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DEGRADATION OF CHLORPYRIFOS AND CARBARYL IN SOIL: INFLUENCE OF TEMPERATURE AND SOIL MOISTURE.

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ABSTRACT

The degradation of chlorpyrifos and carbaryl in clay loam soil (5μg/g) was evaluated under laboratory conditions to determine the effect of temperature and soil moisture on their degradation rates. They were both affected by temperature and soil moisture. Half-lives ($t_{1/2}$) were calculated by assuming that degradation of both insecticides follows first-order kinetics. The $t_{1/2}$ values of chlorpyrifos decreased from 148-76 days at 15°C and from 60 to 32.5 days at 25°C with soil moisture increase from 15 to 30%; the $t_{1/2}$ of carbaryl, in the same conditions, decreased from 100 to 44.6 days at 15°C and from 52.5 to 28.8 days at 25°C. At 35°C, the effects of an increase in soil moisture from 15 to 30% were larger on the degradation of either insecticide, as $t_{1/2}$ decreased from 56.1 to 21.9 days of chlorpyrifos and from 38.1 to 11.5 days of carbaryl. The analysis of residues showed that there were at least 4 degradation products of carbaryl and 2 only of chlorpyrifos were detected by HPLC.

Keywords: *Insecticides; chlorpyrifos; carbaryl; soil; degradation.*

INTRODUCTION

Pesticides are used in agriculture to improve crop yields mainly by eliminating or controlling the harmful effects of pests, weeds or the normal growth characteristics of the crop plants. When applied in the field for these purposes, pesticides can enter or move into the soil, air and water compartments of the environment. Perhaps the most important of these is the soil. Some pesticides are applied directly to soil. Others reach the soil during spraying of crop plants, through run off from decaying plant remains. Thus, most pesticides will reach the soil, directly or indirectly, and in greater or lesser amount, according to use pattern and characteristics of the applied chemical.

The fraction of a pesticide, which as a result of its practical use has found its way to the soil and is present there either in the form of the parent compound, or a significant degradation product(s), or as a bound residue, is regarded as a soil residue.

The transformation of organic chemicals in soil can occur by photochemical, chemical or microbiological action (Walia *et al.*, 1988; Racke *et al.*, 1990).

In fact, published reports confirm that members of several classes of pesticides (organophosphorus and carbamate insecticides, phenoxy herbicide esters) may be affected by many environmental factors (such as pH, temperature and soil moisture) (Cantier *et al.*, 1988; Fuesler and Hanafey 1990; Walker, 1994; Hafez, 1994; Capri *et al.*, 1995; Gaynor *et al.*, 1997).

Chlorpyrifos(O,O-diethyl(O-3,5,6-trichloro–2-pyridyl) phosphoro thioate) and carbaryl (1-naphthyl methylcarbamate) are insecticides widely employed for control of agricultural pests, and they examined as residues in many substances (Espinosa- Mansilla *et al.*, 1995; Racke *et al.*, 1996).

In the current experiments, chlorpyrifos and carbaryl were added to clay loam soil and incubated under laboratory conditions at different temperatures and with different soil moisture contents to determine the effect of temperature and moisture on the degradation rates of these insecticides.

MATERIALS AND METHODS

Chemicals. The analytical grade of chlorpyrifos (O, O- diethyl (O - 3, 5, 6- trichloro – 2 –pyridyl) phosphorothioate) and carbaryl (1-naphthyl methylcarbamate) (99% purity) were used in this study. The other chemicals for the chemical analysis were HPLC grade solvents.

Soil. A clay loam soil was collected from an area has not history of either chlorpyrifos or carbaryl treatment. Soil samples were air-dried and sieved through a 2-mm mesh sieve. Physical and chemical characteristics are given in (Table 1).

Incubation Conditions. The method described by Mikami *et al.*, (1984) with some modification was used in this experiment. Fresh soil samples (450g each) were incubated in glass containers (600ml capacity) at 25±2°C in the dark in incubation cabinets. After two weeks incubation time, a freshly acetone solution of each standard insecticide was applied with a pipette to the soil surface at a concentration of 5µg/g of dry soil. The containers included the soil samples were closed with "parafilm".

