CHLORPYRIFOS AND MALATHION RESIDUES IN SOILS OF A TERENGGANU GOLF COURSE: A CASE STUDY

(Residu Klorpirifos dan Malathion Dalam Tanah di Padang Golf Terengganu: Satu Kajian Kes)

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Abstract

A preliminary study was conducted to determine the residues of organophosphorus insecticides, Chlorpyrifos and Malathion, in soils of a local 18-hole golf course in order to evaluate their dissipation rate and half-life values under field condition. Soils samples were collected from 18 stations (greens) three times within a period of one month after its application. The insecticide residues were extracted using soxhlet technique and determined using gas chromatography fitted with a nitrogen phosphorus detector (GC-NPD). Results obtained indicated that dissipation of these insecticides were fairly fast, with amount dissipated within 30 days ranging from 65.0 to 96.6 % for chlorpyrifos and 63.5 to 95.8% for malathion. The dissipation of these insecticides from the soils seemed to follow a first order kinetic with half-life values ranging from 3.4 to 15.3 days with average of 6.5 days and 6.8 to 31.3 days with average of 13.5 days for chlorpyrifos and malathion, respectively. It appears that soil physico-chemical properties such as organic matter content, pH, particle size distribution, cationic exhange capacity and moisture content do not exert an influence on the dissipation of these insecticides.

Keywords: chlorpyrifos, malathion, residues in soils, golf course, Kuala Terengganu

Abstrak

Satu kajian awal telah dilakukan bagi menentukan residu insektisid organofosforus, Klorpyrifos dan Malathion, dalam tanah padang golf 18-lubang tempatan bagi menilai kadar lesapan dan separuh-hayat insektisid tersebut pada keadaan lapangan. Sampel tanah diambil dari 18 stesen (‘greens’) sebanyak tiga kali sepanjang satu bulan selepas racun tersebut digunakan. Residu insektisid diekstrak dengan menggunakan teknik soxhlet dan ditentukan dengan kromatografi gas dengan pengesan nitrogen fosforus (GC-NPD). Keputusan yang didapati menunjukkan lesapan insektisid ini adalah cepat, iaitu dalam jangkamasa 30 hari, 65.0 hingga 96.6 % klorpirifos dan 63.5 hingga 95.8% malathion telah melesap. Kelesapan kedua-dua insektisid ini dari tanah adalah mengikut kinetik tertib pertama dengan nilai separuh-hayat masing-masing di antara 3.4 hingga 15.3 hari dengan purata 6.5 hari dan 6.8 hingga 31.3 hari dengan purata 13.5 hari, bagi klorpirifos dan malathion. Kajian ini juga menunjukkan ciri fizik-kimia tanah seperti kandungan bahan organik, pH, taburan saiz partikel, kapasiti penukaran kation dan kandungan lembapan tidak mempengaruhi lesapan insektisid-insektisid tersebut.

Kata kunci: klorpirifos, malathion, residu dalam tanah, padang golf, Kuala Terengganu

Introduction

The demand for golf is rapidly expanding worldwide and the number of golf courses around the world has increased tremendously; for instance, it is estimated that in the United States alone, there are approximately 16,000 golf courses across the country [1]. In the South East Asian countries of Thailand, Malaysia, Indonesia and the Philippines, the popularity of golf has led to the spread of golf tourism in these countries where golf courses has become a central part of many hotels and resorts development projects. In Malaysia, it is also now becoming a trend to use golf courses as a central part of many new housing development projects; in Kuala Terengganu alone, there are at least two housing developments with such concept.

Golf courses are highly managed locations. Generally, turf grass receives almost daily applications of irrigation water and frequent applications of fertilizers in order to stimulate plant growth. In addition pesticides are used in large quantities on turf grass to control damage caused by insects, weeds and fungus-borne diseases. All these additions are needed in order to maintain a high quality turf grass playing surface. Golf course is often presumed to be a significant contributor to nonpoint source water pollution and an increased attention on the possible environmental effects of chemical applications on golf courses has occurred with the increase in

public's concern for the environment. This has led to several studies being conducted worldwide particularly in the United States on these issues [2-12].

