sample had not difference between the dry season and the wet season ($p > 0.005$).

Mean chlorpyrifos concentrations in either the wet or dry seasons did not exceed the level of 0.2 mg/m^3 as recommended by American Conference of Governmental Industrial Hygienist (ACGIH). In the same way mean of dicrotophos concentrations in both wet and dry did not exceed the level of 0.25 mg/m^3 as recommended by the National Institute for Occupational Safety and Health (NIOSH). But in the dry season, the highest concentration of individual sample of chlorpyrifos from farm areas contained up to 2.27 times of the recommend value of ACGIH and 9% of samples exceed recommended values. In addition in the wet season, individual sample of dicrotophos from farm area contained up to 1.06 times of the recommend value of NIOSH and 3% of samples exceed recommend values. The analytical results

found that OPPs (chlorpyrifos, dicotophos and profenofos) was not detected in reference area during both the dry and wet season.

TABLE 4.10 Organophosphate Pesticide Concentrations in Working Air Condition (mg/m^3) collected from farm area and reference area at Bang Rieng Sub-District, Khuan Neing District, Thailand.

	Recommended Value (mg/m^3)	Dry Season		Wet Season	
		Farm	Reference	Farm	Reference
Chlorpyrifos					
Mean	0.20*	0.070	<LOD	0.035	<LOD
Range		<LOD-0.454	<LOD	<LOD-0.197	<LOD
Dicotophos					
Mean	0.25**	0.028	<LOD	0.024	<LOD
Range		<LOD-0.244	<LOD	<LOD-0.264	<LOD
Profenofos					
Mean	-	0.034	<LOD	0.026	<LOD
Range		<LOD-0.329	<LOD	<LOD-0.491	<LOD

*Using the recommended value of American Conference of Governmental Industrial Hygienist (ACGIH) $0.20 \text{ mg}/\text{m}^3$

**Using the recommended value of National Institute for Occupational Safety and Health (NIOSH) $0.25 \text{ mg}/\text{m}^3$

4.3.3 Soil Samples

Agricultural farm workers are likely to have high potential for pesticide exposure when they are involved in farm activity. Pesticide exposure could occur from a number of sources such as contaminated soil. The farmer contact contaminated soil when they walk to the field for watering and harvesting vegetable.

Altogether, 99 soil samples were collected; 50 were collected during the dry season (April-June 2006) and 49 during the wet season (September - October 2006). During the dry season, 33 soil samples were collected in working farm areas and 17 soil samples were collected from reference areas. During the wet season, 32 soil samples were collected from farm areas and 17 soil samples were collected from reference areas.

Soil samples were found to contain chlorpyrifos, dicotophos, and profenofos. Table 4.11 shows the mean OPPs concentration in soil (mg/kg) with the maximum and minimum values. The concentrations of chlorpyrifos, dicotophos and profenofos were significantly higher in the farm areas compared to the reference areas, in both the wet and dry seasons ($p \leq 0.05$). In the agricultural area and reference area, concentrations of all three pesticides were not different during the wet and dry season. It is because of the soil sample was collected after vegetable grower spraying pesticide. The reason to collect soil at that time because of after spraying pesticide the vegetable growers would reentry to farm for watering vegetable. The researcher though the soil collecting after spraying is the most dangerous to contact

Table 4. 11 Organophosphate Pesticide Concentrations in soil (mg/kg) collected from farm area and reference area at Bang Rieng Sub-District, Khuan Neing District, Thailand.

	Dry Season		Wet Season	
	Farm	Reference	Farm	Reference
Chlorpyrifos				
Mean	0.444	0.008	0.881	0.009
Range	0.006-2.842	<LOD-0.019	0.008-5.579	<LOD-0.067
Dicrotophos				
Mean	0.004	<LOD	0.004	<LOD
Range	<LOD-0.087	<LOD	<LOD- 0.050	<LOD
Profenofos				
Mean	0.071	0.002	0.108	0.002
Range	<LOD-0.513	<LOD-0.022	<LOD-1.224	<LOD-0.015

4.3.4 Hand Wipe Samples

Most of vegetable growers in Bang Rieng Sub-District did not wear gloves while they were loading, mixing and spraying pesticides. The OPPs can be exposed to their hands. The hand wipe samples were collected from both hands. The mean OPPs concentrations on the hands (μg / two hands) with the maximum and minimum values are present in Table 4.12 . The levels of chlorpyrifos, dicrotophos and profenofos were appeared on hand of vegetable growers higher than those of reference during both dry and wet seasons ($p \leq 0.05$). The concentrations of all three pesticides were not different during the wet and dry seasons ($p \leq 0.05$).

TABLE 4.12 Organophosphate Pesticide Concentrations on Vegetable Growers' hands (mg /twohands) in Bang Rieng Sub- District, Khuan Neing District, Thailand

	Dry Season		Wet Season	
	Farm	Reference	Farm	Reference
Chlorpyrifos				
Mean	0.070	0.0002	0.086	0.0003
Range	<LOD-0.491	<LOD- 0.004	<LOD-0.852	<LOD
Dicrotophos				
Mean	0.061	<LOD	0.059	<LOD
Range	<LOD-0.306	<LOD	<LOD-0.682	<LOD
Profenofos				
Mean	0.024	<LOD	0.059	<LOD
Range	<LOD-0.144	<LOD	<LOD-0.859	<LOD

4.3.5 Patch samples

Limited quantitative information in Thailand is available on dermal exposure during farm activities. The potential dermal exposure was measured during three different tasks: loading, mixing and spraying OPPs. Potential whole body exposure was measured using self-constructed cotton patch on 7 body locations. Position 1 is the hat as close to the top of the head. Position 2 is over sternum, on outside of normal clothing. Position 3 is on sternum, inside of normal clothing. Position 4 is upper surface of right forearm held with elbow bent at right angle across body, midway between elbow and wrist, on outside of normal clothing. Position 5 is front of left leg, mid – thigh on outside of normal clothing. Position 6 is front of left leg, above ankle, on outside of normal clothing. Position 7 is on the back between shoulder blades, on outside of normal clothing. Patches samples were collected to determine the concentration of OPPs on body skin. Each patch from each body part was determined. The mean, maximum and minimum of OPPs was combined among patches position 1, 2,4,5,6 and 7 was present in Table 4.13.

The mean of combined would be used to calculate the average daily dose of pesticide exposure to body skin. The patches at position 3 would be calculated the level of penetration through the coveralls, calculate from the amount of spray fluid on patches 3 compare to patches 2.

Patches samples were found to contain chlorpyrifos, dicotophos, and profenofos. Table 4.13 shows the mean OPPs concentration on patches ($\mu\text{g}/\text{cm}^2$) with the maximum and minimum values. The concentrations of chlorpyrifos, dicotophos and profenofos were significantly higher in the farm areas compared to the reference areas, in both the wet and dry seasons ($p \leq 0.05$). In the agricultural area, concentrations of all three pesticides were not different during the dry and the wet season. The concentration of patches showed in this table were divided by two for calculate unevenness of deposition in the area where direct exposure was less likely, e.g. crease in the overalls, the insides of leg and underarms (Johnson *et al.*, 2004).

Table 4.13 Organophosphate pesticides on dermal contact on body skin ($\mu\text{g}/\text{cm}^2$) of vegetable farmer and reference group in Bang Rieng Sub- District, Khuan Neing District, Thailand

	Dry Season		Wet Season	
	Farm	Reference	Farm	Reference
Chlorpyrifos				
Mean	1.315	0.027	2.027	0.020
Range	0.021-7.778	<LOD-0.292	0.049-8.787	<LOD-0.271
Dicotophos				
Mean	2.112	<LOD	1.855	<LOD
Range	<LOD-28.531	<LOD	0.019-15.843	<LOD
Profenofos				
Mean	1.082	<LOD	0.588	0.014
Range	<LOD-6.896	<LOD	<LOD-4.061	<LOD-0.114

4.4 The Relationship among Potential Exposure Variable

4.4.1 Correlation Residue among OPPs Pesticide Residues in Different Exposure Media

Spearman correlation coefficients were calculated to examine the relationship between of target OPPs in different environmental and personal samples of vegetable growers during the dry and wet season. It is found significant correlation for pesticide in environmental media and personal media. There were significant correlate between for sum of three pesticides (chlorpyrifos, dicotophos and profenofos) in air and sum of three pesticide on hands and OPPs on body skin show in Table 4.14. There were quite low significant correlated between OPPs in air and OPPs in soil with the relevant of r at 0.039. There were moderate significant correlated between OPPs in air and OPPs on hands with the relevant of r at 0.446. And there were quite high significant correlated between OPPs in air and OPPs on body skin, $r = 0.682$. The contaminants representing in soil, hand and body skin may originate from OPPs in air during applying pesticides.

Table 4.14 Spearman rank correlation coefficient (r) between OPPs levels in air, on hand and body skin

	Sum of OPPs in hand		Sum of OPPs on body Skin		Sum of OPPs in soil	
	p	r	p	r	p	r
Sum of OPPs in air	0.446	0.01	0.682	<0.001	0.039	0.256

4.4.2 Relationship between OPPs residues variable and OPPs exposure (DAP metabolite)

The result of multiple regression model to examine the association of OPPs in environmental and personal samples with the total of urine metabolites (DAP) for the vegetable growers are presented in table 4.15 and 4.16

Table 4.15 Linear regression model estimating the correlation of OPPs in environmental and total urinary metabolites in the dry season

Variable	Parameter Estimate	Standard Error	Standard Coefficient	P-value
Intercept	236.671	69.928		0.003
Sum of chlorpyrifos, dicotophos and profenofos in water	1223.625	453.594	0.483	0.013
Sum of chlorpyrifos, dicotophos and profenofos in air	446.896	215.10	0.372	0.050

Correlation of model; $R = 0.559$, $R^2 = 0.313$, adjust $R^2 = 0.250$; p -value = 0.016

Table 4.16 Linear regression model estimating the correlation of OPPs in environmental and total urinary metabolites in the wet season

Variable	Parameter Estimate	Standard Error	Standard Coefficient	P-value
Intercept	361.313	64.309		<0.0001
Sum of OPPs (chlorpyrifos, dicotophos and profenofos) in water	236.269	43.261	0.715	<0.0001
Sum of OPPs (chlorpyrifos, dicotophos and profenofos) on hand	135.703	57.349	0.327	0.029

Correlation of model; R= 0.837, R²= 0.700, adjust R²= 0.617; p-value =<0.0001

The model for the OPPs exposure of vegetable growers was elaborate as follows:

Dry Season

$$\text{DAP metabolites} = 236.7 + 1223.6 \text{ Sum of OPPs in water} + 446.9 \text{ Sum of OPPs in air}$$

Wet Season

$$\text{DAP metabolites} = 361.3 + 236.3 \text{ sum of OPPs in water} + 135.7 \text{ Sum of OPPs on hand}$$

The model in the dry season indicated that the level of sum of OPPs (chlorpyrifos, dicotophos and profenofos) in the water samples and air samples were significantly associated with increasing of urinary metabolite in the vegetable growers. It seem to be that the predictor in the model involved ingestion pathway with measure through the water media and inhalation pathway which measure through the air media. The regression model explained about 25.0 % of the variability in exposure. It can be observed that there was a wide variability in OPPs measurement in subject. One reason to explain because the condition of protective equipment, high frequency of splashed and spill onto the body and ambient air temperature effect may be influence the correlation between OPPs in air and DAP metabolite quite low. (Cattani *et al*, 2001). Another reason can be explained is that all data input in the model were derived from cross sectional investigation, result is lack of the correlation between environmental and biological measurement (Rappaport *et al*, 1995)

The model in the wet season indicated that the level of sum of OPPs in the water sample and on hands were significant associated with increasing of urinary metabolite in the vegetable growers. It can be seem that the predictor in the model involved ingestion pathway with measure through water media and dermal contact which measure through the hand wipe (personal media). The regression model

explained 61.7% of the variability. It can be noted that water and hand contact measurement within subject are important variable for exposure in wet season. Some study had found positive correlations between pesticide hand exposure and urinary level among green house pesticide applicator and agricultural worker (Apera *et al.*,1994; Tuomanien *et al.*, 2002)

In particular, OPPs level in soil and on body skin was not significant in the model. It might be the vegetable growers were not contact directly OPPs in soil and on body skin because they wore boot and clothes during they worked in the farm. Chester and Hart monitored a group of mixer/loader/applicator with urine and WBDs (synthetic coveralls, cotton gloves and face mask). It found that no correlation was found between the estimate dermal exposure (WBDs) and the fluazifob residues recovered from the urine ($R^2=0.009$).

4.5 Estimation of Dose and Risk

This approach is used to estimate farmers exposed to OPPs and OPPs dose by ingestion, inhalation and dermal contact exposure pathways. To assess exposure for each pathway, the route-specific mathematical algorithms were used and expressed as functions of pesticide concentration in the exposure medium, intake or contact rate, rate of transfer from the exposure medium to the portal of entry, and exposure duration (Cohen *et al.*, 2000).

The average daily dose (ADD) was used to estimate the exposure for non carcinogenic exposure as describes in each exposure pathway. The default or recommend exposure value to estimate dose were obtained from US EPA. Some factors were estimated based on chemical analysis such as OPPs in each exposure media or from vegetable grower interviewing such as body weight, water intake rate, bathing time.

The dose estimations were expressed as the mean for describing the distribution of exposure for the study population. The values at the extreme upper-end were presented for described the most individual exposed persons in the population. The statistic 95% confidential interval (CI) was also present. The concentration values in each media were less than LOD estimating to zero.

4.5.1 Water Ingestion Exposure

Dietary exposure from water ingestion was calculated by the following algorithm.

$$ADD = (C_s \times IR \times EF \times ED \times UCF) / (BW \times AT)$$

Where:

ADD	= average daily dose for water ingestion (mg/kg day)
C_s	= concentrations of pesticide in water ($\mu\text{g/L}$)
IR	= water ingestion rate (L/day)
EF	= exposure frequency (days/year)
ED	= exposure duration (years)
BW	= body weight (kg)
AT	= averaging time (days)

C_s : The Pesticide concentration; for example the mean chlorpyrifos concentration of water in vegetable farm in dry season = 0.035 $\mu\text{g/L}$
IR: from the interview, IR for vegetable growers' drinking water equals 2.2 L/day and IR for reference group equals 2.0 L/day.
EF: 365 days/year
ED: from the interview, farming period equals to 45 years
BW: body weight (65kg; average body weight of vegetable growers and reference group from interview)
AT: average time (16,425 days calculated by multiplying exposure duration = 45 year with the exposure frequency = 365 day/year)
UCF: Unit Conservation Factor ($10^{-3}\text{mg}/\mu\text{g}$)

The average daily dose (ADD) and hazard quotients (HQ) for vegetable farmers and reference are illustrated in Table 4.17 and Table 4.18 respectively for the dry and wet season. The HQ, is a ratio of the exposure dose to the reference dose (RfD); an HQ value greater than 1 indicates that the exposure has exceeded the RfD. The chronic oral RfDs recommended by the US EPA Integrated Risk Information System (IRIS, 1994) for chlorpyrifos, dicofol, and profenofos are 0.003, 0.0001, and 0.0001 mg/kg-day, respectively (IRIS,1994; HCRA,2004).

