

AN ABSTRACT OF THE THESIS OF

Pongsri Biadul for the degree of Master of Science in  
Soil Science presented on August 1, 1986

Title : Degradation and Behavior of Chlorpyrifos-methyl  
and Propoxur in Soil : a Comparison between Thailand and  
Oregon Soils.

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Chlorpyrifos-methyl, an organophosphate insecticide, and propoxur, a carbamate insecticide both widely used in Thailand, were studied in the laboratory for degradation and behavior in two Thai and two Oregon soils. The purpose of the study was to ascertain the comparative persistence and to measure behavior such as adsorption, evaporation and leaching in the soil environment as a background for predicting or estimating the hazard that may be presented by these two chemicals.

The degradation studies of chlorpyrifos-methyl were conducted on four different soils; clay and loamy sand from Thailand, and silt loam and loam soil from Oregon. The variables used included three different temperatures: 1.7 C (35 F), 23 C (70 F), and 32 C (89.6 F); three

moisture contents: saturation, field capacity, and midway between field capacity and wilting point at a temperature of 30 C; and pH of 6.5 and 7.3 for the loamy sand at moisture content midway between field capacity and wilting point at 30 C temperature.

The effect of the two chemicals on microorganismal activity was studied using  $^{14}\text{C}$ -glucose as an indicator in clay and silt loam soils at 30 C at saturated moisture content.

The adsorption of chlorpyrifos-methyl on clay and silt loam soils was determined at 23 C. The vapor pressure of propoxur at 23 C and 32 C was determined. The evaporation rate of chlorpyrifos-methyl and propoxur from clay and silt loam soils at 32 C was measured. Leaching of the two chemicals in clay and silt loam was measured in soil columns to compare their mobility.

Considerable variation at different sampling intervals in the degradation study made precise calculation of half-life and rate impossible. However, a consistent trend in degradation as affected by each environmental factor was apparent. The chlorpyrifos-methyl degradation rate responded to temperature: 32 C > 23 C > 17 C; and moisture: midway between field capacity and wilting point > field capacity > saturation; soils: loamy sand > clay > silt loam > loam. Both chlorpyrifos-

methyl and propoxur showed degradation in loamy sand at pH 7.3 > pH 6.5.

The effect on microbial activity as evidenced by <sup>14</sup>C-glucose metabolism was chlorpyrifos-methyl > propoxur on silt loam and propoxur > chlorpyrifos-methyl on clay soil. The microbial activity depended on the concentration of these two chemicals, and was 100 ppm > 500 ppm > 1000 ppm for a 1-3 hours incubation period. Metabolism with the chemicals was higher than the control after 4 hours.

The distribution coefficient (Kd) of chlorpyrifos-methyl was 93.1 on clay and 76.9 on silt loam.

The relative evaporation rate of chlorpyrifos-methyl was field capacity > air dry soil and silt loam > clay soil.

The vapor pressure of pure propoxur determined at 23 C was  $3.5 \times 10^{-6}$  mm Hg and  $1.5 \times 10^{-5}$  mm Hg at 32 C. The calculated latent heat of evaporation was 29 Kcal/mole.

Chlorpyrifos-methyl was less mobile than propoxur. The leachate of chlorpyrifos-methyl contained less than 0.1 % and 0.5 % of the initial concentration for the clay and silt loam soils respectively, but 56 % and 60 % of propoxur was found leached from the clay and silt loam soils.

Degradation and Behavior  
of Chlorpyrifos-methyl and Propoxur in Soil:  
a Comparison between Thailand and Oregon Soils

by

Pongsri Biadul

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

Completed August 1, 1986

Commencement June 1987

APPROVED:

*Redacted for Privacy*

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Date thesis is presented August 1, 1986

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## ACKNOWLEDGEMENTS

I would like to express my deep appreciation to the International Atomic Energy Agency in Vienna, Austria and National Research Council of the United States who provide the opportunity and support to study at Oregon State University. Also, I thank the department of Agriculture in Thailand for permission to do so.

I am sincerely grateful to both of my advisors; Dr. B.P. Warkentin, Soil Science, and Dr. V.H. Freed, Agricultural Chemistry, for their advice and encouragement throughout my program of study and research work. Also thanks is due to Department of Agricultural Chemistry for space and facilities. Special thanks is given to Dr. Ralph Berry, Dr. L.A. Norris, Dr. David Hannaway, and Dr. E.D. Palmes for their valuable assistance.

