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Bioactivity, Persistence and Mobility of Picloram in Selangor and Serdang Soil Series

ISMAIL B.S. and K. KALITHASAN
School of Environmental Science and Natural Resources
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM, Bangi, Selangor
Malaysia

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ABSTRAK

Kesan faktor persekitaran ke atas bioaktiviti, kekekalan dan mobiliti pikloram telah dikaji dalam makmal dan rumah hijau dengan menggunakan kacang panjang (Vigna sinensis Endl. ex Hassk), sebagai spesies bioasai. Dua jenis tanah iaitu siri Selangor (loam liat berkelodak) dan siri Serdang (liat berkelodak) digunakan dalam kajian ini. Bioaktiviti pikloram (Tordon®) didapati berkorelasi songsang dengan kandungan bahan organik tanah dan meningkat dengan bertambahnya kepekatan herbisid. Separuh hayat pikloram berkurangan daripada 33.1 kepada 24.1 hari apabila suhu tanah meningkat daripada 25°C kepada 35°C dalam tanah siri Selangor dan daripada 28.1 kepada 17.7 hari dalam tanah siri Serdang. Kadar penguraian pikloram meningkat dengan peningkatan kelembapan dalam kedua-dua siri tanah. Bagaimanapun, pikloram kekal lebih lama dalam tanah siri Selangor berbanding siri Serdang. Mobiliti ke arah bawah melalui profil tanah mempunyai kaitan songsang dengan kandungan organik tanah. Kuantiti dan kekerapan hujan mempengaruhi kadar larut-lesap pikloram. Mobiliti pikloram ke arah bawah didapati tinggi dalam tanah siri Serdang yang mengandungi bahan organik yang kurang berbanding tanah siri Selangor.

ABSTRACT

The effects of environmental factors on bioactivity, persistence and mobility of picloram were studied in the laboratory and greenhouse using long beans (Vigna sinensis Endl. ex Hassk), as a bioassay species. Two soils were used, namely Selangor series (silty clay loam soil) and Serdang series (silty clay soil). The bioactivity of picloram (Tordon®) was inversely correlated with the organic matter content of the soil and increased with increasing herbicide concentrations. The half-life of picloram decreased from 33.1 to 24.1 days as soil temperature increased from 25°C to 35°C in the Selangor series, and from 28.1 to 17.7 days in the Serdang series soil. The degradation rate of picloram also increased with increasing moisture level in both soil series. However, picloram persisted longer in Selangor series soil than in Serdang series. Downward mobility through the soil profile was inversely related to the organic matter content of the soil. The quantity and frequency of simulated rain directly influenced the extent of leaching of the herbicide. Downward movement of picloram was greater in Serdang series which contains less organic matter but high sand than Selangor series longest available vessel.

INTRODUCTION

The fate of herbicides in soils is greatly influenced by their interaction with the soil environment. It is now well established that the behaviour of most herbicides is influenced by the organic matter content of the soil (Blumhorst *et al.* 1990). Generally, adsorption and decomposition are the two major factors that influence the bioactivity of most herbicides (Aldrich 1984). It has been suggested that variation in the phytotoxicity of the herbicides in soil is caused by differences in the adsorption capacity of the soil (Okafor *et al.* 1983).

Herbicides dissipate in the soil through a combination of microbiological and chemical processes. Microbial degradation of herbicides increases with increasing soil temperature (Bouchard *et al.* 1982) and soil moisture levels (Hurle and Walker 1980). Temperature can, therefore, be an important factor affecting the persistence of herbicides in the soil, especially in the tropics. Herbicide degradation in soil generally increases with increasing moisture levels up to field capacity, probably reflecting increased microbial activity (Hurle and Walker 1980).

Picloram (4-amino-3,5,6-trichloropicolinic acid) is an effective herbicide used to control of most annual and perennial broadleaf weeds in crops and woody plants. However, the susceptibility of certain crops to extremely small quantities of picloram makes study of persistence very imperative. Picloram is rapidly absorbed by leaves and roots and causes epinasty and leaf curling.

As a soil-applied herbicide, picloram's behaviour and interaction with various soil components merit study. Although many reports have been published, only limited information is available on its behaviour in Malaysian soils. Therefore, experiments were conducted to determine the persistence of picloram in two soils, viz. Selangor series and Serdang series. The effects of soil organic matter content on the bioactivity and adsorption of this herbicide were also examined.

