

## Potential of Agricultural By-product in Reducing Chlorpyrifos Leaching Through Soil

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**Abstract:** This study was conducted to determine the minimization of chlorpyrifos, an organophosphate pesticide, in leachate after spraying onto plants by agricultural by-product. Agricultural by-product samples including coconut husk, peat moss, rice husk and peanut shell were investigated in comparison to a sandy soil sample taken from orange grove. Batch partitioning experiments were initially conducted to evaluate sorption capacity of these sorbents. The experiments revealed that peat moss could sorp chlorpyrifos higher than coconut husk, rice husk and peanut shell, respectively. For soil, sorption obviously gave lower values than all agricultural-by product samples. Sorption coefficient ( $K_d$ ) values were increased with increasing organic carbon contents in sorbent, which indicated that organic carbon played an important role in sorption of chlorpyrifos. Half-life ( $t_{1/2}$ ) of chlorpyrifos in coconut husk was 8.6 days, which was reported to be the fastest among the tested biomass, whereas; its half-life was 56.8 days in soil. The results suggested that the sorped chlorpyrifos could be degraded afterward. To find the optimum depth before use in the field, leaching experiments were carried out by packing 2, 3 and 4 cm coconut husk in columns and sprayed with  $0.25 \text{ kg ha}^{-1}$  chlorpyrifos to the column surface. Results indicated that 97.02, 99.62 and 99.96% of chlorpyrifos mass could be retained in coconut husk at 2, 3 and 4 cm depth, respectively. Therefore, coconut husk was recommended as sorbent material due to the combination of high sorption capacity and enhanced biodegradation properties.

**Key words:** Coconut husk, half-life, chlorpyrifos

### INTRODUCTION

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate) is used worldwide as an agricultural organophosphate insecticide. Its environmental fate has been extensively studied and the reported half-life in soil varies from 10 to 120 days (Singh, 2003). Agricultural land is major source of pesticides due to the run off and leaching events that could affect the soil surface. In order to protect the environment and human health, the study focused on the protection of ground water by prevention of contaminant transport in infiltrating water from the soil surface to the water table. One of these challenges is achieving pesticide longevity in the sorptive or immobilizing zones by the incorporation of the appropriate sorbent in the affected area of soil (Xu *et al.*, 1997; Vischetti *et al.*, 2004). It is important that pesticide should sorbed well and retained long enough to provide an available condition for microbial degradation.

Application of agriculture by-product, which is exogenous organic matter to soil, is being use as an alternative method for disposal. Organic carbon or organic matter in agricultural by-product is one key of parameters in the sorption and degradation process of pesticides in soils (Dennis *et al.*, 2004). According to the high organic matter, agricultural by product cannot only promote sorption of pesticides by retarding their movement but also affect the biodegradation of pesticides by enhancing microbial activity and consequently, promoting biodegradation (Perrin-Ganier *et al.*, 2001; Albarain *et al.*, 2004; Vischetti *et al.*, 2004; Jensen *et al.*, 2004). Therefore, the purpose of this study was to assess the possibility of using agricultural by-product; namely coconut husk, peat moss, rice husk and peanut shells as sorbent material to prevent leaching from sprayed chlorpyrifos to soil. Sorption capacity of chlorpyrifos was investigated by batch partitioning behavior in comparison with native soil from tangerine orchard in Mae Ai,

Chiangmai Province. The degradation of chlorpyrifos after sorption was also determined. Finally, the appropriate depth of the selected biomass on soil to prevent chlorpyrifos discharge was obtained from leaching test.

## MATERIALS AND METHODS

**Materials:** Four agricultural by-products under this study are coconut husk, rice husk, peat moss and peanut shell. They were air dried, sieved through 500  $\mu\text{m}$  and stored in the sealed plastic containers at room temperature. One sample of soil was collected from the tangerine orchard at Mae Ai, Chiangmai, Thailand. The top 15 cm of the soil was collected by using a shovel and sample scoop and stored in plastic bag before air dried, stones and debris were removed and the remaining soil was sieved to 500  $\mu\text{m}$  prior to use. The biomass and soil were analyzed for their physical and chemical properties as shown in Table 1.

Standard chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate (> 99%)), was purchased from Chem Service Inc., West Chester, PA, U.S.A. Its solubility is 2 mg L<sup>-1</sup>. Figure 1 shows the chemical structure of the test compound.

