

ADSORPTION OF FORMULATED CHLORPYRIFOS ON SELECTED AGRICULTURAL SOILS OF TERENGGANU

(Penjerapan Rumusan Klorpirifos ke atas Tanah Pertanian Terpilih di Terengganu)

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Abstrak

Penjerapan insektisid klorpirifos (rumusan komersil berjenama Kensban®, 20% bahan aktif) pada tiga jenis siri tanah (0-25cm) dari kebun sayur-sayuran di negeri Terengganu, Malaysia telah dikaji menggunakan kaedah penjerapan kelompok. Analisis insektisid dijalankan menggunakan kaedah kromatografi gas dilengkapi dengan pengesanan nitrogen and fosforus. Keputusan menunjukkan bahawa tanah yang mengandungi lebih banyak jirim organik dan lempung mempunyai keupayaan menjerap insektisid yang lebih kuat. Selain itu, pH tanah juga mempengaruhi keupayaan penjerapan insektisid di mana penjerapan adalah lebih tinggi pada tanah yang mempunyai nilai pH yang rendah. Secara keseluruhannya, kandungan jirim organik, kandungan lempung dan pH memainkan peranan yang penting dalam penjerapan insektisid klorpirifos. Walau bagaimanapun, tidak boleh dinafikan bahawa keupayaan penjerapan yang diperolehi dalam kajian ini mungkin juga dipengaruhi oleh interaksi di antara klorpirifos, pelarut, pengemulsi, air dengan tapak penjerapan tanah memandangkan klorpirifos yang digunakan adalah formulasi komersil.

Kata kunci: penjerapan, klorpirifos, insektisid organofosforus, tanah pertanian, GC-NPD

Abstract

In this study, the adsorption of commercially formulated chlorpyrifos (trade name Kensban®, 20% a.i.) in three soil samples (0-25cm depths) collected from vegetable farms in the state of Terengganu, Malaysia has been investigated using a batch technique. Analysis of the insecticide was carried out using gas chromatography equipped with nitrogen and phosphorus detector. Result indicated that, soils contained higher organic matter and clay content exhibited a much stronger adsorption affinity for the insecticide. In addition, soil pH was also observed to play a role in influencing the adsorption affinity of this insecticide where a higher adsorption was observed for soils with lower pH values. Results from this study clearly showed that, in agreement with previously reported studies, soil properties particularly organic matter content, clay content and pH play an important role in controlling the sorption behaviour of chlorpyrifos insecticide. However, it must be conceded that the measured adsorption in this study might also be influenced by a number of processes occurred in the soil, such as complex interaction between chlorpyrifos, solvent, emulsifier, water and the soil sorption sites since the applied chlorpyrifos was a commercial formulation.

Keywords: adsorption, chlorpyrifos, organophosphorus insecticide, agricultural soil, GC-NPD

Introduction

Chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothionate) (Figure 1) is a broad-spectrum insecticide whose mode of activity is as a cholinesterase inhibitor. It is used to kill a wide variety of insects including cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice by disrupting their nervous system. It is also used as a soil treatment (pre-plant and at planting), as a seed treatment and as a foliar spray, directed spray and dormant spray. It has been speculated that the bioaccumulation ability of chlorpyrifos and other organophosphorus pesticides in living tissues may spell a potential environment risk to marine organisms and humans [1]. Recently, the U.S. Environmental Protection Agency (USEPA) and the manufacturers of chlorpyrifos have agreed to eliminate nearly all-household applications of chlorpyrifos, but agriculture use continues [2]. Because of its low water solubility and relatively high log K_{ow} (Table 1), the sorption of chlorpyrifos will play a crucial role in determining its fate and transport in the environment. This adsorption process in turn, is influenced by the soil properties, chemical nature of the insecticide and also climatic factors.

Although the sorption behaviour of this insecticide has been well studied under temperate climate, similar information under tropical climate is still limited, especially on formulated chlorpyrifos. Several reports have been published in recent years on the dissipation of chlorpyrifos in Malaysian soils [3-4] but very limited report on adsorption study. The objective of this study was to investigate the adsorption of chlorpyrifos in selected agricultural soils of Malaysia in order to provide data to assess the potential risk of pollution to the environment.

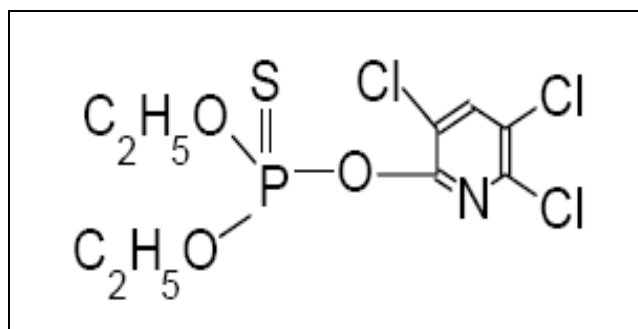


Figure 1: Structure of chlorpyrifos.