Table 1. Physical and Chemical Characteristics of Soil

Characteristics	
PH in (H_2O)	7.80
Organic matter,%	1.14
Clay,%	45.17
Silt,%	36.36
Sand,%	18.20
Field capacity*,%	70.20
Phosphorus,%	0.26
Total nitrogen,%	0.11

* Dry weight

Influence of Temperature and Soil Moisture on insecticides Degradation Rates.

The influence of temperature and soil moisture on the degradation rate of insecticides in conditions similar to field conditions was evaluated. Trails with 15, 20, and 30% soil moisture were incubated at temperatures of 15, 25, and 35°C. at 1,3,7,14,28,45, and 60 days after insecticide treatment, 25g of soil was sampled from each container for insecticide determination. (Samuel *et al.*, 1988; Racke *et al.*, 1996). Trials lasted 60 days to avoid a depression of the microbial activity, as reported by authors (Anderson, 1987). The temperatures and moisture values used during these trials were approximately representative of our countries weather conditions in the winter to summer. Soil weights were taken periodically to check for moisture loss.

Extraction of Chlorpyrifos.

Samples (25g each) of soil treated with chlorpyrifos were extracted with acidified acetone (98% acetone, 1% water, 1% concentrated phosphoric acid)(Racke *et al.*, 1996). A 50-ml aliquot of extraction solvent was added to soil sample in 250-ml conical flask and shaken for 4 h. After 15 min of centrifugation at around 2000 rpm; the extract was decanted into a glass vial.

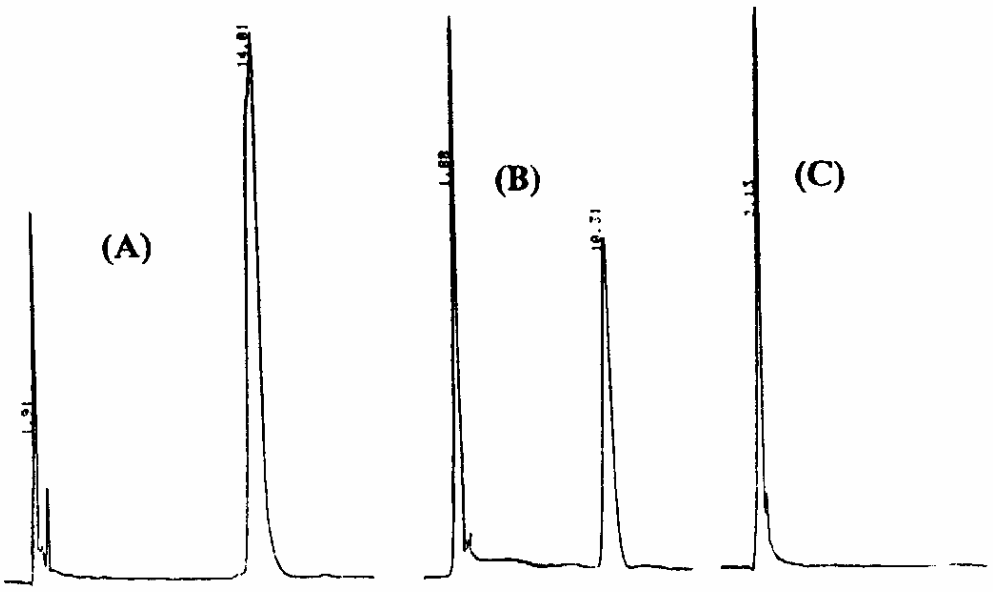
Extraction of Carbaryl.

Carbaryl was extracted from soil according to the method of Singh and Senthunathan (1992) with some modifications. Samples of treated soil (25g each) were transported into a wide mouth conical flask 250 ml. 50-ml of chloroform- diethyl ether (1:1,v/v) was added to each flask. The flasks were covered with " para film" and then the contents macerated at a high speed for 10 min. then the flasks were transported to a mechanical shaker and shacked for 10 min. at 20°C. The flasks were allowed to stand for several minutes to obtain separation phase. The separation phase was achieved by gently swirling the contents of the flasks in centrifuge tubes for centrifugation, and then the extract was decanted into a glass vial. Recoveries of chlorpyrifos and carbaryl from

soil samples fortified in the range 0.1- 1.0 µg/g were 98.3 ±1.2 and 97.4 ± 2.2 % for chlorpyrifos and carbaryl, respectively.