This paper presents results of a preliminary study conducted to determine residues of organophosphorus insecticides, Chlorpyrifos and Malathion, in soils of a local 18-hole golf course in order to evaluate their dissipation rate and half-life values under field condition. It is hope that the findings reported would provide some baseline information on the fate of pesticides applied on golf courses.

Experimental

Study area and sampling sites

The 18 holes golf course is located in Tok Jembal, approximately 15km north of Kuala Terengganu. The golf course was built on a reclaimed municipal landfill. The site was initially a swamp land used by Kuala Terengganu municipal as their landfill site and when the landfill was decommissioned, it was reclaimed and converted into a golf course in the late 90's. The golf course is actually part of a housing development project known as Kuala Terengganu Golf Resort managed by KT Golf Resort Berhad, a subsidiary of UDA Holdings Sdn Bhd. A variety of pesticides are applied to the turfgrass on this golf course (Table 1) and two types of insecticide was chosen for this study *viz*. malathion and chlorpyrifos.

Table 1. List of pesticides used on the golf course

Pesticides Classification	Trade Name	Active Ingredients
Insecticides	ACM DIAZINON	Diazinon 55%
	CH MALAXION	**Malathion 88%**
	DURSBAN 75	**Chlorpyrifos 21.2%**
	KONSEP 550	**Chlorpyrifos 46.3%,** Cypermethrin 4.6%
Herbicides	STARANE 200	Fluroxypyr, 1-Methyl Heptyl Ester 29.6%
	FUSILADE	Fluazifop-butyl 26% (pyridyloxyl phenoxy propionic ester)
	MEWAHTOX	2,4- Butyl Ester 45%
Fungicides	Ultracide 0.3EC	Methidation 20.6%
	KENLATE	Benomyl 24.7%
	TERAZOLE 25EC	Etridiazole 24.7%
	TERRACHLOR 75 wp	Quintozene 75%
	Cuprawit 85wp	Copper oxychloride 85% (metallic copper 50%)
	CH MANCOZEB	Zinc 62%, Manganese ion 16%
	Bavistin (BASF)	Carbendazim 50%

Surface soils (0-5 cm) were collected from a total of 18 sampling sites (Fig. 1) using metal spades; each sampling site represents one green. Samplings were carried out three times, *viz*. one day (1st sampling), fifteen days (2nd sampling) and thirty days (3rd sampling) after pesticide application. The soils collected were packed in plastic bags and transported immediately to the laboratory and once in the laboratory, they were kept cool in the fridge until further analysis to minimise degradation. Analysis of pesticides in soils was carried out using a method based on USEPA method 3542B [13]. Briefly, pesticides were soxhlet extracted using 1:1 mixture of hexane and acetone for 12hrs and the extracts concentrated using rotary evaporator. Determination and quantification of the two pesticides were carried out using gas chromatography fitted with nitrogen phosphorus detector (GC-NPD) based on the retention times compared to that of external malathion and chlorpyrifos standards.