**Batch sorption studies:** Sorption studies were performed in triplicate partitioning experiments at room temperature. The partitioning experiments were carried out at the concentrations ranged from 0.05, 0.12, 0.18 and 0.25 times the maximum aqueous solubility of chlorpyrifos in Phosphate Buffer pH 7. The 20 g soil or 2 g of each biomass were mixed with 40 mL of chlorpyrifos solution. This experiment operated at 48 h. Differences between initial chlorpyrifos concentration (C<sub>i</sub>) and equilibrium chlorpyrifos concentration (C<sub>e</sub>) were assumed to be the amount sorbed by biomass and soil. Sorption isotherms were fit to the linear equation and distribution coefficients, K<sub>D</sub> were calculated.

**Biodegradation studies:** Portions of 5 g of soil and 0.5 g of each biomass at optimum particle size were packed and adjusted moisture at 70% of water holding capacity in 22 mL vial to make soil microcosm. Chlorpyrifos was spiked at concentration of normal agricultural application rate of dry soil and biomass. The microcosms were maintained at room temperature. The changes of chlorpyrifos concentration were monitored in soil and biomass from 0, 7, 14, 21, 28 and 35 days. Chlorpyrifos residues were extracted and determined by Gas Chromatography. Half-life of chlorpyrifos was determined by kinetic equation.

**Leaching studies:** Coconut husk were added to the separate glass columns (70 mm × 38.5 id mm) at 2, 3 and

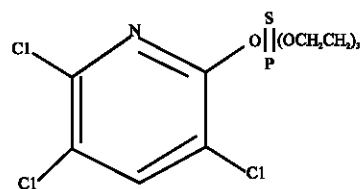


Fig. 1: Structure of chlorpyrifos

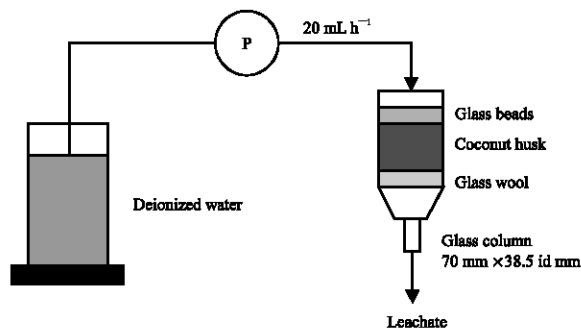


Fig. 2: Diagram of leaching studies

Table 1: Properties of the four agricultural by-product and soil

Properties	Coconut husk	Rice husk	Peat moss	Peanut shell	Soil
Organic carbon (% dry weight)	45.39	35.44	49.42	41.61	1.29
Organic matter (% dry weight)	78.62	61.10	85.20	70.73	2.22
pH	5.30	6.30	5.20	5.50	4.40
Nitrogen (%)	4.63	4.01	4.77	3.42	0.07
Phosphorus (mg kg <sup>-1</sup> )	369.00	118.00	310.00	373.00	229.00
Price kg <sup>-1</sup> (\$)	0.25	0.25	1.25	0.25	none

4 cm depths. The columns were lined below with glass wool to avoid biomass leakage and small glass beads on top in order to distribute water evenly over the biomass surface (Fig. 2). All column samples were spiked with chlorpyrifos 0.0291 mg. Its mass is equivalent to the actual application rates at 0.25 kg ha<sup>-1</sup> of chlorpyrifos employed on a tangerine orchard in Thailand. The columns were then left 24 h before leaching. Deionized water was simultaneously added at 20 mL h<sup>-1</sup>, the current average watering regime in the orchard. Leachate collection was started after about 30 mL drained out and afterwards every pore volume until no chlorpyrifos was occurred in the collected water.

**Analysis of samples:** Solvent extraction was used to extract chlorpyrifos from both liquid and solid samples. This method is modified from extraction of organochlorine pesticides in soil and water (Kraijitmate, 2004). The solvent used in this experiment is a mixture of hexane and acetone at 8:2 ratio. For liquid samples, 20 mL solution samples were transferred into a new 125 mL flask and then

20 mL of solvent were added, for soil samples, 20 g of soil samples were added with 40 mL of solvent and 5 mL of 15% Triton x-100. For biomass samples, 2 g of biomass samples were mixed with 40 mL of solvent and 5 mL of 15% Triton x-100. The samples were mixed and shook at 250 rpm for 4 h. After the samples are being shaken, the flasks were frozen at  $-4^{\circ}\text{C}$  to solidify the lower aqueous layer and then solvent were transferred to vial where 2-3 g of  $\text{Na}_2\text{SO}_4$  were added to dewater the sample. Chlorpyrifos dissolved in solvent fraction were concentrated using nitrogen 99.5% blower. Then the extracted samples were transferred to gas chromatography vials for analysis using gas chromatography equipped with an electron capture detector (GC-ECD) and a HP-5 (5% Phenyl Methyl Siloxane) fused-silica capillary column (30 m  $\times$  0.32 mm ID; thickness 0.25  $\mu\text{m}$ ). The following operating conditions were used: injector temperature  $250^{\circ}\text{C}$ , detector temperature  $250^{\circ}\text{C}$ , initial column temperature  $120^{\circ}\text{C}$  then, programmed at 120 to  $250^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C min}^{-1}$  (3 min) and 250 to  $300^{\circ}\text{C}$  at a rate of  $\text{min}^{-1}$  (4 min). A post column temperature of  $325^{\circ}\text{C}$  were held for 3 min. The carrier gas is helium with gas flow  $20\text{ mL min}^{-1}$  and a 5:1 split ratio. The make up gas is  $\text{N}_2$  at  $60\text{ mL min}^{-1}$ .

