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Improved Method for the Determination of Cypermethrin in Sarawak Soils

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ABSTRACT A gas chromatographic method was developed to determine cypermethrin residues in top and subsoil horizons of three types of Sarawak soils, viz. Semongok (*Paleudults*), Tarat (*Udorthents*) and Balai Ringin (*Kandiudults*) soils. Fourteen different horizons of top and subsoils varying in content of clay (6 – 67 %) and soil organic carbon (0.22 – 2.20 %) were used in the study. Soil samples were spiked with cypermethrin at three concentration levels (0.01, 0.1 and 1 mg/kg) and subsequently extracted for one hour with hexane and acetone at room temperature. This extraction was then followed by liquid-liquid extraction with dichloromethane before determination of cypermethrin by use of GC-ECD. There were no interfering peaks seen in GC chromatograms and therefore no clean-up of the extracts was needed. The recoveries ranged between 80.0 % and 101.2 % with standard deviations ranging between 0.6 % and 9.9 %. It was found that addition of 10 ml water per 10 gram of soil prior to the extraction improved the recovery substantially. The recoveries decreased with soil depth as the clay content increased. The limits of detection were in the range of 1.1 µg/kg to 5.9 µg/kg, which is as good as the similar ECM method used for determination of deltamethrin. In conclusion the method is versatile for rapid determination of cypermethrin in clayey tropical top and subsoils of Sarawak.

ABSTRAK Satu kaedah kromatografi gas telah dihasilkan untuk menentukan residu cypermethrin di dalam pelbagai lapisan tanah di Sarawak. Tiga jenis tanah iaitu Semongok (*Paleudults*), Tarat (*Udorthents*) and Balai Ringin (*Kandiudults*) terdiri daripada empatbelas lapisan tanah yang mengandungi kandungan tanah liat (6 - 67 %) and karbon organic tanah (0.22 - 2.20 %) yang berlainan telah digunakan di dalam kajian ini. Sampel tanah dicampurkan dengan tiga kepekatan cypermethrin (0.01, 0.1 and 1 mg/kg) dan diekstak dengan aseton dan hexana pada suhu bilik. Kemudian ia diekstrak dengan dwiklorometana dan ditentukan dengan GC-ECD. Perolehan semula yang diperolehi adalah di antara 80.0 % dan 101.2 % dan deviasi standardnya adalah di antara 0.6 % dan 9.9 %. Penambahan 10 ml air kepada sampel tanah sebelum extraksi dapat memperbaiki kadar perolehan semula. Perolehan semula berkurangan apabila kedalaman tanah meningkat. Tahap penentuan yang diperolehi adalah di antara 1.1 µg/kg to 5.9 µg/kg iaitu lebih kurang sama dengan kaedah ECM yang digunakan untuk menentukan deltamethrin.

(Gas chromatography, cypermethrin, pyrethroid insecticides, tropical soils)

INTRODUCTION

Cypermethrin [(RS)-α-cyano-3phenoxy benzyl(1RS)-*cis,trans*-3-(2,2-dichlorovinyl)2,2-dimethyl cyclopropane carboxylate] (Figure 1) is a pyrethroid insecticide effective against a wide range of insect pests. Cypermethrin has a very low aqueous solubility of 4 µg/L and a corresponding high octanol-water partitioning coefficient (log K_{ow} of 6.6) [1] indicating that it has a high affinity for sorption to soil organic matter [2]. It is used widely in agriculture because of its desirable environmental properties of relatively short persistence and non-toxicity to mammals. It is active against a broad spectrum of insects and comparatively low application rates are needed for insect control. These properties have made the pyrethroids useful alternatives to other groups of pesticides. The main concern with pyrethroids has been due to its high toxicity to fish and aquatic invertebrates. The LC_{50} (96 hour) for cypermethrin in rainbow trout is 0.82 mg/L and in bluegill sunfish as low as 1.8 mg/L [3]. There is only sparse data on the fate of pyrethroids in tropical environments, including tropical soils and thus it is difficult to evaluate to which extent pyrethroids may present a risk to sensitive species in aqueous and terrestrial tropical environments.