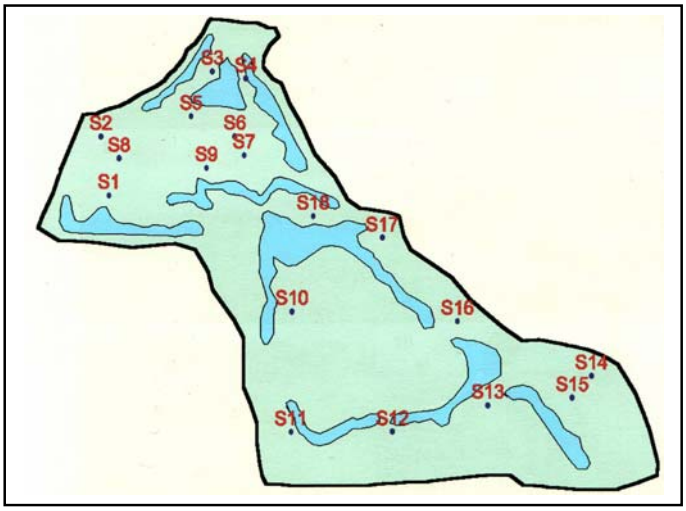

Figure 1. Locations of soil sampling stations

The GC-NPD operating conditions were modified slightly from the recommended method in order to improve separation of the two peaks of interest (Fig 2) and they were as follows: 2 µl extract was injected onto ETX-5 column (30m x 0.25 mm i.d; 0.25µm filmed thickness); injection temperature was set at 250°C; column temperature was programmed in the following manner: hold at 120°C for 2 min, first temperature ramp of 120 - 170°C at 20°C min^{-1} followed by the second and third temperature ramp of 170 - 180°C at 0.5°C min^{-1} and 180 – 270°C at 30°C min^{-1} before maintaining at 270°C for 1 min resulting in a total run time of 28.5 mins; helium was used as the carrier gas with a flow rate at 1.0ml. min^{-1}; detector temperature was set at 300°C. Recoveries of malathion and chlorpyrifos from six replicates of soils fortified with 10 µg/g (soil dry weight) insecticide standards was between 88.5 to 99.9% and 78.5 to 85.6% with mean recovery of 95.1% (±3.7%) and 83.4 % (±2.6%), respectively. Recoveries obtained for malathion were within those recommended by the EPA method (>85%). Recoveries for chlorpyrifos on the other hand were slightly below those recommended by EPA (85%) but are still acceptable since method reproducibility is very good.

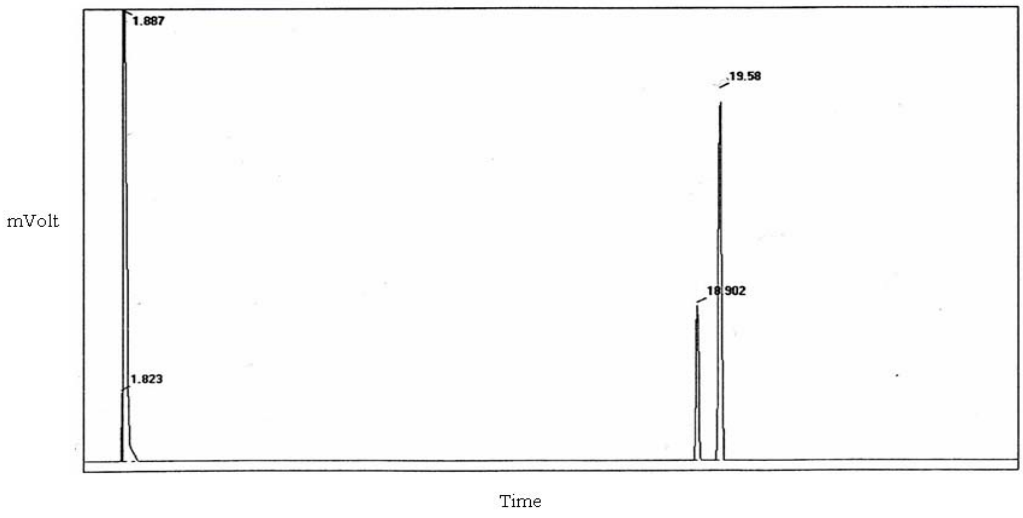

Figure 2. Typical chromatogram of malathion (18. 90 min) and chlorpyrifos (19.58) obtained

Physical characteristics, viz. particle size analysis (PSA), total organic content, cationic exchange capacity (CEC), moisture content and pH were determined using procedure described by Lim, H.K. [14].

Results and Discussion

Table 2 shows the results of soil physical-chemical characteristics. Soil texture for the whole course is sandy with very low silt and clay content. Generally, soil organic carbon content was low whilst the moisture content of the course was relatively high; very small variation of organic carbon and moisture content were found in these soils and statistical analysis showed that the variation between the 18 greens were insignificant. On the hand, the soil pH and CEC values showed significant variation ($p<0.05$) with sampling stations. The pH values ranged from 3.48 to 4.65 with mean value of 4.25; generally these soils were in the acidic range and it is not surprising that the greens on this golf course were regularly limed by the green keeper as part of the turf treatment and management. The CEC was found to range from 0.0257 to 0.0766 cmol/kg. Very strong correlation between these two soils parameters ($r= 0.95$) was found and this is generally an indication that pH exerts a strong influence on the CEC of the soils.