MATERIALS AND METHODS

Soil Samples

The phytotoxicity and adsorption studies were conducted in a glasshouse using sand and peat soil. In the persistence and mobility studies, two soils, Selangor series (silty clay) and Serdang series (sandy clay loam), were used. Soil characteristics are shown in Table 1. Samples of Selangor series soil were collected from Jenderata Estate, Teluk Intan, Perak, Malaysia, while the soil samples of Serdang series were from the experimental plot at Universiti Putra Malaysia, Serdang, Selangor, Malaysia. The soils were collected from the 0-10 cm depth, air-dried and sieved through a 1.0-cm mesh prior to use.

Phytotoxicity Study

Sand, peat or their mixtures containing 5, 10, 20 or 50% (v/v) were treated to obtain a final picloram concentrations (Tordon 22K®, contained 240 gm a.i/L) of 0, 0.05, 0.1 or 1.0 mg/kg. The treated soils were placed in 6.5 cm diameter plastic pots into each of which six long bean (*Vigna sinensis*) seeds were sown at a depth of 0.5 cm. The soil in each pot was watered to 80-90% field capacity and maintained at this level throughout the experiment. After emergence, the seedlings were thinned to four per pot. Seven days after emergence, the plants were harvested by cutting at soil level and fresh weights were recorded. The data were expressed as a percentage of the untreated control.

Adsorption Study

Two g samples of peat (100% organic matter), 5 g samples of sand or peat-sand mixtures containing 5, 10 or 20% (v/v) peat and 4 g sample of 50% (v/v) peat-sand mixture were weighed into 50 mL conical flasks, to which 20 mL of 0, 0.05, 0.1 or 1.0 mg/kg picloram were then added. Control samples were prepared without adding any soil. The flasks were sealed immediately with aluminium foil. The samples were allowed to equilibrate for 12 hours on an orbital shaker at 150 rpm and then centrifuged for 20 minutes at 4000 rpm to obtain a clear solution. Seven mL of the supernatant were transferred to 9 cm diameter petri dishes, each

TABLE 1
Physico-chemical characteristics of the soils

Characteristics	Selangor Series	Serdang series
pH	4.0	4.6
silt (%)	53.5	14.6
sand (%)	3.1	50.6
clay (%)	43.4	34.8
organic matter (%)	4.3	0.8
CEC (cmol (+) kg–1)	23.7	4.7
Texture	Silty clay loam	Silty clay

lined with one sheet of Whatman No. 3 filter paper. Ten long bean seeds were placed in each petri dish and incubated at 28°C for seven days. After incubation, the length of the longest root was measured and was expressed as a percentage of the untreated control value.

Standard Curve for Bioassay

Long beans were used to define a linear relationship of the concentration range of the herbicide in the soils used for the persistence and mobility studies in the greenhouse. Concentrations used for picloram in the two soils were 0, 0.001, 0.005, 0.01, 0.3, 0.5, 1.0, 2.0, and 3.0 ppm (w/w). The required volume of the herbicide was thoroughly mixed with air-dried soil to obtain a final concentration. The soil samples were bioassayed in the greenhouse under natural light. Five pots were filled with 200 g of treated soil each, in which five long bean seeds were planted at a depth of 0.5 cm in each pot. Soil moisture was maintained at about 90% field capacity throughout the experimental period. After emergence the seedlings were thinned to three per pot. Seven days after emergence, the plants were harvested by cutting at soil level and fresh weights were recorded. The fresh weight of five replicates (expressed as a percentage of the control value) was plotted against log herbicide concentration.

Persistence Study

About 45 kg of air-dried soils of either Selangor or Serdang series were treated with picloram to obtain final concentrations of 1 ppm (w/w). For the control treatment, soils were not treated with picloram. After mixing, four 1.5 kg samples of treated soil was kept in each of 24 polyethylene bags. The bags were then divided into three groups and incubated at either 25°C, 28°C or 35°C. The final soil moisture level was maintained by adding adequate water at weekly intervals to obtain 50% of field capacity. One 1.5-kg bag of soil for each soil at each temperature level was put in a refrigerator at 4°C on Day 0, 15, 30, 45, 60, 75, 90 and 105.

