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Composition of Insecticidal Residues in Total Suspended Particulate and Rain Water at an Agricultural Area in Kedah, Malaysia

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ABSTRACT
A study was conducted to determine the most common insecticides found in the total suspended particulate and rainwater, in an agricultural area in Kedah, Malaysia where insecticides such as endosulfan, chlorpyrifos and cypermethrin were commonly used. The samples of total suspended particulate and rain water were collected using a High Volume Sampler (HVS) equipped with fiber glass filter and glass bottles respectively, for a specific period (September 2010-March 2011) at four different sampling sites within the agricultural area in Kedah. The composition of the insecticides (cypermethrin, endosulfan and chlorpyrifos) in both suspended particulate and rain water samples were determined by a Gas Chromatograph (GC) equipped with a micro electron capture detector (μ-ECD) after extraction with acetone and toluene (9:1). Results showed that chlorpyrifos was recorded as having the highest concentration in the suspended particulate matter (543.6 pg m^{-3}) and cypermethrin, the highest concentration in rain water. The concentrations of the insecticides showed seasonal dependence based on the application periods. This study also indicated that basic training on precautionary measures and correct usage and handing of insecticides should be undertaken by the Muda Agricultural Development Authority to ensure that the level of insecticidal residues in the air and rain water of the agricultural area remained safe.

Key words: Cypermethrin, endosulfan, chlorpyrifos, particulate matter, insecticide

INTRODUCTION
The development of agricultural activities leads to higher usage of pesticides such as insecticides to protect crops from pests and to ensure increased yields (Salameh *et al*., 2001). Due to their widespread use, pesticide waste/residues can be detected in various environmental matrices such as soil, water and air (Konstantinou *et al*., 2006). Insecticides are widely used in agriculture and their properties provide many benefits in terms of higher production and quality, but their usage could cause harmful effects on human health (Avino *et al*., 2011; Kannan *et al*., 1994). Most insecticides exhibit a high degree of persistence in the environment and this could result in various health and pollution problems (Jelinek, 1985; Kosikowska and Biziuk, 2010).

Organophosphorus insecticides such as chlorpyrifos are widely used in agriculture and their properties provide many benefits in terms of yield and quality of agricultural produce (Avino *et al*., 2011; Kannan *et al*., 1994). As they exhibit a high degree of persistence in the environment, this could lead to various health and safety problems (Jelinek, 1985; Kosikowska and Biziuk, 2010).

Meanwhile, toxicological experiments carried out have proven that the metabolites of pyrethroids are relatively non-toxic or low in toxicity compared to the parent pyrethroid compounds (Chen and Wang, 1996; Sharif *et al.*, 2006). Pyrethroids have been reported to have relatively low toxicity compared to organophosphorus, organochlorine and carbamate insecticides (Colume *et al.*, 2001; Sharif *et al.*, 2006). In Malaysia, the use of organochlorine insecticides which are organic pollutants, have been prohibited for general use and only permitted for specific purposes. For example, the used of aldrin, endrin and DDT were discontinued since 1998. The use of insecticides such as heptachlor, hexachlorobenzene, mirex, toxaphene and endrin has not been reported in Malaysia (Zakaria *et al.*, 2003). Although, the use of organochlorine insecticides is prohibited in Malaysia, reports show that these compounds are present in river water, sediments and the aquatic environment in Malaysia (Cheah and Lum, 1994; Lee, 1994; Huat *et al.*, 1991). In most studies, the sources of contamination have yet to be determined.

Insecticides can be released into the atmosphere through volatilization, evaporation and wind erosion on land (Gil and Sinfort, 2005; Glotfelty, 1978; Glotfelty *et al.*, 1989). Besides that, spray drift also can transfer the insecticide away from the application site. Spray drift can be defined as the rate of loss from the sprayer which deviates from the target area because of wind action (Gil and Sinfort, 2005; Waxman, 1998; Yusa *et al.*, 2009). In the atmosphere, insecticides can be redistributed, degraded, transferred and resettled on the surface of the earth again through wet and dry deposition (Muir *et al.*, 2004; Wania and Mackay, 1996). However, information on insecticides in the total suspended particulate is rarely reported compared to reports of their presence in other matrixes. Since the 1960s, several studies (Halimah *et al.*, 2005; Primental and Levifan, 1986; Ismail *et al.*, 2009) on insecticidal contamination of soil and water resources at agricultural areas in Malaysia have been carried out. Such studies were undertaken in numerous countries and according to Primental and Levifan (1986), 50% of the insecticides sprayed on crops were carried by the wind into the atmosphere. Many organochlorine insecticides are known to be persistent in the environment for a long time after application and distributed long distances in the atmosphere (Alegria *et al.*, 2008; Wania and Mackay, 1996; Al-Wabel *et al.*, 2011).

The main scope of the present study was the identification and determination of the concentration levels of the residues of commonly used insecticides, namely α-endosulfan, β-endosulfan, endosulfan sulphate, chlorpyrifos and cypermethrin in the total suspended particulate and rain water during the wet and dry seasons of the largest rice growing area in Malaysia, under Muda Agricultural Development Authority (MADA) in Kedah, Malaysia. The study aimed to determine the possible impact of insecticides in the atmosphere through their concentration in the total suspended particulate and rain water of the agricultural area.

MATERIALS AND METHODS

Apparatus: The gas chromatograph used was Hewlett Packard GC 5890 Series II, fitted with a micro electron capture detector (μ-ECD). One microliter samples were injected manually into the GC-μ-ECD through a 0.2 μm filter (Minisart, USA). A capillary column chromatograph with high Achievement HP-5 (Crosslinked 5% phenyl Methyl Siloxane) 30.0 ×0.25 mm and thickness of 0:25 μm, was used. The study was conducted following the method of operation of the GC-ECD with injector temperature of 250°C, a temperature detector (280°C) and splitless time of 0.75 min. The initial temperature of 100°C, was increased at a rate of 10°C min^{-1}, up to 250-280°C followed at the rate of 3°C min^{-1}. The carrier gas was nitrogen at 1 mL min^{-1} and the same gas at a flow-rate of 1.4 mL min^{-1} was used as the make-up.