I deeply appreciate the advice and assistance of Dr. S.C. Fang, Agricultural Chemistry in the experiments on microbial activity. Many thanks are given to D.W. Schmedding, Gene Johnson, Yousef El. Madhun, Susan Cheng, and researchers in Agricultural chemistry for their help during the course of the research. I also appreciate the kind help of Dr. Herb Huddleton from Soil Science in sampling soil samples.

Sincere thanks is due to Prof. Manat Suchawipun from Kasetsart University and Sivaporn Sakulthiengtrong from

Agricultural Toxic Substances Division, Department of  
Agriculture, Thailand in providing information and soil  
samples from Thailand and their continued encouragement  
through out the program.

Thanks to all my friends who helped make my time  
and studies at OSU so enjoyable and rewarding.

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# Degradation and Behavior of Chlorpyrifos-methyl and Propoxur in Soil: a Comparison between Thailand and Oregon Soils.

## INTRODUCTION

Pesticides are one of the most valuable tools for controlling losses from insects, diseases and weed infestations in agricultural, forest and housing areas if wisely used. Many classes of organic chemicals such as organochlorines, organophosphates and carbamates have been used as pesticides beginning before World War II. As people discovered that the organochlorine pesticides have long persistence in the environment, the organophosphates and carbamates which are shorter lived became more widely used.

Chlorpyrifos-methyl [o,o-dimethyl o-(3,5,6-trichloro-2-pyridyl) phosphorothioate]; one of the most widely used organophosphate pesticides was developed by the Dow Chemical Company in 1965 (Spencer,1981). It is a broad spectrum insecticide that is active against stored grain pests, rice stem borer, plant and leaf hoppers, and mosquitoes (Spencer,1981).

Propoxur [2-(1-methyl ethoxy) phenyl methylcarbamate] was developed by Chemagro's parent Company, Levenkusen, West Germany (Anderson,1973). It is effective against insects affecting man and animal such as cockroaches, flies and mosquitoes, for control of aphids, lygus bugs,

grasshoppers and other insects on various crops, as well as root maggots and root worms on many crops in soils (Anderson, 1973.)

These two chemicals are widely used both in Thailand and the United States for controlling the insects described above. The concerns are whether continued foliar and soil application of these two pesticides, or others, and their accumulation in the soil, will constitute a source of impact on the environment. A chemical may persist, adsorb, dissipate, leach, and evaporate in/from soil. With different soils, characteristics, and variation in climatic situations, there is the question whether these factors will result in a different behavior of the pesticides in soil. Thus, it is of great interest to study the degradation and behavior of these two pesticides in soils from different places. Two soil samples each, from Thailand and Oregon were chosen for this study.

The objectives of this study are to answer the following research questions;

1. What is the effect of temperature, moisture content, organic matter, and clay content on the rate of degradation of chlorpyrifos-methyl in different soils from Thailand and Oregon?
2. What is the effect of pH on the degradation rate of chlorpyrifos-methyl and propoxur in Thailand soil?



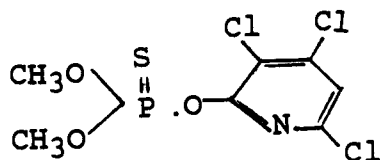
3. Does either chlorpyrifos-methyl or propoxur affect microbial activity in Thailand and Oregon soils, and is there a difference due to origin of the soil?

4. Is there a demonstrable difference in the behavior of chlorpyrifos-methyl in adsorption and chlorpyrifos-methyl and propoxur in evaporation and leaching in Thailand and Oregon soils?