After 2 days in refrigerator, samples were removed and air-dried overnight before bioassayed in the laboratory. All soil samples were bioassayed in the greenhouse under natural light. One 1.5-kg bag of soil for the each soil-temperature combination was then split into four portions, each of which was then placed in a pot into which 5 long bean seeds were then planted at a depth of 0.5 cm. The soils were watered twice a day to maintain the moisture level at about 90% of field capacity. After emergence the seedlings were thinned to three per pot. Seven days after emergence, the plants were harvested by cutting at soil level and fresh weights were recorded and expressed as a percentage of the control value. The concentration of herbicide in the soil was estimated by referring to a dose-response curve developed concurrently (Ismail and Kalithasan 1997). The herbicide concentrations calculated for each data point using the dose-response curve were log transformed and plotted against time, from which the half-life was calculated by assuming first-order kinetic reaction.

In a different set of experiments, the soil samples were divided into three groups with soil moisture levels of either 30, 50 or 70% field capacity and kept in a room at 28°C. The bags were weighed weekly and, when necessary, water was added to restore the initial moisture level. The soil samples in the refrigerator were thawed and air-dried overnight. All soil samples were bioassayed in a greenhouse to determine the half-life of picloram as described above.

Effect of Organic Matter (peat) in Soil on Mobility of Picloram

A PVC column (30 cm long and 11 cm diameter) was filled to a depth of 25 cm with either sand, peat or sand-peat mixtures containing 5, 10, 20 or 50% (w/w) peat. Once the column had settled, a 5-cm-thick layer of soil (350 g Selangor series or 500 g Serdang series) treated with picloram (0 or 1 mg/kg) was placed on top of the peat mixture and the column was lined with one sheet of Whatman No. 3 filter paper. Five hours after adding the treated soil, the soil column was watered with 20 mL water (equivalent to 2.1 mm of rain) every day for 16 days. On day 17, the column was separated into 5- cm segments and the herbicide in soil was bioassayed as described above.

Effects of Amount and Frequency of Simulated Rain on the Mobility of Picloram

PVC columns were uniformly packed to a depth of 25 cm with 0.74 g/cm^3 Selangor series or 1.05 g/cm^3 Serdang series soil at 50% field capacity. After equilibrating, a 5-cm layer of soil treated with picloram was placed on top of the peat mixture and the column was lined with Whatman No. 3 filter paper. Five hours after adding treated soil, the soil column was watered with either 10, 20 or 40 mL water (equivalent to 1.0, 2.1 or 4.2 mm of rain respectively) either every day or every 4 days for 16 days. On day 17, the distribution of herbicide in each soil segment was determined using the bioassay method as described.

The design of mobility and persistence experiments was a randomized block with four replications except for the mobility study which had three replicates. Elsewhere a complete randomized design with four replications was used for bioassay studies. All data were subjected to analysis of variance and means were compared with an LSD test at the 5% level of significance.

RESULTS AND DISCUSSION

The phytotoxicity of picloram decreased with increasing levels of peat soil (*Fig. 1*). A significant increase in percentage fresh weight of long beans was also recorded between each level of peat soil at 0.05 ppm. The growth of long bean was inhibited in the presence of 0.1 mg/kg picloram in soil containing 10% peat soil, but was observed in soil containing 20% peat or more. In the presence of 1.0 mg/kg picloram, growth of long bean was only observed in soil containing 100% peat soil. This demonstrates that the phytotoxicity of picloram decreased as organic matter content increased. Organic matter in soil increased the adsorption process, reducing herbicide phytotoxicity to the plant. The length of the seedling radicle reduced with increasing herbicide concentrations. *Fig. 2* shows that the radicle length was completely inhibited in the presence of 1 ppm picloram in soil containing 5% peat or less, but it grew when peat increased above 10%. This result shows a positive correlation between adsorption and soil organic matter among the herbicides, as has also been confirmed in previous studies (Cheung and Biggar 1974; Gaynor and Volk 1976). Grover (1971) points out that adsorption involves hydrogen bonding or coulombic attraction between protonated picloram molecules and the hydrophobic surfaces of the organic matter.