Analysis of Chlorpyrifos and Carbaryl.

Extracts of chlorpyrifos or carbaryl were analyzed quantitatively by high- performance liquid chromatography (HPLC) to determine the relative proportions of these insecticides and metabolites present. HPLC instrument was used for the analysis under the following conditions: µ Bondapak C18 column (25 cm length x 4.5 mm i.d.), 75% acetonitrile as a mobile phase, flow rate of 1.5 ml/min. Samples of 0.1-0.5 ml were injected. Detection of standards was by UV absorbance at 300 nm. Known standards were injected each day for identification purposes. The retention times of chlorpyrifos and carbaryl under these conditions were approximately 14 and 10 min, respectively (Figure 1). The amount of these insecticides was calculated on the basis of the peak areas obtained with standardized authentic samples analyzed under the same HPLC conditions.



Figure(1). HPLC chromatograms of (A): Standard chlorpyrifos; (B): Standard carbaryl; (C): Extract of untreated soil.

Statistical Analysis of Data.

The data presented here are based on dry weight of soil and corrected for recovery efficiency of the analytical methods. The data were subjected to a kinetic analysis, assuming that degradation of both insecticides follow first- order kinetics. The integrated form of the first-order kinetic equation (Atkins, 1994) is:

$$C_t = C_0 e^{-kt}$$

Where: t is the time after application, C_0 is the estimated initial concentration, Ct is the concentration of the pesticide in soil at time t, and k is the rate constant (min). The rate constant was derived from the slope of the linear regression of the logarithms of the concentration against time, assuming the linear relationship. Time for 50% loss ($t_{1/2}$) was calculated from this rate constant and the above equation becomes:

$$t_{1/2} = -0.6932/k$$ (Trubey *et al.*, 1998).

RESULTS AND DISCUSSIONS

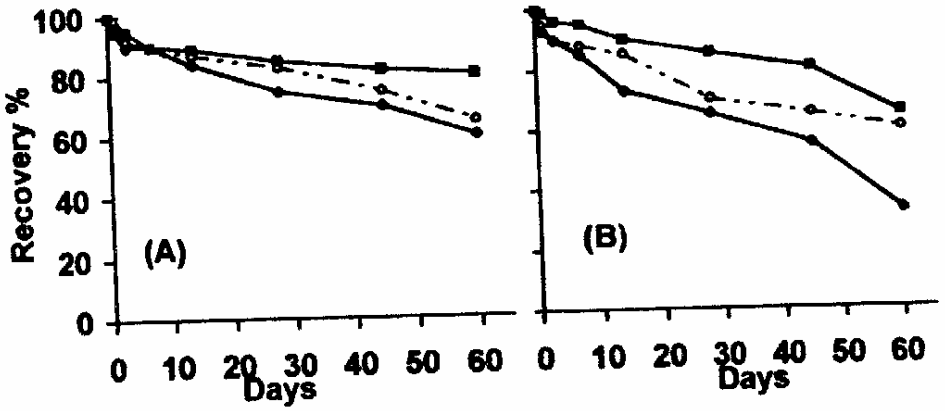
Chlorpyrifos and Carbaryl Degradation.

All the degradation rates were calculated from the assumption that the degradation of each compound followed first-order kinetics. The first- order rate constants and half-lives are showed in (Table 2). The recovery percentages from soil treated with either chlorpyrifos or carbaryl at different temperatures with different moisture contents are shown in (Figures 2,3 and 4). For chlorpyrifos, soil moisture and temperature had a different effect on degradation. When the soil moisture was made to vary from 15 to 20 to 30% at 15°C, degradation was slowly increased, and the half-lives were decreased from 148 to 90.1 to 76 days, respectively. At 25°C there was a high degradation rate and the half-life decreased by a factor of 1.9 (60÷32.5 days) as the soil moisture increased from 15 to 30%. Increasing the temperature to 35°C increases degradation by a factor of 2.6 (56.1÷21.9). Strongly increase occurs with a temperature variation from 15 to 35°C by factors of 3.2 (90.1÷28.1 days) and 3.5 (76-21.9 days) as soil moisture increased from 20% to 30% (Table2).