The mean ADDs for chlorpyrifos, dicofol and profenofos that vegetable growers were exposed during both wet and dry season were significantly higher than the mean ADDs for the reference group ($p \leq 0.05$). The results also indicate that ADD of three pesticides exposed to vegetable was significantly higher during the wet season compared to the dry season ($p \leq 0.05$). Mean ADDs for both the vegetable growers and the reference groups during the dry and wet season were below the mentioned oral RfDs. HQs calculated using the mean ADDs for the vegetable growers and the reference groups during both the dry and wet seasons were less than 1, suggesting that the vegetable growers and the reference group may not be at high risk from consuming OPPs in contaminated well water. This shows that agriculture communities consume the drinking water contaminated with OPPs such as chlorpyrifos, dicofol and profenofos without adverse effects. However, in this study we found OPPs in drinking water, the amount of pesticide may be increased in the future. So environmental monitoring and health surveillance should still be applied to this area to prevent possible future risks associated with these OPPs. The government mitigation plan suggested that the communities be made aware of such things as proper application of pesticides to effectively reduce pesticide contamination in drinking water.

Table 4.17 Average daily dose (ADD) of organophosphate pesticide residues due to water ingestion for the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the dry season.

	Oral RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.003						
Mean		0.035	1.18E-06	0.0004	0.003	9.23E-08	0.00003
Maximum		0.111	3.76E-06	0.0013	0.011	3.39E-07	0.0001
95%CI				0.0003-0.0005			0.000009- 0.00004
Dicrotophos	0.0001						
Mean		0.011	3.72E-07	0.0037	<LOD	0	0
Maximum		0.067	2.27E-06	0.0227	<LOD	0	0
95%CI				0.0017-0.0061			-
Profenofos	0.0001						
Mean		0.039	1.32E-06	0.0132	0.001	3.08E-08	0.0003
Maximum		0.461	1.56E-05	0.1560	0.008	2.46E-07	0.0025
95%CI				0.0034-0.0232			0.00014-0.0011

^a Oral chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

Table 4.18 Average daily dose (ADD) of organophosphate pesticide residues due to water ingestion for the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Oral RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.003						
Mean		0.069	2.33E-06	0.0008	0.003	9.23E-08	0.00003
Maximum		0.511	1.73E-05	0.0058	0.011	3.39E-08	0.0001
95%CI				0.0001-0.0014			0.000004-0.00005
Dicrotophos	0.0001						
Mean		0.132	4.47E-06	0.0447	<LOD	0	0
Maximum		1.738	5.88E-05	0.5883	<LOD	0	0
95%CI				-0.047-0.0929			-
Profenofos	0.0001						
Mean		0.217	7.36E-06	0.0735	0.001	3.08E-08	0.0003
Maximum		1.323	4.48E-05	0.4478	0.008	2.46E-07	0.002
95%CI				0.0296-0.1170			0.00014-0.0011

^a Oral chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

4.5.2 Air Inhalation Exposure

Air inhalation exposure was calculated by the following algorithm

$$ADD = (C_s \times IR \times EF \times ED \times AF) / (BW \times AT)$$

Where: ADD = average daily dose for air inhalation (mg/kg.day)
C_s = concentration of pesticides in air (mg/m³)
IR = inhalation rate (m³/day)
EF = exposure frequency (days/year)
ED = exposure duration (years)
BW = body weight (kg)
AT = averaging time (days)
AF = absorption factor

C_s: pesticide concentration in air

IR: for vegetable growers' average breathing rate

dry season vegetable growers average breathing rate = 1.443 m³/day, calculated from breathing rate in heavy activity (3.2 m³/hr; EPA,1997) and multiply by 0.451 hr/day for average spraying pesticide period of vegetable farmers in dry season.

wet season vegetable growers average breathing rate = 1.699 m³/day, calculated from breathing rate in heavy activity (3.2 m³/hr; EPA,1997) and multiply by 0.531hr/day for average spraying pesticide period of vegetable farmers in wet season..

for reference group breathing rate and breathing time use as same as vegetable growers in both dry and wet seasons

EF: 64.5 days/year (average spraying days from the interview)

ED: farming period equals to 45 years (from the interview)

BW: body weight (65kg; average body weight of vegetable growers and reference group from interview)

AT: average time (2,902 days calculated by multiplying exposure duration = 45 years with the exposure frequency = 64.5 days/year)

AF: absorption factor equal to 1

The average daily dose (ADD) and hazard quotients (HQ) for vegetable growers and controls' are illustrated in Table 4.19 and Table 4.20, respectively for the dry and wet seasons. The HQ is a ratio of the exposure dose to the reference dose; RfD; an HQ value greater than 1 indicates that the exposure has exceeded the RfD. The inhalation RfDs was modified from no-observed-adverse-effects level (NOAEL) or lowest-observed-adverse-effects level (LOAEL) or lowest-effect level (LEL) and uncertain factor (UF) recommended by the US EPA. The NOAEL of chlorpyrifos for inhalation in chronic effect was 0.03 mg/kg.day (US EPA, 1999). The LOAEL of dicotophos for chronic effect was 0.02 mg/kg.d (US EPA, 1999). There was lowest effects level (LEL) of profenofos for inhalation route for chronic effect was 11.2 mg/kg.d (US EPA, 1998). The UFs of chlorpyrifos, dicotophos and profenofos were 100, 1000 and 100 respectively (US EPA 1998; US EPA 1999). So the estimated RfDs for chlorpyrifos, dicotophos and profenofos were 0.0003, 0.00002 and 0.112 mg/kg.day respectively.

The mean ADDs for chlorpyrifos, dicotophos and profenofos that vegetable growers were exposed to during both wet and dry seasons were significantly higher than the mean ADDs for the reference group ($p \leq 0.05$). The results indicated that ADD of three pesticides exposed to vegetable was not significantly different between the dry season and the wet season ($p \geq 0.05$). Mean ADDs of chlorpyrifos and dicotophos of the vegetable growers during the dry and wet season were above the mentioned inhalation RfD or HQ higher than 1 whereas the mean ADD of profenofos was below in halation RfD or HQ less than 1, suggesting that the vegetable growers may be at higher risk from chlorpyrifos and dicotophos from breathing air at working condition. But the finding indicated that HQ of the chlorpyrifos, dicotophos, and profenofos were less than 1 in reference area, suggesting that the reference group may not be at higher risk from breathing air from their working condition.

Table 4.19 Average daily dose (ADD) of organophosphate pesticide residues due to air ingestion for the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the dry season.

	Inhalation RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (mg/m ³)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (mg/m ³)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.0003						
Mean		0.070	1.54E-03	5.144	<LOD	0	0
Maximum		0.454	1.00E-02	33.333	<LOD	0	0
95%CI				1.880-9.400			
Dicrotophos	0.00002						
Mean		0.028	6.17E-04	30.864	<LOD	0	0
Maximum		0.244	5.38E-03	268.963	<LOD	0	0
95%CI				10.660-57.470			
Profenofos	0.112						
Mean		0.034	7.50E-04	0.007	<LOD	0	0
Maximum		0.329	7.25E-03	0.065	<LOD	0	0
95%CI				0.0006-0.0158			-

^a Inhalation chronic reference dose was modified from EPA. The RfD = NOAEL or LOAEL or LEL /UF; NOAEL Chlorpyrifos 0.03, LOAEL dicrotophos 0.02 and LEL profenofos 11.2 mg/kg.day. Uncertainty factor (UF) for chropyrifos = 100, dicrotophos = 1000, profenofos = 100

Table 4.20 Average daily dose (ADD) of organophosphate pesticide residues due to air ingestion for the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Inhalation RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (mg/m ³)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (mg/m ³)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.0003						
Mean		0.035	9.15E-04	3.050	<LOD	0	0
Maximum		0.197	5.14E-03	17.164	<LOD	0	0
95%CI				1.348-3.848			-
Dicrotophos	0.00002						
Mean		0.024	6.27E-04	31.366	<LOD	0	0
Maximum		0.264	6.90E-03	345.028	<LOD	0	0
95%CI				8.85-57.75			-
Profenofos	0.112						
Mean		0.026	6.80E-04	0.006	<LOD	0	0
Maximum		0.491	1.28E-02	0.114	<LOD	0	0
95%CI				-0.023-0.0137			-

^a Inhalation chronic reference dose was modified from EPA. The RfD = NOAEL or LOAEL or LEL /UF; NOAEL Chlorpyrifos 0.03, LOAEL dicrotophos 0.02 and LEL profenofos 11.2 mg/kg.day. Uncertainty factor (UF) for chropyrifos = 100, dicrotophos = 1000, profenofos = 100

4.5.3 Dermal Contact Exposure

4.5.3.1 Water Dermal Contact (bathing) Exposure

Dermal exposure from water (bathing) contact was calculated by the following equation.

$$\text{ADD} = C_s \times SA \times PC \times ET \times EF \times EP \times CF / BW \times AT$$

Where:

ADD = average daily dose for dermal contact (mg/kg.day)
Cs = concentration of pesticide in water ($\mu\text{g/L}$)
SA = skin surface area available for contact (cm^2)
PC = pesticide specific permeability coefficient (cm/hr)
ET = exposure time (hrs/event)
EF = exposure frequency
EP = exposure duration
ED = exposure duration (years)
CF = conversion factor
BW = body weight (kg)
AT = averaging time (days)
CF = conversion factor

The dose estimates generated using the algorithms presented above are based on some US EPA's default values (i.e. skin surface area available for contact, permeability coefficient)

SA: 19,400 cm^2 (male), 16,900 cm^2 (female)

PC : chlorpyrifos = 0.046 cm/hr (IRIS, 2008)

for dicotophos and profenofos, the data are not available. The EPA had recommend to calculate from equation

$\log K_p(\text{PC}) = 0.72 \log Kow - 0.0061 MW - 2.72$ (US. EPA, 1992a);

MW = Molecular Weight; Kow = partition coefficient

dicotophos = 0.0037 cm/hr (Kow = 2.455, MW = 237.21)

profenofos = 0.00016 cm/hr (Kow = 1.7, MW = 373.65)

ET: 0.5 hrs (0.25 hrs/event \times 2 events/day; bathing time 0.25 hrs/event, bathing 2 events/day)

EF: 365 days/year

ED: 45 years (farming period from the interview)

BW: body weight (65kg; average body weight of vegetable growers from interview)

AT: average time (16,425 days calculated by multiplying exposure duration = 45 year with the exposure frequency = 365 day/year)

CF: (10^{-3} mg/ μg , 1L/1000 cm^3)

The average daily dose (ADD) and hazard quotients (HQ) for vegetable growers and controls are illustrated in Table 4.21 and Table 4.22 respectively for the dry and wet season. The HQ, is a ratio of the exposure dose to the reference dose (RfD); an HQ value greater than 1 indicates that the exposure has exceeded the dermal RfD. The dermal RfDs recommended by the US EPA Integrated Risk Information System (IRIS, 1994) for chlorpyrifos, dicotophos, and profenofos are 0.0015, 0.00005, and 0.00005 mg/kg-day, respectively.

The finding indicated that all of ADDs of chlorpyrifos, dicotophos and profenofos for vegetable growers and reference were below the US EPA dermal reference dose in both dry and wet season. This shows that the vegetable growers and reference group were not at risk from bathing contaminated water with OPPs. However, the mean ADDs of dicotophos, chlorpyrifos, and profenofos were exposed to vegetable growers by bathing water higher than reference group during the both dry season and wet season significantly ($p \leq 0.05$).

Table 4.21 Average daily dose (ADD) of organophosphate pesticide residues due to dermal contact by bathing water from artesian well of the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the dry season.

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.0015						
Mean		0.035	2.40E-07	0.00016	0.003	2.06E-08	0.00001
Maximum		0.111	7.62E-07	0.00051	0.011	7.55E-08	0.00005
95%CI				0.00015-0.03			0.000001-0.00002
Dicrotophos	0.00005						
Mean		0.011	6.07E-09	0.00012	<LOD	0	0
Maximum		0.067	3.70E-08	0.00075	<LOD	0	0
95%CI				0.000005-0.000020			-
Profenofos	0.00005						
Mean		0.039	9.31E-10	0.00002	0.001	2.39E-11	0.0000005
Maximum		0.461	1.10E-08	0.00022	0.008	1.91E-10	0.000004
95%CI				0.00004-0.00003			0.00000001-0.000001

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

Table 4.22 Average daily dose (ADD) of organophosphate pesticide residues due to dermal contact by bathing water from artesian well of the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (µg/L)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.0015						
Mean		0.069	4.74E-07	0.0003	0.003	2.06E-08	0.00001
Maximum		0.511	3.51E-06	0.0023	0.011	7.55E-08	0.00005
95%CI				0.00004-0.001			0.000001-0.00002
Dicrotophos	0.00005						
Mean		0.132	7.29E-08	0.0014	<LOD	0	0
Maximum		1.738	9.60E-07	0.0192	<LOD	0	0
95%CI				0.00015-0.003			-
Profenofos	0.00005						
Mean		0.217	5.18E-09	0.0001	0.001	2.39E-11	0.0000005
Maximum		1.323	3.16E-08	0.0006	0.008	1.91E-10	0.000004
95%CI				0.00004-0.0002			0.00000001-0.000001

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

4.5.3.2 Soil Dermal Contact Exposure

Dermal exposure from soil contact was calculated by the following equation.
$$ADD = (C_s \times CF \times SA \times AF \times ABS \times EF \times ED) / (BW \times AT)$$

Where: ADD = average daily dose for dermal contact (mg/kg.day)

C_s = concentration of pesticide in soil (mg/kg)

CF = conversion factor (10⁻⁶ kg/mg)

SA = skin surface area available for contact (cm²/day)

AF = soil to skin adherence factor (mg/cm²)

ABS = absorption factor (unitless)

EF = exposure frequency (days/year)

ED = exposure duration (years)

BW = body weight (kg)

AT = average time (days)

The dose estimates based on some US EPA's default values as following

SA: 5,700 cm²/day (EPA, 1997)

AF: 0.2 mg/cm² (CDTOC, 2005)

ABS: 0.03 for chlorpyrifos (US.EPA, 1999), 0.15 for dicotophos (US.EPA.,1999), and 0.5 for profenofos (US. EPA., 1998)

EF: 300 days/year (The vegetable growers worked and cultivated product in their farms approximately 10 months, another 2 months farm areas were flooding)

ED: 45 years (farming period from the interview)

BW: body weight (65kg; average body weight of vegetable growers from interview)

AT: average time (13,500 days calculated by multiplying exposure duration = 45 years with the exposure frequency = 300 days/year)

The average daily dose (ADD) and hazard quotients (HQ) for vegetable farmers and controls' by soil dermal contact exposure are illustrated in Table 4.23 and Table 4.24 respectively for the dry and wet season. The HQ, is a ratio of the exposure dose to the reference dose (RfD); an HQ value greater than 1 indicates that the exposure has exceeded the dermal RfD. The dermal RfDs recommended by the US EPA Integrated Risk Information System (IRIS, 1994) for chlorpyrifos, dicotophos, and profenofos are 0.0015, 0.00005, and 0.00005 mg/kg-day, respectively.