Sampling location: Kedah, located in north west Peninsular Malaysia is known as the rice bowl of Malaysia accounting for one third of Malaysia's total production of rice. It has an area of 97,000 hectares of paddy fields under the supervision of the Muda Agricultural Development Authority (MADA) and a population of about 1,890,098 (Department of Statistics Malaysia, 2010) inhabitants. Kedah produces 2,384 000 tons of rice (2008) with the average yield of 3556 kg ha^{-1} (paddy). As the agricultural area under MADA is large, it is divided into different zones (Zone 1 to 4). The sampling locations for the current study were chosen randomly from the different zones and named as S1, S2, S3 and S4, in an attempt to evenly distribute the sampling operation over the entire rice growing region. The total suspended particulate samples were obtained from the 4 sampling sites (Zone 1 to 4) within the MADA area, Kedah (Fig. 1).

Sample collection

Total suspended particulate matter: A High-Volume air Sampler (HVS) model Grasbey, fitted with fiber glass filter (20.4×28.1 cm) was operated for 24 h at a constant air flow of 1:13 m^3 min^{-1}. The HVS was placed randomly within the study area and the total suspended particulate sampling was carried out for 3 consecutive days. Sampling was done during the two seasons, namely the rainy season (September -December 2010) and the dry season (January 2011-March 2011). The filters from the sampler were removed and kept in desiccators prior to extraction and analysis for insecticide residue.

Rain water samples: Monthly samples of wet-only deposition were collected using modified amber bottles. These collector bottles were equipped with filter funnels, diameter 15 cm. Samples were transported to the lab. From the sampling site, 60 rain water samples were taken from September 2010 until March 2011 from the 4 stations. Each station had 3 replicate samples. The rain water samples were transferred into a refrigerator with the temperature maintained at 4°C, prior to analysis.

Recovery test

Total suspended particulate: The fiber glass filters (20.4×28.1 cm) were cut into small pieces and put into 250 mL Schott bottles. Then, 1 mL of insecticide solution per bottle was added from a series of standard concentrations of 0.01, 0.08, 0.1, 0.5 and 1.0 μg m^{-3}. The bottles were left at room temperature for 24 h to reach equilibrium. The organic solvent, acetone/toluene (9:1) was added into the Schott bottles, which were shaken on an orbital shaker (Model Infors Multiron HT) for 1 h. The fiber glass filter mixture was then sonicated for 1 h. A total of 50 mL of the extract were filtered through a glass column containing 40 g anhydrous sodium sulphate and dried using a rotary evaporator. The sample was concentrated to 1 mL and injected into the GC-ECD (Elflein *et al.*, 2003).

Rain water: To determine the presence of insecticides in the rain water samples, the cartridge C18 was used for Solid-Phase Extraction (SPE). The SPE cartridges were connected to a vacuum manifold and rinsed with 3 mL of acetonitrile and 3 mL of distilled water. Then, 1 mL of the insecticide solution (per bottle) was added from a series of standard concentrations of 0.01, 0.08, 0.1, 0.5 and 1.0 μg mL^{-1} into 500 mL of deionizer water. The solution was shaken until it reached equilibrium. The SPE tube was placed into the water and the pump was turned on. When suction occurred, the water samples were drawn through the C_{18} cartridge into the vacuum manifold. The