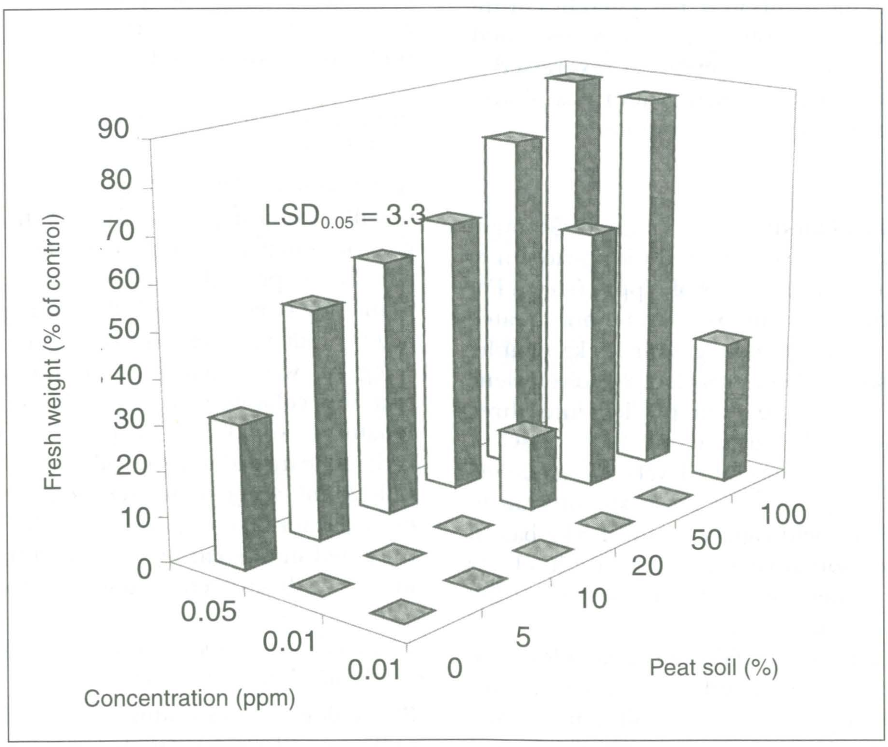

Fig 1. Fresh weights of long bean seedlings (% control 7 days after sowing) grown in soils with varying peat content and treated with varying concentrations of picloram

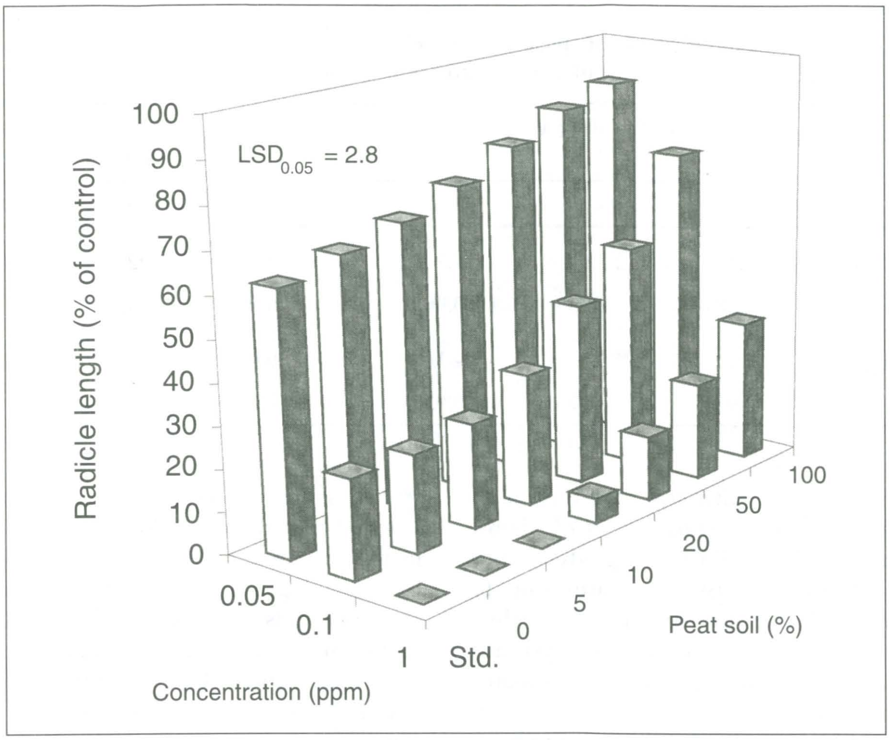

Fig 2. Radicle length of long bean seedlings (% control 7 days after sowing) grown in soils with varying peat content and treated with varying concentrations of picloram