The finding indicated that the all ADDs of chlorpyrifos, dicotophos and profenofos for soil dermal contact of vegetable growers and reference group were below the US EPA dermal reference dose in both wet and dry season. This shows that the vegetable growers and reference group contacted soil contaminated with the three OPPs without adverse effects. However, the mean average daily doses of dicotophos, chlorpyrifos, and profenofos were exposed to vegetable growers by soil dermal contact higher than reference group during the both dry season and wet season significantly ($p \leq 0.05$).

Table 4.23 Average daily dose (ADD) of organophosphate pesticide residues due to dermal contact by contaminated soil for the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the dry season.

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (mg/kg)	ADD (mg/kg.d)	HQ (ADD/RfD)	Cs (mg/kg)	ADD (mg/kg.d)	HQ (ADD/RfD)
Chlorpyrifos	0.0015						
Mean		0.444	2.34E-07	0.0002	0.008	4.21E-08	0.000003
Maximum		2.842	1.50E-06	0.0010	0.019	1.00E-09	0.000006
95%CI				0.0001-0.002			0.0000001- 0.000002
Dicrotophos	0.00005						
Mean		0.004	1.05E-08	0.0002	<LOD	0	0
Maximum		0.087	2.29E-07	0.0045	<LOD	0	0
95%CI				-0.0001-0.0006			-
Profenofos	0.00005						
Mean		0.071	6.23E-07	0.0124	0.002	1.75E-08	0.0003
Maximum		0.513	4.50E-06	0.0900	0.022	1.93E-07	0.004
95%CI				0.0056-0.19			0.0002-0.0008

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

Table 4.24 Average daily dose (ADD) of organophosphate pesticide residues due to dermal contact by contaminated soil for the people in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (mg/kg)	ADD (mg/kg.d)	HQ (ADD/RfD)	Cs (mg/kg)	ADD (mg/kg.d)	HQ (ADD/RfD)
Chlorpyrifos	0.0015						
Mean		0.881	4.64E-07	0.0003	0.0087	4.58E-09	0.000003
Maximum		5.579	2.94E-06	0.0020	0.067	3.53E-08	0.00002
95%CI				0.0002-0.0005			0.0000008-0.000006
Dicrotophos	0.00005						
Mean		0.004	1.05E-08	0.0002	<LOD	0	0
Maximum		0.050	1.32E-07	0.0026	<LOD	0	0
95%CI				0.0001-0.0004			-
Profenofos	0.00005						
Mean		0.108	9.47E-07	0.0189	0.0016	1.40E-08	0.0003
Maximum		1.224	1.07E-05	0.2147	0.015	1.32E-07	0.003
95%CI				0.0043-0.027			0.001-0.0007

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

4.5.3.3 Pesticides Dermal (Hand) Contact Exposure

Dermal exposure from hand contact to pesticides was calculated by the following equation.

$$\text{ADDs} = (\text{Cs} \times \text{ABS} \times \text{ET} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT})$$

Where:

ADDs	= average daily dose for dermal contact (mg/kg/day)
Cs	= Concentration of pesticide on hand (mg/two hands)
ABS	= absorption factor
ET	= exposure time (event/side-d)
EF	= exposure frequency (day/year)
ED	= exposure duration (years)
BW	= body weight (kg)
AT	= averaging time (days)

The dose estimates generated using the algorithms presented above are based on some US EPA's default values (i.e. hand surface area available for contact, absorption factor)

ABS: 0.03 for chlorpyrifos (US.EPA, 1999), 0.15 for dicotophos (US.EPA.,1999), and 0.5 for profenofos (US. EPA., 1998)

ET: 1 event/day (data from field work)

EF: 64.5 days/year (average spraying days from the interview)

ED: from the interview, farming period equals to 45 years

BW: body weight (65kg; average body weight of vegetable growers from interview)

AT: average time (exposure frequency (64.5 days) multiply with exposure duration (45 years) equal to 2,902 day)

The average daily dose (ADD) and hazard quotients (HQ) for vegetable farmers and controls' are illustrated pesticides dermal (hand) contact exposure in Table 4.25 and Table 4.26 respectively for the dry and wet season. The HQ, is a ratio of the exposure dose to the reference dose (RfD); an HQ value greater than 1 indicates that the exposure has exceeded the dermal RfD. The dermal RfDs recommended by the US EPA Integrated Risk Information System (IRIS,1994) for chlorpyrifos, dicotophos, and profenofos are 0.0015, 0.00005, and 0.00005 mg/kg-day, respectively.

The mean ADDs of chlorpyrifos of vegetable growers was below RfD whereas the mean ADDs of dicotophos and profenofos were above RfD in both dry and wet season. It concluded that vegetable growers might be at risk from hand contact to dicotophos and profenofos during farm activities including mixing, loading and spraying pesticides. In addition, the vegetable growers in the dry season contained the highest ADDs of individual chlorpyrifos up to 0.151 times the Rfd or

HQ equal to 0.151, the highest ADDs of individual dicotophos up to 14.123 times the RfD and the highest ADDs of individual profenofos up to 22 times the RfD . The finding indicated that some of the individual vegetable growers expose dicotophos and profenofos were much greater than 1 in the dry season. In addition in the wet season the vegetable growers contained HQ of chlorpyrifos equal to 0.26, HQ of dicotophos equal to 31.477, and HQ of profenofos equal to 132.158. The finding indicated that some of the individual vegetable growers expose dicotophos and profenofos were much greater than 1 in the wet season. It can be suggested that some of vegetable growers might be at higher risk from hand contact to dicotophos and profenofos residues during loading, mixing and spraying.

Table 4.25 Average daily dose of organophosphate pesticide residues to hand contact exposure of vegetable grower and reference group in Bang Rieng Sub- District, Khuan Nieng District, Thailand dry season

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (mg/two hands)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (mg/two hands)	ADD (mg.kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.0015						
Mean		0.070	3.23E-05	0.021	0.0002	9.23E-08	0.00006
Maximum		0.491	2.27E-04	0.151	0.004	1.85E-06	0.001
95%CI				0.009-0.033			-0.00008-0.0002
Dicrotophos	0.00005						
Mean		0.061	1.41E-04	2.815	<LOD	0	0
Maximum		0.306	7.06E-04	14.123	<LOD	0	0
95%CI				1.245-4.024			-
Profenofos	0.00005						
Mean		0.024	1.85E-04	3.692	<LOD	0	0
Maximum		0.143	1.10E-03	22.000	<LOD	0	0
95%CI				1.866-5.620			-

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

Table 4.26 Average daily dose of organophosphate pesticide residues hand contact of vegetable grower and reference group in Bang Rieng Sub-District, Khuan Nieng District, Thailand wet season.

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (mg/two hands)	ADD (mg/kg.day)	HQ (ADD/RfD)	Cs (mg/two hands)	ADD (mg/kg.day)	HQ (ADD/RfD)
Chlorpyrifos	0.0015						
Mean		0.086	3.97E-05	0.026	0.0003	1.38E-07	0.00009
Maximum		0.852	3.93E-04	0.260	0.004	1.85E-06	0.001
95%CI				0.009-0.043			-0.00006-0.0002
Dicrotophos	0.00005						
Mean		0.059	1.36E-04	2.723	<LOD	0	0
Maximum		0.682	1.57E-03	31.477	<LOD	0	0
95%CI				0.456-4.633			-
Profenofos	0.00005						
Mean		0.059	4.54E-04	9.077	<LOD	0	0
Maximum		0.859	6.61E-03	132.158	<LOD	0	0
95%CI				0.521-17.398			-

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

4.5.3.4 Liquid Pesticides Dermal (Body Skin) Contact Exposure

$$ADD = (Cs \times SA \times TE \times ABS \times ET \times EF \times ED) / (BW \times AT \times UCF)$$

Where:

ADD = average daily dose for dermal contact (mg/kg/day)
Cs = Concentration of pesticide on body skin ($\mu\text{g}/\text{cm}^2$)
SA = body skin surface area available for contact (cm^2)
TE = transfer efficiency from clothes to body skin
ABS = absorption factor
ET = exposure time (event/d)
EF = exposure frequency (day/year)
ED = exposure duration (years)
BW = body weight (kg)
AT = averaging time (days)
UCF = Unit Conservation Factor

The dose estimates generated using the algorithms presented above are based on some US EPA's default values (i.e. skin surface area available for contact, absorption factor). Each patch would be used to calculate with each part of skin area contact such as patch at position 1 should multiply with head surface area (1450 cm^2). The combined ADD of each patch were represented ADD of body skin contact (Johnson *et al.*, 2004).

SA: Skin Surface Area (Head $1,450 \text{ cm}^2$, Chest $4,620 \text{ cm}^2$, Arm $2,020 \text{ cm}^2$, Upper Leg $3,640 \text{ cm}^2$, Lower Leg $3,640 \text{ cm}^2$, Back $4,620 \text{ cm}^2$) (Johnson *et al.*, 2004)

TE: 0.1 (Cal-EPA, 2004)

ABS: 0.03 for chlorpyrifos (US EPA, 1999), 0.15 for dicofol (US EPA, 1999), and 0.5 for profenofos (US EPA, 1998)

ET: 1 event/d (data from field work)

EF: 64.5 days/year (average spraying days from the interview)

ED: from the interview, farming period equals to 45 years

BW: body weight (65kg; average body weight of vegetable growers from interview)

AT: average time (exposure frequency (64.5 days) multiply with exposure duration (45 years) equal to 2,902 day)

UCF: Unit Conservation Factor (1,000 $\mu\text{g}/\text{mg}$)

The average daily dose (ADD) and hazard quotients (HQ) for pesticides dermal (body skin) contact exposure for vegetable farmers and controls' are illustrated in Table 4.27 and Table 4.28 respectively for the dry and wet season. The HQ, is a ratio of the exposure dose to the reference dose (RfD); an HQ value greater than 1 indicates that the exposure has exceeded the dermal RfD. The dermal RfDs recommended by the US EPA Integrated Risk Information System (IRIS, 1994) for chlorpyrifos, dicofol, and profenofos are 0.0015, 0.00005, and 0.00005 mg/kg-day, respectively.

The mean ADDs of chlorpyrifos, dicotophos and profenofos were above RfD in both dry and wet season. It concluded that vegetable growers might be at risk from body contact to Chlorpyrifos, dicotophos and profenofos during farm activities including mixing, loading and spraying pesticides. In addition, the vegetable growers in the dry season contained the highest ADDs of individual chlorpyrifos up to 0.797times the Rfd, the highest ADDs of individual dicotophos up to 438.726 and the highest ADDs of individual profenofos up to 353.448 times the RfD. The finding indicated that some of the individual vegetable growers exposed to Chlorpyrifos, dicotophos and profenos were much greater than 1 in the dry season. In addition in the wet season the vegetable growers contained HQ of chlorpyrifos equal to 0.900, HQ of dicotophos equal to 243.63, and HQ of profenos equal to 222.386. The finding indicated that some of the individual vegetable growers exposed to chlorpyrifos, dicotophos and profenos were much greater than 1 in the wet season. It can be suggested that some of vegetable growers might be at higher risk from dermal contact to chlorpyrifos, dicotophos and profenofos residues during loading, mixing and spraying.

Table 4.27 Average daily dose of organophosphate pesticide residues to dermal (body skin) contact exposure of vegetable grower and reference group in Bang Rieng Sub- District, Khuan Nieng District, Thailand dry season

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs (µg/cm ²)	ADD	HQ	Cs (µg/cm ²)	ADD	HQ
Chlorpyrifos	0.0015						
Mean		1.315	2.02E-04	0.135	0.027	4.10E-06	0.003
Maximum		7.778	1.20E-03	0.797	0.292	4.21E-05	0.028
95%CI				0.071-0.199			-0.0014-0.007
Dicrotophos	0.00005						
Mean		2.112	1.62E-03	32.400	<LOD	0	0
Maximum		28.531	2.19E-02	438.000	<LOD	0	0
95%CI				4.049-60.894			-
Profenofos	0.00005						
Mean		1.082	2.77E-03	55.400	<LOD	0	0
Maximum		6.896	1.76E-02	352.000	<LOD	0	0
95%CI				17.276-93.69			-

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>))

Table 4.28 Average daily dose of organophosphate pesticide residues to dermal(body skin) contact exposure of vegetable grower and reference group in Bang Rieng Sub- Disict, Khuan Nieng District, Thailand wet season

	Dermal RfD ^a (mg/kg.day)	Vegetable Growers			Reference		
		Cs ($\mu\text{g}/\text{cm}^2$)	ADD	HQ	Cs ($\mu\text{g}/\text{cm}^2$)	ADD	HQ
Chlorpyrifos	0.0015						
Mean		2.022	3.37E-04	0.224	0.020	2.08E-05	0.014
Maximum		8.787	1.35E-03	0.900	0.271	2.82E-04	0.187
95%CI				0.128-0.298			-0.001-0.039
Dicrotophos	0.00005						
Mean		1.855	1.41E-03	28.200	<LOD	0	0
Maximum		15.843	1.21E-02	243.613	<LOD	0	0
95%CI				9.372-49.232			-
Profenofos	0.00005						
Mean		0.588	6.68E-03	32.183	0.014	1.79E-05	0.003
Maximum		4.016	1.11E-02	222.386	0.115	3.82E-05	0.030
95%CI				11.472-51.513			-0.0014-0.007

^a Dermal chronic reference dose (from Integrated Risk Information system Database, IRIS EPA 1994; Toxicity & Chemical Specific Factors Database (<http://risk.lsd.ornl.gov/cgi>)).