Analytical methods for the determination of pyrethroid pesticides have been reported for fruits and vegetables, crops, milk, fish and honey [4 - 10]. The analytical methods for the determination of pyrethroid pesticides in soil have also been reported [11 - 17]. Many of the analytical methods reported in the literature refer to determination of pyrethroid pesticides in top soils and usually involves cleanup steps. In these methods, pyrethroid pesticides have been extracted from the soils using different types of solvents such as acetronitrile, methanol, ethyl acetate, hexane or acidified acetone or combination of two solvents. Solid-phase extraction, solvent partitioning or use of Florisil has been used for cleanup. The pyrethroids are usually determined by gas chromatography, or liquid chromatography.

In this study, a method based on the Environmental Chemistry Method (ECM) provided by the Environmental Protection Agency (EPA) [12] for the determination of deltamethrin in soil has been evaluated and modified for the analysis of cypermethrin in top and subsoil of Sarawak soils. In the ECM method, the soil samples were extracted with hexane:acetone (1:1) and cleaned-up by use of silica gel cartridges. Since soil texture, mineralogy and contents of organic matter may change with depths and varies for soils in different regions, these may affect the efficiency of the method. The objective of the present study was to develop a simple, efficient and accurate method for the determination of cypermethrin in different types and depths of Sarawak soils.

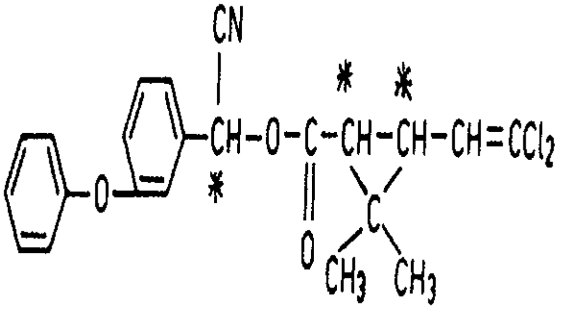


Figure 1. Chemical structure of cypermethrin. Asterisks denote asymmetric carbons. *cis* A = (1 *R-cis-αR*; 1 *S-cis-αS*), *cis* B = (1 *R-cis-αS*; 1 *S- cis-αR*), *trans* C = (1 *R-trans-αR*; 1 *S-trans-αS*) and *trans* D (1 *R- trans-αS*; 1 *S-trans-αR*)

MATERIALS AND METHODS

Reagents and chemicals

Cypermethrin standard (purity 91 %) was obtained from Ehrenstorfer, Germany. Analytical grade acetone and dichloromethane and analytical and residue grade *n*-hexane were purchased from J. T. Baker, USA. Standard pesticide stock solution (500 μg/mL) was prepared by dissolving the cypermethrin standard in residue grade n-hexane. Appropriate aliquots of the stock solutions were diluted with the same solvent to make pesticide stock solutions with concentrations of 10 μg/mL, 1 μg/mL, 0.1 μg/mL and 0.01 μg/mL of cypermethrin, respectively.

Apparatus

Gas Chromatography (GC): An Agilent Model 6890 GC equipped with electron capture detector (ECD) was used for the analysis of cypermethrin. A non polar fused-silica capillary column, Ultra 1 (25 m x 0.32 mm I.D and 0.5 μm film thickness) purchased from J & W Scientific (USA) was used with nitrogen as the carrier gas at a flow of 1.2 ml/min. The column temperature was maintained at 120°C for 0.5 min followed by an increase to 180°C at a rate of 10°C/min followed by a second temperature ramp of 6°C/min to 240°C and subsequently 10°C/min to 280°C and held at 280°C for 12 min. The injector and detector temperatures were maintained at 260°C and 300°C, respectively. The total content of cypermethrin was calculated based on the sum of four individual cypermethrin diastereoisomers as shown in Figure 1.

Extraction and evaporation equipments: An orbital Shaker (Lab-line Instruments Inc., USA) was used in the extraction procedure. A Rotavapor RE 111 rotary evaporator (Switzerland) coupled to a Buchi 461 water bath (Switzerland) and a refrigerated cooler (Polyscience, USA) was used to concentrate the extracts.