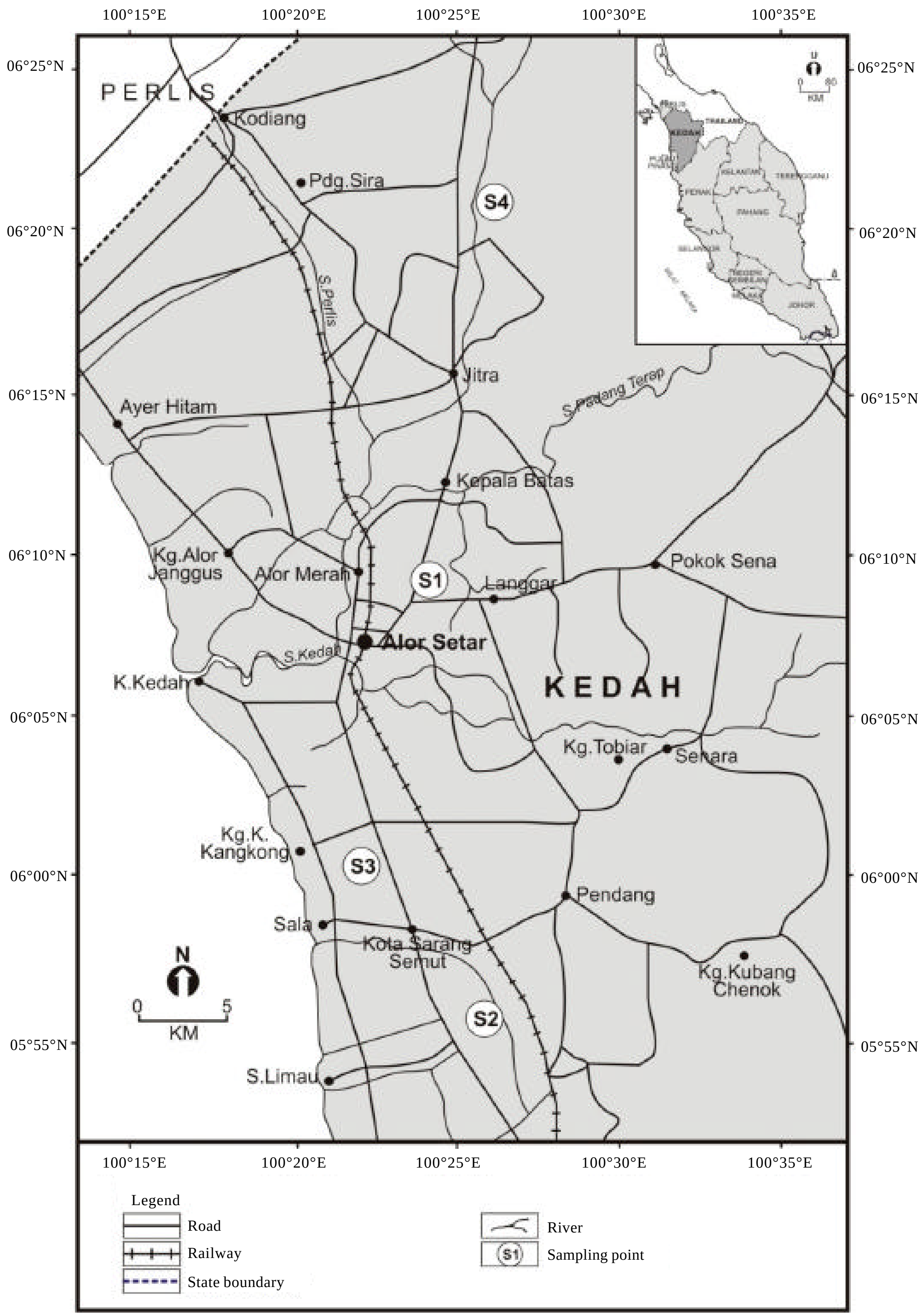

Fig. 1: Location of sampling sites

flow through the SPE cartridge was controlled using a pressure knob. Samples were eluted from the cartridges with a solvent (6 mL of acetone) and analyzed for the specific, test insecticides. The insecticides were analyzed by GC (Hewlett Packard 5890 Series II) fitted with a micro electron capture detector (μ-ECD) (Halimah *et al.*, 2005).

Insecticide analyses

Total suspended particulate: Analyses of endosulfan, chlorpyrifos and cypermethrin in the TSP were carried out by cutting the fiber glass filters (20.4×28.1 cm) into small pieces and placing them into 250 mL Schott bottles. Insecticide extraction from the fiber glass was carried out first, assisted by the orbital shaker (Model Infors Multiron HT) and then sonicated for 1 hour, using acetone: toluene (9:1 mL). A total of 50 mL of the extract were filtered through a glass column containing 40 g anhydrous sodium sulphate and dried using a rotary evaporator. Insecticide residues were determined by GC-ECD under the conditions described above (Elflein *et al.*, 2003).

Rain water: One liter rain water was withdrawn and passed through a C-18 solid phase extraction cartridge for isolation of the compounds of interest. Samples were eluted from the cartridges with a solvent and analyzed for the test insecticides. The insecticides were analyzed by GC (Hewlett Packard 5890 Series II) with a micro electron capture detector (μ-ECD).

RESULTS AND DISCUSSION

Overall recovery test: The percentage recovery of cypermethrin, chlorpyrifos and endosulfan in the suspended particulate is shown in Table 1. The recovery for cypermethrin ranged from 86 to 98%, chlorpyrifos from 94 to 112% and endosulfan from 85 to 100%. Based on statistical analysis (ANOVA), the recovery levels of cypermethrin, chlorpyrifos and endosulfan were significantly different (at $p<0.05$). Overall, the percentage recovery of cypermethrin, chlorpyrifos and endosulfan were in the range of 85-112%. Therefore, it was concluded that the method of extraction for cypermethrin, chlorpyrifos and endosulfan from the air samples is acceptable. The limit of detection of cypermethrin, endosulfan and chlorpyrifos, was 0.002, 0.02 and 0.0005 μg mL^{-1}, respectively for the GC-ECD.

Insecticide concentration in TSP: The concentration of insecticides in the Total Suspended Particulate (TSP) for the rainy and dry seasons is presented in Table 2. During the rainy season, the concentration of insecticides in the TSP ranged from 180.8 - 17.7 pg m^{-3}, meanwhile for the dry season, the concentration of insecticide in the TSP ranged from 543.6-34.3 pg m^{-3}. Chlorpyrifos was found to be the main insecticide in the TSP for both the rainy and dry seasons with concentrations of 180.8±28.2 and 543.6±63.4 pg m^{-3}, respectively. Meanwhile the concentration of endosulfan

Table 1: Recovery studies of cypermethrin, chlorpyrifos and endosulfan in the air

	Insecticide percentage recovery		
Concentration (μg mL^{-1})	Cypermethrin	Chlorpyrifos	Endosulfan
0.01	98.33±8.09	94.63±6.47	100.37±4.32
0.08	85.76±7.62	97.88±1.04	98.12±2.75
0.1	94.01±6.59	94.40±2.07	102.80±1.35
0.5	90.94±4.74	93.74±6.40	98.98±1.40
1.0	86.29±5.87	111.75±12.96	85.32±3.17

Values are Mean±SD

Table 2: Concentration of insecticides in the ambient air of the MADA agricultural area in, Kedah

Compound	TSP ($pg\ m^{-3}$) Raining season (September-December)	TSP ($pg\ m^{-3}$) Dry season (January-March)
α-Endosulfan	63.1±6.3	37.5±17.7
β-Endosulfan	84.5±8.5	34.3±15.0
Endosulfan Sulphate	17.7±3.5	146.2±23.2
Cypermethrin	28.1±5.5	69.1±18.1
Chlorpyrifos	180.8±28.2	543.6±63.4
Total	374.2	830.6

sulphate was the lowest during the rainy season and **β**-endosulfan the lowest for the dry season in the TSP with values of 17.7±3.5 pg m^{-3} and 34.3±15.0 pg m^{-3}, respectively.

Table 3 shows the concentration of insecticides in the TSP during the dry and rainy seasons at the four different locations. During the rainy season, the concentrations ranged from 8.3±0.4 to 15.6±0.9 pg m^{-3} for α-endosulfan, 11.1±0.5-31.8±0.3 pg m^{-3} for **β**-endosulfan, 3.3±1.2-7.4±0.3 pg m^{-3} for endosulfan sulphate, 5.3±2.0-11.8±0.5 pg m^{-3} for cypermethrin and 9.7±0.6-78.5±2.3 pg m^{-3} for chlorpyrifos. For total concentration of insecticides, the highest was chlorpyrifos followed by **β**-endosulfan, α-endosulfan, cypermethrin and endosulfan sulphate with values of 180.8, 84.5, 63.1, 28.1 and 17.7 pg m^{-3}, respectively.