4.6 Occupational Handler Risk Characterization

The farmer always used high amount of pesticide in short and long time. The occupational exposures to OPPs can occur during handling, mixing, loading and application activities. Based on toxicological criteria and potential for exposure, Health Effect Division (HED) has conducted dermal and inhalation exposure assessments for: occupational dermal, and inhalation exposure to worker. The duration of exposure is expected to be short term and intermediate term and in some instances long term for pest control operator. The dermal and inhalation risk assessment, risk estimates are expressed in terms of the Margin of Exposure (MOE), which is the ratio of the NOAEL selected for the risk assessment to the exposure. For occupationally exposed workers, MOEs >100 for chlorpyrifos and profenofos; and MOEs >1000 for dicotophos. The MOEs below these levels would represent a risk concern. The NOAELs of chlorpyrifos for inhalation in acute effect and chronic effect were 0.1 and 0.03 mg/kg.d respectively. The LOAELs of dicotophos (used LOAELs instead of NOAELs as US EPA recommendation) for inhalation in acute and chronic effect were 0.5 and 0.02 mg/kg.d respectively. There was LEL of profenofos for inhalation route for both acute and chronic effect was 11.2 mg/kg.d.

4.6.1 Inhalation Exposure

The average daily doses and MOEs of acute effect and chronic effect of OPPs due to air inhalation for vegetable growers during the dry and wet season are illustrated in Table 4.29 and Table 4.30 respectively. The MOEs, is a ratio of the NOAELs to the average daily dose (ADD); an MOEs value for chlorpyrifos, dicotophos and profenofos less than 100, 1000 and 100, respectively would represent a risk concern.

For acute effect in the dry season, the result indicated that NOAEL compare to mean ADDs of chlorpyrifos and dicotophos were less than 100 and 1000 respectively. It indicated that the vegetable might be at risk from consuming chlorpyrifos and dicotophos in working air condition. But the MOE of profenofos greater than 100 suggested that the vegetable growers might not be at risk from breathing profenofos in short time. In the wet season, the result indicated that MOEs of acute effect of chlorpyrifos and profenofos were greater than 100 whereas MOEs of dicotophos less than 1000. It concluded that in the wet season the vegetable growers might be at risk only from consuming dicotophos in working air condition.

For chronic effect, the ADDs of chlorpyrifos and profenofos for chronic effect should multiply by absorption factor before using to compare with NOAEL. The absorption factor for all pesticides in halation pathway was 100%. So ADDs using to calculate for acute effect and chronic effect were the same value. In both dry and wet season, the result indicated that MOEs of chlorpyrifos and dicrorophos were less than the values as recommended by EPA. It indicated that the vegetable growers might be at risk from breathing working air contaminated with these pesticides in long period.

Table 4.29 Average daily dose (ADD) of organophosphate pesticide residues due to air ingestion for vegetable growers in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the dry season.

	Cs in air (mg/m ³)	Acute Effect			Chronic Effect		
		ADD _{pot} ^a (mg/kg.day)	NOAEL LOAEL / LEL ^b (mg/kg.day)	MOE	ADD _{int} ^c (mg/kg.day)	NOAEL/ LOAEL / LEL ^d (mg/kg.day)	MOE
Chlorpyrifos			0.1	>100		0.03	>100
Mean	0.070	1.54E-03		64.80	1.54E-03		19.43
Maximum	0.454	1.00E-02		9.99	1.00E-02		3.00
Diclotophos			0.5	>1000		0.02	>1000
Mean	0.028	6.17E-04		809.99	6.17E-04		32.40
Maximum	0.244	5.38E-03		92.94	5.38E-03		3.72
Profenofos			11.2	>100		11.2	>100
Mean	0.034	7.50-04		14941.92	7.50-04		14941.92
Maximum	0.329	7.25E-03		1544.15	7.25E-03		1544.15

^aADD_{pot} = Potential average daily dose ADD = (C_s x IR x EF x ED)/(BW x AT), the air inhalation exposure algorithm, and estimation value from page 60 and not using absorption factor (AF) to calculate potential exposure (EPA, 1992). The ADD_{pot} was used to compare with NOAEL_{chlorpyrifos}/LOAEL_{diclotophos}/LEL_{profenofos} of acute effect.

^bNOAEL_{chlorpyrifos}/LOAEL_{diclotophos}/LEL_{profenofos} for acute inhalation effect are available from US. EPA.,1998 and EPA, 1999, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments.

^cADD_{int} = Internal or Absorbed dose, ADD = (C_s x IR x EF x ED x AF)/(BW x AT); the air inhalation algorithm and estimation value from page 60 (EPA, 1992). The ADD_{int} was used to compare with NOAEL/LOAEL/LEL of chronic effect.

^dNOAEL_{chlorpyrifos}/LOAEL_{diclotophos}/LEL_{profenofos} for chronic inhalation effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments.

Table 4.30 Average daily dose (ADD) of organophosphate pesticide residues due to air ingestion for vegetable growers in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Cs in air (mg/m ³)	Acute Effect			Chronic Effect		
		ADD _{pot} ^a (mg/kg.day)	NOAEL / LOAEL / LEL ^b (mg/kg.day)	MOE	ADD _{int} ^c (mg/kg.day)	NOAEL/ LOAEL / LEL ^d (mg/kg.day)	MOE
Chlorpyrifos			0.1	>100		0.03	>100
Mean	0.035	9.15E-04		109.31	9.15E-04		32.79
Maximum	0.110	5.15E-03		19.42	5.15E-03		5.82
Dicrotophos			0.5	>1000		0.02	>1000
Mean	0.024	6.27E-04		797.04	6.27E-04		31.88
Maximum	0.264	6.90E-03		72.46	6.90E-03		2.89
Profenofos			11.2	>100		11.2	>100
Mean	0.026	6.80E-04		16480.28	6.80E-04		16480.28
Maximum	0.491	1.28E-02		872.68	1.28E-02		872.68

^aADD_{pot} = Potential average daily dose ADD = (C_s x IR x EF x ED)/(BW x AT), the air inhalation exposure algorithm, and estimation value from page 60 and not using absorption factor (AF) to calculate potential exposure (EPA, 1992). The ADD_{pot} was used to compare with NOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ LEL_{profenofos} of acute effect.

^bNOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ LEL_{profenofos} for acute inhalation effect are available from US. EPA.,1998 and EPA, 1999, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments.

^cADD_{int} = Internal or Absorbed dose, ADD = (C_s x IR x EF x ED x AF)/(BW x AT); the air inhalation algorithm and estimation value from page 60 (EPA, 1992). The ADD_{int} was used to compare with NOAEL/ LOAEL /LEL of chronic effect.

^dNOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ LEL_{profenofos} for chronic inhalation effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments.

4.6.2 Dermal Exposure

4.6.2.1 Hand Contact Exposure

The average daily doses and MOEs of acute effect and chronic effect of OPPs due to hand contact for vegetable growers during the dry and wet season are illustrated in Table 4.31 and Table 4.32 respectively.

For acute effect both in the dry and the wet season, the result indicated that $\text{NOAEL}_{\text{chlorpyrifos}} / \text{LOAEL}_{\text{dicotophos}} / \text{NOEL}_{\text{profenofos}}$ compared to mean potential average daily dose (ADD_{pot}) of chlorpyrifos, dicotophos and profenofos were greater than 100, 1000 and 100 respectively. It indicated that the vegetable growers may not be risk from hand contact chlorpyrifos and dicotophos during working in their farms, in short period in both dry and wet season. However, the vegetable growers in the dry and wet seasons contained the MOEs of individual dicotophos was less than EPA's recommendation. In addition in the wet season MOEs of individual profenofos was less than EPA's recommendat values. It can be suggested that some of vegetable growers might be at higher risk from hand contact to dicotophos and profenofos residues during loading, mixing and spraying in short period.

For chronic effect due to hand contact OPPs residues, the internal average daily dose (ADD_{int}) of chlorpyrifos and profenofos for chronic effect should be multiplied by absorption factor before using to compare with NOAEL. The absorption factors for chlorpyrifos and profenofos are 0.03 and 0.5, respectively. (EPA, 1999). For dicotophos the ADDs to compare to LOAEL in chronic effect were the same ADDs values to compare to acute effect (EPA, 1998; EPA, 1999). This study found that the mean MOEs of dicotophos and profenofos was less than MOEs recommended values whereas the mean MOEs of chlorpyrifos was greater than MOEs recommended values. It means that the vegetable growers might be at risk from hand contact to dicotophos and profenofos in long period. Although the mean of chlorpyrifos above recommend value but the individual chlorpyrifos were lower than EPA's recommend value. In addition this result indicated that some individual vegetable growers might be at risk from hand contact to chlorpyrifos.

Table 4.31 Average daily dose (ADD) of organophosphate pesticide residues due to dermal (hand) contact for vegetable growers in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the dry season.

	Cs on hands (mg/two hands)	ADD _{pot} ^a (mg/kg.day)	Acute Effect		Chronic Effect		
			NOAEL/ LOAEL / NOEL ^b (mg/kg.day)	MOE	ADD _{int} ^c (mg/kg.day)	NOAEL/ LOAEL/ NOEL ^d (mg/kg.day)	MOE
Chlorpyrifos			5	>100		0.03	>100
Mean	0.070	1.07E-03		4642.86	3.23E-05		928.57
Maximum	0.491	7.55E-03		661.91	2.27E-04		132.38
95%CI							
Dicrotophos			0.5	>1000		0.04	>1000
Mean	0.061	1.41E-04*		3551.9	1.41E-04*		284.15
Maximum	0.306	7.06E-04*		708.06	7.06E-04*		56.64
Profenofos			1	>100		0.005	>100
Mean	0.024	3.69E-04		2708.33	1.85E-04		27.08
Maximum	0.143	2.20E-02		454.54	1.10E-03		4.54

^a ADD_{pot} (potential average daily dose) = (C_s x ET x EF x ED) / (BW x AT); the dermal exposure algorithm and estimated value from page 72 (EPA, 1992), the dermal exposure algorithm, not using absorption factor (ABS) to calculate (EPA, 1992).

^bNOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ NOEL_{profenofos} for acute dermal effect are available from US. EPA. 1998, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

^cADD_{int,(Chlorpyrifos, Profenofos)} (internal average daily dose) = (C_s × ABS × ET × EF × ED) / (BW × AT) the dermal exposure algorithm and estimated value from page 72 (EPA, 1992) ; absorption factor (ABS) of chlorpyrifos and profenofos equal to 0.03 and 0.5 respectively(US. EPA for equal to 0.The ADD_{int} was used to compare with MOE of chronic effect.

^dNOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ NOEL_{profenofos} for chronic dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

* The ADD_{pot, dicrotophos} using to compare to LOAEL of acute dermal effect and chronic effect (EPA, 1999).

Table 4.32 Average daily dose (ADD) of organophosphate pesticide residues due to dermal (hand) contact for vegetable growers in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Cs on hand (mg/m ³)	Acute Effect			Chronic Effect		
		ADD _{pot} ^a (mg/kg.day)	NOAEL/ LOAEL / NOEL ^b (mg/kg.day)	MOE	ADD _{int} ^c (mg/kg.day)	NOAEL/ LOAEL / NOEL ^d (mg/kg.day)	MOE
Chlorpyrifos			5	>100		0.03	>100
Mean	0.086	1.32E-03		3779.07	3.97E-05		755.81
Maximum	0.852	1.31E-02		381.45	3.93E-04		76.29
Dicrotophos			0.5	>1000		0.04	>1000
Mean	0.059	1.36E-04*		3672.32	1.36E-04*		293.78
Maximum	0.682	1.57E-03*		317.69	1.57E-03*		25.42
Profenofos			1	>100		0.005	>100
Mean	0.059	9.08E-04		1101.70	4.53E-04		11.01
Maximum	0.859	1.32E-02		75.67	6.60E-03		0.76

^a ADD_{pot} (potential average daily dose) = (C_s × ET × EF × ED) / (BW × AT); the dermal exposure algorithm and estimated value from page 72 (EPA, 1992)., the dermal exposure algorithm, not using absorption factor (ABS) to calculate (EPA, 1992).

^b NOAEL_{chlorpyrifos} / LOAEL_{dicrotophos} / NOEL_{profenofos} for acute dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

^c ADD_{int,(Chlorpyrifos, Profenofos)} (internal average daily dose) = (C_s × ABS × ET × EF × ED) / (BW × AT) the dermal exposure algorithm and estimated value from page 72 (EPA, 1992); absorption factor (ABS) of chlorpyrifos and profenofos equal to 0.03 and 0.5 respectively (US. EPA for equal to 0. The ADD_{int} was used to compare with MOE of chronic effect.

^d NOAEL_{chlorpyrifos} / LOAEL_{dicrotophos} / NOEL_{profenofos} for chronic dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

* The ADD_{pot, dicrotophos} using to compare to LOAEL of acute dermal effect and chronic effect (EPA, 1999).

4.6.2.2 Skin body contact exposure

The average daily doses and MOEs of acute effect and chronic effects of OPPs due to body contact for vegetable growers during the dry and wet seasons are illustrated in Table 4.33 and Table 4.34, respectively. Both in the dry and the wet seasons, the results indicated that NOAEL of acute effects compared to mean ADD_{pot} of chlorpyrifos and profenofos were greater than MOE recommend value (100) whereas the LOAEL of acute effect compared to mean ADDs of dicotophos was less than MOEs recommend values (1000). It indicated that the vegetable might be acute risk from body contact to only dicotophos during working in their farm. Addition, the vegetable growers in the dry and wet seasons contained the MOEs of individual dicotophos was less than EPA's recommendation. In the wet season MOEs of individual profenofos was also less than EPA's recommended values. It can be suggested that some of vegetable growers might be at higher risk from body contact to dicotophos and profenofos residues during loading, mixing and spraying in short period.