Soil samples for recovery studies

Three types of soils were sampled, viz. undisturbed mineral soil, disturbed mineral soil and sandy soil, from the fields at Semongok in Kuching division, Tarat and Balai Ringin in Samarahan division of Sarawak, respectively. The Semongok soil is a red-yellow podzolic soil (*Typic Paleudult;* very fine, mixed, isohyperthermic) and formed from sedimentary rock. The Tarat soil is an alluvial soil formed from basic/intermediate igneous parent material (*Typic Udorthents*; clayey, siliceous, isohyperthermic). The Balai Ringin soil is the grey-white podzolic soil (*Typic Kandiudults*; fine, mixed, isohyperthermic) also formed from alluvium. Debris, plant roots, plant remnants and stones were removed from the soil samples. The soils were air dried and sieved through a 2 mm sieve for the analysis of their physicochemical properties using standard soil analysis methods [18]. For the determination of recovery, naturally moist soil samples were fortified with known amounts of cypermethrin standards. 10 μg, 1 μg and 0.1 μg of cypermethrin were added separately to 10 g of soil to obtain spiking levels of 1 mg/kg, 0.1 mg/kg and 0.01 mg/kg, respectively. The samples were mixed homogenously and left for one hour to allow the solvent to evaporate and to ensure sufficient contact between the pesticide and the soil material. Each sample was prepared in four replicates.

Extraction and GC determination

Fortified soil samples (10 g) were weighed into a 500 ml shaking glass flask. Double deionized water (10 ml) and hexane:acetone (1:1) (150 ml) were added to the flask and the resulting mixture was shaken for one hour on an orbital shaker at 300 rpm. The extract was left to settle and then filtered through a glass filter paper (Whatman GF/C, 1.2 μm) into a receiving flask. The shaking flask and its contents were rinsed twice with the extraction solvents and the supernatant decanted to the filter and all extracts collected in the same receiving flask. The filtrate was evaporated to almost dryness on a rotary evaporator at 40 °C and made up with *n*-hexane (10 ml). In cases where water was found to be present in the final extract after evaporation, the extract was re-extracted twice with dichloromethane (50 ml). The dichloromethane layer was then collected, evaporated to almost dryness and made up with *n*-hexane (10 ml). The final extract (2 μl) was injected into GC-ECD for determination of cypermethrin.

Statistical Analysis

Differences between depths and spiking levels were compared at $p < 0.05$ level using two-way analysis of variance (PC-STAT, University of Georgia, 1985). Multiple linear regressions were used for analysis of correlations between the recovery and the combined effect of clay and organic matter content (recovery (%) = a*clay % + b*carbon %).

RESULTS AND DISCUSSION

Soil Analysis

The data on physiochemical properties of the three soils used in this study are shown in Table 1. The three soils used in this study were all acidic soils with high clay contents in the subsoils. The carbon content in all the top soils were more than 1.5 % and the subsoils also contained relatively high organic carbon except for the Balai Ringin soil. Calcium is the dominating exchangeable cation and larger amounts are found in the top soils of Semongok and Balai Ringin and all the soil horizons of the Tarat soil. Lower amounts of exchangeable Mg, K and Na were found in all horizons of the soils. The cation exchange capacity (CEC_7) was relatively high for the clayey Semongok and Tarat soil profiles whereas the CEC_7 was lower for all horizons of the Balai Ringin soil even the clayey horizons demonstrating that this soil is rather weathered and is dominated by clay minerals with low CEC's, e.g. kaolinite. The base saturation decreased with depth for all three soils. The base saturation was relatively high for all layers of Tarat soil and the topsoils of

Semongok and Balai Ringin. The subsoil of Semongok had lower base saturation than the Balai Ringin soil. In general the base saturation was well correlated with soil pH, lower pH being correlated with lower base saturation percentages. The Semongok and Tarat soils had the highest contents of aluminium oxide which increased with soil depth. A similar trend was observed for the iron oxides found in these soils except for Semongok soil which showed decreasing contents with increasing depth. The differences in soil properties were mainly attributed to the degree of weathering of the soil parent materials.