Table 1: The physical and chemical properties of chlorpyrifos.

Insecticide	Melting point (°C)	Molecular weight	Vapour pressure (mPa at 25°C)	Water solubility (ppm at 25°C)	Log K _{ow} (at 25°C)
chlorpyrifos	41-43	350.6	3.35	2	4.98

Materials and methods

Three surface (0-25cm) soil samples were obtained from vegetable farms in Marang (*Nami* and *Chempaka* series) and Kuala Terengganu (*Sabrang* series). Bulk soils were air-dried, ground and passed through a 2mm sieve. Sub-samples of freshly collected soils were dried at 110°C until there is no significant change in weight (approx. 24h) to determine the initial soil moisture content. Soil pH was determined in a 1:2.5 soil/water suspension; soil organic matter (OM) by Walkley and Black's Titration Method [5]; particle size distribution by using pipette method; clay mineralogy analysed using Philips X-ray diffraction system.

The commercial formulation of chlorpyrifos (trade name Kensban®) which contains 20% of active ingredient was used in this study. All insecticide solutions were prepared in 0.02M calcium chloride and its concentration was determined by using ThermoFinnigan Gas Chromatography (GC) fitted with ATTM-1 Capillary Column (0.25µm x 0.25mm x 30m Alltech) and a Nitrogen Phosphorus Detector (NPD). The column temperature was programmed from 125 to 230°C at rate of 30°C/min, held at 230°C for 6 min, the detector and injector temperatures were 300 and 200°C, respectively. Adsorption study was carried out using a batch equilibrium method. Triplicate samples of the air-dried soil (1g) were equilibrated with 5ml of insecticide solutions (initial concentration, C_i = 0-25 mg/L), shaken for 2h and 24h, allowed to stand followed by centrifugation. The clear supernatants obtained were extracted three times using n-Hexane (10mL, 5mL and 5mL, respectively) and analysed for their insecticide content using GC-NPD technique described above. The amount of insecticide adsorbed by the soil was estimated as the differences between that initially present in solution (C_i) and that remaining after equilibration with soil (C_e).

Results and discussion

The physicochemical properties of the soils are given in Table 2. The *Chempaka* soils was observed to have significantly lower ($p < 0.05$) pH value compared to other soil series. Results showed that all soil studied exhibited similar OM content and statistical analysis showed the differences were insignificant ($p > 0.05$). Clay mineral analysis showed that muscovite-3, kaolinite and gibbsite is the most abundant mineral in soil samples.

Table 2: Physicochemical properties of soil samples.

Soil	moisture content (%)	pH in water	pH in CaCl ₂	% OM	% sand	% clay	% silt	texture	Clay mineralogy*
<i>Chempaka</i>	20.4	4.52	4.07	2.08	30.1	31.7	38.2	Clay loam	M, K, Q
<i>Sabrang</i>	13.9	4.91	4.34	1.92	69.6	10.1	20.3	Sandy Loam	M, K, G, Q
<i>Nami</i>	15.7	5.32	4.51	1.94	48.5	10.2	41.3	Loam	K, G, Q

*M = Muscovite-3, K = Kaolinite, G = Gibbsite, Q = Quartz

The adsorption isotherms for chlorpyrifos in the soil samples are shown in Figure 2 and Figure 3. Two different equilibration times (2h and 24h) has been chosen for comparison. The distribution coefficient (K_d), which represents the partitioning of the insecticide between liquid (C_e) and solid phases (C_s) in equilibrium and typically known as a linear adsorption isotherm, was calculated using equation $C_s = K_d C_e$. The empirical Freundlich adsorption isotherm ($C_s = K_f C_e^{1/n}$), which allows the evaluation of experimental constants K_f and n , was also calculated using the linearised form of the equation ($\text{Log } C_s = \text{Log } K_f + 1/n \text{ Log } C_e$). The Freundlich isotherm takes into consideration the non-linearity of sorption at increasing concentration and the value of K_f will equal K_d when n equals 1. The values of the K_d and Freundlich constants K_f and n thus obtained are given in Table 3. Evaluation of the values shows that the linear adsorption isotherm could fit the data better than the Freundlich adsorption isotherm.

Table 3: Distribution coefficient (K_d) and Freundlich constants (K_f and n) for adsorption of chlorpyrifos on various soil samples.