For chronic effect due to body contact OPPs residues, the ADD_{int} of chlorpyrifos and profenofos for chronic effect should be multiply by absorption factor before comparing it with NOAEL. The absorption factors for chlorpyrifos and profenofos are 0.03 and 0.5, respectively (EPA, 1999). For dicotophos the ADDs used to compare to LOAEL in chronic effect were the same ADDs values as the acute effect (EPA, 1999). From this study, we found that the mean MOEs of dicrophos and profenofos were less than MOEs recommended values whereas the mean MOEs of chlorpyrifos was greater than MOEs recommended values. It means that the vegetable growers might be at risk from body contact to dicotophos and profenofos in long period. Although the mean MOEs of chlorpyrifos above MOEs, the individual MOEs of chlorpyrifos were above EPA's recommend value. This result indicated that some individual vegetable growers might be at risk from dermal contact to chlorpyrifos.

Table 4.33 Average daily dose (ADD) of organophosphate pesticides residues due to dermal (body) contact for vegetable growers in Bang Rieng Sub-District, Thailand during the dry season.

	Cs of patch on body skin (mg/m ³)	Acute Effect			Chronic Effect		
		ADD _{pot} ^a (mg/kg.day)	NOAEL/LOAEL / NOEL ^b (mg/kg.day)	MOE	ADD _{int} ^c (mg/kg.day)	NOAEL/LOAEL / NOEL ^d (mg/kg.day)	MOE
Chlorpyrifos			5	>100		0.03	>100
Mean	0.012	6.73E-03		742.57	2.02E-04		149.00
Maximum	0.071	4.00E-02		125.00	1.20E-03		25.00
Diclotophos			0.5	>1000		0.04	>1000
Mean	0.097	1.62E-03*		308.64	1.62E-03*		24.70
Maximum	1.316	2.19E-02*		22.83	2.19E-02*		1.83
Profenofos			1	>100		0.005	>100
Mean	0.166	5.54E-03		180.50	2.77E-03		1.81
Maximum	1.060	3.52E-02		28.41	1.76E-02		0.003

^a ADD_{pot} (potential average daily dose) = (C_s x SA x TE x ET x EF x ED)/(BW x AT x UCF); the dermal exposure algorithm and estimated value from page 74 (EPA, 1992)., the dermal exposure algorithm, not using absorption factor (ABS) to calculate (EPA, 1992).

^b NOAEL_{chlorpyrifos}/ LOAEL_{diclotophos}/ NOEL_{profenofos} for acute dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

^c ADD_{int,(Chlorpyrifos, Profenofos)} (internal average daily dose) = (C_s x SA x ABS x TE x ET x EF x ED)/(BW x AT x UCF) the dermal exposure algorithm and estimated value from page 74 (EPA, 1992) ; absorption factor (ABS) of chlorpyrifos and profenofos equal to 0.03 and 0.5 respectively(US. EPA for equal to 0.The ADD_{int} was used to compare with MOE of chronic effect.

^d NOAEL_{chlorpyrifos}/ LOAEL_{diclotophos}/ NOEL_{profenofos} for chronic dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

* The ADD_{pot, diclotophos} using to compare to LOAEL of acute dermal effect and chronic effect (EPA, 1999).

Table 4.34 Average daily dose (ADD) of organophosphate pesticide residues due to dermal (body) contact for vegetable growers in Bang Rieng Sub-District, Khuan Nieng District, Thailand during the wet season.

	Cs (mg/m ³)	Acute Effect			Chronic Effect		
		ADD _{pot} ^a (mg/kg.day)	NOAEL/ LOAEL / NOEL ^b (mg/kg.day)	MOE	ADD _{int} ^c (mg/kg.day)	NOAEL/ LOAEL / NOEL ^d (mg/kg.day)	MOE
Chlorpyrifos			5	>100		0.03	>100
Mean	0.020	1.12E-02		445.10	3.37E-04		89.00
Maximum	0.081	4.50E-02		111.11	1.35E-03		22.00
Dicrotophos			0.5	>1000		0.04	>1000
Mean	0.102	1.41E-03*		354.61	1.41E-03*		354.61
Maximum	0.731	1.21E-02*		41.32	1.21E-02*		41.32
Profenofos			1	>100		0.005	>100
Mean	0.401	1.32E-02		310	6.68E-03		0.75
Maximum	5.42	2.22E-02		45	1.11E-02		0.45

^a ADD_{pot} (potential average daily dose) = (C_s x SA x TE x ET x EF x ED)/(BW x AT x UCF); the dermal exposure algorithm and estimated value from page 74 (EPA, 1992)., the dermal exposure algorithm, not using absorption factor (ABS) to calculate (EPA, 1992).

^b NOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ NOEL_{profenofos} for acute dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

^c ADD_{int,(Chlorpyrifos, Profenofos)} (internal average daily dose) = (C_s x SA x ABS x TE x ET x EF x ED)/(BW x AT x UCF) the dermal exposure algorithm and estimated value from page 74 (EPA, 1992) ; absorption factor (ABS) of chlorpyrifos and profenofos equal to 0.03 and 0.5 respectively(US. EPA for equal to 0.The ADD_{int} was used to compare with MOE of chronic effect.

^d NOAEL_{chlorpyrifos}/ LOAEL_{dicrotophos}/ NOEL_{profenofos} for chronic dermal effect are available from US. EPA. 2007, Office of Pesticide Program, Special Docket for Pesticide Reregistration Risk Assessments

* The ADD_{pot, dicrotophos} using to compare to LOAEL of acute dermal effect and chronic effect (EPA, 1999).

4.7 Non- Carcinogen Hazard Index Estimation

Both Margin of Exposure (MOE) and Hazard Quotient (HQ) method were used to estimate risk. The degree of risk of vegetable growers due to chronic effect from both methods are the same. The vegetable grower might be risk from inhale chlorpyrifos and dicotophos and dermal effect from contacting dicotophos and profenofos. This part the researcher will identify risk from all route exposure by using Hazard Index (HI).

Sum of the hazard quotient for all pesticides in each exposure pathway including water ingestion, air inhalation, water dermal contact, soil contact, hand contact and body contact for vegetable growers was presented as the population distribution in Table 4.35 and 4.36. The degree of risk from expose from each exposure pathway also presented. The highest risk is the body contact to pesticide, follow by air inhalation, hand contact, water ingestion, soil dermal contact and water dermal contact respectively. During the dry and the wet seasons, the risk estimation indicated that the non carcinogen hazards as average from total exposure HI of 129.78 and 103.61 exceeded 1. The vegetable growers might be got higher risk from pesticide for all exposure routes. Focus to each route of exposure for both wet and dry seasons. It found that the mean HI of hand dermal contact was 6.399 and 11.535 respectively which was above 1. In addition, the mean HI of body skin dermal contact was 88.096 and 62.357 respectively was above 1. Considering the individual risk, the total exposure HI at high-end level which above 90th percentile of the population distribution was much above the acceptable index in range of 353.047–486.48 in the dry season and 245.89 – 615.53 in the wet season, indicating a great potential for adverse non-carcinogen health impact to the vegetable growers.

In view of hazard index for each pesticide including chlorpyrifos, dicotophos and profenofos, during the dry season it was found that the first single greatest contributor to the high end HI for the individual resulted from dicotophos with HI 201.886 - 438.96. The second following contributor to high-end HI was profenofos with HI of 257.903-355.78. The last contributor to high end was chlorpyrifos contributor high HI of 15.70- 55.99. In addition during the wet season the first single greatest contributor to the high end HI for the individual result from dicotophos with HI 193.85 -599.83 The second following contributor to high-end HI was profenofos with HI of 156.057 -237.96. The last contributor to high end was chlorpyrifos contributor to high end 5.56-8.04. It can suggest that the dicotophos is the most dangerous pesticide, followed by profenofos and chlorpyrifos.

However, data on the distribution of non-carcinogenic hazards was not available for the reference group. It presented only for the average value of the total exposure HI in the dry and wet season was 0.004 and 0.015 respectively. These values were less than the acceptable level of 1. It can concluded that exposure through water ingestion, air inhalation, water dermal contact, soil contact hand contact and body contact did not appear to be a problem for the reference group.

Table 4.35 The distribution of hazard index for a given exposure pathway among the vegetable growers

	Mean	25th	50th	75th	90 th	Max	% above 90 th Percentile (n) ^a
Dry Season							
Water Ingestion	0.017	0.0027	0.009	0.0195	0.040	0.16	-
Air Inhalation	38.390	1.064	6.197	56.206	123.847	298.21	12%(4)
Water Contact	0.0003	0.0001	0.0003	0.0004	0.0006	0.0010	12%(4)
Soil Contact	0.013	0.002	0.005	0.0191	0.034	0.09	12%(4)
Hand Contact	6.399	1.7658	4.378	9.867	15.898	21.91	12%(4)
Skin body Contact	88.096	11.241	22.803	134.022	316.213	450.38	12%(4)
Total Exposure HI	129.779	27.261	73.082	239.986	353.047	486.48	12%(4)
Wet Season							
Water Ingestion	0.119	0.0049	0.0175	0.1668	0.4479	1.04	12%(4)
Air Inhalation	36.263	1.048	4.472	32.191	104.875	332.89	12%(4)
Water Contact	0.002	0.00005	0.0002	0.001	0.0007	0.01	12%(4)
Soil Contact	0.019	0.0017	0.0065	0.0166	0.0505	0.22	12%(4)
Hand Contact	11.535	1.350	3.693	11.794	31.099	131.71	12%(4)
Skin body Contact	62.3568	8.847	32.573	89.946	177.412	248.87	12%(4)
Total Exposure HI	103.613	16.107	32.308	133.132	245.8987	615.53	12%(4)

^a Individuals at the high end of the risk distribution; n=number of vegetable growers

Table 4.36 The distribution of aggregate hazard index for each OPPs among the vegetable farm

	Mean	25th	50 th	75th	90 th	Max	% above 90 th Percentile (n) ^a
Dry Season							
Dicrotophos	64.717	12.300	19.697	77.079	201.886	438.96	12%(4)
Chlorpyrifos	5.800	0.568	2.522	6.777	15.700	55.99	12%(4)
Profenofos	59.262	3.164	10.944	23.358	257.903	355.78	12%(4)
Total Exposure HI	129.779	27.261	73.082	239.986	353.047	486.48	12%(4)
Wet Season							
Dicrotophos	61.076	2.592	9.624	53.529	193.859	599.83	12%(3)
Chlorpyrifos	2.127	0.368	1.619	3.302	5.564	8.04	12%(3)
Profenofos	37.863	1.923	12.141	53.993	156.057	237.96	12%(3)
Total Exposure HI	103.613	16.107	32.308	133.132	245.898	615.53	12%(3)

^a Individuals at the high end of the risk distribution; n=number of vegetable growers

The contributions of each route to the total amount of pesticides dose of chronic effect were investigated. As expected, the result show an important difference in the ranking of routes by their contribution to the total dose in the figure 4.4. For three pesticides absorbed dose, the route that contributes the most is the dermal contact (sum of hand, body skin, water and soil dermal contact) about 65.23 %, follow by the inhalation 34.88% and the ingestion 0.03% in the dry season. In the wet season also show the same pattern the routes that contributes the most is the dermal contact (65.29%), follow by the inhalation 34.09 % and the ingestion 0.2%. Percentage contributions of three pesticides to the risk in each route are based on the sum of HQ or HI in each route as shown in figure 4.5. For three pesticides risk, the routes that contribute the most is dermal contact 70.78%, follow by inhalation 29.20% and ingestion 0.01 % in the dry season and dermal contact 67.01%, follow by inhalation 32.87 % and ingestion 0.11% in the wet season. The finding the dermal route put in the largest portion of dose and it is the most contribution to the risk, followed by inhalation routes.

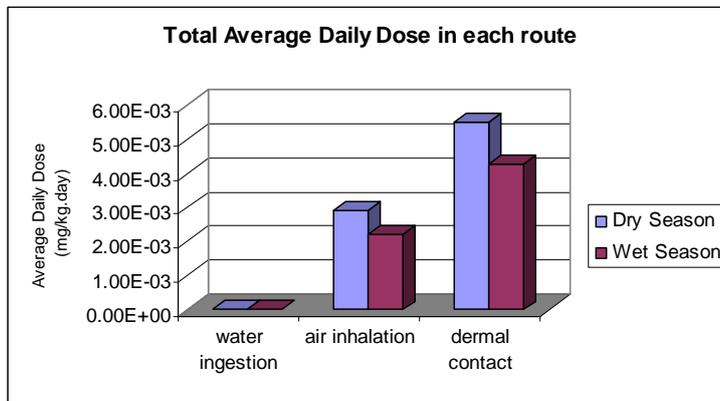


Figure 4.4 Contribution of each route to the absorbed dose by OPPs

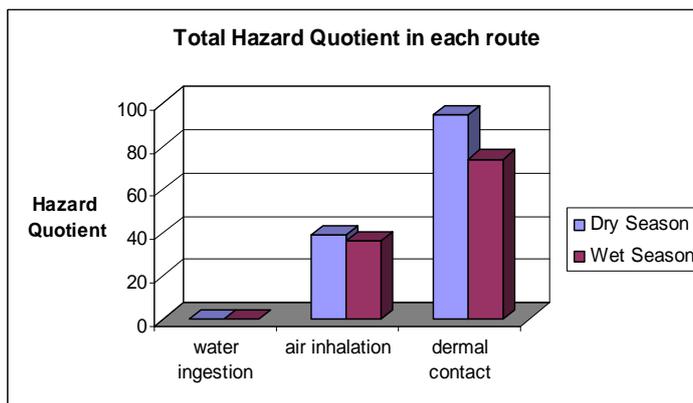


Figure 4.5 Contribution to the estimated risk of each route by OPPs

4.8 Comparison between Dialkyl Phosphate and Exposure dose

Spearman correlation coefficients were calculated to examine the relationship between of total exposure dose and dialkyl phosphate (DAP) in urine as shown in table 4.37. It is found significant correlation between exposure dose and dialkyl phosphate in the dry season. There were moderate significant correlated between expose dose (ADD) in air and dialkyl phosphate. In addition there were moderate significant correlated between sum of expose dose from all route exposure. It might be conclude that dialkylphosphate in urine came from OPPs in working air condition.

Table 4.37 Spearman rank correlation coefficient (r) between dialkyl phosphate and exposure dose in the dry season.

