CHAPTER 1

INTRODUCTION

1.1 Statement and significance of problem

Synthetic pyrethroids are produced to mimic the effective action of natural pyrethrins in exhibiting effect on insects. In the view of their character, synthetic pyrethroids are more chemically and biochemically stable than natural pyrethrins. Moreover, synthetic pyrethroids are mostly solids, low water solubility and neurotoxic to target insects. The neurotoxic effect is determined by a prolonged opening of the sodium channel which evokes a repetitive nerve action associated with hyperactivity, tremor, ataxia, convulsions and possible paralysis (Dyck et al. 1984; Soderlund et al., 1989). In addition, some pyrethroids' metabolites are capable to interact with the human estrogen receptor (Parvez et al., 2006).

Pyrethroids were manufactured in the 1970's after the removal of organochlorine, organophosphorus and carbamate insecticides from the markets. Synthetic pyrethroid insecticides are widely used in agriculture and public health to control diseases transmitted by vectors or intermediate hosts. Formulations that are commercially available include aerosols, dips, emulsifiable concentrates, wettable powders, granules, and concentrates for ultra low volume applications targeting mosquitoes. The commercially synthetic pyrethroids that have been commonly used include permethrin, cypermethrin, fenvalerate and deltamethrin (Heudorf et al., 2006).

Thailand is a leader in food producer and the world's largest exporter of agricultural and foodproduces which worth more than 199.24 billion dollar in 2010 (Office of Agricultural Economics., 2011). The amount of imported pesticides rose from 60,541 tons in 2001 to 117,698 tons in 2010. This amount represented herbicides (80,278 tons or 68%), followed by insecticides (23,417 tons or 20%), while other pesticides comprised only 12% of the total use (Department of Agriculture, 2011a). Thus, herbicides and insecticide were the major market share comprising over 80% of all imported pesticides.

The usage of synthetic pyrethroids in Thailand have been increased and widely used in agriculture, public health and households. The Department of Agriculture reported synthetic pyrethroid active ingradients imported of 148.4 tons (estimated 6.11 million dollar) in 1996 and dramatically increased to 844.9 tons (estimated 12.49 million dollar) in 2010. This data indicated that synthetic pyrethroids' residues in agricultural produces might be one of the exposure pathways among Thai population.

The detection of synthetic pyrethroid residues can be done by chromatographic techniques such as gas chromatography with electron capture detection (GC-ECD) and gas chromatography with mass spectrometry (GC-MS). In 2006, Department of Agriculture detected cypermethrin residues in exported vegetables (9.1% of kale and collard) and fruits (4.7% of longan and lychee) at the levels of exceeding Thailand maximum residue limits (MRLs. The MRLs of cypermethrin is 1 mg/kg in kale and collard and 0.5 mg/kg in longan and lychee. Hence, monitoring of pyrethroid insecticides' residues will be essential in protecting of health risk among consumers.

Meanwhile, biological monitoring which determines individual internal exposure of pyrethriod in urine sample has several advantages against the analysis in plasma (Leng et al., 1997). Urinary pyrethroid metabolites can be detected by gas chromatography with electron capture detection (GC-ECD) (Aprea et al., 1997) and gas chromatography with mass spectrometry (GC-MS) (Fortin et al., 2008; Leng et al., 1996; Chensheng et al., 2006; Marsha et al., 2007). Aprea et al. (2000) reported that children had higher possibility in exposure to pesticide than adults. Dietary exposure to pesticide residues is also potentially higher for children. Chensheng et al., (2006) reported that 8 - 11 years old experienced higher pyrethroid exposures than 3 - 7 years old children.

This study was divided into 3 sections as following.

Section 1: Developing a method for detecting synthetic pyrethroid insecticides in vegetables and fruits using GC-ECD.

Section 2: Developing a method for detecting a common synthetic pyrethroid insecticides metabolite in urine using GC-ECD.

Section 3: Assessing the exposure of synthetic pyrethroid insecticides among school children.

1.2 Objectives

1.2.1 The main objective of this study was to develop two analytical rapid methods, one for detecting synthetic pyrethroids' residues in vegetables and fruits and the other one for detecting a common metabolite of synthetic pyrethroids in human urine. Then, two developed methods were applied in assessment of exposure to synthetic pyrethroids among school children in an agricultural community in Fang district, Chiang Mai province.

1.2.2 Specific objectives were divided into 3 sections as following.

(1) To develop a method for detecting synthetic pyrethroid residues in vegetables and fruits using GC-ECD.

(2) To develop a method for detecting a common metabolite of synthetic pyrethroids in human urine using GC-ECD.

(3) To assess the exposure of synthetic pyrethroid insecticides among school children in an agricultural community.

1.3 Definitions

1.3.1 Exposure assessment is to identify the exposures that quantified in the residue in food (vegetable and fruit) and exposure internal dose in urine.

1.3.2 Synthetic pyrethroid insecticides include two types: Type I pyrethroids are non- α -cyano group: permethrin and Type II pyrethroids are containing α -cyano group: lambda-cyhalothrin, cypermethrin, cyfluthrin, fenvalerate, and deltamethrin.

1.3.3 A common synthetic pyrethroid metabolite is 3-phenoxybenzoic acid (3-PBA)

1.3.4 School children are children studied in grade 5 to 6 in four subdistricts of Fang district, Chiang Mai province.

1.4 Conceptual frame works

1.4.1 Section 1

Development of an extraction of synthetic pyrethroid insecticide residues in vegetables and fruits. Consists of a solvent used to extract samples. Compare the effectiveness of the clean up the extract for eliminating the interference in the sample and to validate the method for the detection of residues. As shown in Figure 1.1.

To develop a method for detecting synthetic pyrethroid residues in vegetables and fruits

- Selection of the solvent extraction

- To compare the effectiveness of extraction/clean up procedure for

eliminating interference in the sample

- To validate the method for determining
- Solvent for extraction were selected for optimization
 - The effectiveness of extraction clean up procedure
- A new, simple, and sensitive method for quantitative
 - determination synthetic pyrethroid residues in vegetable and fruit

Figure 1.1 Conceptual framework of section 1: Development of a method for detecting synthetic pyrethroid residues in vegetables and fruits 1.4.2 Section 2

To Develop a method of synthetic pyrethroid metabolite in the urine extract. For the development consists of a solvent used to extract samples. Compare the effectiveness of the clean up the extract for eliminating the interference in the sample and validate methods for detection of synthetic pyrethroid metabolite in urine samples, as shown in Figure 1.2.

> To develop a method for detecting synthetic pyrethroid metabolite in urine

- Selection of the solvent extraction
- The effectiveness of extraction clean up procedure
 - To validate the method for determining
- Solvent for extraction were selected for optimization
- The effectiveness of extraction clean up procedure
- A simple, and sensitive method for quantitative determination
 - synthetic pyrethroid metabolite in urine

Figure 1.2 Conceptual framework of section 2:

Development of a method for detecting a common metabolite of synthetic pyrethroids

in human urine

1.4.3 Section 3

Assessment of exposure to synthetic pyrethroid insecticides in children in agricultural communities, Fang district, Chiang Mai. Exposure assessment will be monitored in the environment and in humans. As shown in Figure 1.3.



Figure 1.3 Conceptual framework of section 3:

Assessment of an exposure to synthetic pyrethroid insecticides among school children

in an agricultural community