The degradation of picloram was faster at higher temperatures, and a significant effect of temperature on degradation was observed in both soil series (Table 2). The half-life of picloram decreased by 10.4 days to 17.7 days in Serdang series when temperature increased from 25 to 35°C. Similarly, in Selangor series, the half-life decreased by 9 days as the temperature increased by 10°C from 25 to 35°C. This observation is in line with previous reports by Hamaker *et al.* (1967) and Merkle *et al.* (1967). An increase in temperature probably increases both biological and non-biological activity of herbicides. High temperature also favours microbial growth, which increases microbial degradation. Youngson *et al.* (1967) showed that picloram degrades in soil by microbial activity. In addition, the increased dissipation of herbicides at higher temperatures could also be attributed to volatility and photodecomposition of the compounds (Aldrich 1984; Ashton and Monaco 1991) but it may not occur under laboratory conditions.

The degradation rate of picloram increased significantly also with increasing soil moisture levels (Table 2). At 70% field capacity, the half-life of picloram in Selangor and Serdang series was 18 and 14 days respectively, which is about half of that at 30% field capacity. Increased degradation at higher soil moisture levels is expected as a result of the consequent weaker adsorption of herbicide molecules by the soil particles; increasing herbicide concentration in the soil solution would make herbicide molecules more readily available to microbial degradation. Under aerobic conditions, the degradation rate increased with increasing soil moisture content and tended to plateau at high moisture content (Hamaker 1972; Zimdahl and Clark 1982).

Our results show that the half-life of picloram was longer in the Selangor series than in the Serdang series. The difference may be attributed to the lower pH value and considerably higher organic matter content in Selangor series (Table 1). These results are in line with earlier reports by Grover (1971), Cheung and Biggar (1974) and Merkle *et al.* (1967). In view of the fact that the fate of picloram in soil is dependent on the degree of adsorption of picloram onto the soil particles, it has been reported that adsorption

TABLE 2
Half-life (days) of picloram in Selangor and Serdang series at different temperatures and moisture levels

Soil series	Temperature (°C)			Soil Moisture (% of Field capacity)		
	25	28	35	30	50	70
Serdang	28.1	22.5	17.7	32.2	22.5	14.0
r^2	0.987	0.858	0.963	0.970	0.858	0.937
Selangor	33.1	28.5	24.1	36.0	28.5	18.0
r^2	0.985	0.973	0.957	0.989	0.973	0.942

was greatest for soils with low pH and high organic matter contents (Hamaker *et al.* 1966). Gaynar and Volk (1976) suggested that adsorption increases as pH decreases due to protonation of the picloram molecules, decreasing its solubility. Generally, compounds with lower solubility are adsorbed to a greater extent on soil organic matter than are compounds of high water solubility (Carringer *et al.* 1975).

In sandy soil column (0% peat), picloram leached to a depth of 30 cm (*Fig. 3*). However, in the presence of 5 or 10% peat soil, it moved only to a depth of 25 and 10 cm, respectively. As peat contents increased to 50 or 100% peat, picloram was not leached deeper than 10 cm. An accumulation of the residue on the top layer had reduced the fresh weight of the bioassay species.