## REVIEW OF LITERATURE

Insecticide characteristicsChlorpyrifos-methyl <sup>1</sup>

o,o - dimethyl o - (3,5,6 - trichloro - 2 pyridyl),  
phosphorothioate



Alternative names: Reldan (Dow Chemical Company), Zertell

Molecular weight: (C<sub>7</sub>H<sub>7</sub>Cl<sub>3</sub>NO<sub>3</sub>PS) 322.6

Physical properties: melting point 45.5 - 46.6 C

vapor pressure 4.22 x 10<sup>-5</sup> mm Hg at 25 C

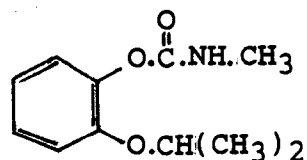
solubility in water 0.4 ppm at 25 C

partition coefficient, octanol-water <sup>2</sup>

20,200

Propoxur <sup>1,3</sup>

2-(1-Methylethoxy) phenyl methylcarbamate



Alternative names: Baygon, Blattanex, Under (Bayer)

(Mobay/Chemagro), aprocarb (common)

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1. E.Y. Spencer, 1982    2. Freed et al., 1979

3. C.A. Anderson, 1973

name approved by BSI), PHC (Japan),  
Sendran (animal health), Suncide,  
Aracarb, Tugar Fliegenkugel

Molecular weight: ( $C_{11}H_{15}NO_3$ ) 209.2

Physical properties: melting point 91.5 C

vapor pressure  $10^{-2}$  mm Hg at 120 C

solubility in water 2,000 ppm at 20 C

### Degradation

The bulk of a chemical applied as a pesticide comes in contact with soil, where it may play an important role as a contaminant to the soil environment. The important consideration is the role of degradation in reducing the concentration. Goring et al. (1975) described the three important aspects of pesticide degradation; these are 1) the causes of degradation, 2) the pathways of degradation, and 3) the rates of degradation. The two major degradation pathways for chemicals in soil are biodegradation and photolysis, of which biodegradation represents the major route and occurs simultaneously with chemical degradation (Goring et al., 1975).

The degradation of pesticide in soil depends upon its persistence and therefore influences the disappearance rate from the environment. The rate constant in decomposition appears to follow the first-order power rate model as given by Hamaker (1972):

$$\ln C_t = kt + \ln C_0$$

where  $C_0$  = initial concentration;  $C_t$  = concentration at time,  $t$ ; and  $k$  = first order rate constant. The rate constant has been related to the half-life ( $t_{1/2}$ ), the time required for one half of the chemical to disappear, as

$$t_{1/2} = 0.693 / k$$

which is useful for comparing the persistence of one chemical to another. Freed et al. (1979) showed the half-lives of phosmet and chlorpyrifos in moist Willamette soil were 60 and 120 days respectively, which indicated the greater persistence of chlorpyrifos compared with phosmet. Also the study of Page (1983) showed a half-life of 43 days for gamma-HCH, which was shorter than 102 days for chlorpyrifos-methyl, in Ponderosa pine bark.

There are many factors that affect the rate of degradation. Goring et al. (1975) discussed sorption, climatic factors of temperature and moisture, and soil factors of pH, organic matter, clay and soil biological population. Felsol et al. (1982) showed that the effect of temperature was more important than moisture in influencing the dissipation of terbufos. Chapman et al. (1986) indicated that moisture was important in affecting the persistence of carbofuran in soils. Helweg (1981) concluded from his work on the influence of temperature, moisture, clay and organic material on degradation of  $^{14}\text{C}$ -labelled maleic hydrazide (MH) in soil that: "between 1

and 30 C at a constant moisture content (full field capacity), the mean degradation rate increased by a factor of 3 for each temperature increment of 10 C. Above 35 C, the degradation rate decreased. At soil moisture contents between wilting point and 80-90 % of field capacity, the degradation rate doubled with an increase in moisture content to 50 % of field capacity (constant temperature, 25 C). Above field capacity, the degradation rate was either unchanged or decreased. Below wilting point the degradation was very slow, even after 2 months. The rate of decomposition of MH at all temperatures and moisture contents was lowest in the soil with the highest content of organic matter and the lowest clay content".

Miles et al. (1984) studied the influence of moisture on the persistence of chlorpyrifos and chlorfenvinphos in sterile and untreated mineral and organic soils. He found that chlorpyrifos was fairly stable in sterile soils, but disappeared most rapidly from air-dry natural soil, and slightly less rapidly from soil at 20, 40, and 60 % of moisture holding capacity at 28 C. Chlorfenvinphos, in contrast to chlorpyrifos was more stable in air-dry natural soils and fairly stable in sterile soil. He pointed out that there was specific microbial degradation in natural soils.