Recovery studies

In our earlier studies, the recoveries obtained for Semongok, Balai Ringin and Tarat soil at a spiking level of 0.01 mg/kg using the ECM method without modification were 63.2 to 80 %, 65.0 to 100.7 % and 54.6 to 98.5 % respectively, depending on the horizons of the soils. The general trend observed was that the recoveries decreased as the soil depth increased. However, the recovery strongly improved after modifications were made to the method. Examples of chromatograms for the fortified Semongok, Balai Ringin and Tarat soils are shown in Figure 2. No interfering peaks were seen in the interval between 9 to 10 minutes where the cypermethrin isomers eluted.

Tables 2 - 4 list the recoveries of cypermethrin in Semongok, Balai Ringin and Tarat soil at different horizons and at the three fortification levels, respectively using the optimized method. Recoveries obtained for Semongok soil at 1, 0.1 and 0.01 mg/kg fortification levels were 90.6 - 97.5 %, 89.0 - 98.1 % and 80.0 - 92.0 %, respectively whilst for Balai Ringin soil the recoveries were 82.4 - 95.1 %, 89.8 - 98.2 % and 80.2 - 101.2 %, respectively. In the case of Tarat soil, recoveries were in the range of 84.8 - 93.9 %, 85.6 - 92.4 % and 88.7 - 98.5 % for 1, 0.1 and 0.01 mg/kg fortification levels, respectively. In general, these results showed that the recoveries of cypermethrin from the soils were good and comparable to the recovery values reported in the ECM method for deltamethrin for which recoveries were 100% and 89%, respectively for spking levels of 0.002 and 0.02 mg/kg. Relatively small standard deviations between replicates at each fortification level for the three soils (< 8.9%) indicate that the modified method developed in this study has a good reproducibility.

The results of the statistical analysis are shown in Table 5. The two-way analysis of variance which was applied to each soil type separately showed there were no significant differences between recoveries at the three different spiking levels except for the Semongok soil. For this soil the recoveries decreased with decreasing amount of spiked cypermethrin. The Semongok soil is characterized by having the highest amounts of clay and CEC_7 and thus the lower recoveries at low spiking levels may be due to high sorption affinity to clay-organic complexes [19]. There are significant differences seen between recoveries determined for the different horizons (depths) of the three soil profiles. Multiple linear regressions showed that in general there were no significant correlation between recoveries and the combined effect of carbon and clay content in Semongok and Balai Ringin soils at the three levels of fortifications except for Balai Ringin soil fortified at the 0.01 mg/kg level. For this soil, the recoveries decreased with soil depth as clay content increased. Multiple linear regression analysis was not done for the Tarat soil as the soil has only few horizons.

Table 6 reports the limits of detection (LOD) of cypermethrin in the three soils for different horizons. In this study, the LOD is defined as three times the standard deviation of the results of the analysis of four soil samples fortified at the lowest spiking level of 0.01 mg/kg. The LOD's for Balai Ringin and Tarat soil materials were similar and slightly lower than the LOD's obtained for Semongok soil materials. In general, the LOD's obtained in the present study were comparable to the LOD reported for deltamethrin in the ECM method which was 2 μg/kg [12].

Modification of the ECM method as carried out in this study involved the addition of 10 ml of water to 10 gram of soil prior to the extraction procedure. It was found that the addition of water substantially improved the recovery of cypermethrin. It has been reported that the presence of water helps to disperse the structure of the soil in the extraction of simazine from soil [19]. The presence of water allows the extractant to work on a larger surface area of the soil particles. In our earlier study, attempts were made to improve the recovery of cypermethrin by adding 3 ml of 2N ammonium acetate to the clayey soil to improve desorption of pesticides from the soil particles [20] but no significant improvement was observed. The mass of soil sample was reduced by five times and the volume of extraction solvent reduced by half as compared to the original method without loss of accuracy. As the extract did not contain any compounds which may interfere with the GC analysis, SPE cleanup was also omitted in the current method. Instead, solvent partitioning using dichloromethane was used to remove water and interfering compounds from the final extract. The above results clearly document that the modified ECM method is efficient for the determination of cypermethrin in tropical soils of varying types, textures and soil organic matter contents.