Table 2. Physical-chemical characteristics of turf soils

Soil characteristics	Results
Organic matter content*	2.85 ± 0.08%
Moisture content*	10.3 ± 0.19%
Soil texture	Sandy (<2.23 ± 0.66% silt+clay content)
pH*	4.25 ± 0.29
Cationic exchange capacity*	0.0579 ± 0.0173 cmol/kg

* Mean value

Table 3 summarises the results obtained for chlorpyrifos and malathion residues in soils within 30 days after their application on the greens while Figure 3 and 4 shows their distribution in soils with sampling stations for the three samplings.

Table 3. Concentration range of chlorpyrifos and malathion residues in soils

Days after application	Malathion / ppm	Chlorpyrifos / ppm
0	0.08 – 2.36	0.74 – 2.24
15	0.02 – 0.09	0.08 – 0.43
30	0.02 – 0.05	0.02 – 0.18

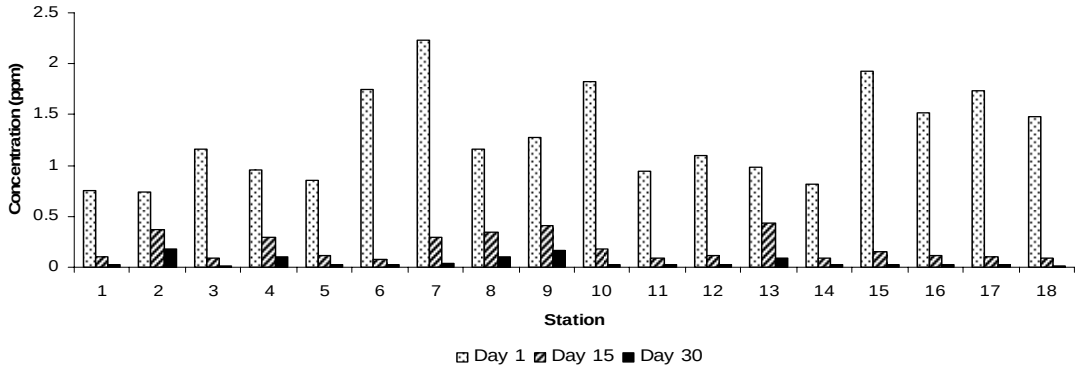

Figure 3. Concentration of chlorpyrifos residues in soils for a period of 30 days after application

Statistical analysis (ANOVA) shows that differences observed between stations were insignificant ($p>0.05$) whilst significant differences were obtained ($p<0.05$) between the three samplings for both insecticides. These results show a fairly rapid dissipation of the two insecticides under field condition where 65.0-96.6% of the chlorpyrifos and 63.5-95.8% of the malathion have dissipated from the top soils within 30 days after their application. Correlation analysis between measured soil physical-chemical characteristics and the insecticides concentrations and their dissipation rates suggests that these parameters do not play an important role in influencing the dissipation of the two insecticides from the soils.