The station S1 had the highest concentration of chlorpyrifos with 78.5±2.3 pg m^{-3} and the lowest concentration of endosulfan sulfate of 3.3±1.2 pg m^{-3}. Statistical analysis showed significant differences in the insecticide concentrations among the stations ($p<0.05$). This could also be due to different (increased levels) levels of application by farmers during the rainy season to prevent pest attack including the golden snail (*Pomacea* sp.). It could also be related to increased volatilization of previously applied compounds from the surface and/or seasonal/local/regional application of the currently used insecticides namely endosulfan and chlorpyrifos (Table 3).

During the dry season, the concentration of insecticides in the TSP ranged from 0.3±0.1-35.9±4.9 pg m^{-3} for α-endosulfan, 0.3±0.1-31.0±20.8 pg m^{-3} for **β**-endosulfan, 6.1±4.2-55.0±10.3 pg m^{-3} for endosulfan sulphate, 3.3±3.3-42.3±27.1 pg m^{-3} for cypermethrin and 67.7±1.6-220.8±13.3 pg m^{-3} for chlorpyrifos. With regard to total concentration of insecticides, the highest was chlorpyrifos followed by endosulfan sulphate, cypermethrin, α-endosulfan and **β**-endosulfan with values of 543.6, 146.3, 69.2, 37.5, 34.3 pg m^{-3}, respectively. Station S4 had the highest concentration of chlorpyrifos (220.8±13.3 pg m^{-3}) and the lowest concentrations of α-endosulfan and **β**-endosulfan (0.3±0.1 pg m^{-3}) a low value of endosulfan was also obtained at station S3 (0.3±0.0 pg m^{-3}). Statistical analysis showed that there were no significant differences among the stations ($p>0.05$) for insecticidal concentration (Table 3).

The correlation analysis was done of TSP for α-endosulfan, **β**-endosulfan, endosulfan sulphate, cypermethrin and chlorpyrifos. The results showed that α-endosulfan was significantly correlated with **β**-endosulfan ($r = 0.893$) and cypermethrin ($r = 0.503$) at ($p>0.01$). A study showed that α-endosulfan was always detected in lesser amounts than the α-isomer. The technical mixture is enriched with the a-isomer, plus the α-isomers is more volatile (vapor pressure: 0.0061 for α-endosulfan vs. 0.0032 Pa for α-endosulfan) at 25.1°C (Hinckley *et al.*, 1990). Therefore the **β**-isomer could be converted to the α-isomer. This conversion was observed in laboratory experiments (Rice *et al.*, 1997; Schmidt *et al.*, 1997) but has still not been observed under field conditions. Atmospheric washout ratios for each isomer are still difficult to predict. Although, vapor pressure of the **β**-isomer was lower compared to that of the α-isomer, it is more easily removed from the

Table 3: Concentration (pg m^{-3}) of insecticides in the total suspended particles during the dry and rainy seasons at the four sampling stations

Sampling site	α- Endosulfan	β- Endosulfan	Endosulfan sulphate	Cypermethrin	Chlorpyrifos	Total
Raining season						
S1	15.6±0.9	21.0±1.3[a]	3.3±1.2[a]	5.3±2.0[a]	78.5±2.3[a]	123.7
S2	8.3±0.4[a]	11.1±0.5[a]	7.4±0.3[a]	11.8±0.5[a]	44.4±0.6	83.0
S3	23.8±0.2[b]	31.8±0.3[a]	6.9±1.1[a]	11.0±1.7[a]	48.4±3.4	121.8
S4	15.4±11.0[a]	20.6±13.4[a]	nd	nd	9.7±0.6[a]	45.7
Total	63.1	84.5	17.7	28.1	180.8	374.2
Dry season						
S1	0.9±0.2[a]	2.7±0.4[a]	55.0±10.3[a]	18.8±9.9[a]	67.7±1.6[a]	145.1
S2	35.9±4.9[a]	31.0±20.8[b]	54.2±14.2[b]	42.3±27.1[a]	122.6±16.0[a]	285.9
S3	0.4±0.2[b]	0.3±0.0[a]	6.1±4.2[a]	3.3±3.3[b]	132.5±17.9[a]	142.5
S4	0.3±0.1[a]	0.3±0.1[a]	31.0±20.1[a]	4.8±0.4[b]	220.8±13.3[a]	257.1
Total	37.5	34.3	146.3	69.2	543.6	830.6

Mean followed by the same letter within a column are not significantly different at $p<0.05$, nd: Not detected

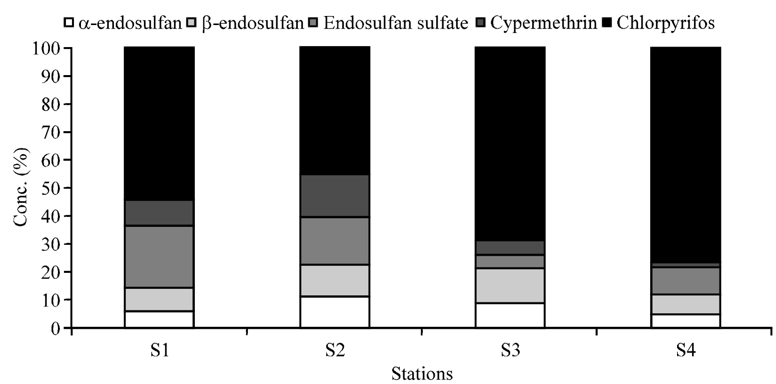

Fig. 2: Concentration of insecticides in TSP at all stations

atmosphere by precipitation. This hypothesis was proven in a study by Tuduri *et al.* (2006) where the results showed higher concentration of the **β**-isomer in precipitation.