For carbaryl, at 15°C increasing soil moisture increases the degradation rate as for chlorpyrifos; increasing soil moisture from 15 to 30% increases degradation by a factor of 2.3 (100÷44.6). When the temperature was made to vary from 15 to 35°C degradation increased by a factor of 2.6 at 15% and with a constant factor of 3.9 at either of 20% or 30% moisture content. (Table 2).

Table (2): Rate Constant (K) and Half-life ($t_{1/2}$) Values for Chlorpyrifos and Carbaryl Degradation in Soil at Different Temperatures with Different Soil Moisture Contents.

			Chlorpyrifos			Carbaryl		
Trial	Temp, °C	Soil moisture, %	kx10^{-5} (min)	$t_{1/2}$, (days)	R^2	kx10^{-5} (min)	$t_{1/2}$, (days)	R^2
1	15	15	0.33	148.0	0.85	0.48	100.0	0.97
2		20	0.53	90.1	0.88	0.68	70.8	0.93
3		30	0.63	76.0	0.96	1.08	44.6	0.96
4	25	15	0.80	60.0	0.96	0.92	52.5	0.96
5		20	1.30	37.5	0.99	1.48	32.5	0.98
6		30	1.48	32.5	0.98	1.67	28.8	0.96
7	35	15	0.86	56.1	0.97	1.25	38.1	0.98
8		20	1.71	28.1	0.97	2.66	18.0	0.99
9		30	2.19	21.9	0.93	4.17	11.5	0.96



Figure(2). Degradation of (A) chlorpyrifos and (B) carbaryl at 15°C with (■): 15%; (○): 20%; (◆): 30% soil moisture contents.

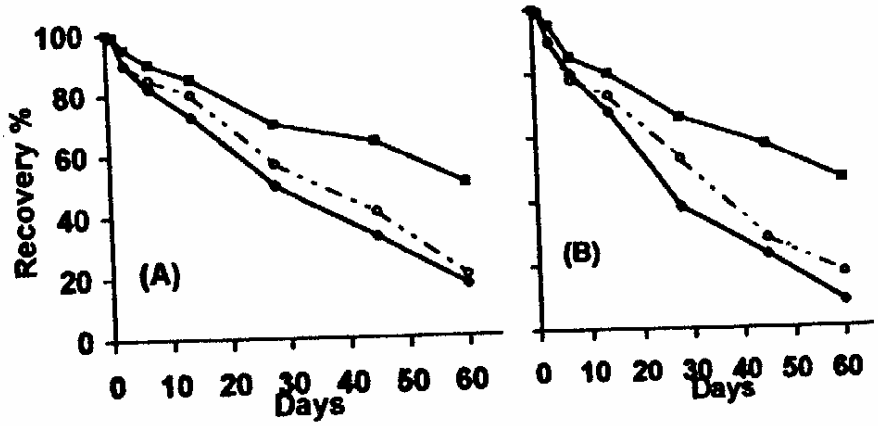


Figure 3. Degradation of (A) chlorpyrifos and (B) carbaryl at 25°C with, (■): 15%; (○): 20%; (◆): 30% soil moisture contents.