## RESULTS AND DISCUSSION

**Batch sorption studies:** Batch sorption studies were conducted to determine sorption coefficient ( $K_D$ ) of chlorpyrifos in each sorbent and soil. In this experiment,  $K_D$  values were obtained from the slope of linear isotherm which theoretically observed if the equilibrium aqueous phase organic compound concentrations are below  $10^{-5}\text{ M}$  or one-half the aqueous phase solubility (whichever is lower) and the organic content of the solid is greater than 0.1% (LaGrega *et al.*, 2001; Smith *et al.*, 2003; Suthersan, 2002). In addition, isotherms of nonionic organic compounds (e.g., organophosphate pesticides) are often assumed to be linear (Chiou, 1989; Hamaker and Thomson 1972; Karickhoff, 1984; Smith, 2003). A linear relationship represented by the following equation;

$$K_D = C_s/C_w \quad (1)$$

Where,  $C_s$  and  $C_w$  are the concentrations of the chlorpyrifos sorbed by biomass or soil ( $\text{mg kg}^{-1}$ ) and dissolved in aqueous phase ( $\text{mg L}^{-1}$ ), respectively. Units of  $K_D$  are given as  $\text{L kg}^{-1}$

The sorption isotherm revealed that all sorption data fitted well to linear isotherm. All regression generated had  $R^2 > 0.95$ . The results were reported in Table 2. The sorption coefficient of soil was  $107.9\text{ L kg}^{-1}$ , while  $K_D$  of

coconut husk, peat moss, rice husk and peanut shell were 1,475.4, 3,371.4, 1,316.5 and  $1,072.2\text{ L kg}^{-1}$ , respectively. As a result, sorption capacities of all biomass were higher than soil. The results showed that  $K_D$  values were correlated with organic carbon contents in soil and biomass; for instance, soil had lowest sorption coefficient value due to its lower organic content than every biomass. This relationship indicated that organic carbon played a major role in the sorption of chlorpyrifos in soil and biomass prior to Dennish *et al.* (2004) reported on a positive linear correlation between sorption of non-ionic organic chemicals and soil organic matter content. Riaz *et al.* (2001) also confirmed that organic carbon is the most important component of soil controlling sorption. However, sorption behavior is not only influenced by the organic carbon, but shape and properties of biomass, polarity, solubility of pesticides are also the factors that could affect this behavior.

**Degradation of chlorpyrifos:** One of the major way for chlorpyrifos breakdown is through bacterial metabolism, usually though a consortium of microbes rather than a single species. The pesticides degradation in soil and biomass could be described with the first-order kinetic equation as  $dC/dt = -kt$ . From the equation, we can obtain the following equations:

$$\ln C = -kt + \ln C_0 \quad (2)$$

$$t_{1/2} = 0.693/k \quad (3)$$

Where  $C$  is concentration of chlorpyrifos in biomass,  $\text{mg kg}^{-1}$ ,  $k$  is degradation rate constant,  $\text{d}^{-1}$ ,  $C_0$  is the initial concentration of in biomass,  $\text{mg kg}^{-1}$  and  $t_{1/2}$  is half life, days (Table 3).

It has been revealed that the increasing of organic matter is varied directly to microbial degrading activities (Sánchez *et al.*, 2004). By comparing the degradation of

Table 2: Sorption coefficient ( $K_D$ ) of chlorpyrifos in agricultural sorbent and soil

Sorbent	$K_D$ ( $\text{L kg}^{-1}$ )	$R^2$
Coconut husk	1,475.4	0.98
Peat moss	3,371.4	0.98
Rice husk	1,316.5	0.98
Peanut shell	1,072.2	0.97
Soil	107.9	0.98

Table 3: Half-life of chlorpyrifos in agricultural sorbent and soil

Sorbent	Kinetic equation	$t_{1/2}$
Coconut husk	$\ln C = -0.0808t + 3.3962$	8.6
Peat moss	$\ln C = -0.0115t + 2.9630$	60.3
Rice husk	$\ln C = -0.0130t + 2.8843$	53.3
Peanut shell	$\ln C = -0.0149t + 2.9420$	46.5
Soil	$\ln C = -0.0122t + 0.7156$	56.8

