Residues of synthetic pyrethroid pesticides in vegetables, fruit, sediment and water from an intensive agricultural area (Fang district, Chiang Mai, Thailand)

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Abstract

This study was conducted in four intensive agricultural areas of the Fang district, Chiang Mai, northern Thailand. The objective of this study was to determine synthetic pyrethroid residues in vegetable, fruit, sediment, and surface water samples. Fruit and vegetables were purchased from local markets in the study areas. The vegetables in this study included cabbage, kale, water spinach, cauliflower, Chinese cabbage, Chinese mustard, yard long bean, cucumber, and sugar pea, while the fresh fruit included tangerine, guava, apple, dragon fruit, mango, sand pear, rose apple, lychee and grape. Sediment and surface water samples were collected from main streams of the four studied areas. The pyrethroid residues in vegetables, fruit, and sediment samples were extracted with dichloromethane in an ultrasonic bath and cleaned up on a graphite carbon cartridge. Liquid – liquid extraction technique was used to prepare pyrethroid compounds from surface water samples. The extracted samples were determined by using gas chromatography – electron capture detection (GC-ECD). Six synthetic pyrethriod pesticides in this study consist of lambda cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, and deltamethrin.

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Cypermethrin was found to be the highest detection percentage in surface water, vegetables, and fruit samples at 33.3, 75.8 and 95.3%, respectively. Meanwhile, permethrin was the highest detection percentage in sediment samples at 66%. However, lambda cyhalothrin was detected in sediment and surface water samples with the highest levels at 0.38 and 1.61 mg/kg, respectively. Deltamethrin was detected in vegetable samples with the highest level at 9.97 mg/kg and cypermethrin was detected in fruit samples with the highest level at 11.83 mg/kg. Furthermore, this study is an application of the developed method providing a high sensitivity with the limit of detection (LoD) of permethrin at 0.11 mg/kg, cyfluthrin at 0.11 mg/kg, fenvalerate at 0.22 mg/kg, lambda cyhalothrin at 0.26 mg/kg, cypermethrin at 0.51 mg/kg and deltamethrin at 0.65 mg/kg.
Keywords: synthetic pyrethroid pesticides, intensive agricultural area, northern Thailand.

1 Introduction

The tendency of pesticide usage has been increasing worldwide due to the expansion of pesticide-based mono-cropping agriculture either for food or for energy. After the 1990s the usage of highly toxic and persistent pesticides were reduced by the implementation of regulations. Most of organochlorine pesticides have been banned because of their high persistence in the environment, bio-accumulation through the food chain, and risk in causing harmful effects on wildlife and humans.

Synthetic pyrethroid pesticides are the most frequently used in agricultural application, residential areas and commercial facilities [1]. There is a new group of pesticides which has similar chemical formula to pyrethrum [2]. It has greater photostability, enhanced insecticidal activity, and relatively low toxicity when compared to organochlorine and organophosphate pesticides. Synthetic pyrethroid pesticides are non-systemic as they cannot penetrate into the plant. The extraction of these pesticides is rather simple compared to the systemic organophosphate and carbamate pesticides because they form a deposit on the surface of the leaf after treatment. In Thailand, a great amount of pesticides have been imported and the active chemical ingredient has continued to increase from 60,541 tons in 2001 to 117,698 tons in 2010. The use of synthetic pyrethroid pesticides is approximately 5–7% of the total amount of pesticides used in Thailand [3]. They are widely used in growing fruit and vegetables and these chemicals are accumulated in the environment such as water streams and soil sediments [4, 5]. This paper focused on synthetic pyrethroid residues in fruit, vegetables, sediment, and surface water of the Fang district, an intensive agricultural area of the Chiang Mai province, northern Thailand.

2 Experiments

2.1 Study area

This study was conducted in an intensive agricultural community in the Fang district, Chiang Mai province, northern Thailand (19° 47′ 00.86″ N latitude and

99° 03′ 14.64″ S longitude). The study areas for sediment and surface water sampling were located in Mon Pin subdistrict (20° 06′ 22.93″ N 99° 05′ 02.08″ S), Mae Kha subdistrict (19° 47′ 16.02″ N 99° 14′ 32.42″ S), Mae Ngon subdistrict (19° 46′34.87″ N 99° 05′ 51.70″ S), and Wiang subdistrict (19° 50′ 44.79″ N 99° 20′ 18.68″ S).

