VOL. 10, NO. 15, AUGUST 2015 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

COMPARISON OF PESTICIDE RESIDUE LEVELS IN THE SURFACE WATER OF BERTAM RIVER IN CAMERON HIGHLANDS, PAHANG

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ABSTRACT

The presence of pesticide residues in the surface water of Bertam River located amidst the agricultural areas of Cameron Highlands in Pahang, Malaysia was monitored from May to October in 2014. The sampling sites were located at 10 sampling points along the Bertam River in the agricultural areas. The method of extraction of the insecticides (organophosphate/pyrethroid) from the water samples consist of solid phase extraction followed by gas chromatography (with electron capture detector, ECD). As expected, insecticides, namely cypermethrin and chlorpyrifos were found in the surface water of Bertam River. High level concentrations of insecticides in the surface water were observed during the period from May to October 2014, a period which included both seasons (wet and dry seasons). The highest concentration of 2.66 µg/ml and 1.23µg/ml for cypermethrin was observed during the wet and dry seasons respectively. This could be due to the frequent usage of the above-mentioned insecticides coupled with contamination that could have originated from the application sites. Meanwhile, the lowest concentration detected in the surface water was for chlorpyrifos (0.11µg/ml and 0.17µg/ml) during the dry and wet seasons, respectively.

Keywords: pesticide, insecticide, modification, gas chromatography, environmental analysis.

INTRODUCTION

Cameron Highlands is one of the most important agricultural areas in Malaysia with an estimated 2, 140 hectares of vegetable farms. Farmers in Cameron Highlands supply more than half the vegetable needs of Malaysia in addition to that, this industry also generate significant foreign income where between RM 56 to RM100 million was made from vegetables and RM 20 million was earned from flower production in 1996. However, there are concerns over the long-term environmental impacts on the production of vegetables in general and especially in the highlands. The focus of concern is not only seen in soil erosion (Ali *et al*., 2014a), which can be clearly seen in the vegetable production areas in Cameron Highlands (sedimentation, loss of soil structure and nutrients) but also in the indiscriminate and uncontrolled use of many pesticides thus leading to health hazards, pesticide residues, resistant insects and soil contamination (Khalid *et al*., 2015) (Rahman *et al*., 2014).

In Malaysia, many studies have been done to show the concentration of pesticide residues in the environment, hence, there are now several studies being conducted on pesticides in environmental conservation, agro-ecosystems which include water (Yang and Su, 2013), (Hela *et al*, 2009), (Ali *et al*., 2014b), soil (Andrew *et al*. 2003), (Barcela *et al*, 1991) and air (Barrionuevo and Lanasas, 2002), (Bonwick *et al*, 2005). However, reports and studies of insecticidal pyrethroid and organophosphate that were widely used are limited in Malaysia. The purpose of the study was to investigate the seasonal variation and distribution of pesticides in the surface water of the Bertam River agricultural areas in Cameron Highlands, Pahang for a period of 6 months (from May to October 2014). The choice of pesticides studied was based on those frequently used by the farmers in the area.

MATERIALS AND METHODS

Study area

Cameron Highlands which is situated in the state of Pahang has an estimated area of 712km^2. Cameron Highlands share its borders with the states of Kelantan and Perak, in the north and west, respectively (see Figure-1). The economic activities of the highlands are largely driven by agriculture and tourism. Cameron Highlands is one of the significant agricultural areas producing not only for the domestic market but also for exportation. The average temperature recorded at Cameron Highlands is about 17.9°C while, the mean minimum temperature is about 15.3°C.

Sampling procedure

Sampling

Ten sampling sites for surface water were selected along the Bertam River. Selected sampling sites were divided into ten sampling points along the Bertam

River (Figure-1). All sampling sites are located in the intensive vegetable cultivation areas (Table-1).

Seasonal field samplings were carried out during both the dry season (May-July) and wet season (August-October) throughout the 6 month period (2014). Three replicates of 1-L volumes of water were collected in glass bottles from each sampling site. In situ measurements (pH, temperature, dissolved oxygen, salinity and conductivity) were taken prior to storing the samples in 1 L amber glass bottles. The containers were pre-rinsed with the river water sample before being filled just to overflowing. Samples reached the laboratory 1 day after sampling, stored at 48˚C prior to extraction, normally within 48 h.

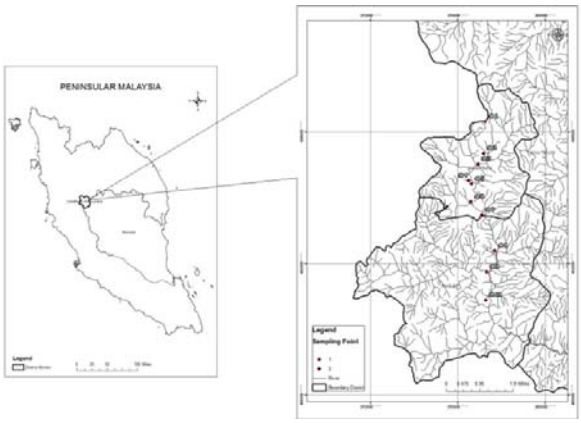

Figure-1. Map of Cameron Highlands showing the location of sampling stations.