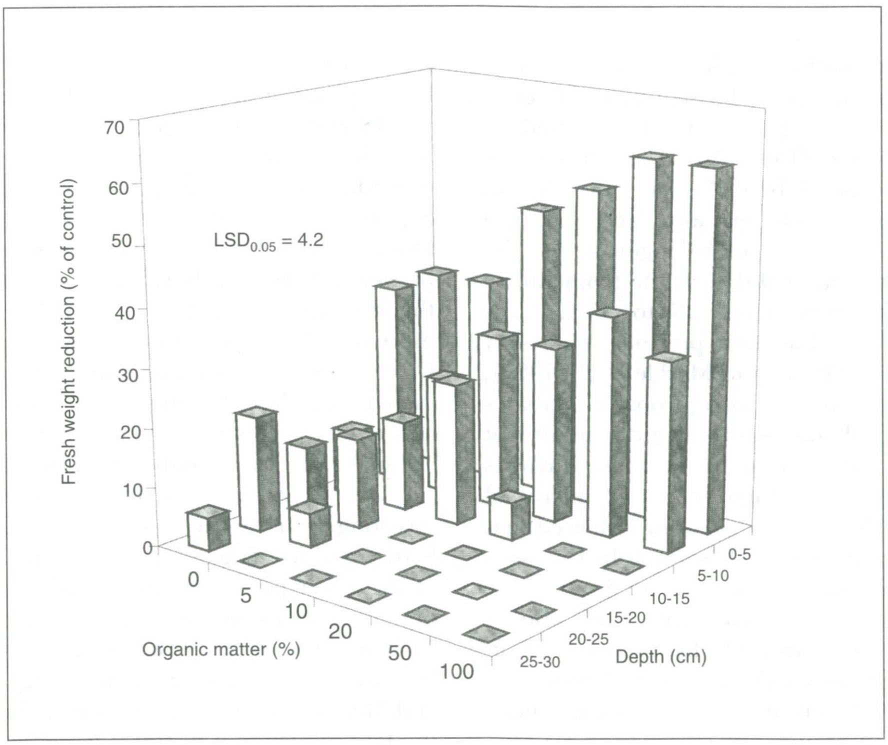

Fig 3. Fresh weight reduction of long beans (% control 7 days after sowing) at various depths with varying peat content in the presence of picloram

Increased quantity and frequency of simulated rain increased downward movement of picloram residue. There was a trend towards a greater downward movement of picloram when simulated rain was given daily rather than at 4-day intervals (*Fig. 4*). Picloram leached down to only the 5 cm depth in soil column watered with 10 mL water either daily or 4-day interval in Selangor series. However it was detected down to 25 cm and 15 cm depth, respectively with daily or 4-day intervals of 40 mL water. Greater reduction in fresh weight was observed when the bioassay species was grown in soil taken from 0-5 cm zone. This shows that a large amount of the residue persisted on the top layer of soil, irrespective of the amount and frequency of watering.

In Serdang series columns, daily watering at 40 mL resulted in greater movement of picloram down to the 25 cm depth than there was to 15 cm with watering at 4-day intervals (*Fig. 5*). Watering with 40 mL caused greater movement of picloram than did either 20 or 10 mL of water at either daily or 4-day intervals. Picloram was detected at 25 cm depth when 40 mL of water was applied daily compared to only at 10 cm depth for 10 mL daily.

The rate of downward movement of picloram in the soil column was inversely related to the organic matter content of the soil. In the medium containing only sand, the picloram moved to the lowest zone tested (25 – 30 cm depth), but this did not occur in soils with higher organic matter contents (*Fig. 3*). Increased adsorption of picloram onto soil organic matter can be expected to reduce the concentration of herbicide available in the soil solution as the percentage of organic matter increases, leading to reduced downward movement in mass flow of water. This would account for the limited mobility of picloram in Selangor series soil, which contains a greater amount of organic matter than does Serdang series soil. Oppong and Sagar (1992) also observed high herbicide activity in gravelly sand soil, and Rahman (1976) reported that organic matter had a greater influence on the duration of bioactivity and on leaching of alachlor.