### Adsorption

Haque (1975) found that the adsorption process plays

an important role in determining the fate and behavior of pesticides and related chemicals in a soil environment. Adsorption influences leaching, diffusion, vapor loss, degradation and biological availability in soil (Bailey and White, 1964; Hamaker and Thompson, 1972; Freed and Haque, 1973; Haque, 1975).

The soil-pesticide interaction is commonly represented with an isotherm. Freed and Haque (1973) indicated that a Freundlich type isotherm had been found to apply widely to the adsorption of pesticides by soils. The isotherm is shown as follows:

$$x/m = KC^n \quad (1)$$

where  $x$  = the amount of chemical sorbed

$m$  = the mass of soil

$C$  = the equilibrium concentration of the chemical

$K$  = a constant describing the extent of adsorption

and  $n$  = a constant describing the nature of the

adsorption (Hamaker and Thompson, 1972).

Taking logarithms, Eq. (1) become:

$$\log x/m = n \log C + \log K$$

which shows a linear relationship between  $\log x/m$  and  $\log C$ .

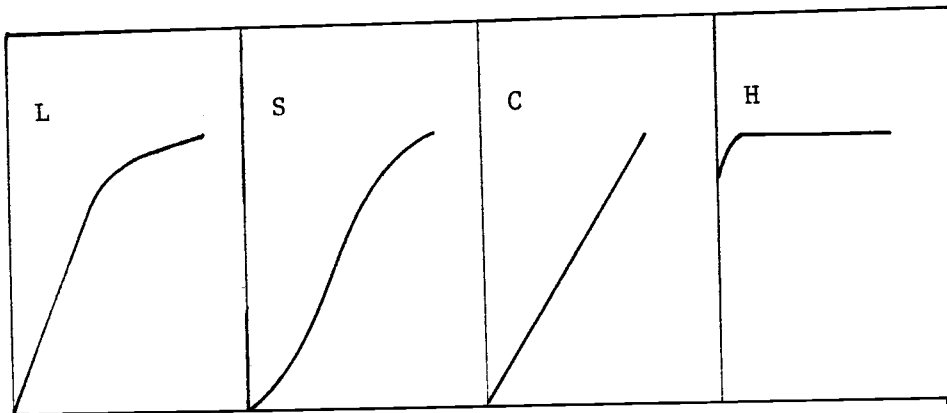
The slope,  $n$  indicates the nature of the adsorption.

Green (1974) and Weed and Weber (1974) discussed the

classification of adsorption isotherms developed from

Giles et al. In the curves, amount adsorbed is plotted

as a function of solution concentration.



Curve illustrating degree of adsorption (Green, 1974).

The L-type is most common and represents a relatively high affinity between the solid and the solute, in which the  $n$  value is less than or equal unity. The S-type indicates cooperative adsorption, with the  $n$  value greater than one. The C-type represents constant partition between solution and surface, and adsorption is always directly proportional to solute concentration. The H-type represents a very high affinity between solute and solid, which is quite uncommon.

Since  $n$  is often approximately one, the isotherm will represent the distribution coefficient of pesticide between two phases, by the equation;

$$x/m = K_d C$$

where  $K_d$  = distribution coefficient between two phases. This  $K_d$  value is an index to compare pesticides sorbed in

different soils.

Bailey and White (1964) and Hamaker and Thompson (1972) have shown the factors influencing the adsorption process. These were: structural characteristics of the chemical, the organic content of the soil, the pH of the medium, particle size, ion exchange capacity and temperature. Hamaker and Thompson (1972) found that correlation of adsorption with pH in a series of soils is poor compared with organic matter and other factors. Green (1974) showed that the pH of the system was particularly important for bases and acids. Umino and Suzuki (1984) found that chlorpyrifos-methyl suspension adsorbed more readily to coarse sand than to fine sand, and the release of the once-adsorbed chemical into water was intermediate to that of temephos and fenitrothion.

#### Evaporation

Evaporation or volatilization is a common phenomenon of organic chemicals. Thus pesticides released from application, disposal, moving as wind-blown particles, or from manufacture undergo vaporization to the environment. Although the majority of pesticides have vapor pressures that are low by the standards of practical organic chemistry, the ability of these chemicals to pass into the vapor phase is significant in relation to the quantities applied annually and also to their biological effects (Plimmer, 1976). Spencer and Farmer (1980) indicated that



air transport is probably the principle method of their dispersion over wide areas and into bodies of water far removed from sites of manufacture, use or disposal.