Equilibration time (hour)	Soil	K_d	R^2	K_f	n	R^2
2h	<i>sabrang</i>	195	0.62	153	1.36	0.32
	<i>chempaka</i>	241	0.76	200	1.26	0.56
	<i>nami</i>	185	0.30	0.71	-0.21	0.30
24h	<i>sabrang</i>	289	0.69	700	0.56	0.38
	<i>chempaka</i>	346	0.42	82.0	6.29	0.00
	<i>nami</i>	231	0.84	493	0.57	0.83

The adsorption capacity of the soils towards chlorpyrifos was evaluated by comparing the values of K_d obtained. The isotherm was S-type for all samples investigated indicating a low herbicide-soil affinity at low herbicide concentrations. However, once the chlorpyrifos molecule begins to adsorb it is easier for additional amounts to become stabilized on the soil surface and lead to enhanced affinity of the soil surface for chlorpyrifos with increasing amounts adsorbed. Great difference between K_d values obtained using 2h and 24h equilibration time

indicated that the adsorption of formulated chlorpyrifos is characterized by a rapid initial process, followed by a slower stage and needed longer time to reach equilibrium.

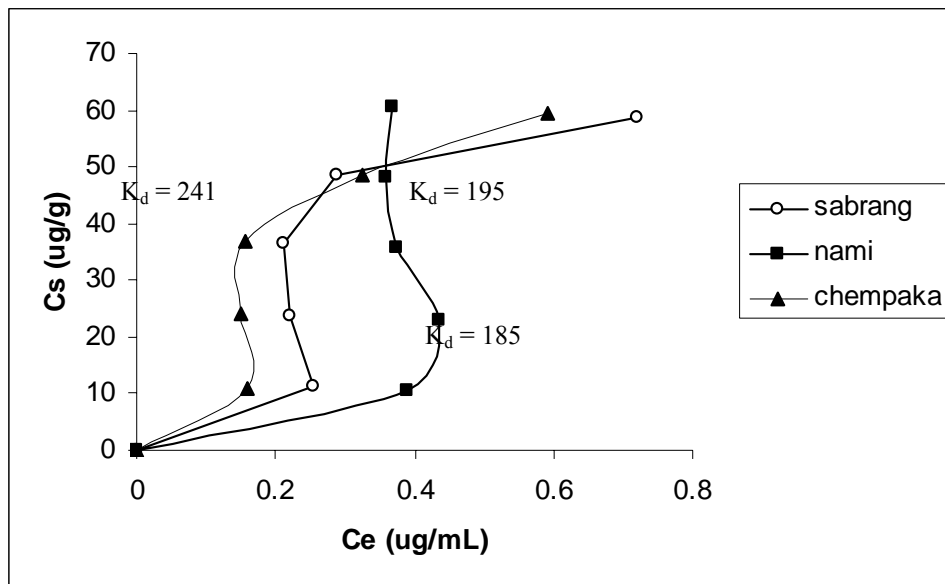


Figure 2: Adsorption isotherm of chlorpyrifos in soil samples with 2h equilibration time.

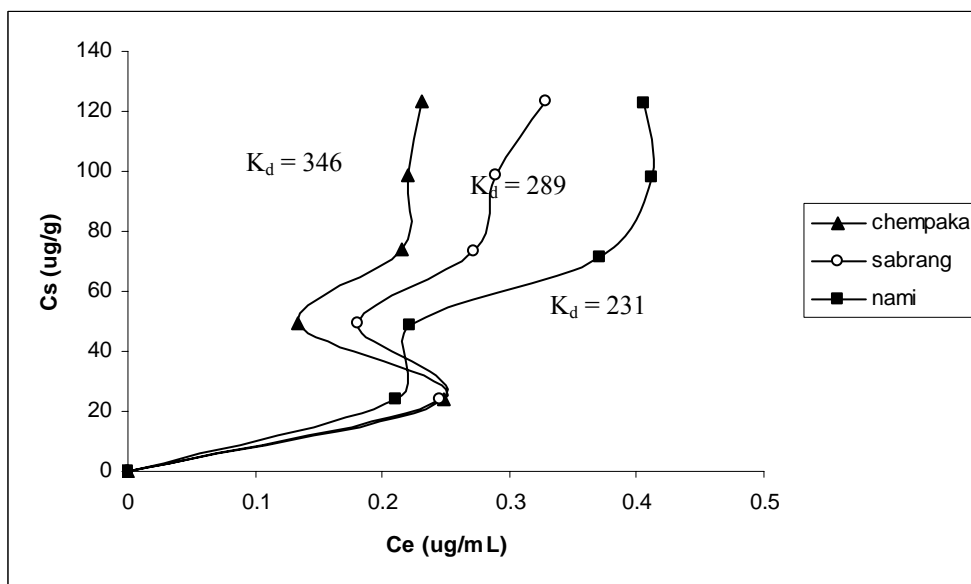


Figure 3: Adsorption isotherm of chlorpyrifos in soil samples with 24h equilibration time.