Table 1. Physiochemical properties of the soils investigated

	SEMONGOK SOIL					**TARAT SOIL**			**BALAI RINGIN SOIL**					
	0-20 cm	**20-50 cm**	**50-80 cm**	**80-95 cm**	**95-115 cm**	**0-5 cm**	**5-35 cm**	**35-50 cm**	**0-12 cm**	**12-20 cm**	**20-30 cm**	**30-70 cm**	**70-80 cm**	**80-110 cm**
Horizon	A	B_1	B_2	B/C	C	A_1	B_1	B/C	A/Bo	B_1	B_1	B_2	C	C
pH[a]	4.8	4.5	4.6	4.5	4.5	5.6	5.2	5.1	5.6	4.8	4.3	4.1	4.0	4.0
% carbon[b]	2.20	0.92	0.64	0.81	0.80	1.78	1.43	0.88	1.42	0.35	0.22	0.26	0.27	0.27
% clay[c]	23.1	34.2	55.3	66.4	65.7	13.9	37.2	41.6	5.9	11.4	21.8	48.8	67.3	67.4
% silt	29.6	20.5	19.7	17.2	21.7	15.4	18.0	13.3	16.4	15.2	12.9	12.8	9.3	11.4
% fine sand	9.8	6.4	4.1	3.5	3.9	44.1	23.1	26.1	27.9	26.1	26.8	16.4	8.8	7.6
% coarse sand	37.6	30.6	21.0	12.4	8.8	26.6	21.8	19.1	49.9	47.3	38.6	22.0	14.7	13.7
Ca (cmol/kg)	3.7	1.3	0.8	0.7	0.5	8.6	6.6	4.9	3.6	1.2	1.0	0.9	0.7	0.5
Mg (cmol/kg)	0.7	0.2	0.1	0.2	0.2	1.5	1.0	0.8	0.5	0.4	0.4	0.4	0.3	0.2
K (cmol/kg)	0.2	0.1	0.2	0.3	0.3	0.9	0.7	0.7	0.1	0.1	0.1	0.2	0.2	0.2
Na (cmol/kg)	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.4	0.2	0.1	0.2	0.3	0.2	0.3
CEC_7[d] (cmol/kg)	11.8	12.1	17.2	21.6	23.3	16.2	16.2	14.4	5.0	5.0	5.9	8.1	7.6	9.2
% base saturation	40	15	8	6	4	70	53	47	88	34	29	21	18	12
Al oxides[e] (mmol/kg)	56.4	78.9	111.6	133.2	146.4	63.0	98.5	155.2	12.0	7.5	12.5	19.2	27.4	35.0
Fe oxides[e] (mmol/kg)	196.5	238.6	239.6	136.0	96.4	117.7	143.1	167.3	29.1	21.7	32.6	55.0	48.5	53.2

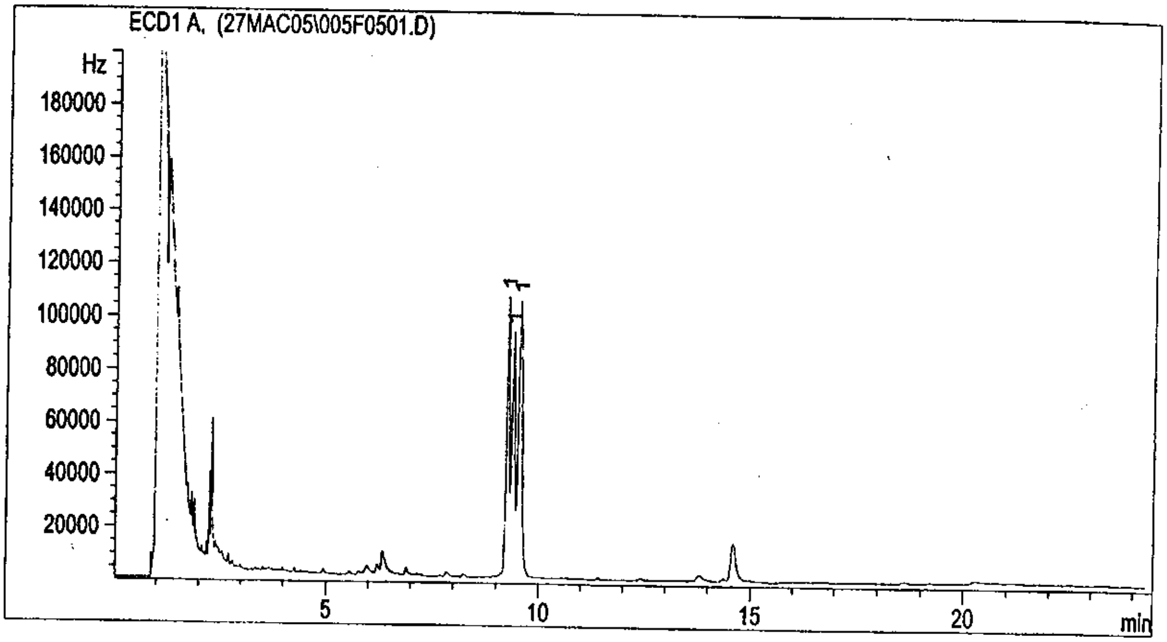
[a] pH determined in 0.01 M $CaCl_2$ in a 1:1 soil:water suspension