Figure 2 shows the percentage insecticide in the Total Suspended Particulate (TSP) TSP at all the stations. Chlorpyrifos was present in the highest percentage for all the stations ranging from 12 to 19% compared to the percentage of the other insecticides. The next higher was endosulfan sulphate with 5% at stations S1 and S2. The other insecticides were present in values of ≤4%.

The total amount of detected insecticides in the dry season was slightly higher than that in the rainy season. This is partly due to the fact that the insecticides used in the rice fields were diluted by the rain water. In Japan, during the dry season (summer) the air temperature is higher than that in the spring and a larger amount of insecticides are vaporized in summer compared to that in spring (Kawahara *et al.*, 2005). During the dry season in Kedah the temperature reached 29-34°C, the relative humidity was low and there was almost no wind movement (0 msec) recorded. According to Haenel and Siebers (1995), high temperatures, low relative humidity and low air movement affect the vaporization process. From a study by Klingman and Ashton (1982), the vaporization process increases as the temperature increases. Vaporization processes improve the content of insecticides in the air.

Air circulation/movement will carry insecticides that have been vaporized in the air to other locations (Muir *et al.*, 2004). In the dry season, the records show that the wind speed was very low, particularly at the S2 and S3 stations; therefore, both stations recorded a high content of insecticide residues compared to that at the other stations. As sampling occurred during the planting season, the concentrations reported in the paper are probably related to the higher insecticidal application at planting. In addition the S2 and S3 stations were located along the main road, where there was movement of many vehicles transporting rice and weeds plus they were also surrounded by extensive rice fields where insecticide spraying activities were being carried out and these activities could have been the cause of the high insecticide content in the air.

Insecticide levels in the dry season were higher than those in the rainy season because rainfall during the rainy season (1205.4 mm month^{-1}) was much higher than that in the dry season (50.77 mm month^{-1}). The total suspended particles, including insecticides can be removed from the air/atmosphere by rain through the process of 'rainout' and 'washout' (Sham, 1979). According to Vesilind *et al.* (1988) rain can clear up the suspended particles under the clouds through 'washout' processes. The cleaning effect of rain water is the reason the concentration of insecticides in the atmosphere during the rainy season was lower than that during the dry season. In addition, the ground being wet due to rain, caused a reduction in the amount of dust scattered into the atmosphere.

The concentration of insecticides in the study area was higher compared to the concentration of insecticides detected in ambient air (TSP) over the Turkey, the Great Lakes (α-endosulfan- 83.0 pg m^{-3}) and Chiapas, Mexico (α-endosulfan- 367 pg m^{-3}) (Bozlaker *et al.*, 2009). Meanwhile the concentration of endosulfan was lower than that detected over Guangzhou, China (2.63 μg mL^{-1}) (Huang *et al.*, 2010).

The toxicity of chlorpyrifos as classified by the WHO (World Health Organization, WHO), comes under Class II and is not listed among the virulent, banned and restricted insecticides (TACTRI/COA, 2009), therefore chlorpyrifos is currently not considered a highly toxic insecticide. The present study found that the chlorpyrifos concentration in the TSP at the rice fields within the study area was lower than the value reported in Jacksonville (Florida),Tokyo (Japan), Québec (CAN) and Springfield/Chicopee, Massachusetts (United States), a decade ago (Kawahara *et al.*, 2005; Sadiki and Poissant, 2008; Tulve *et al.*, 2008; Whitemore *et al.*, 1994) and lower than that reported by Harnly *et al.* (2005) for Tulare County, California. However it is still considerably higher than the chlorpyrifos concentrations at other rural or agricultural areas over the past decade (Clayton *et al.*, 2003; Mukerjee *et al.*, 1997; Raina and Sun, 2008).

Insecticides in rain water: The concentrations of insecticides in rain water for the rainy and dry seasons are presented in Table 4. For rain water, during the rainy season, the concentrations of insecticides ranged from 2861.7±43.4-139.4±1.5 μg L^{-1}, meanwhile in the dry season insecticidal concentration ranged from 3597.5±276.8-0.1195±0.2 μg L^{-1}. Cypermethrin was found to be the dominant insecticide in rain water for the rainy and dry seasons with the concentrations of 2861.7±43.4 μg mL^{-1} and 3597.5±276.8 μg L^{-1}, respectively. Meanwhile, chlorpyrifos was recorded to have the lowest concentration in rain water in the rainy and dry seasons with values of 139.4±1.5 and 119.5±0.2 μg L^{-1}. The five tested insecticides were detected in all the rain water samples from the different sampling sites. The distribution pattern of the insecticides in the rain water samples for both the dry and rainy seasons are shown in Table 5. During the rainy season, the insecticide concentration ranged from 65.8±0.4-90.7±4.2 μg L^{-1} for α-endosulfan,

Table 4: Concentration of insecticides in rain water in the MADA agricultural area in, Kedah

	Insecticide ($\mu g\ L^{-1}$)	
Compound	Raining season (September-December)	Dry season (January-March)
α-Endosulfan	305.6±5.1	240.1±0.2
β-Endosulfan	304.8±4.9	283.1±1.1
Endosulfan Sulphate	324.4±1.4	308.5±0.1
Cypermethrin	2861.7±43.4	3597.5±276.8
Chlorpyrifos	139.4±1.5	119.5±0.2
Total	3936.0	4548.7

Table 5: Average concentration of insecticides ($\mu g\ L^{-1}$) dissolved in rain water during the dry and rainy seasons