Plimmer (1976) also states that pesticides, as air pollutants, form a part of the total burden of organic pollutants that result from human activity. They may contribute directly to plant injury or damaging effects on wildlife far from the site of pesticide application.

Potential volatility of a chemical is related to its vapor pressure (Spencer and Cliath, 1975; 1981). The vapor pressure of a chemical is an important physical property and is useful in defining the extent to which a chemical will be transported into the atmosphere (Hague et al., 1980). It can be determined from the Gas Law as

$$PV = nRT$$

where

- P = vapor pressure of pure chemical
- V = volume of saturated chemical
- n = W/MW = moles of chemical
- R = gas constant, 1.9865 cal/mole K
- T = absolute temperature, K

Theoretically, the thermodynamic treatment is based on the relationship between vapor pressure and temperature known as the Clapeyron-Clausius equation (Plimmer, 1976):

$$dP/dT = \Delta H/T^2V$$

where  $dP/dT$  = change in vapor pressure with temperature  
 $\Delta H$  = heat absorbed during the change in state

(solid to vapor), which is equal to  
latent heat of evaporation

$\Delta V$  = volume change

$T$  = absolute temperature, K

If the behavior of the vapor is assumed to be that of an ideal gas, then

$$d \ln P/dT = \Delta H/RT^2 \quad (1)$$

Hartley and Graham-Bryce (1980) stated that over a small range of temperature,  $\Delta H$  can be assumed to be independent of temperature and calculated by deriving Eq. (1) as follows:

$$\begin{aligned} \ln P_1/ P_2 &= \Delta H/R ( \Delta T/ T_1 T_2 ) \\ \text{or } \log P_1/ P_2 &= \Delta H/2.303R ( \Delta T/ T_1 T_2 ) \end{aligned}$$

The actual vaporization rate depends on environmental conditions and all factors that modify the effective vapor pressure of the chemical (Spencer and Cliath, 1975,1981). Volatilization from soil is much more complicated and difficult to predict because of the many parameters affecting adsorption, movement and persistence (Spencer and Cliath, 1981). Factors affecting vaporization rate are the equilibrium distribution between air, water and soil matrix phases, and such soil and environmental factors as adsorption coefficient, solubility and rate of movement to the soil surface (Spencer et al. 1973). The rate of movement to the soil surface in a dry soil depends upon diffusion due to a concentration gradient. Mass flow

or a wick effect occurs in moist soil in which any chemical in the soil solution moves toward the surface with the water (Hartley, 1969). Spencer and Cliath (1973) stated that the solubility of lindane, which is greater than that of dieldrin was enhanced through volatilization by concurrent evaporation of water from the soil surface.

Spencer and Farmer (1980) stated that vaporization of a chemical from a surface of constant area is independent of the depth of the chemical layer, and under constant conditions the loss rate will be constant until so little substance remains that it no longer can cover the surface. They also stated that incorporation of an organic chemical into the soil decreases its concentration at the evaporation surfaces, thereby greatly reducing the volatilization rate. Farmer et al. (1972) showed that the rate of volatilization of dieldrin from Gila silt loam increased with increasing soil pesticide concentration until it reached the concentration to give a maximum saturation vapor density equivalent to that of the pure compound. They also found that increasing temperature by 10 C increased the rate of volatilization approximately four fold. Increasing the rate of air movement over the soil surface from 0.005 to 0.018 mile/hour increased the rate of volatilization two fold. Dieldrin volatilization from Gila silt loam depended on soil water content, but did not dependent on rate of water loss from the soil.

Volatilization decreased rapidly as the soil water content decreased and was essentially zero below a soil water content of 2.8 %.

Even though the measurement of volatilization from soil is somewhat arbitrary because of the many variables affecting rate of volatilization, measurements under a uniform set of conditions can be extremely helpful in comparing relative volatility of chemicals and as a research tool in establishing the parameters needed to predict volatilization from soil or soil covered land fills under various conditions (Spencer and Cliath, 1981).