	Exposure Dose in air		Sum of Exposure Dose In all route	
	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>
DAP	0.003	0.525	0.002	0.554

4.9 Comparison between Pesticide Exposure Questionnaires to Average Daily Dose and Hazard Index

4.9.1 Comparison between Pesticide Exposure Questionnaire and Total Average Daily Dose

Table 4.38 illustrated relationship between the question from pesticide exposure questionnaire and average daily dose (ADD). The total average daily dose was sum of ADD from water ingestion, air inhalation, water dermal contact, hand contact and body skin contact. The questions that perform as quality data and the ADD were modified to nominal scale. The Cramer's (C) correlation was used to find relationship between these nominal scales of quality question and ADD. The range of C value 0- 0.25 indicate low correlate, 0.26-0.50 indicate medium correlate, 0.51-0.75 indicate moderately high correlate, and 0.76-1.0 indicate high correlate. The relation between questions that perform as quantity data and the ADD was using Spearman's correlation. The R is correlation value. The correlation value from -1 to +1, indicating perfect negative correlation at -1, absence of correlation at zero and perfect positive correlation at +1. From this questionnaire the main factor for pesticides exposed to vegetable growers depend on pesticide mixing, mixed pesticide by themselves, farm area, duration of vegetable farming, residence location, annual working day in farm and averaging time to applying pesticide for a month.

In addition the correlation between health effect score, pesticide exposure assessment score and ADDs were significantly were 0.626 and 0.648 respectively. The health effect score was depended on its severity and frequency of sign and symptom that vegetable growers affect from such as headache, muscle weakness. The pesticide exposure assessment score was calculate from degree of vegetable grower exposes to pesticide by giving high score to each serious exposure item in

questionnaire. From this study it can be conclude that the pesticide exposure questionnaire can be use as indirect method to estimate the pesticide exposure to vegetable growers at the beginning.

Table 4.38 Test of correlation between each question of pesticide exposure questionnaire and average daily doses (ADDs) from field collection

Question from pesticide exposure Questionnaire	Average Daily Dose (mg/kg.d)	
	R/C	<i>p-value</i>
1.Age	0.148	0.160
2.Education	0.223	0.449
3. Residence location	0.506	0.000
4.Farm area	0.529	0.001
5.Duration of vegetable farming	0.532	0.001
6.Mix or spray pesticides by yourself	0.661	0.000
7.Average time for applying pesticide for a month	0.426	0.001
8.Daily working hour in the vegetable farms	0.284	0.006
9.Annual working day in farm	0.476	0.001
10. Pesticide mixing (where, what method, how)	0.879	0.000
11.Equipment use for spraying pesticides	0.204	.081
12.Pesticide spill on your clothes (how quick to change cloth, how to wash cloth)	0.279	0.020
13. If your last pesticide application is ineffective, what will you do with the first pest control?	0.251	.049
14. Disposing the pesticides container.	0.231	0.040
15.Washing the pesticide equipment after used	0.242	.070
16. Repairing your own spraying or mixing equipment.	0.228	0.110
17. Where do you store the pesticides?	0.223	0.031
18. Where is the source of water used?	0.279	0.020
19. Normally, what kind of drinking water do you usually drink?	0.252	0.047
20. Where do you have lunch?	0.203	0.083
21. Do you smoke while working in the farm?	0.222	0.132
22. Do you drink while working in the farm?	0.185	0.143
23.Health Effect Score from pesticide Exposure	0.626	0.000
24.Pesticide Exposure Score	0.648	0.000

4.9.2 Comparison between Pesticide Exposure Questionnaire and Hazard Index

All of exposure variable from questionnaire were input in multiple regression model to examine the association with HI of vegetable growers.

Table 4.39 Linear regression model estimating the correlation of HI and exposure variable

Variable	Parameter Estimate	Standard Error	Standard Coefficient	P-value
Intercept	2.29	17.588		0.897
Pesticide Exposure Assessment Score	1.888	0.402	0.438	<0.001
Dicrotophos	131.501	52.809	0.233	0.015

Correlation of model; R= 0.531, R²= 0.282, adjust R²= 0.265; p-value =<0.0001

$$HI = 2.29 + 1.88 \text{ Pesticide Exposure Assessment Score} + 131.5 \text{ Dicrotophos}$$

This model indicated that the pesticide exposure assessment score and level of dicrotophos were significant associated with the increasing of hazard index in the vegetable growers. It can be said that the predictor of model involve the behavior of farmer with related to the pesticide exposure and chemical that was used in the farm. The regression model explains only 26.5 % of the variable of exposure.

4.10 Exposure Model for Study Pesticide Exposure for Vegetable Growers

In summary, it can be note that there are several factors essential to occupational pesticide exposure for vegetable growers at Bang Rieng (Figure 4.6). The personal background such as mixing pesticide by themselves, duration time for applying pesticide (year), frequency for applying pesticide (time/month), number of farm area (rai). In addition, the farmer behavior such as apply pesticide near home, use bare hand to mix pesticide, do not wear protective equipment, drink water from well located in field and disposing the pesticide container on the ground. Moreover the level of pesticide exposure assessment score and health effect score could be related to pesticide exposure (average daily dose). OPPs of concern were measured parent compound (chlorpyrifos, dicrotophos and profenofos) and their metabolites (dialkyl phosphate). The parent compounds were measured from direct exposure from personal media e.g. hand contact and body contact and environmental media from working air condition The parent compounds were also measured from indirect exposure from environmental media e.g. water, air and soil. The parent compounds were showed degree of exposure occur. Combination of biomonitoring, personal, environmental exposure measurements, and related exposure factors relative contributed the exposures as internal dose (average daily dose) through the different routes and exposure media. The potential exposure routes for farmer in this study consist of dermal exposure from direct body contact to pesticide, inhalation exposure from working air condition, direct hand contact to pesticide, ingestion exposure from drinking underground water, dermal soil contact and water dermal contact.

The model that we use to study in Bang Rieng as shown in figure 4.7. It is a good model to tell degree of risk in each exposure route and tell the OPP metabolites in farmer but it need high budget, human resources and consume time. From this study the research try to modified new model that more appropriate to use for study pesticide exposure to farmer. As the result from the study in the dry HI of water

ingestion, soil dermal contact and water dermal contact was only 0.017, 0.013 and 0.0003 respectively. Addition the result in the wet season HI of water ingestion, soil dermal contact and water dermal contact was only 0.119, 0.019 and 0.002 respectively. It was not showed the effect to vegetable growers. So it can be exclude water ingestion, soil dermal contact and water dermal contact from the model to study pesticide exposure to farmer as shown in Figure 4.7. For the model presented in figure 4.6 we need to screen exposure factor by using questionnaire. If you found there are no exposure factor. You do not need to find exposure dose in model of figure 4.7. If you found exposure factors, you can follow another step in this model to study.

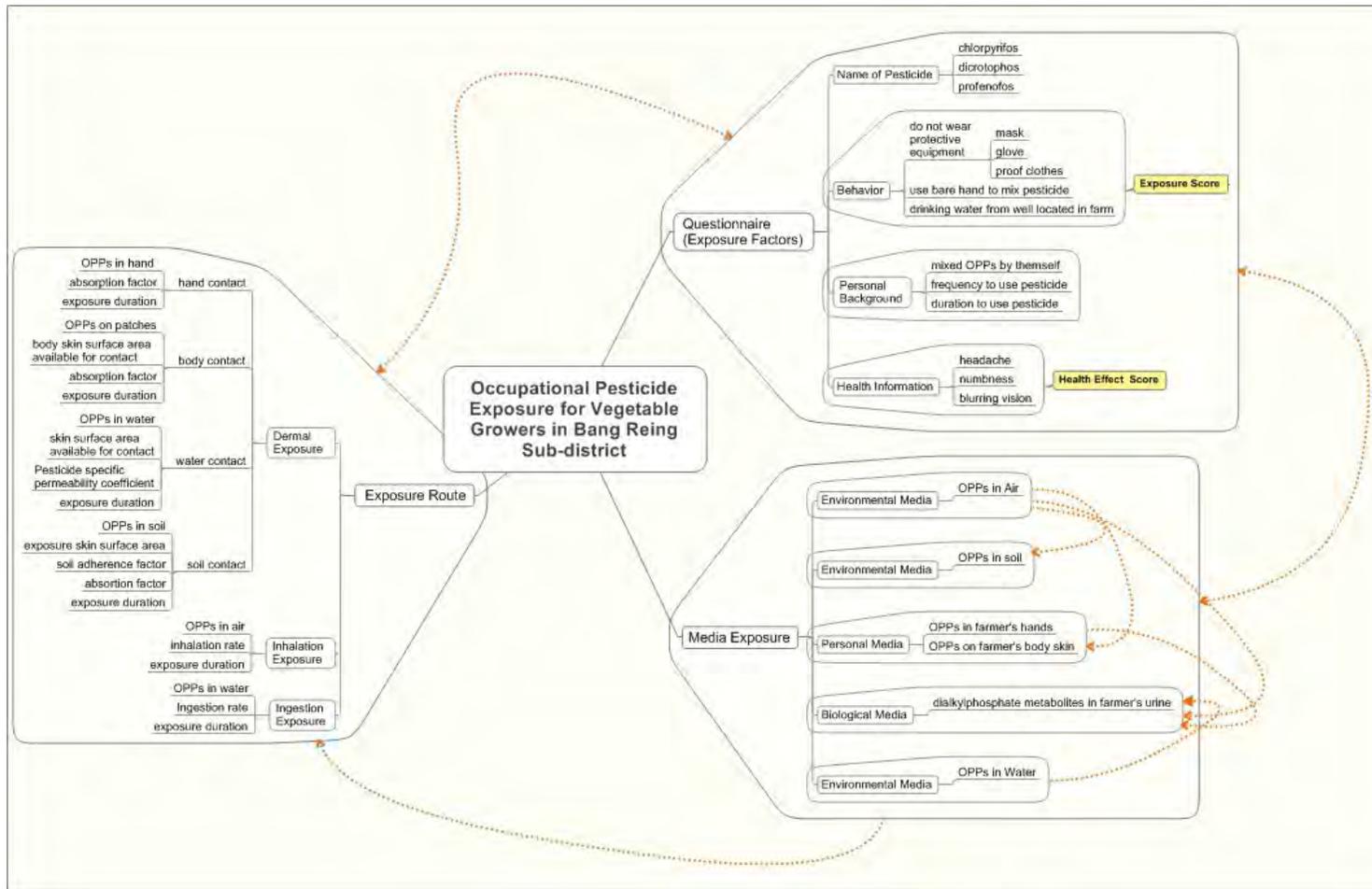


Figure 4.6 Occupation pesticide exposures to vegetable growers in Bang Rieng community.

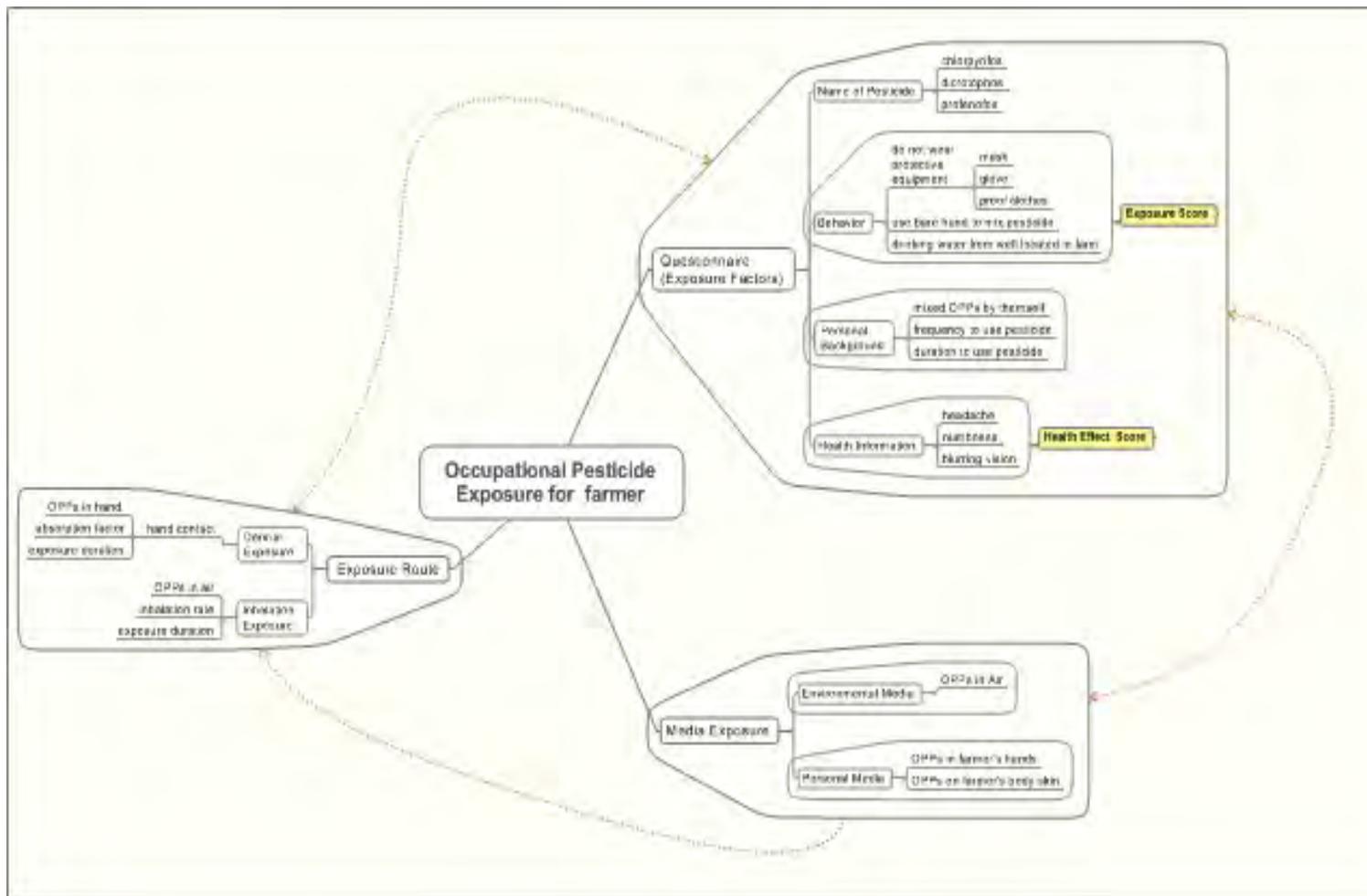


Figure 4.7 Optimal models for study pesticide exposure to vegetable grower

4.11 Uncertainty in the Dose Estimation

Risk assessment is a scientific tool to manage uncertainty. Uncertainty in risk assessment primarily arises from natural variability. Humans and the environment are constantly exposed to hazardous chemicals. Human reaction to varying degrees of hazard depends on the magnitude of exposure and the biological sensitivity of individual members to the hazardous dose. Variability of the natural world makes it difficult to determine the exact amount of hazardous dose an individual may be exposed to in a given time. It is essential to address uncertainty in the assessment. The following items summarize sources of uncertainty in the exposure and risk estimation in this study (Teshfamichael and Kaluarachchi, 2004)

This study used the field specific data to calculate dose for example; pesticide concentration in exposure media, water intake rate, spraying pesticide time, exposure duration and average body weight), but some factors were not available (e.g.). The use of surrogate data is common when field specific data are not available (US EPA 1992). Therefore, this study required the use of available measurements in combination with actual data and surrogate data (for professional judgment). This is one of sources of uncertainty because the data may not represent the exposure scenario being analyzed.