[b] Mass percentage of carbon determined by dry combustion

[c] Particle size distribution determined by sieving and sedimentation (clay < 2 μm, 2 μm < silt < 20 μm, 20 μm < fine sand < 200 μm, 200 μm < coarse sand < 2000 μm)

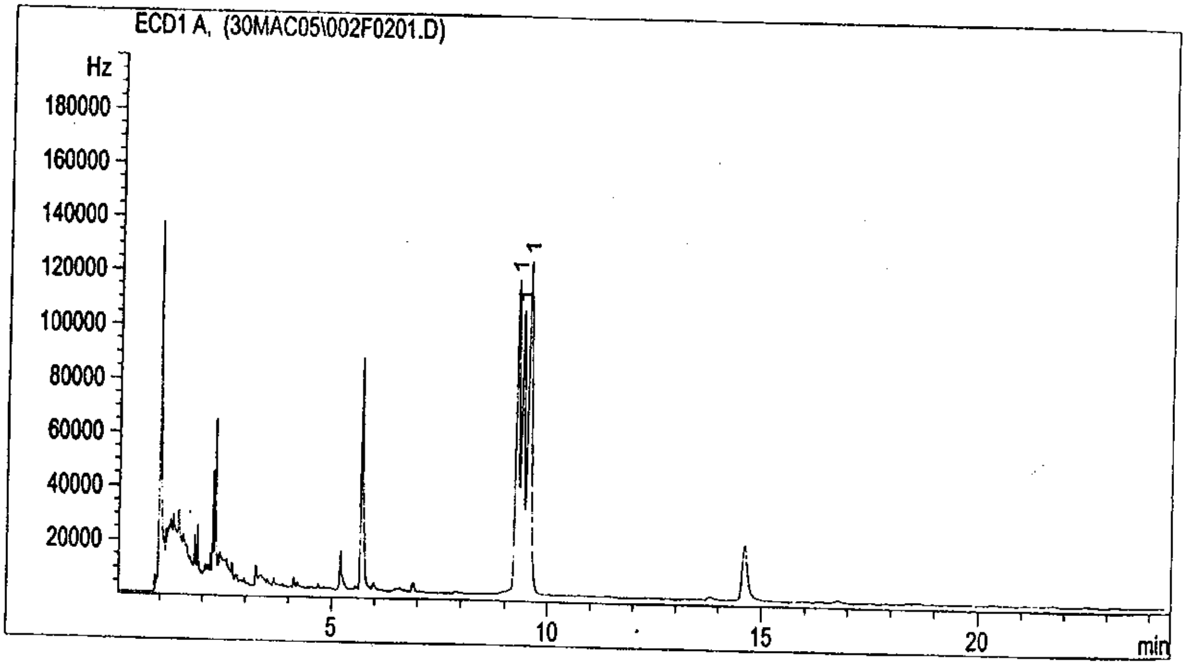
[d] CEC_7 : cation exchange capacity determined by the ammonium acetate method (pH 7)