Sampling site	α- Endosulfan	β- Endosulfan	Endosulfan sulphate	Cypermethrin	Chlorpyrifos	Total
Raining season						
S1	65.8±0.4^{a}	79.0±0.9^{a}	80.3±0.4^{a}	1265.5±138.0^{a}	37.0±0.1^{a}	1527.6
S2	70.1±12.1^{a}	79.1±10.1^{b}	79.7±3.3^{b}	471.0±44.1^{a}	41.2±3.7^{a}	741.1
S3	79.0±2.5^{a}	73.1±0.4	79.2±0.6^{c}	334.3±64.0^{a}	31.3±1.0^{a}	596.9
S4	90.7±4.2^{a}	73.6±0.1	85.1±0.5^{a}	790.9±50.5^{a}	30.0±1.1^{a}	1070.3
Total	305.6	304.8	324.3	2861.7	139.5	3935.9
Dry season						
S1	59.9±0.0^{a}	71.7±2.5^{a}	76.4±0.1^{a}	1095.1±589.3^{a}	31.2±0.3^{a}	1334.2
S2	59.9±0.1^{b}	70.1±0.1^{a}	77.7±0.1^{a}	637.3±35.7^{a}	32.4±0.6^{a}	877.4
S3	60.3±0.4^{c}	70.8±0.3^{b}	76.8±0.1^{a}	593.6±84.3^{a}	28.1±0.4^{a}	829.6
S4	59.9±0.2^{a}	71.7±0.5^{c}	76.4±0.3^{a}	705.8±351.5^{b}	27.8±0.1^{a}	941.6
Total	240.1	283.1	308.5	3031.9	119.5	3983.1

Mean followed by the same letter within a column are not significantly different at $p<0.05$

73.1±0.4- 79.1±10.1 $\mu g\ L^{-1}$ for β-endosulfan, 79.2±0.6-85.1±0.5 $\mu g\ L^{-1}$ for endosulfan sulphate, 334.3±6.0 $\mu g\ L^{-1}$-1265.5±13.8 $\mu g\ L^{-1}$ for cypermethrin and 30.0±1.1-41.2±3.7 $\mu g\ L^{-1}$ for chlorpyrifos. With regards to the total concentration of insecticides, the insecticide with the highest concentration was cypermethrin followed by endosulfan sulphate, α-endosulfan, β-endosulfan and chlorpyrifos with values of 2861.7, 324.3, 305.6, 304.8 and 139.5 $\mu g\ L^{-1}$, respectively. Station S1 recorded the highest concentration of cypermethrin @ 1265.5±138.0 $\mu g\ L^{-1}$; the lowest concentration of chlorpyrifos, 30.0±1.1 $\mu g\ L^{-1}$, was recorded at station S4. Statistical analysis showed significant differences in the concentration of insecticides among the stations ($p<0.05$). During the rainy season there were significant differences among the stations for insecticide concentration ($p<0.05$). This indicated that the amount of insecticides recorded in the rain water was affected by the meteorological parameters (i.e., wind speed, air temperature and atmospheric stability) for every station.

For the dry season, the insecticide concentrations ranged from 59.9±0.0- 60.3±0.4 $\mu g\ L^{-1}$ for α-endosulfan, 70.1±0.1-71.7±2.5 $\mu g\ L^{-1}$ for β-endosulfan, 76.4±0.1-76.8±0.1 $\mu g\ L^{-1}$ for endosulfan sulphate, 593.6±84.3-1095.1±589.3 $\mu g\ L^{-1}$ for cypermethrin and 27.8±0.1-32.4±0.6 $\mu g\ L^{-1}$ for chlorpyrifos. For total concentration of insecticides, the highest was cypermethrin followed by endosulfan sulphate, β-endosulfan, α-endosulfan and chlorpyrifos with values of 308.5, 283.1, 240.1 and 119.5 $\mu g\ L^{-1}$, respectively. Station S1 recorded the highest concentrations of cypermethrin @ 1095.1±589.3 $\mu g\ L^{-1}$ while the lowest concentration was recorded for chlorpyrifos @ 27.8±0.1 $\mu g\ L^{-1}$ at S4. Statistical analysis showed significant differences among the stations during the dry season ($p>0.05$).

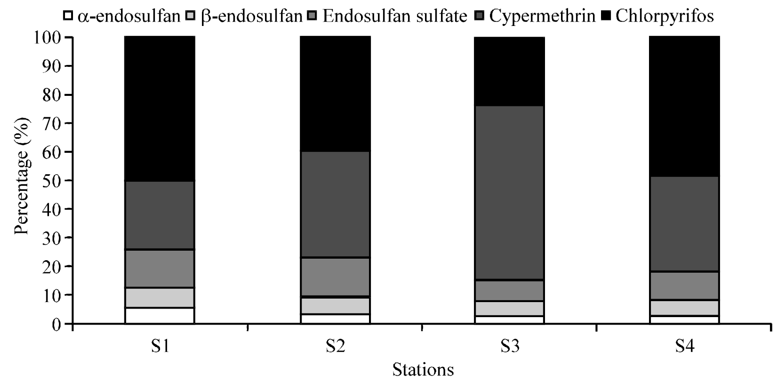

Fig. 3: Concentration of insecticide in rain water at all stations

Figure 3 shows the percentage insecticide in rain water at all the stations. Cypermethrin and chlorpyrifos were recorded to be in the highest concentration in rain water for all the stations compared to the concentration of the other insecticides, with 5-15% for cypermethrin and 6-12% for chlorpyrifos. Meanwhile α-endosulfan, β-endosulfan and endosulfan sulphate had concentrations of 4-1% in rain water.

The relationship between the total concentration of insecticides in the total suspended particulate samples (n = 48) were investigated. Statistically significant correlations ($p<0.01$) were found among α- endosulfan, β- endosulfan ($r^2 = 0.919$) and endosulfan sulphate ($r^2 = 0.858$). This indicated that the related insecticides in the air could possibly have been affected by the same sources and/or meteorological conditions. However, there was no statistical significance ($p>0.05$) but a relatively weak negative correlation between α-endosulfan with chlorpyrifos ($r^2 = -0.271$) and cypermethrin ($r^2 = -0.281$).

The total concentration of insecticides was one-fold higher at the dry season reflecting the heavy use of agricultural chemicals during that season. The insecticide with high percentage total concentration in rain water for the both seasons was cypermethrin. The concentration of insecticide residues in the rain water samples at the S4 station was high during the dry season as the low rainfall caused bioconcentration of the insecticide residues in the raindrops (63.5 mm month^{-1}) while during the rainy season the samples from S1 station had the highest insecticide residue derived from frequent rain (1051.7 mm month^{-1}) compared to that in the other stations.