4.12 Risk Management

The result showed that the vegetable growers could have risk from non-cancer risk due to OPPs contaminants such as chlorpyrifos, dicofol and profenofos. The contaminants have been found on water ingestion, air inhalation, water dermal contact, hand contact and body skin contact. The appropriate risk management recommendation could be in helping vegetable growers to protect themselves.

4.12.1 Individual awareness

High risk in air inhalation was found. The vegetable growers should wear chemical proof masks to protect themselves from the improper usage of the toxic chemicals. Dermal contact via hand was another route of high exposure. The growers should wear gloves during mixing the chemicals and wash their hands properly after the usage. Moreover, they should protect themselves from body contact to the chemicals by using the appropriate cloth during spraying and mixing the pesticides.

4.12.2 Community Awareness

Eventhough water contaminated by pesticides was found in low level, it has to be concerned. The cause of contamination might be due to the improper disposal of the empty containers. Hence, these are hazardous waste therefore they should be proper collected. Dropping points and collection systems should be initiated in the area to collect the containers and return them to the manufacturers to further suitable management.

Time of pesticide spraying should be planned among the neighborhood. Different time of spraying might be lower the risk of exposure.

First aid training to the farmers should be set up. The farmers could immediately response to the scenario of pesticide intoxication.

4.12.3 Government Agencies Concern

Since dicrotophos is the high risk in inhalation and dermal routes and is a class IB highly toxicity, it should be banned in Thailand.

Continuous awareness and monitoring system, including recommendation of pesticides usage should be launched by the government to reduce pesticide utilization.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The investigation of occupational pesticide exposure of vegetable growers working in vegetable farm area at Bang Rieng Sub-district, Khuan Neing District, Songkhla Province can be concluded as following.

1. The considerable finding predicted that the major occupational exposure pathway for vegetable growers contain of air inhalation, hand contact, body contact, while the minor of occupational pathway of vegetable growers consist of soil dermal contact, water ingestion and bathing water contact.

2. The vegetable growers as occupational group should be concerned about acute effect of inhalation pathway from non-carcinogenic hazard of OPPs because the margin of exposure (MOEs) values of OPPs were less than the EPA's recommend values.

3. The hazard indices (HI) of chronic effect of air inhalation, hand contact and body contact were greater than 1. The vegetable growers might be at risk from breathing contaminated air and contacting OPPs pesticide residues during loading, mixing and spraying pesticides.

4. The vegetable growers should be concerned about non-carcinogen hazard of total exposure of OPPs with the total exposure hazard index above the acceptable index (HI) of 129.7 above the acceptable index of unity. Considering the individual risk, the total exposure HI at high-end level range from 245.8-615.5, indicating a great potential for adverse on non-carcinogenic health impact to vegetable growers.

5. Based on dose estimation of OPPs due to ingestion, inhalation and dermal contact route of vegetable growers was higher than reference group. The vegetable growers have been exposed to OPPs greater than reference group.

6. Based on dose estimation from attribution of DAP metabolites related to parent OPPs pesticide supporting the vegetable grower have potential hazard from OPPs exposure through all routes higher than reference group.

7. The correlation between question of pesticide exposures and average daily doses was relative moderately. So this questionnaire can be use as indirect method to estimate the pesticide exposure to vegetable growers at the beginning.

8. The reference groups have less OPPs exposure for all routes exposure comparing with vegetable growers. The total hazard index was less than 1 indicting the reference group might not be harm form water ingestion, air inhalation, water dermal contact, soil dermal contact , hand contact and body contact to OPPs.

5.2 Contribution of This Work

This research showed the evidence of occupational exposure of farmers working in vegetable farm area. Although there were several researches studied about farmer exposed to pesticide in developed country but most of them had been not studied all pesticide and all route together. This study will provide information or guidance to investigate the pesticide exposure of all routes exposure among farmer in different agriculture settings in Thailand. Some of specific parameter relevant farmer

based on the values of Thai farmers such as body weight, pesticide spraying time, water intake rate, bathing time. This information are representing for Thai farmer database to use in risk estimation. The risk information obtained from this study can be further useful for risk management and risk communication performing in Bang Rieng agricultural community, and also provides baseline information served for initial making of local and national government decision relevant to farmer health risk. The researcher also took some accountability to do risk communication by reporting individual health risk to each vegetable grower and give a guidance to protect themselves from pesticide exposure (Appendix E). In addition the researcher gave some opinion to manage risk for Bang Rieng agricultural communities in the previous chapter.

5.3 Recommendations for Future Work

1. According to vegetable growers in Bang Rieng agricultural area face risk from OPPs exposure at high level. The risk communication process should be introduced to this area for making vegetable growers awareness of using pesticides. Continuous awareness and monitoring system, including recommendation of pesticides usage should be launched by the government to reduce pesticide utilization.

2. This study was focused on the organophosphate pesticides. The farmers used other types of pesticide in their farm especially the herbicides and pyrethroid. Further research should be conducted to study exposure assessment of these pesticides.

3. This study focused on most of volunteer male. Exposure assessment should be concerned about female because the different in their structure, hormone and behavior give interested result.

4. This study focused on farmer spraying pesticide to plant setting below head. So the exposure assessment for spraying pesticide setting above head should be concerned because head area and chest area is the important part of body.

5. Determination of urinary OPPs metabolite in general population would be needed because these data could be used of reference data to compare with exposed farmer.

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APPENDICES

APPENDIX A

Pesticides Exposure Questionnaire

Description

This questionnaire is combined with open and close questions and consisted with 4 parts as following:

Part 1: General Information; to ask about general and personal background of the farmers.

Part 2: Health Information; to assess farmer's health problems, which may be causes from exposure with organophosphate pesticide, including some related signs and symptoms.

Part 3: Pesticide Exposure Assessment; it contains with 26 items for assess farmer's behaviors and their activities related with pesticide exposure. Each item consists with ranking score for evaluation of each behavior's content.

Questionnaire Manual

Part 3 is the major part, which used to assess the pesticide exposure. In each item of this part, there are the ranking score that determined for assessing the behavior which related to the pesticide exposure (the score in each item is shown at the end of answer choice).

The maximum score in this part is 92 points while the minimum is 22 points. The scores from the calculation can be assessed the exposure level by comparing with the following criteria. The researcher assigned and calculated the pesticide exposure score into 5 levels by categorizing the scores in the following standard

Level	Exposure Score (point)	Description
1	22 – 36	Low Exposure
2	37 – 50	Moderately Low Exposure
3	51 – 64	Medium Exposure
4	65 – 78	Moderately High Exposure
5	79 – 92	High Exposure

Officer

Part 2 Health Information

1. Have you ever had blood examination for pesticides residues test?

1. Yes, Result is _____ 2. No

2. During 1 month, do you have any sign or symptom?

Score (0) (1) (2) (3) (4) (5)

Advers effect	None	Mild but occasional	Mild but frequent	Moderate but occasional	Moderate but frequent	Severe
1. Headache, Vomiting						
2. Abdomen cramp, Vomiting						
3. Muscle seizure						
4. Muscle weakness, Numbness						
5. Blurring vision, Tearing						
6. Chess pain, Difficult breathing						
7. Loss consciousness						

Officer

. Do you know, what the causes of that sign and symptoms are?

1. Yes 2. No

. If you experience those symptoms, do you know the names of such pesticides?

Part 3 Pesticides Exposure Assessment

Where do you apply pesticides?

- 1. Near the home (5)
- 2. Near the drinking water sources (4)
- 3. In the farm and near the water well (3)
- 4. Near the farm which use only for growing (2)
- 5. In the farm but far from the water source (1)

What is the method that you select for apply pesticide?

- 1. Mix less than the instruction (1)
- 2. Follow the instruction (2)
- 3. Mix more than the instruction (3)
- 4. Follow the neighborhood's suggest (4)
- 5. Mix with the individual decision (Mix more than one type of pesticide) (5)

How do you mix the pesticides?

- 1. By wearing rubber gloves and using stirring stick (1)
- 2. By wearing fabric gloves and using stirring stick (2)
- 3. By using hand and stirring stick (3)
- 4. By hand only (4)

9. If your last pesticides application is ineffective, what will you do with the first pest control?

- () 1. Change the new one (2)
 () 2. Mix higher dose pesticides (3)
 () 3. Mix more than one type of pesticides (4)
 () 4. Spray again in the same concentration (2)
 () 5. Liberate (1)
 () 6. Other _____

10. After applying pesticides, when do you usually change into clean clothes?

- () 1. Immediately (1)
 () 2. At lunch (2)
 () 3. At the end of that working day (3)
 () 4. At the end of the next working day (4)
 () 5. Later in the week (5)

11. In your household, how do you wash your clothes, you wore during applying pesticide?

- () 1. Wash separated from family's clothes (1)
 () 2. Rinse separately then wash with family's clothes (2)
 () 3. Wash with family's clothes (3)

12. After mixing or applying pesticides, where do you usually wash up or shower?

- () 1. Bathroom at home (2)
 () 2. Outside shower or well (1)

13. What is the method in disposing the pesticides container?

- () 1. Dispose on the ground (5)
 () 2. Collect for the individual landfill (4)
 () 3. Dispose in the hole (1)
 () 4. Dispose to the natural water source (6)
 () 5. Dispose with the sanitary waste (2)
 () 6. Burn (3)

14. How often do you washing the pesticide equipment after using?

- () 1. Not at all (1)
 () 2. Occasionally wash (2)
 () 3. Frequently (3)

15. What is the method for washing the pesticide equipment?

- () 1. Clean nozzle only (1)
 () 2. Rinse tank (2)
 () 3. Hose down sprayer with water (3)

16. Do you usually repair your own spraying or mixing equipment?

- () 1. Yes (3)
 () 2. Occasionally (2)
 () 3. No (1)

APPENDIX B

OPTIMAL CONDITION OF ORGANOPHOSPHATE MEASUREMENT AND OPTIMAL CONDITION OF DIALKYL PHOSPHATE MEASUREMENT

B-1 Instrumental Condition

Instrument: Hewlett – Packard gas chromatography (HP6890) with flame photometric detector (FPD)

Column: column: Zebron 1701 fused silica capillary column (30 m x 0.32 mm I.D. x 0.25 μm film thickness) coated with 14% cyanopropyl phenyl and 86% dimethyl polysiloxane.

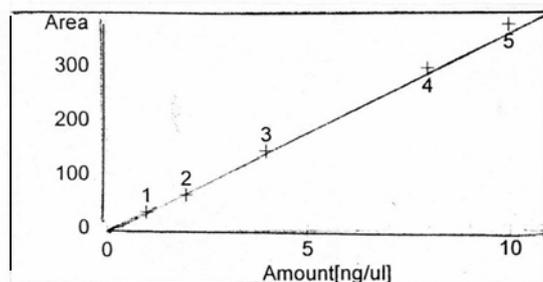
Oven: The initial oven temperature was set at 80°C for 2 min and then increased at a rate of 15°C/min until it reached 180°C, where it remained for 2 min. The temperature was then increased at a rate of 6°C/min. until it reached 260°C, where it remained for 2 min using this temperature program.

Injection temperature: 250 °C

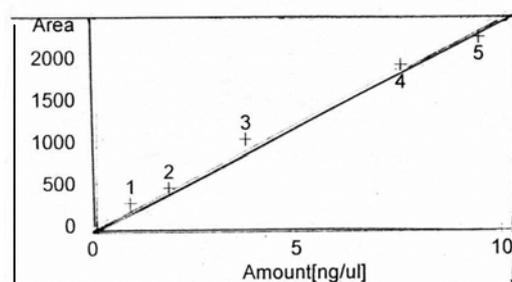
Inject volume: 2 μL

Detector: FPD temperature 250 °C

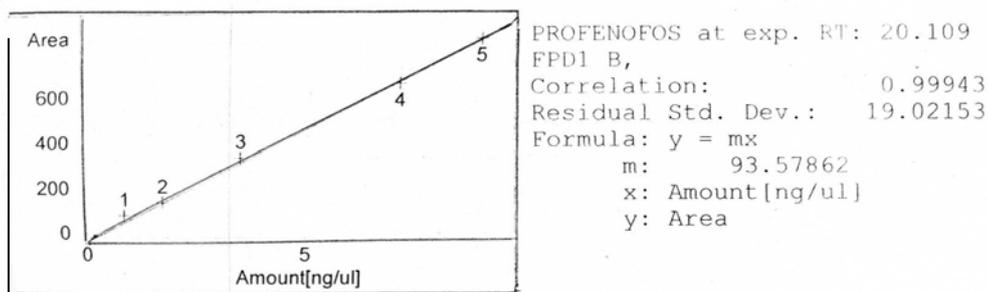
B-2 Calibration Curve for Target Organophosphate Pesticide



DICROTOFOS at exp. RT: 13.864
FPD1 B,
Correlation: 0.99910
Residual Std. Dev.: 10.47528
Formula: $y = mx$
m: 36.51284
x: Amount [ng/ul]
y: Area



CHLOPYRIFOS at exp. RT: 16.917
FPD1 B,
Correlation: 0.99903
Residual Std. Dev.: 69.17519
Formula: $y = mx$
m: 244.92863
x: Amount [ng/ul]
y: Area



B-3 Instrument Condition

Instrument: Hewlett – Packard gas chromatography (HP6890) with flame photometric detector (FPD)