[e] Aluminum and iron oxides determined by dithionite-citrate-bicarbonate method



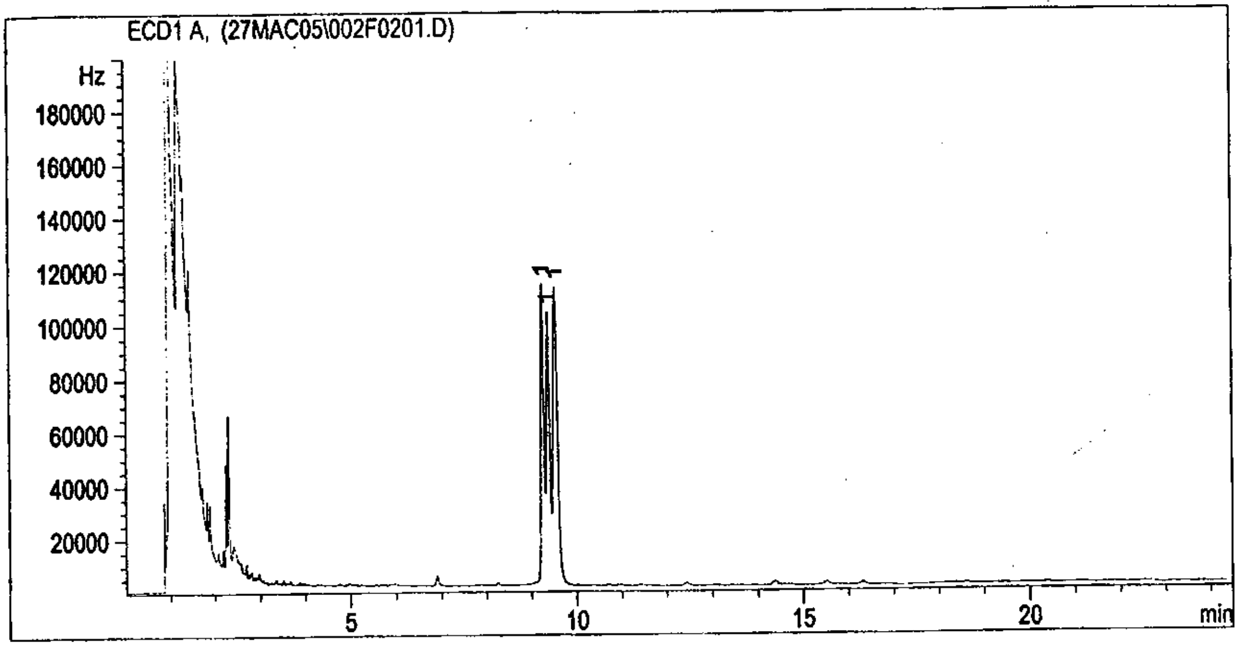
Y axis: Detector response **x axis: Time (min)**

Figure 2a. Chromatograms for cypermethrin (1) fortified at 1 mg/kg for top soil of Semongok. First peak (*cis* A), second peak (*trans* C) and last peak (*cis* B + *trans* D)



Y axis: Detector response **x axis: Time (min)**

Figure 2b. Chromatograms for cypermethrin (1) fortified at 1 mg/kg for top soil of Balai Ringin. First peak (*cis* A), second peak (*trans* C) and last peak (*cis* B + *trans* D)



Y axis: Detector response **x axis: Time (min)**

Figure 2c. Chromatograms for cypermethrin (1) fortified at 1 mg/kg for top soil of Tarat. First peak (*cis* A), second peak (*trans* C) and last peak (*cis* B + *trans* D)

Table 2. Recovery of cypermethrin from fortified Semongok soil

DEPTH OF SOIL	**TEXTURE**	**% RECOVERY[a] ± SD**		
		1 mg/kg	**0.1 mg/kg**	**0.01 mg/kg**
0 - 20 cm	Loam	93.8 ± 4.6	96.0 ± 6.1	81.1 ± 2.6
20 - 50 cm	Clay loam	97.5 ± 4.0	91.6 ± 4.2	92.0 ± 7.4
50 - 80 cm	Clay	90.6 ± 7.3	89.0 ± 8.3	82.5 ± 7.9
80 - 95 cm	Clay	94.9 ± 2.6	98.1 ± 4.6	80.0 ± 4.9
95 - 115 cm	Clay	95.3 ± 7.5	91.9 ± 4.1	85.8 ± 5.9