In order to assess the factors that affect the adsorption of formulated chlorpyrifos by soil, the K_d values were correlated with the soil properties (Table 4). *Chempaka* soil with higher OM and lower pH exhibited the highest value of K_d (for both 2h and 24h equilibration time) compared to *Sabrang* and *Nami* soil series. OM has been reported to be one of the major factors that influence the extent of pesticide adsorption on soils and results obtained in this study are in agreement with earlier reports [6-8]. The correlation coefficient was found to be 0.96 and 0.81 for 2h and 24h adsorption, respectively, indicating strong positive correlation between OM and adsorption even though the OM content in soil samples was low.

It has also been reported that for soils with low OM content the interactions of pesticides with soil inorganic matrix may become more important [9]. Correlation analysis between K_d and % clay in this present study gives value of 0.99 and 0.86 for 2h and 24h equilibration time, indicating strong correlation between clay content and adsorption affinity of chlorpyrifos. However, the correlation was not statistically significant ($p>0.05$). Interaction study of acephate (an organophosphorus insecticide) with montmorillonite (a mineral of the group of smectites) by Gonzalez-Pozuelo *et al.* in 1991 [10] showed that the pesticide is adsorbed into the interlayer space of the smectite forming a stable complex. Similar finding had been reported by Hernández-Soriano *et al.* [9], in which the adsorption of malathion (an organophosphorus insecticide) was enhanced for clayey soils. However, soil samples used in this study are dominated by kaolinite, gibbsite, muscovite-3 (mica group) and quartz which do not contain the microporous structure that is present in montmorillonite. Haderlein and Schwarzenbach [11] found a specific adsorption of nitroaromatic compounds (NACs) to the silanol surface sites of kaolinite. They proposed that an electron donor-acceptor complex (i.e., a π complex) between electron donor functions at the siloxane surface and the aromatic ring system of the NAC is responsible for the observed specific adsorption. This may also be a plausible mechanism for the adsorption of the uncharged chlorpyrifos investigated in this study.

Table 4: Correlation coefficients between K_d values and soil parameter.

Soil parameter	<i>r</i>	
	2h equilibration time	24h equilibration time
% organic matter	0.96	0.81
% clay	0.99	0.86
pH in CaCl ₂	-0.98	-0.99*

*: correlation is significant at the 0.05 level.

Study by Van Emmerik *et al.* [2] showed that the adsorption of chlorpyrifos on gibbsite is dependent on pH (adsorption decreased when pH increased) but only has little effect on chlorpyrifos adsorption by kaolinite. The result obtained in this present study showed that soil with lower pH (*Chempaka* series) exhibited higher adsorption capacity for chlorpyrifos, with correlation coefficient of -0.98 and -0.99 between K_d and pH (for 2h and 24h equilibration time, respectively). The reduction in chlorpyrifos adsorption as the pH increases might be due to an increase in negative surface charge at the edges of clay.

However, it must be conceded that the measured adsorption in this study may also involve a number of other processes that occurred in the soil because the chlorpyrifos applied was a commercial formulation containing aromatic hydrocarbons as a co-solvent. Complex interaction between chlorpyrifos, solvent, emulsifier, water and the soil sorption sites may have occurred, in which chlorpyrifos and solvent may compete for the same sorption sites. Since chlorpyrifos has greater affinity for solvent than water ($\text{Log } K_{ow} = 4.98$), solvent adsorption at soil surface may also enhance chlorpyrifos adsorption at that site. Therefore, the measured sorption may be the result of simple sorption, competitive or cooperative sorption involving chlorpyrifos and solvent. Comparison with previous studies using non-formulated chlorpyrifos (Baskaran *et al.*, 2003; Huang, 1999) showed that formulated chlorpyrifos exhibited higher adsorption coefficient (K_d). This result indicated that the presence of additive(s) in commercial formulation could enhance chlorpyrifos adsorption at soil surface.

Conclusions

Results obtained in present study indicated the influences of soil organic matter content, clay content and soil pH on the adsorption of formulated chlorpyrifos in selected Terengganu agricultural soils. In general, soils with higher organic matter content, higher clay content and lower pH value exhibited stronger adsorption affinity for the insecticide. Consistent with previously reported work, soil properties particularly organic matter content, clay content and pH play an important role in controlling the sorption behaviour of chlorpyrifos. However, the measured adsorption in this study may also involve a number of processes that occurred in the soil because the chlorpyrifos applied was a commercial formulation. Complex interaction between chlorpyrifos, solvent, emulsifier, water and the soil sorption sites may have occurred, in which solvent may enhance chlorpyrifos adsorption at that site. Although formulated chlorpyrifos is mainly used for environmental fate studies rather than sorption studies, results obtained in this study suggest that mechanisms for sorption of formulated chlorpyrifos should also be more thoroughly investigated as sorption processes will undoubtedly influence the fate of this pesticide in the environment.

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