2.2 Experimental

2.2.1 Reagent and calibration

Standard reagents for calibration in this study consist of lambda cyhalothrin, bifenthrin (as an internal standard), permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin, with a different range of purity from 92.5 to 99.5% (Dr. Ehrenstorfer, Augsburg, Germany). Methylene chloride and ethyl acetate were both organic residue analysis graded from J.T. beaker (Philipsburg, NJ, USA) and used for extraction and solvation. Anhydrous sodium sulfate was obtained from Merck (Germany). Standard stock solution was prepared in ethyl acetate and stored at -20°C. Intermediate and working standard solutions of a mixture of synthetic pyrethroid pesticides and internal standard solution was prepared in ethyl acetate. The standard solutions were prepared at 5, 10, 20, 100, 150, 200, 250 and 300 ng/mL.

2.2.2 Instrumental analysis

The samples were analyzed by Gas Chromatography with Electron Capture Detector (GC-ECD, HP6890 series, USA). The separation was accomplished by capillary column, HP-5 (5% phenylmethylpolysiloxane phase with 30 m × 0.25 mm, 0.25 μm film thickness). Injection was operated in the splitless mode. The injection port and detector temperature were set at 250°C and 300°C, respectively. The HP-5 column temperature was chronologically adjusted as follows: the initial sample temperature of 100°C was increased at the rate of 15°C/min to 250°C and the sample was detained for 1 min at 250°C. After that, the sample was heated up from 250°C to 280°C at the rate of 5°C/min and held for 3 min at the final temperature. Helium (99.994% purity) at flow rate of 1.5 mL/min was used as the gas carrier. GC-ECD make-up gas for ECD was OFN (99.999% purity) flow rate at 14.7.mL/min.

2.3 Sampling

2.3.1 Vegetable and fruit samples

Fruit and vegetables were purchased from local markets in four sub districts of the studied areas. The vegetables in this study included cabbage, kale, water spinach, cauliflower, Chinese cabbage, Chinese mustard, yard long bean, cucumber, and sugar pea, while the fresh fruit included tangerine, guava, apple, dragon fruit, mango, sand pear, lychee, rose apple and grape. The sample weight was at least one kilogram for small and medium sized fresh produce and two kilograms for large size fresh produce [6]. In addition, the samples of pears, oranges and apples were purchased for ten each. One kilogram

of the collected vegetables and fruit were quartered and half of them were randomly selected (approximately 500 grams) to homogenize by blender (IKA ULTRA-TURRAX T25 digital, Germany). Then, 50 grams aliquot of blended sample was kept and reserved in a plastic container at a temperature of -20°C prior to analysis.

2.3.2 Sediment and surface water samples

Sediment and surface water samples were collected at ten different sites within the main streams of four sub districts during August–September 2009. Sediments which collected from depositional zone were wrapped with foil and placed in zip lock plastic bags. Sediments were air dried at room temperature, ground and graded through a metal sieve (35 mesh). Large-volume of surface water samples were collected by Kemmerer water sample at 20 centimetres deep and kept in pre-cleaned PETE plastic bottles.

2.4 Sample treatment and extraction

2.4.1 Vegetable, fruit, and sediment extraction and clean-up

Five grams of sample was loaded into 50 mL Teflon centrifuge tube and extracted with 10 mL dichloromethane (DCM) for 30 seconds with a vortex mixer. The mixture was further extracted in an ultrasonicate bath for 5 min and re-extracted with 10 ml DCM with vortex for 30 seconds. The whole samples were filtrated through a glass funnel with Whatman No.1 filter paper and passed onto 50 mL centrifuge tube. The extract was transferred onto the 250 mg graphite carbon clean up column and eluted with 8 ml DCM, drop by drop, in a 15 mL graduated test tube. Extracts were evaporated to dry off by rotary evaporation at 37°C under reducing pressure. The final volume of concentrated extract was 1 mL with ethyl acetate and determined by gas chromatography with electron capture detection [7–11].

2.4.2 Surface water extraction

Each of the water samples was loaded into a separating funnel for 50 mL then 30 grams of sodium chloride was added and shaken with 50 mL dichloromethane/ethyl acetate (1:1, v/v). The solvent extraction procedure was repeated twice. The extracted solution was filtered with sodium sulphate and evaporated under vacuum rotary evaporation at 37°C until about 2 mL and dried-off using a stream of nitrogen gas. The final volume of the solution was adjusted to 1 mL with ethyl acetate prior to gas chromatography with electron capture detection [5, 12, 13].