#### Leaching

Leaching is defined as the movement of a chemical through a soil matrix with water (Freed and Haque, 1973) or the water transport of a chemical in a soil profile (Helling and Dragun, 1980). Leaching of chemicals through soil is an environmental concern because of the possibility that chemicals will reach the water table and contaminate the ground water (Hamaker, 1975). A knowledge of leaching can help to prevent undesired environmental consequences from the use, manufacture, distribution in commerce, or disposal of the chemical (Helling and Dragun, 1980).

The simplest index for leaching is the adsorption coefficient (Hamaker, 1975). McCall et al. (1981) presented a simple relationship to predict leaching of a

chemical if the soil adsorption coefficient is known along with the organic carbon content of the soil. Hamaker and Thompson (1972) compiled a ranking of pesticides using  $K_{oc}$ , the adsorption coefficient in response to the organic carbon content, as follows:

$$K_{oc} = K_d \times 100 / \% \text{ organic carbon}$$

when, organic carbon = 1/1.728 organic matter.

Their data are shown below:

<u>Chemical</u>	<u>Koc</u>	<u>Mobility</u>
Chloramben	12.8	mobile
2,4-D	32	↓ immobility
Propham	51	
Atrazine	172	
Chlorpropham	245	
Prometryne	513	
Chloroxuron	4,986	
Paraquat	20,000	
DDT	243,000	

Many other factors affect leaching (Freed and Haque, 1973; Helling and Dragun, 1980) such as temperature, solubility, partition coefficient, distribution coefficient, type of soil, moisture or rain fall, adsorption, and rate of degradation. Since many factors affect leaching of a chemical through soil, it is difficult to predict the distribution of a chemical in the soil profile from simple laboratory tests (McCall et al., 1981). However such tests can serve to assess qualitatively the leaching tendencies of chemicals in order to rank and compare them (Hamaker, 1975; McCall et al., 1981), and therefore make use of available experience with leaching of chemicals under field conditions.

## MATERIALS AND METHODS

### Soil sampling and preparation

Four different soil samples were taken from agricultural areas where pesticides are used. Two different soils, a clay and a loamy sand from Thailand, and the other two, a Woodburn silt loam (Fine-silty, mixed, mesic Aquultic Argixeroll) and a Metholius loam (Coarse-loamy, mixed, mesic Durixerollic Camborthid) from Oregon were collected. Soils were sampled from the top 6-8 inches, air dried one week, and ground to pass a 20 mesh sieve. The soils were stored at room temperature.

Each soil sample was analyzed for physical and chemical properties by the Soil Physics and Soil Testing Laboratories, Department of Soil Science, Oregon State University. The physical and chemical properties of the four soils are shown in Tables 1 and 2.

### Recovery of chlorpyrifos-methyl and propoxur in soil

Duplicate ten grams samples of each soil were fortified with chlorpyrifos-methyl (1 µg/ml in hexane) and propoxur (10 µg/ml in hexane) to obtain 0.1 and 1.0 ppm chlorpyrifos-methyl and propoxur in soil respectively. Chlorpyrifos-methyl, technical grade, 96.5 % from Dow Chemical Company and propoxur, analytical grade, 98 % from Applied Science Laboratories, were used. Samples of soils were placed in cellulose thimbles (45 mm x 123 mm) and extracted with 200 ml of hexane : acetone (4:1) in soxhlet

Table 1. The physical properties of soils.

Location	Code	Textural class	Particle size(%)			Moisture content (%)			
			Sand	Silt	Clay	0.3 bar <sup>1</sup>	15 bar	1/2(0.3-15)bar	air dry
Nonthaburi, TH Thailand	TH	clay	4.3	29.6	66.0	49.4	25.0	37.2	8.3
Parkchong, Thailand	TL	loamy sand	81.7	14.4	3.9	19.9	2.7	11.3	0.2
Corvallis, Oregon	OH	silt loam	7.2	67.4	25.4	35.9	10.5	23.2	1.9
Central Oregon	OL	loam	47.1	29.8	23.1	34.2	11.8	23.0	2.4

<sup>1</sup> 1 bar = 10 MPa

Table 2. The chemical properties of soils.