Table-1. Description of Bertam River sampling locations in Cameron Highlands.

Station	Longitude	Latitude
1	N04°30'17.0"	E101°23'14.7"
2	N04°29'30.1"	E101°23'12.5"
3	N04°29'14.4"	E101°23'4.3"
4	N04°28'49.9"	E101°22'50.2"
5	N04°28'44.7"	E101°22'54.5"
6	N04°28'18.0"	E101°22'54.0"
7	N04°27'58.4"	E101°23'10.1"
8	N04°27'5.4"	E101°23'29.1"
9	N04°26'34.40"	E101°23'17.20"
10	N04°25'52.70"	E101°23'16.40"

Sample extractions and analysis

Solid Phase Extraction (SPE) and chromatographic techniques were applied to quantify pesticides. The collected samples were pre-filtered on 0.45-mm HVLP filters (Millipore Bedford, MA, USA) to eliminate particulate matters. Prior to the extraction, the C bonded phase (J.T. Baker) and poly (styrene-divinylbenzene) disks of 47 mm diameter and 0.5 mm thickness containing 500 mg of the bonded phase were washed with 10 ml of acetone under vacuum followed by 3 ml of acetonitrile and 3 ml of distilled water. The disks were not allowed to dry, as recommended (Casas *et al*, 2006), (Esteve-Turrillas *et al*, 2004). The samples were mixed well and allowed to percolate through the disks at a flow-rate of 1.5 ml/min under vacuum. SPE tubes were immersed in the water samples and the pump is turned on. During inhalation, the water samples are drawn into the C_{18} cartridge. Water flow through the SPE cartridge was controlled using the pressure knob so that the pressure drop of water samples extracted was drop by drop. After extraction, the pesticide residues trapped in the disk cartridge were collected using 6 ml of acetone as eluting solvent. The fraction was evaporated to 1 ml by vacuum before being injected into the GC-ECD. Three replicates were carried out for each sample and with each replication, 1 µL was injected twice (Halimah *et al*, 2003).

Rainfall data

The monthly rainfall data of Cameron Highlands within the period of May - October 2014 was obtained from the Malaysian Meteorological Department as presented in Figure-2. A scale of between 50-400 mm of rainfall was recorded during the dry season (May to July 2014) at the time of sampling. While, 200-400 mm of total rainfall was recorded during the wet season (August to October 2014). The total number of wet days for both seasons were 66 (dry season) and 74 (wet season), respectively.

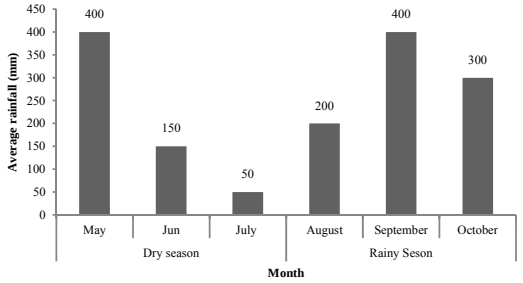

Figure-2. Monthly rainfall data of Cameron Highlands within the period of May - October 2014.

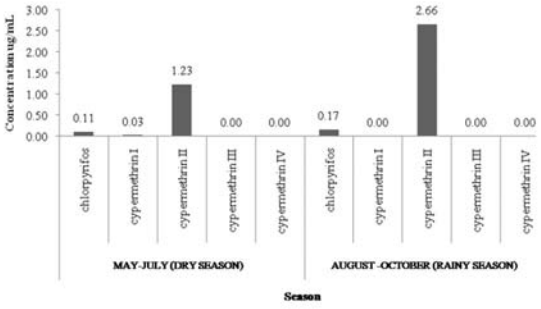

Figure-3. Seasonal variation of insecticides in surface water detected at sampling sites, from May-July 2014 (Dry Season) and August–October2014 (Wet Season).

Analysis

Statistical analysis of the present data were interpreted using single factor analysis of variance (one way - ANOVA, $p<0.05$) to measure significant differences between sampling stations. Pearson correlation (r) test was analyzed to identify the association between pairs of variables for sampling stations.

RESULTS AND DISCUSSIONS

The seasonal variation of insecticides detected with high frequency at higher concentrations in the surface river water is shown in Figure-3. The insecticides that was present in higher concentrations in the surface water was cypermethrin II for both the dry (1.23 µg/ml) and wet (2.66 µg/ml) seasons. During the wet season, it was observed that a significant amount of cypermethrin was transported to areas relatively far from the application sites. Higher amounts of cypermethrin were used during the wet season for the control of insect pests.