3 Results and discussion

This monitoring study was conducted in vegetables, fruit, surface water and sediment of four sites in the agricultural area of the Fang district where synthetic pyrethroid pesticides were vastly applied throughout the year and really need at least a reference here.

3.1 Synthetic pyrethroid residues in vegetables and fruit

Table 1 shows the common name, scientific name, and synthetic pyrethroid residues which have been found in the vegetable and fruit samples analyzed. The vegetable residue samples showed the pesticide ranging between 30.8 to 100% of samples analyzed while the fruit samples were detected 100%. In most of the vegetable samples one or more residues were detected at 100%, except cucumber, Chinese cabbage, and cabbage which found 30.8, 88.9, and 92.3% respectively.

Table 1: Name of sample and incidence of pyrethroid residues in vegetables and fruit.

Common name	Scientific name	No. of samples	% samples with one or more residues
Vegetable N=66			
Cabbage	*Brassica oleracea* L. var. *capitata*	13	92.3
Kale	*Brassica oleracea* L.var.*acephala* DC.	8	100
Water spinach	*Impomoea aquatica* Forsk.	2	100
Cauliflower	*Brassica oleracea* L.var.*botrytis* L.	3	100
Chinese cabbage	*Brassica rapa* L. subsp. *pekinensis* (Lour.) Olsson.	9	88.9
Chinese mustard	*Brassica.camprestris* L. ssp. *Chinensis* (Lour.) Ruprecht.	5	100
Yard long bean	*Vigna unguiculata* var. *sesquipedalis* (*Vigna sinensis* var. *sesquipedalis* L. Verdc.)	10	100
Cucumber	*Cucumis sativus* L.	13	30.8
Sugar pea	*Pisum sativum* var.*macrocarpon* Ser.	3	100
Fruit N=55			
Tangerine	*Citrus reticulate*	10	100
Guava	*Psidium guajava*	2	100
Apple	*Malus domestica*	7	100
Dragon fruit	*Hylocereu undatuss*	5	100
Mango	*Mangifere india* Linn.	5	100
Sand pear	*Pyrus pyrifolia*	3	100
Grape	*Vitis venefera*	2	100
Lychee	*Litchi chinensis* Sonn.	5	100
Rose apple	*Syzygium samarangense (Blume)* Merr.&L.M.Perry	3	100

The mean level of pyrethroid pesticides in vegetable and fruit samples is presented in table 2. Cypermethrin has the highest positive sample at 50 samples of vegetable and 43 samples of fruit. The result also shows the highest mean value of cypermethrin in fruit at 0.854 mg/kg., while deltamethrin shows the highest mean value in vegetables at 0.874 mg/kg. In addition, the mean value of others pesticides in vegetables are 0.374 mg/kg of lambda cyhalothrin, 0.219 mg/kg of fenvalerate, 0.111 mg/kg of cyfluthrin and 0.065 mg/kg of permethrin. The following mean value of pesticide in fruit samples from cypermethrin are deltamehrin (0.420 mg/kg), fenvalerate (0.323mg/kg), lambda cyhalothrin (0.156mg/kg), cyfluthrin (0.129mg/kg), and permethrin (0.115 mg/kg).

Table 2: Mean levels of six synthetic pyrethroid residues in vegetable and fruit samples in Fang district (mg/kg fresh weight).

Pesticide	Vegetable (n=66)		Fruit (n=43)	
	Mean value (mg/kg)	No. of positive samples	Mean value (mg/kg)	No. of positive samples
lambda cyhalothrin	0.374	25	0.156	20
permethrin	0.065	32	0.115	31
cyfluthrin	0.111	47	0.129	34
cypermethrin	0.530	50	0.854	43
fenvalerate	0.219	38	0.323	33
Deltamethrin	0.874	41	0.420	25

According to the Thai Agricultural Commodity and Food Standard (2006), the maximum residue levels (MRLs) of pesticide were varies by commodities as shown in table 3. The mean values of pesticide in most samples were generally exceeding the MRLs, except cypermethrin in cabbage, fenvalerate in mango and deltamethrin in yard long bean. The highest percentage was found in cypermethrin of sugar pea while deltamethrin of yard long bean showed the lowest percentage. Furthermore, the percentage of sample above MRLs of different international standard has been presented in table 4. Samples with permethrin were not detected when compared to the Codex MRLs. Percentage of the samples above MRLs of Codex and Thailand have similar trend in all pesticides with range from 4.6 to 19.3%. In addition, the European standards which have a lower concentration limit show a higher percentage of sample exceed the MRLs in the range of 22 to 55%.