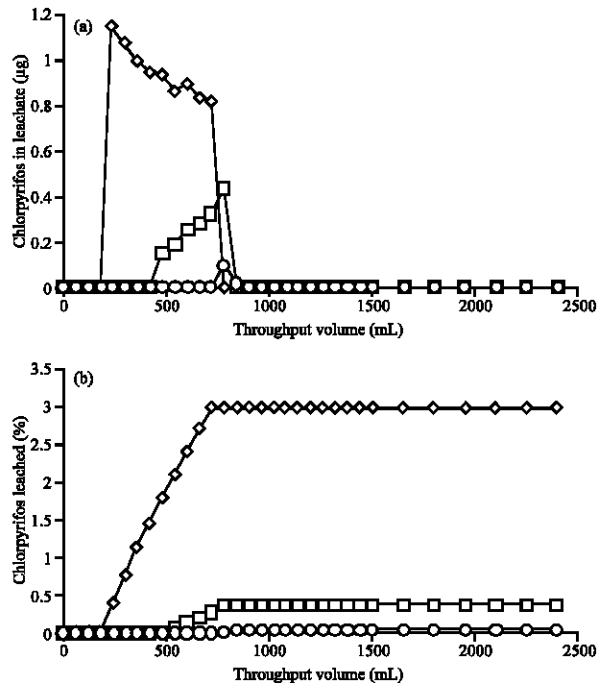


Fig. 3: Chlorpyrifos breakthrough curves (BTCs) in coconut husk 2 cm depth ( $\diamond$ ) 3 cm depth ( $\square$ ) and 4 cm depth ( $\circ$ ): (a) relative BTCs and (b) cumulative BTCs

chlorpyrifos among biomass samples, the results indicated that chlorpyrifos was degraded more rapidly in coconut husk than peanut shell, rice husk and peat moss. Meanwhile, chlorpyrifos was degraded gradually in soil. Many reports had shown that the range of half-life of chlorpyrifos in soil is longer than that in biomass. Generally, microorganisms use carbon as a source of energy and nitrogen for building cell structure. From Table 1, every biomass had higher amount of nutrients (C, N and P) than soil. The amount of nutrients is another important factor that promote microbial growth in biomass. As a result, chlorpyrifos in biomass may degraded more rapid compared to that in soil. However, peat moss had longer half-life than other biomass including soil but composing of higher amount of nutrient. Consequently, the degradation phenomena of peat moss that has lower rate of degradation although having high nutrients maybe explain by higher sorption capacity of organic carbon existed in peat moss. As mention in Boivin *et al.* (2005) high sorption capacity which chlorpyrifos could be bound strongly with organic carbon and sorbed pesticides are generally assumed to be less accessible to microorganisms, which preferentially utilize pesticides in solution.

**Leaching test:** According to the sorption experiment, coconut husk was the best sorbent in term of highest sorption capacity and was very economical due to its lowest price compared to other biomass. Coconut husk also showed the shortest chlorpyrifos half-life. Therefore, coconut husk was selected to determine the leaching behavior of chlorpyrifos which described by breakthrough curve (BTC). Coconut husk columns were leached by DI water until zero discharge. Chlorpyrifos in leachate were showed in relative breakthrough curves of chlorpyrifos (Fig. 3). Figure 3a demonstrated that the amount of chlorpyrifos in 2-cm depth coconut husk bed is higher than amount of chlorpyrifos in 3 and 4 cm depths. Approximately 0.1 µg of chlorpyrifos was leached from 4 cm depth. Figure 3b showed total amount of chlorpyrifos leached from the 2, 3 and 4 cm depth 2.98, 0.38 and 0.04%. Thus, the sorbed chlorpyrifos in 2 cm depth, 3 cm depth and 4 cm depth were 97.02, 99.62 and 99.96%, respectively. The breakthrough was prolonged in the column containing higher depth, which allowed more time for chlorpyrifos to bind to organic carbon in coconut husk.

## CONCLUSION

The study revealed that covering top soil with agricultural by product may be useful to reduce the risk of groundwater contamination. In addition, coconut husk was effective for retarding the mobility of chlorpyrifos and the retained chlorpyrifos could be degraded afterward. The presence of organic carbon in coconut husk played a major role in chlorpyrifos sorption. Degradation of chlorpyrifos in coconut husk was more rapidly than in other agricultural by products and soil. The covering of soil surface with 4 cm depth-coconut husk could be a feasible method to reduce contamination of chlorpyrifos leachate from the sprayed plants through soil.

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