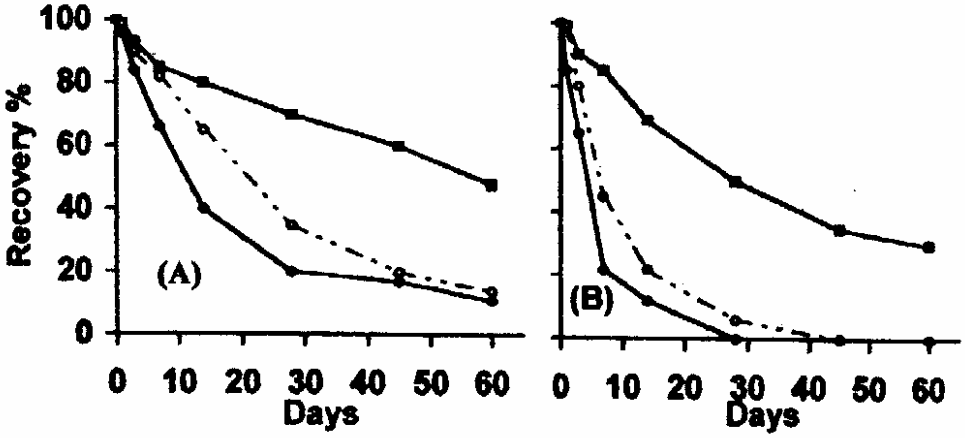
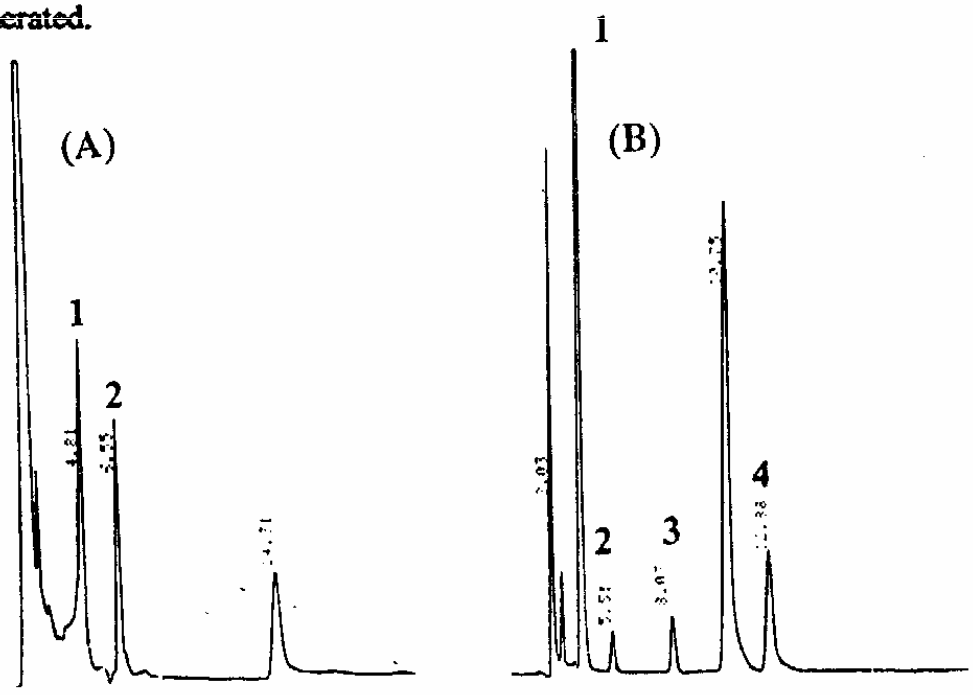


Figure (4): Degradation of (A) chlorpyrifos and (B) carbaryl at 35°C with, (■): 15%; (○): 20%; (◆): 30% soil moisture contents.

Overall, both chlorpyrifos and carbaryl are affected by soil moisture and temperature but different amounts of variation occur with increasing moisture and temperature.

Figure 5 displays a portion of HPLC analysis for both tested insecticides extracted from soil incubated with high moisture content at high temperature. There was at least 4 degradation products were detected for carbaryl, while 2 degradation products only were observed in the case of chlorpyrifos. At low temperature or soil moisture no metabolites were detected by HPLC. Chlorpyrifos is initially degraded in soil to 3,5,6-trichloro-2- pyridinol (TCP) and subsequently to organo chlorine compounds, while carbaryl is degraded to 1- naphthol (Worthing, 1987). The presence of hydrogen peroxide increases the rate of degradation of chlorpyrifos to detectable TCP; in contrast, the degradation product ofcarbaryl (1-naphthol),