SD : standard deviation a : replicate of four samples

Table 3. Recovery of cypermethrin from fortified Balai Ringin soil

DEPTH OF SOIL	**TEXTURE**	**% RECOVERY[a] ± SD**		
		1 mg/kg	**0.1 mg/kg**	**0.01 mg/kg**
0 - 12 cm	Loamy sand	95.1 ± 3.1	89.8 ± 6.8	88.7 ± 4.8
12 - 20 cm	Sandy loam	86.3 ± 4.3	93.5 ± 4.3	101.2 ± 3.7
20 - 30 cm	Sandy clay loam	89.4 ± 1.9	92.3 ± 9.9	97.1 ± 3.9
30 - 70 cm	Clay	82.9 ± 1.8	92.7 ± 5.5	89.0 ± 5.4
70 - 80 cm	Clay	85.5 ± 1.0	92.6 ± 4.8	83.6 ± 5.4
80 - 110 cm	Clay	85.5 ± 5.3	98.2 ± 7.0	80.2 ± 8.0

SD : standard deviation a : replicate of four samples

Table 4. Recovery of cypermethrin from fortified Tarat soil

DEPTH OF SOIL	TEXTURE	% RECOVERY ± SD		
		1 mg/kg	**0.1 mg/kg**	**0.01 mg/kg**
0 - 5 cm	Loamy sand	92.7 ± 4.1	92.4 ± 5.2	98.5 ± 7.6
5 - 35 cm	Sandy clay	93.9 ± 5.3	85.6 ± 0.6	88.7 ± 5.6
35 - 50cm	Sandy Clay	84.8 ± 5.6	89.2 ± 5.4	92.9 ± 4.0

SD: standard deviation a: replicate of four samples

Table 5a. Statistical analysis of recovery data: Two-way analysis of variance

VARIABLE	SEMONGOK SOIL	BALAI RINGIN SOIL	TARAT SOIL
		p VALUES	
Soil depth	1.1017 (d.f. = 4,8)	0.6947 (d.f. = 5,10)	1.8304 (d.f. = 2,4)
Pesticide Concentration	11.1236* (d.f. = 2,8)	1.4985 (d.f. = 2,10)	0.9186 (d.f. = 2,4)

5 % significant level : 3.84 (d.f. = 4,8), 4.46 (d.f. = 2,8), 3.33 (d.f.=5,10), 4.1 (2, 10), 6.94 (d.f. = 2,4) ; * significant difference between recovery and pesticide concentration

Table 5b. Statistical analysis of recovery data: Multiple linear regressions

	SEMONGOK SOIL			BALAI RINGIN SOIL		
	p VALUES					
	1 mg/kg	0.1 mg/kg	0.01 mg/kg	1 mg/kg	0.1 mg/kg	0.01 mg/kg
% carbon, % clay	0.0532 (d.f.=2,2)	0.933 (d.f.=2,2)	1.52 (d.f.=2,2)	5.8779 (d.f.=2,3)	1.3360 (d.f.=2,3)	54.9697* (d.f.=2,3)

5 % significant level : 19 (d.f.=2,2), 9.55 (d.f.=2,3), * significant difference between recovery and the effect of carbon and clay

Table 6. LOD of cypermethrin for Semongok, Balai Ringin and Tarat Soils

SEMONGOK SOIL		BALAI RINGIN SOIL		TARAT SOIL	
DEPTH/cm	**LOD/μg/kg**	**DEPTH/cm**	**LOD/μg/kg**	**DEPTH/cm**	**LOD/μg/kg**
0 - 20	0.8	0-12	1.4	0-5	2.3
20 - 50	3.5	12-20	1.1	5-35	1.7
50 - 80	5.9	20-30	1.2	35-50	1.3
80 - 95	1.5	30-70	1.6		
95 - 115	3.2	70-80	1.6		

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