The concentration of cypermethrin was the highest during both the seasons, because cypermethrin was applied in the powder or granular form to the soil. The amount of cypermethrin released into the air by spray drift or by post application volatilization of the residue in the soil is considered small, because the vapor pressure the cypermethrin is very low (190 nPa). This insecticide might have been subject to wind erosion or heavy application prior to sampling.

The concentration of insecticides during the dry season was higher than that during the rainy season, because raindrops act as bioconcentration agents, one of the main mechanisms for the production of persistent organic chemicals in the atmosphere, namely rainout and washout (Majewski and Capel, 1995). In addition temperature also affects the concentration of insecticide residues in rain water (Coupe *et al.*, 2000). The loss of insecticides from the soil in the tropics is due to high temperature which promotes vaporization processes to occur (Coupe *et al.*, 2000; Matsumura and Murti, 1982), causing the insecticides to then enter the atmosphere and be removed by rain. When the temperature increases, the concentration of insecticides in the gaseous phase will increase with the occurrence of vaporization from the surface, atmospheric particles, water and vegetation (Sofuoglu *et al*., 2004). The concentration of α-endosulfan and β-endosulfan in rain water in Kedah, Malaysia was lower than the concentration detected over the Great Lakes, Canada (α-endosulfan: 520 μg L^{-1}; β-endosulfan: 1260 μg L^{-1}). Chlorpyrifos, has relatively low water solubility (higher Henry's constant) (Majewski and Capel, 1995). Consequently, the less gaseous, insecticide mass would be scavenged, resulting in less frequent detection in rain water, relative to other insecticides that have comparable air concentrations and detection levels in rain (lower Henry's constant) (Coupe *et al*., 2000). Thus, it was shown in the present study that chlorpyrifos was the insecticide with the lowest concentration compared to that of the other insecticides tested. The concentration of chlorpyrifos in the study area was elevated. Meanwhile the concentration of chlorpyrifos in rain water in the study area was higher than that reported for Hinds (9 μg L^{-1}) and Sharkey Counties, Mississippi (40 μg L^{-1}).

Statistical correlation: Correlation analysis between rain water and TSP for all the tested insecticides (α-endosulfan, β-endosulfan, endosulfan sulphate, cypermethrin and chlorpyrifos) was investigated. Figure 4a show ccorrelation of α-Endosulfan concentration between rain water and TSP. Result showed there was negative, very low relationship correlation between insecticides in rain water and TSP ($R = -0.07$, $p<0.05$). This results shows that, high concentration of α-endosulfan in rainwater were not affected by concentration of α-endosulfan in total suspended particle. Figure 4b shows the result correlation of β-Endosulfan concentration in rain water and TSP. The correlation of β-endosulfan ($R = 0.008$) rain water and TSP was positive, but still remained at the low level and insignificant. Compare to α-endosulfan β-endosulfan can easily degrade or degrade more quickly (Schmidt *et al*., 2001), this may be the reason why β-endosulfan concentration in rainwater were higher when the concentration of β-endosulfan in TSP were higher. The difference and insignificant correlation between the insecticide levels in TSP and rain water are probably due to variations in the particle size distribution, solubilisation factors and the meteorological conditions (i.e., wind speed, air temperature and atmospheric stability).

Meanwhile Fig. 4c show the correlation of endosulfan sulphate concentration in rain water and endosulfan sulphate in TSP. the result showed the negative and moderate correlation between rainwater and TSP. this results showed that, as the concentration of endosulfan sulphate become higher in the rainwater, the concentration of endosulfan sulfate in TSP become lower, this may be because the 'rainout'/'snow out' and 'washout process (Sham, 1987). Beside that, report from Vesilind *et al*. (1988), shows that, rainwater can clean out suspended solid under clouds through 'washout' processes. Subsequent from the washout processes causes the concentration of endosulfan sulphate became more lower in TSP than endosulfan sulphate in rainwater.

Correlation of cypermethrin concentration in rain water and TSP were show in Fig. 4d. The results showed that as the concentration of cypermethrin in TSP become higher, the concentration of cypermethrin also become higher were the correlation were positive and relatively have moderate relationship between rainwater and TSP ($R = 0.24$). This is because the farmer spraying cypermethrin gradually and continuously, where it contribute cypermethrin concentration in the air. the farmers had to spray more than 4 times a month to prevent the crop from pests such as insects, mice and snails. In addition the average temperature during the dry season (>30°C) was higher than the rainy season, can cause increased rates of evaporation from the soil, contaminated water and vegetation. According to Klingman and Ashton (1982), evaporation will increase if the temperature rises, the more pesticides found in air.