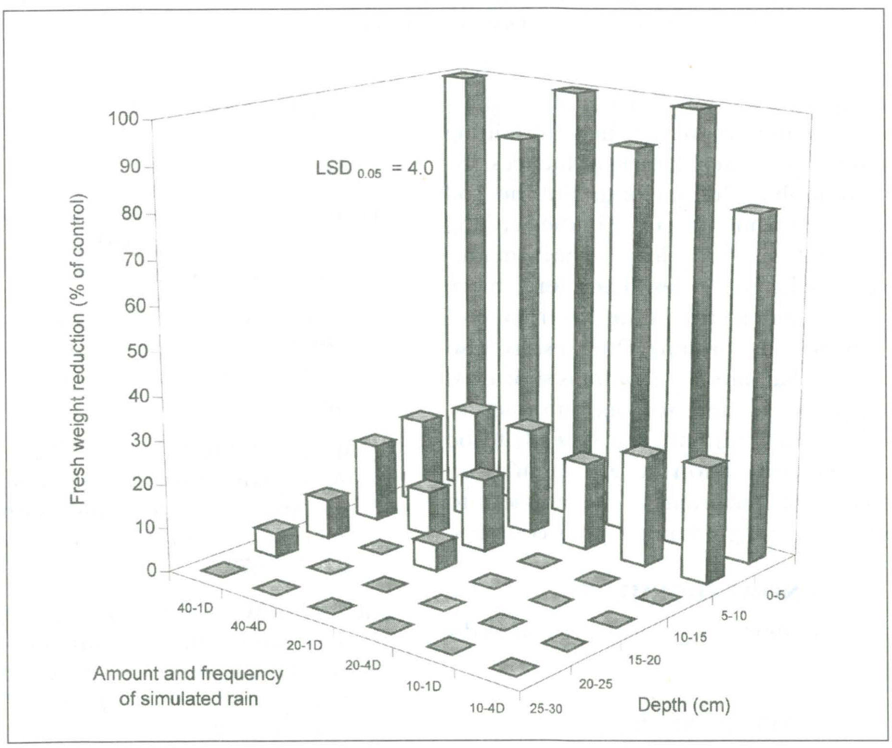

Fig 4. Fresh weight reduction of long beans (% control 7 days after sowing) at various depths under various amounts and frequency of simulated rain (1D = daily; 4D = every 4 days) in Selangor series soil in the presence of picloram

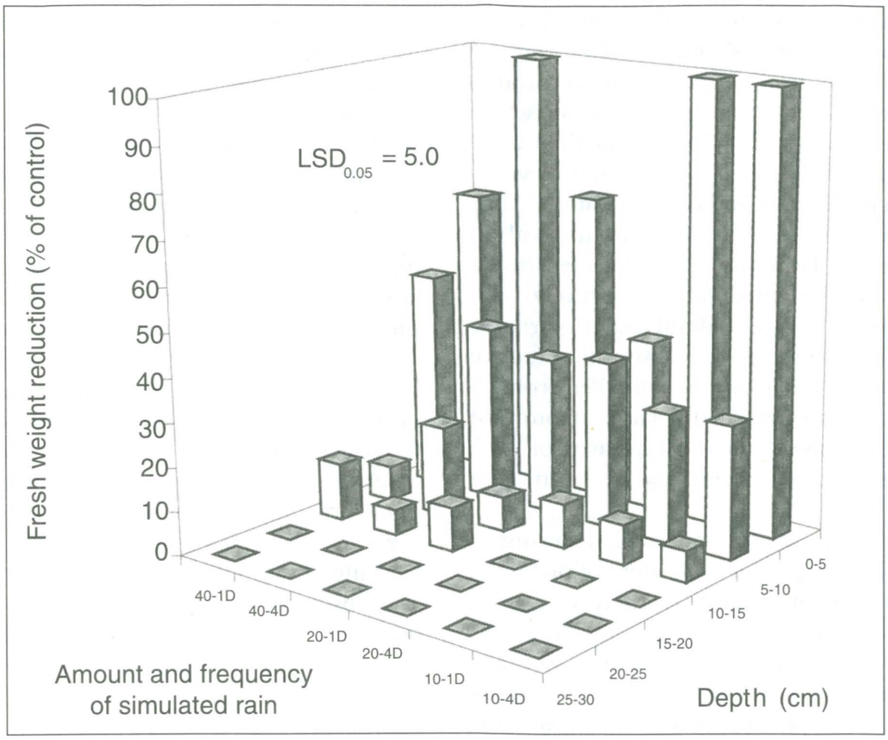

Fig 5. Fresh weight reduction of long beans (% control 7 days after sowing) at various depths under various amounts and frequency of simulated rain (1D = daily; 4D = every 4 days) in Serdang series soil in the presence of picloram

This experiment concludes that organic matter plays an important role in determining the adsorption processes, hence influences the half-life and mobility of picloram in the soil columns. Less adsorption occured in the Serdang series soil which contains less organic matter compared to Selangor series. Therefore, more residues could be detected in the lower zone of Serdang series soil column. Our results also showed that the half-life of picloram is shorter at higher temperatures and soil moisture levels. Soil organic matter content clearly needs to be taken into consideration when calculating concentrations of picloram to be applied to tropical soils of varying organic matter contents.

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