Table 3: The MRLs of pesticide in commodities and number of samples above MRLs.

Pesticide	Commodities	Mean value (mg/kg)	MRLs[a] (mg/kg)	Percentage of samples above MRLs
Lambda cyhalothrin	Cabbage	0.327	0.2	23.1
	Cauliflower	0.273	0.2	66.7
Cypermethrin	Cabbage	0.087	0.1	30.8
	Yard long bean	0.810	0.05	80.0
	Sugar pea	0.751	0.05	100.0
	Chinese cabbage	1.962	1	40.0
Fenvalerate	Mango	0.408	1	20.0
Deltamethrin	Cabbage	0.838	0.2	76.9
	Kale	1.770	0.5	62.5
	Yard long bean	0.192	0.2	10.0
	Cauliflower	0.478	0.1	33.3
	Chinese mustard	1.962	0.5	33.3

[a]Thai Agricultural Commodity and Food Standard (2006).

3.2 Synthetic pyrethroid pesticides in sediment and surface water

More detail about pesticide detected in sediment and surface water was presented in table 5. Synthetic pyrethroids were found in both sediment surface water samples. The overall frequency of occurrence in sediment of all sites are 66.7% in permethrin, 64.1% in cypermethrin, 51.3% in fenvalerate, 25.6% in cyfluthrin, 23.1% in lambda cyhalothrin and 12.8% in deltamethrin. There were no detections in sediment of lambda cyhalothrin in Mae Ngon and Mon Pin sites, and deltamethrin in Wieng site. The overall frequency of occurrence in surface water of all sites are 33.3% in cypermethrin, 30.8% in fenvalerate, 28.2% in permethrin 12.8% in cyfluthrin lambda, 5.1% in lambda cyhalothrin and 2.6% in deltamethrin. There were no detections in surface water of lambda cyhalothrin, and deltamethrin in the Mae Kha, Mon Pin, and Wieng sites.

4 Conclusion

From this study, synthetic pyrethroid residues were found in vegetables, fruit sediment and surface water samples. The data performed showed 32.1% of all samples exceeded the maximum residue limits which indicate that synthetic pyrethroid pesticides were contaminated to sediment and surface water from their wide usage in agriculture. In addition, the standards of permethrin and

Table 4: Compare the percentage of sample above Codex, Thailand, and the European standard.

Pesticide	Codex MRLs[a] (mg/kg)	Percentage of sample above MRLs	Thai MRLs[b] (mg/kg)	Percentage of sample above MRLs	EU MRLs[c] (mg/kg)	Percentage of sample above MRLs
Lambda cyhalothrin	0.05-0.5	4.6	0.2-0.5	4.6	0.02-1	26.6
Permethrin	0.5-5	ND	No	No	0.02-0.05	22.0
Cyfluthrin	0.1-2	0.9	No	No	0.02-0.5	55.0
Cypermethrin	0.2-2	7.3	0.05-2	15.6	0.02-2	44.0
Fenvalerate	0.2-2	0.9	0.1-10	0.9	0.02-0.05	50.5
Deltamethrin	0.02-2	19.3	0.05-0.5	18.3	0.02-0.5	48.6

[a]Codex alimentarius; **Pesticide Residues** in Food. Maximum Residue Limits (MRLs)
[b]Thai Agricultural Commodity and Food Standard (2006).
[c]The European Commission, Council Directive "76/895/EEC" Pesticides MRLs Selected fruit and vegetables.

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Table 5: Mean concentration (mg/kg) and percentage of pesticide residues in sediments and surface water.

Pesticide	Sediment (N=39)		Surface water (N=39)	
	Mean value (mg/kg)	N (%)	Mean value (mg/kg)	N (%)
lambda cyhalothrin	0.058	9 (23.1)	0.813	2 (5.1)
permethrin	0.055	26 (66.7)	0.388	11 (28.2)
cyfluthrin	0.015	10 (25.6)	0.196	5 (12.8)
cypermethrin	0.042	25 (64.1)	0.296	13 (33.3)
fenvalerate	0.028	20 (51.3)	0.291	12 (30.8)
deltamethrin	0.066	5 (12.8)	0.029	1 (2.6)

cyfluthrin in Thailand have not been provided for the control of contamination in fruit and vegetable. Contaminations can affect human health in the case of high accumulation and economic race such as agriculture produce's price and exporting barrier. Furthermore, the Thailand government should be restricted in the usage of synthetic pyrethroid pesticides.

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