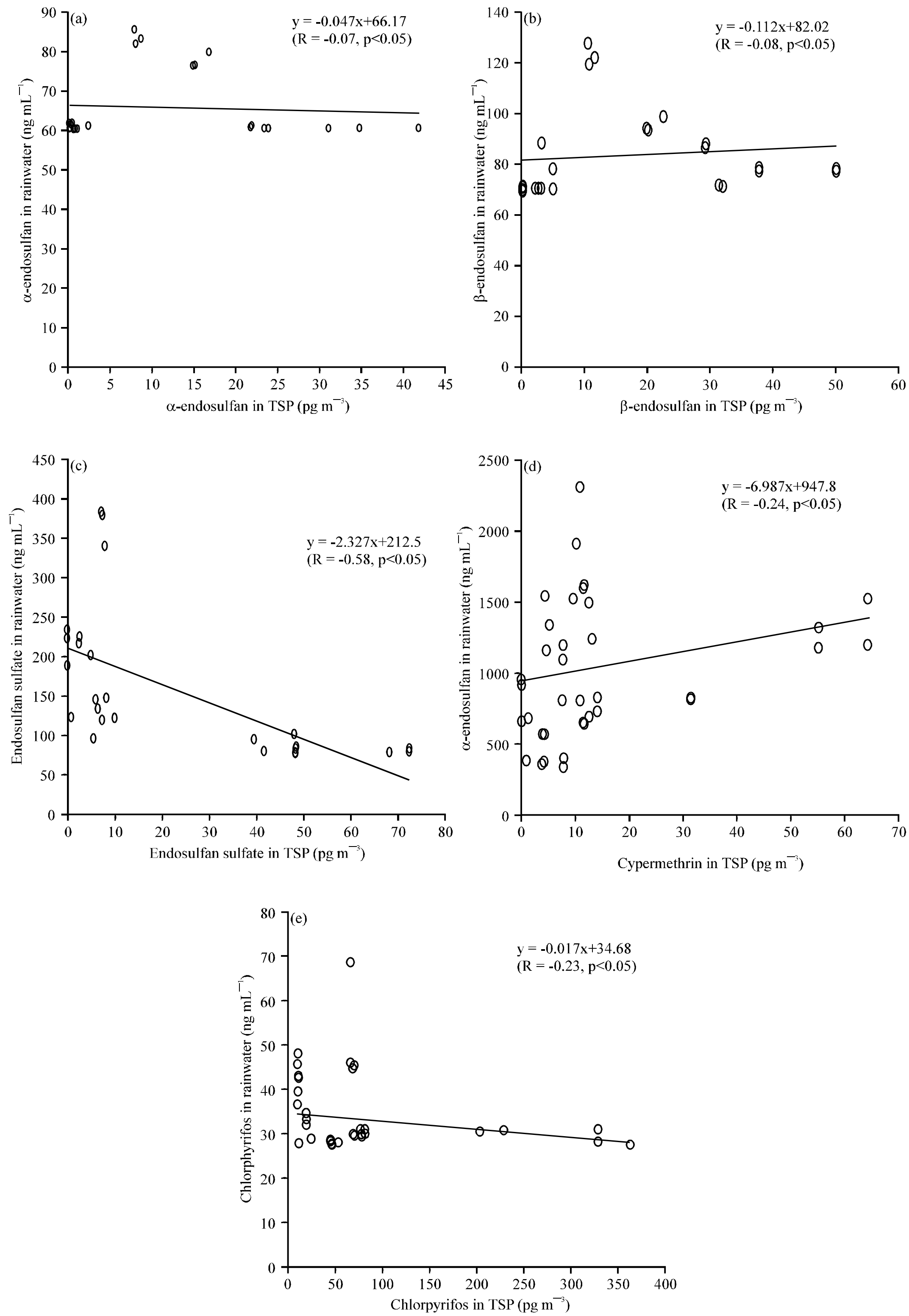

Fig. 4(a-e): Correlation of (a) α-endosulfan, (b) β-endosulfan, (c) Endosulfan sulphate, (d) Cypermethrin and (e) Chlorpyrifos concentration in rain water and TSP

Figure 4e show the negative (low relationship) and insignificant correlation of chlorpyrifos concentration in rain water and TSP ($R = -0.23$, $p<0.05$). as the concentration of chlorpyrifos in rainwater increase, the concentration of chlorpyrifos in TSP decrease. Low concentration of chlorpyrifos in total suspended particles cause the probability of molecule to join with rainwater molecule. In addition, low rainfall during the dry season (50.7 mm) compared to the rainy season (1205.4 mm), resulting in concentrations of chlorpyrifos in the amount of suspended particles in the air that is deposited with rainwater. In addition, the frequency of rain during the dry season cause suspended particles that are deposited in soil, vegetation and surface of the water evaporates into the air (Klingman and Ashton, 1982). Studies have shown that concentration of pesticides showed significant correlation between the concentration of the pesticide in the air with the temperature (Lee and Jones, 1999; Sofuoglu *et al.*, 2001; Scheyer *et al.*, 2005).

Distribution of rainfall in sampling location: The rainfall was recorded at the different sampling stations for the two seasons, namely the dry and rainy seasons. The data showed that, the rainy season occurred from the months of September to December, while the dry season was from January to March. The average rainfall recorded in the dry season was 1.5±1.3 mm month^{-1} while the average rainfall recorded for the rainy season was 8.6±2.8 mm. The total rainfall during the dry season was 82.8 mm while that in the rainy season was 1205.4 mm. The records also showed that the rainfall was a lot higher at all the stations during the rainy season compared to that during the dry season.

CONCLUSION

All rain water and total suspended particulate samples collected from the agricultural site at MADA, Kedah from September 2010-March 2011 had detectable levels of the tested insecticides. The magnitude of the total concentration of insecticides was 0.5 (TSP) to 0.7(rain water) times higher during the dry season, compared to that during the rainy season. The insecticide which was recorded to have the highest concentration in the Total Suspended Particulate (TSP) during the dry and rainy seasons was chlorpyrifos, but for the rain water samples the insecticide with the highest concentration was cypermethrin (for both seasons). The occurrence of insecticides in the rain water and air at the agricultural sites was related to the timing of insecticide application and the method of local use. Information on insecticide concentration in the air (considering the season) and duration in the atmosphere indicate pollution levels, depending on temperature and rainfall, as well as the presence of trees (considered as natural barriers to atmospheric dispersion). Overall, the study showed that the level of insecticide residues in the total suspended particulate was still below the permissible level as stipulated by US NIOSH Recommended Exposure Limits (RELs) (NIOSH, 1992).

The occurrence of insecticides in the rain water and air at the agricultural study sites was related to the timing of application and methodology of local use. Results reported show that concentration of insecticides in the air depends on the season and their duration in the atmosphere. Besides, the pollution levels depend on temperature and rainfall as well as the presence of trees (considered as natural barriers to atmospheric dispersion).

This study suggests that insecticide products must be used according to application and ventilation instructions as stipulated by the manufacturer. A few precautionary measures such as training and advice to the farmers on the correct handling and use of insecticides should be undertaken by MADA to ensure that insecticide residues in the agricultural area remain at a safe level.

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