Cypermethrin

During the dry season, the concentration of cypermethrin in the river water ranged from 0.10-0.29 µg/ml, compared to 0.29-0.30 µg/ml during the wet season (Table-2). It was observed that; the highest concentration of dissolved cypermethrin II was recorded at Stations S5 and S7 (0.29 µg/ml; 0.20 µg/ml) and the lowest at Stations S8 and S9 (0.10 µg/ml). Meanwhile, during the wet season most stations show a higher concentration of cypermethrin with an average of between 0.29-0.30 µg/ml. Statistical analysis showed that there was no significant difference in the concentration levels of this insecticide in the river water ($p>0.05$) between the dry and wet seasons.

The concentration of cypermethrin dissolved in the river water was higher during the wet season compared to that during the dry season. One of the factors contributing to the high level of insecticide residue is the repeated use of insecticides by farmers. There is a possibility that an amount of pesticide sprayed earlier could have been washed away due to rain and entered into the nearby rivers. As seen along the Bertam River there are many illegal farms operating there. This could also contribute to the runoff of insecticides during the wet season.

Table-2. Cypermethrin (µg/ml) in water samples from Bertam River (±SD), (n=180).

	MAY-JULY (DRY SEASON)				**AUGUST-OCTOBER** (WET SEASON)			
Stn.	**cyp I**	**cyp II**	**Cyp III**	**Cyp IV**	**cyp I**	**Cyp II**	**cyp III**	**cyp IV**
1	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	0.11± 0.00	ND	ND	ND	0.29± 0.03	ND	ND
3	ND	0.11± 0.00	ND	ND	ND	0.29± 0.04	ND	ND
4	ND	ND	ND	ND	ND	0.30± 0.03	ND	ND
5	ND	0.29± 0.00	ND	ND	ND	0.29± 0.03	ND	ND
6	ND	0.11± 0.02	ND	ND	ND	0.30± 0.03	ND	ND
7	ND	0.20± 0.00	ND	ND	ND	0.30± 0.04	ND	ND
8	ND	0.10± 0.01	ND	ND	ND	0.30± 0.03	ND	ND
9	ND	0.10± 0.00	ND	ND	ND	0.29± 0.03	ND	ND
10	ND	0.11± 0.01	ND	ND	ND	0.30± 0.03	ND	ND

*Cypermethrin= Cyp

Chlorpyrifos

During the dry season, the concentration of chlorpyrifos in the river water ranged from 0.01-0.02 µg/ml, while during the wet season it was between 0.02-0.08 µg/ml (Table-3). For the dry season, most of the stations showed a low range of concentration (0.01-0.02µg/ml). During the wet season, the highest concentration of chlorpyrifos was recorded at Station S10

(0.08 µg/ml), with the lowest at Stations S6 and S8 (0.02 µg/ml). Statistical analysis showed that there was a significant difference ($p>0.05$) in the concentration of chlorpyrifos between the dry and wet seasons.

A higher concentration of chlorpyrifos dissolved in the river water was observed during the wet season, compared to that during the dry season ($p <0.05$). This may be due to the accumulation of total insecticide during the wet season. The high volume of rainfall during the wet season could have caused runoff from nearby farms into rivers thus, increasing the concentration of chlorpyrifos in the water. Another possibility is that, chlorpyrifos residues could have reached the aquatic environment through surface runoff due to careless and indiscriminate disposal of empty pesticide containers, washing of spraying equipment and other uncontrolled activities of the farmers. It should be noted that the pH of water was 7.0 and the temperature recorded was 25°C. Under these conditions, the insecticides have a half-life of 3-4 weeks in the surface water, and this can only be adversely affected by photolytic processes.

Table-3. Chlorpyrifos concentrations (µg / ml) in water samples from Bertam River (±SD), (n = 180).

	May-July (Dry season)	**August-October** (Wet season)
station	chlorpyrifos	chlorpyrifos
1	ND	ND
2	0.01±0.00	ND
3	0.02±0.01	ND
4	0.02±0.01	ND
5	ND	ND
6	0.01±0.01	0.02±0.02
7	ND	ND
8	ND	0.02±0.03
9	0.02±0.06	0.04±0.02
10	0.02±0.02	0.08±0.03

CONCLUSIONS

This study revealed that the river water in the agriculture areas was contaminated with specific insecticides. The selected insecticides extracted from the water samples collected belonged to the organophosphate and pyrethroid groups. One organophosphate, (chlorpyrifos) and four pyrethroid (cypermethrin) insecticides were found to be present in the river water throughout the study period from May to October 2014. Cypermethrin insecticides were found to be in higher concentrations in the river water for all stations. This finding showed that many of these compounds were transported there from their application sites.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Agriculture, Cameron Highlands (through the Ministry of Agriculture), Ministry of Education (My Brain 15), Malaysian Agricultural Research and Development Institute (MARDI- Grant No. 003) and SWAT Network of Malaysia for their financial and technical support of this research. We are also thankful to the vegetable farmers in Cameron Highlands for their cooperation in making this research successfully.

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