Column: Capillary column, HP5 (30m × 0.32 mm id × 0.25 μm film thickness)

Oven: Initial temp: 80 °C Maximum temp: 210 °C

Initial time: 2.0min Equilibration time 3.0 min

Ramps:

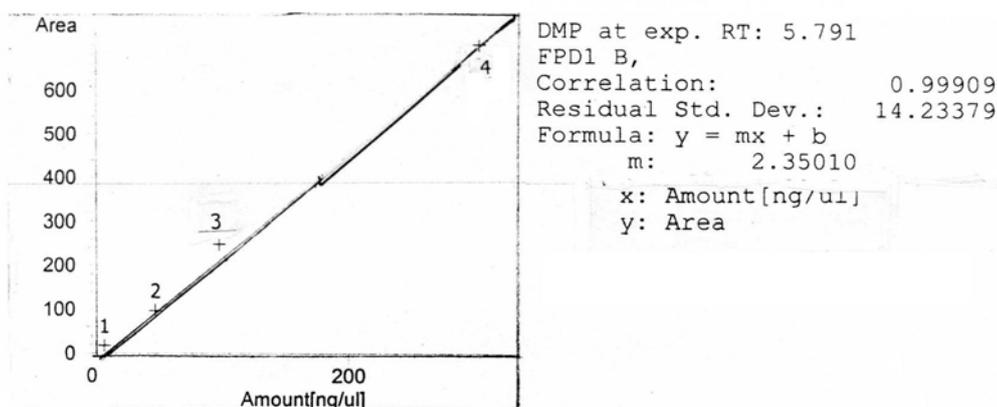
#	Rate	Final temp	Final time
1.	17.0	210.0	1.0
2.	0.0 (Off)		

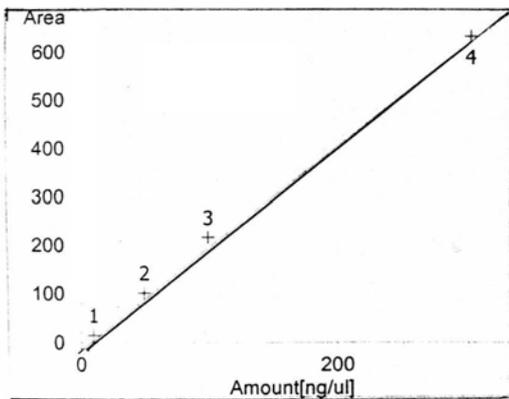
Inlet: 250 °C

Inject volume: 2 μL

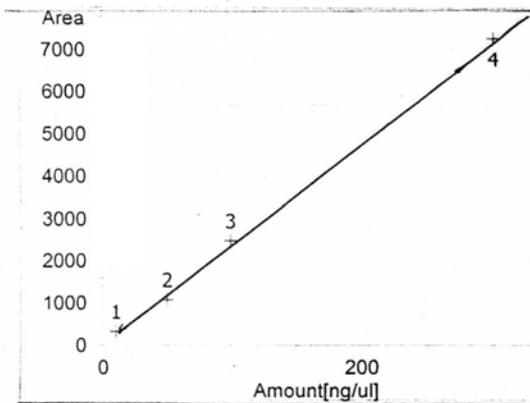
Detector: FPD temperature 250 °C

B-4 Calibration Curve for DAP metabolite

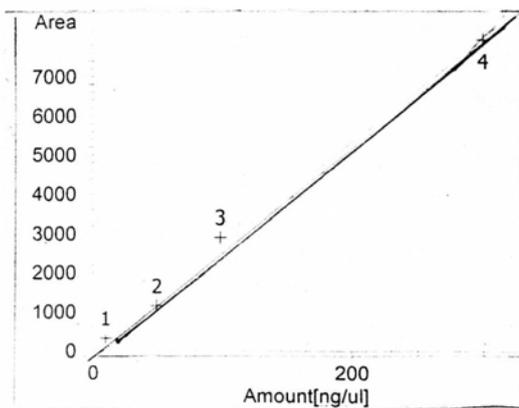




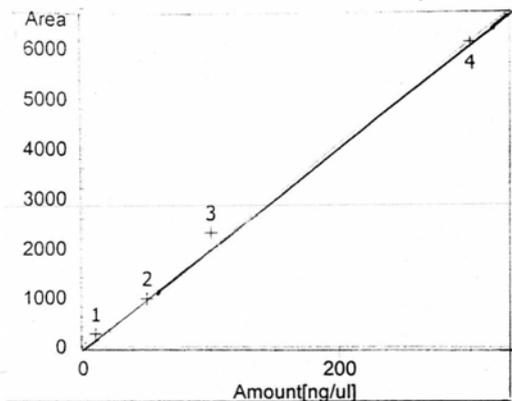
DEP at exp. RT: 6.423
 FPD1 B,
 Correlation: 0.99985
 Residual Std. Dev.: 5.24632
 Formula: $y = mx + b$
 m: 2.11527
 x: Amount[ng/ul]
 y: Area



DMTP at exp. RT: 6.914
 FPD1 B,
 Correlation: 0.99960
 Residual Std. Dev.: 97.40199
 Formula: $y = mx + b$
 m: 24.31448
 x: Amount[ng/ul]
 y: Area



DETP at exp. RT: 7.605
 FPD1 B,
 Correlation: 0.99881
 Residual Std. Dev.: 181.45020
 Formula: $y = mx + b$
 m: 26.23645
 b: 29.26677
 x: Amount[ng/ul]
 y: Area



DEDTP at exp. RT: 8.132
FPD1 B,
Correlation: 0.99898
Residual Std. Dev.: 131.63083
Formula: $y = mx + b$
m: 20.49901
x: Amount[ng/ul]
y: Area

APPENDIX C

FIGURES OF FIELD STUDIES AND SAMPLE ANALYSIS



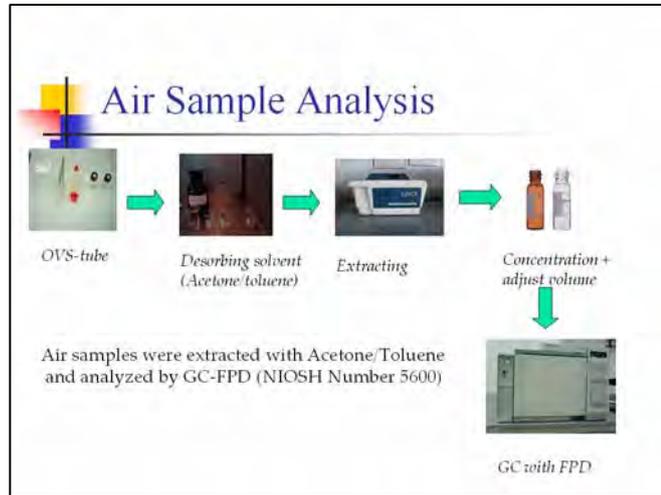
(a) Bang Rieng Vegetable Farm Area



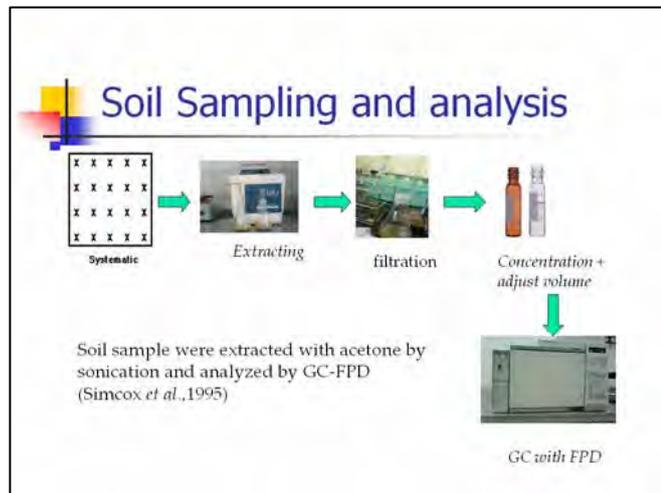
(b) Pesticide Mixing



(c) Pesticide Spraying



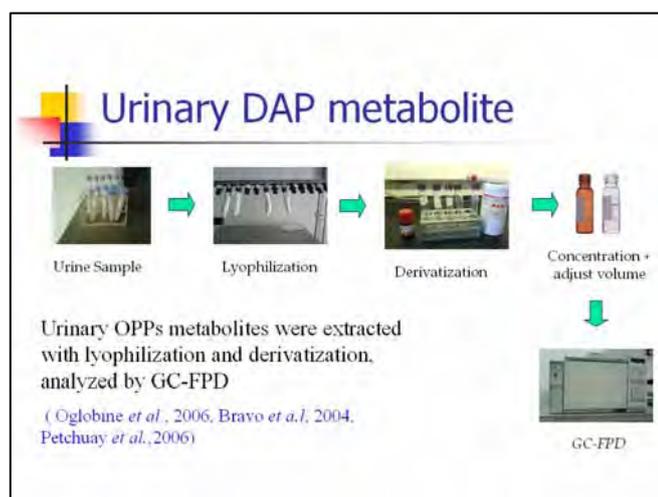
(d) Air Sample Analysis



(e) Soil Sample Analysis



(f) Hand Wipe Sample Analysis



(g) Urine DAP metabolite Analysis

APPENDIX D QUANLITY CONTROL

Table 1-C The limit of detection and recoveries of 3 OPPs in different matrix

Organophosphate Pesticides	LOD (µg/ml)	LOQ (µg/ml)	% Matrices Spike Recovery				
			Water	air	soil	hand	Body skin
Chlorpyrifos	0.01	0.03	77.25	102.79	88.26	89.95	91.54
Dicrotophos	0.10	0.30	90.15	101.82	99.16	99.84	81.10
Profenofos	0.03	0.13	101.25	100.08	86.46	94.19	105.19

APPENDIX E
GUIDANCE TO PROECT FARMERS
FROM PESTICIDE EXPOSURE

คำแนะนำในการใช้สารกำจัดศัตรูพืช กลุ่มออร์กาโนฟอสเฟต
และการป้องกันตนเอง

สารกำจัดศัตรูพืช

สารกลุ่มออร์กาโนฟอสเฟต เป็นสารกำจัดแมลงที่มีฟอสฟอรัส เป็นองค์ประกอบสำคัญ มีพิษค่อนข้างสูง สลายตัวเร็ว มีฤทธิ์ยับยั้งการทำงานของเอนไซม์โคลิเนสเตอเรสแบบถาวร ได้แก่ ไดโครโตฟอส คลอร์ไพริฟอส โพรพิโนฟอส มาลาไทออน

อันตราย

ผู้ป่วยจะมีอาการ คลื่นไส้ วิงเวียน ปวดศีรษะ อ่อนเพลีย กล้ามเนื้อหดตัวเป็นหย่อมๆ แขนงหน้าอก ท้องเดิน ตาพร่า กระตุก เหงื่อ และน้ำตาไหล น้ำลายฟูมปาก อูจจาระ ปัสสาวะราด ชัก หายใจลำบาก อาจหมดสติได้ การเต้นของหัวใจผิดปกติ

การเข้าสู่ร่างกาย

- ทางผิวหนัง
สัมผัสขณะผสม ฉีดพ่น สั่งอุปกรณ์ และละอองสารสัมผัสผิวหนัง
- ทางการหายใจ
ขณะผสมสาร และฉีดพ่นกำจัดศัตรูพืช
- ทางปาก
การกินอาหาร และดื่มน้ำที่ปนเปื้อนสารกำจัดศัตรูพืช



การเลือกใช้สารและเลือกซื้อสาร

- เลือกใช้สารที่ถูกต้องกับชนิดของศัตรูพืช ในปริมาณที่พอดีในแต่ละครั้ง
- ภาชนะที่บรรจุต้องไม่แตกหรือรั่ว มีฝาปิดมิดชิด มีฉลากถูกต้องชัดเจน ประกอบด้วยชื่อเคมี ชื่อสามัญของสารออกฤทธิ์ ประโยชน์ วิธีการใช้ การเก็บรักษา คำเตือนคำอธิบายการเกิดพิษ การแก้พิษเบื้องต้น และคำแนะนำสำหรับแพทย์

การขนส่งและการเก็บรักษา

- แยกการขนส่งสารกำจัดศัตรูพืช จากสิ่งของ อื่นๆ โดยเฉพาะอาหาร
- ควรเก็บสารไว้ในโรงเก็บที่แยกจากที่พักโดยไม่ปะปนกับสิ่งของอื่นๆหรืออาหาร ปลอดภัยห่างไกลจากเด็ก

ข้อปฏิบัติในการใช้สาร

- ก่อนใช้อ่านฉลากโดยตลอดให้เข้าใจ อย่างละเอียดถูกต้อง และปฏิบัติตามคำแนะนำ
- ตรวจสอบ เครื่องพ่นสาร คุรออยรั่วซึม หากพบให้ทำการซ่อมแซม
- สวมใส่ชุดป้องกันสาร ได้แก่ เสื้อแขนยาว กางเกงขายาว รองเท้าบูทยาง ถุงมือยาง แวนตา และหน้ากากให้มิดชิด เพื่อหลีกเลี่ยงสารถูกผิวหนัง ตา หรือหายใจเข้าไป
- ขณะฉีดพ่น ควรอยู่เหนือลมเสมอ
- ระวังไม่ให้ละอองสาร ปลิวเข้าหาตัวคน และบ้านเรือนผู้ที่อาศัยอยู่ข้างเคียง

การทำลายภาชนะบรรจุสารกำจัดศัตรูพืช

- ห้ามนำภาชนะที่ใส่สารกำจัดศัตรูพืชมาใช้โดยเด็ดขาด

- เลือกสถานที่ที่จะชุดหลุมฝังภาชนะบรรจุสารที่ใช้หมดแล้วให้ห่างจากแหล่งน้ำ และที่พักอาศัยอย่างน้อย 50 เมตร และชุดหลุมลึกอย่างน้อย 1 เมตร ใช้ปูนขาวรองก้นหลุม



BIOGRAPHY

Ms. Somsiri Jaipieam was born in Suratthani on November 5, 1964. She received Bachelor Degree in Chemistry from the faculty of Science, Kasetsart University and Master of Environmental Risk Assessment for Tropical Ecosystem from Faculty of Science, Chiang Mai University. She continued her study in the International Postgraduate Program in Environmental management for Doctor of Philosophy in Environmental Management at the Graduate School, Chulalongkorn University in 2004 and completed the program in 2008. .