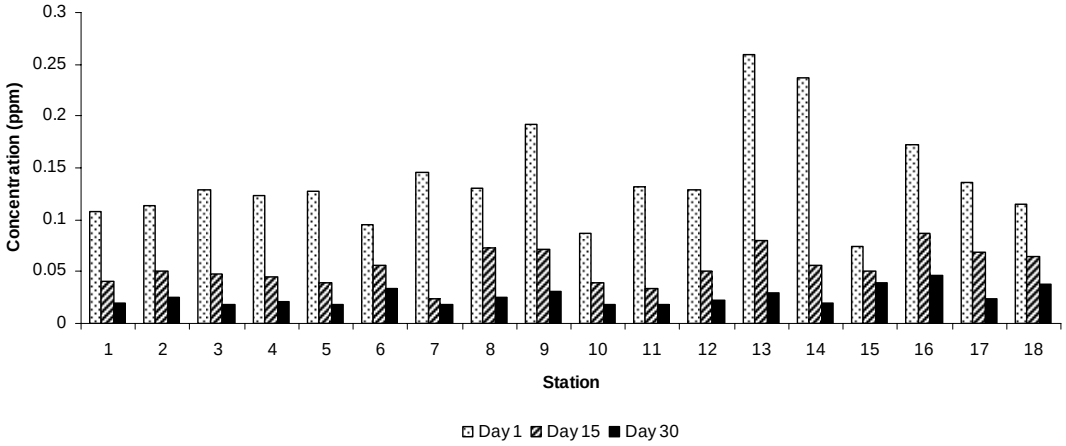

Figure 4. Concentration of malathion residues in soils for a period of 30 days after application

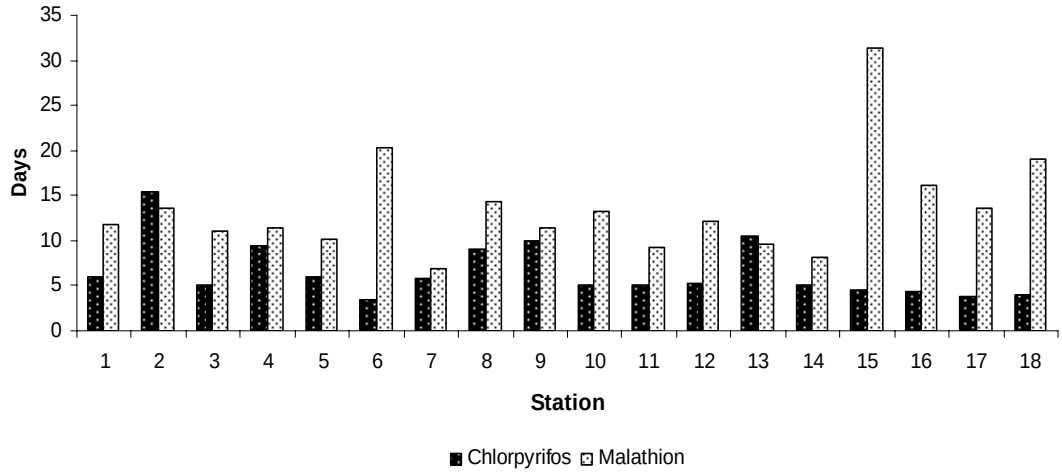

Figure 5. Half-life of chlorpyrifos and malathion under field condition

Using the data obtained, the half-lifes of chlorpyrifos and malathion were calculated assuming the dissipation reaction follows a first order reaction kinetic. The equation used was $C=C_oe^{kt}$ where C is the concentration of insecticide after time t, C_o is the apparent initial concentration, k is the rate constant and t is time in days. A plot of ln C against time would yield a negative slope; the rate constant can thus be obtained from the slope. Good linearity was obtained with R^2 value greater than 0.95 for all the stations suggests that the dissipation rate for these two insecticides actually follows the first order kinetic.

For first order reaction, the half-life ($t_{1/2}$) of a given insecticide is calculated using the equation, $t_{1/2} = 0.693/k$. In this study, the half-life for chlorpyrifos was relatively short with values ranging from 3.4 to 15.3 days with mean value of 6.5 $\pm$ 3.1 days while for malathion, a significantly longer half-life was obtained with values ranging from 6.8 to 31.3 days with mean value of 13.5 $\pm$ 5.6 days (Figure 5).

Conclusions

Results show that dissipation of the two insecticides were relatively fast with chlorpyrifos dissipating faster than malathion under field conditions. It was estimated that 65.0-96.6% of chlorpyrifos and 63.5-95.8% malathion dissipated after 30 days of application to the soils. The dissipation rate of these insecticides appeared to follow a first order kinetic with half-life values ranging from 3.4 to 15.3 days for chlorpyrifos and 6.8 to 31.3 days for malathion. Mean half-life calculated for the two insecticides was 6.50 and 13.5 days, respectively. It appears that soil physico-chemical properties *viz*. organic matter content, pH, particle size distribution, cationic exhange capacity and moisture content do not exert an influence on the dissipation of these insecticides.

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