which is instantaneously formed in alkaline medium, is unstable in the presence of hydrogen peroxide (Espinosa-mansilla *et al.*, 1994a,b). The rapid degradation of these insecticides in moist soil is consistent with results from previous investigations (Patil *et al.*, 1988; Samuel *et al.*, 1988). Normally expect that a faster decay rate of either chlorpyrifos or carbaryl in moist soil than in dry soil because microorganisms contribute to their degradation and microbial activity should be greater in soil with higher moisture contents. The kinetics and pathways have been particular well studied for many insecticides and herbicides. Although mechanisms of pesticides degradation in soil may be either abiotic (hydrolysis and photolysis) or microbiological in nature, it has been the letter which has received the most research focus (Lal, 1984; Racke and Coats, 1990; Miels *et al.*,1984;Racke *et al.*,1990;Hafez1994).In contrast, several investigations have reported no apparent microbial contribution to pesticides degradation in some soils (Jones and Hastings 1981; Yoshioka *et al.*, 1991). However, little information on the important of the hydrolytic degradation mechanism in the soil environment has been generated.



Figure(5): HPLC chromatograms of (A) chlorpyrifos and (B) carbaryl and their degradation products in soil.

Presumably, higher temperature promotes both biological and nonbiological degradation of these insecticides. It is unlikely that volatilization was an important factor at higher temperatures in these experiments because the treated soil were incubated in closed containers.

In conclusion, our results confirm that as with most pesticides, chlorpyrifos and carbaryl degradation rate in soil was faster at high temperature with increasing soil moisture contents, and this will influence the environmental fate of these insecticides in field under similar conditions.

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الملخص العربى

تحطم الكلوربيريفوس والكاربارايل فى التربة: تأثير الحرارة ورطوبة التربة

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الهدف من البحث هو دراسة تأثير كل من الحرارة ورطوبة التربةعلى تحطم مبيدى الكلوربيريفوس والكاربارايل فى التربة الطينية الطميية تحت الظروف المعملية .تم تشبيع عينات من التربة المعاملة بكل مبيد على حدة بالرطوبة عند المستويات ١٥%، ٢٠%، ٣٠% وتم تحضينها بعد ذلك عند كل مستوى رطوبى على درجات حرارة ١٥ ، ٢٥ ، ٣٥ درجة مئوية حتى نهاية التجربة. وقد أظهرت النتائج زيادة معدلات تحطم كلا المبيدين بزيادة كل من الحرارة والرطوبة. حيث انخفضت قيمة نصف العمر لمبيد الكلوربيريفوس من ١٤٨ الى ٧٦ يوم عند درجة الحرارة ١٥ درجة مئوية ، ومن ٦٠ الى ٣٢.٥يوم عند درجة الحرارة ٢٥ درجة مئوية وذلك عند زيادة محتوى رطوبة التربة من ١٥% الى ٣٠%. بينما أنخفضت قيمة نصف العمر لمبيد الكاربارايل تحت نفس الظروف من ١٠٠ الى ٤٤.٦يوم عند ١٥ درجة مئوية ومن ٥٢.٥ الى ٢٨.٨ يوم عند درجة ٢٥ درجة مئوية. كما سجلت النتائج أعلى معدل تحطم لأى من المبيدين عند درجة الحرارة ٣٥ درجة مئوية وذلك عند زيادة محتوى رطوبة التربة من ١٥ الى ٣٠%، حيث أنخفضت قيمة نصف العمر من ٥٦.١ الى ٢١.٩ يوم لمبيد الكلوربيريفوس ومن ٣٨.١ الى ١١.٥ يوم لمبيد الكاربارايل. من ناحية أخرى، أوضحت نتائج التحليل الكروماتوجرافى بأستخدام جهاز الـ HPLC ظهور أربعة نواتج تحطم لمبيد الكاربارايل بينما ظهر ناتجين فقط لمبيد الكلوربيريفوس وذلك تحت ظروف الحرارة والرطوبة المرتفعة بينما لم توجد أى نواتج تحطم لأى من المبيدين عند كل من درجة الحرارة والرطوبة المنخفضة.