Location	Code	Textural class	pH	Organic matter(%)	CEC <sup>1</sup> (meq/100g)
Nonthaburi, Thailand	TH	clay	7.8	2.72	29.0
Parkchong, Thailand	TL	loamy sand	6.5	0.85	2.4
Corvallis, Oregon	OH	silt loam	5.6	2.88	12.4
Central Oregon	OL	loam	5.7	1.65	16.8

<sup>1</sup> cation exchange capacity

extractors at 55-60 C for 8 hours. The extracted solutions were concentrated to 5 ml using a flow of air. The clean-up of chlorpyrifos-methyl for analyses was as follows.

The concentrated solution was passed through a florisil column as described by Szeto and Sundaram (1981) but modified for eluting solvents. Florisil, 100/200 mesh, was activated at 450 C for 10 hours and kept in a 150-200 C oven before use. The florisil was deactivated with 2 % milli - Q water and let stand for 24 hours before using. A chromatographic column (32 cm x 1.5 cm o.d.) was packed with 6 grams of deactivated florisil with one half inch of anhydrous sodium sulfate on top and prewashed with 20 ml benzene followed by 20 ml hexane. The sample was then eluted with 100 ml of 50 % hexane in benzene. The first 30 ml of eluate was discarded, the rest of the eluate (70 ml) evaporated and adjusted to volume for quantitative analysis in a Tracor 550 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron-capture detector. The conditions in gas chromatograph and recovery, the chromatogram and the elution pattern are shown in Table 3, and Figures A.1 and A.2 of the Appendix respectively.

Propoxur clean-up was as follows. One (1) ml of concentrated solution was cleaned in a disposable pasteur pipet (5 3/4 inch x 0.7 mm o.d.) packed with 2 % deactivated florisil 0.5 grams and 1 cm of anhydrous



sodium sulfate on top. The column was prewashed with 3 ml hexane which was discarded and the propoxur eluted with 3 ml acetone. This eluate in acetone was retained and evaporated to dryness before adjusting to volume with hexane for gas chromatographic analysis. The gas chromatography conditions and recovery, the chromatogram and the elution pattern are shown in Table 3, and Figures A.3 and A.4 of the Appendix respectively.

Table 3. Gas chromatography conditions for determining chlorpyrifos-methyl and propoxur.

Condition	Chlorpyrifos-methyl	Propoxur
Column length (feet)	6	6
Column inside diameter (mm)	2	2
Packing	low level carbowax 20 M, 100-200 mesh	low level carbowax 20 M, 100-200 mesh
Mode	RF	RF
Oven temperature(C)	200	170
Detector temperature(C)	290	290
Inlet temperature(C)	220	220
Outlet temperature(C)	205	205
Nitrogen flow (ml/min)	30	60
Recovery in soil +std. deviation(%)	96.9 <sub>±</sub> 4.4	116.1 <sub>±</sub> 4.6
Recovery in water +std. deviation(%)	99.2 <sub>±</sub> 9.9	91.3 <sub>±</sub> 5.3

#### Recovery of chlorpyrifos-methyl and propoxur in water

Water (100 ml) was fortified with chlorpyrifos-methyl (1 µg/ml) and propoxur (50 µg/ml) to make concentrations of 0.01 ppm and 1.0 ppm respectively. The water samples were extracted with 100, 50 and 50 ml of benzene, the

benzene extract combined and filtered through sodium sulfate, evaporated and adjusted to volume with hexane before quantitative analysis with gas chromatography as described above. The results are shown in Table 3.

Effect of temperature on the degradation of chlorpyrifos-methyl

Duplicate 250 gram samples of air-dried soil were placed in one quart Mason jars. All four soils were used. Each sample was incorporated with chlorpyrifos-methyl in hexane to make a concentration of 0.1 ppm in soil. The jars were covered with aluminum foil and closed tightly. The soil in the jars was mixed thoroughly in a shaker for 2 hours and incubated at three different temperatures; 1.7 C (35 F), 23 C (70 F) and 32 C (89.6 F). Each soil was sampled at intervals from zero time (the time from start of incubation), 2, 4 days, 1, 2, 3, 4, 5, 6, 7, and 8 weeks respectively. Samples were analyzed for the chemical remaining by the procedures described above.

Effect of moisture content on the degradation of chlorpyrifos-methyl

Three 500 gram samples of each of the four soils were placed in one quart Mason jars and brought to a concentration of 0.1 ppm with chlorpyrifos-methyl in hexane. The soil was mixed thoroughly in a shaker for 2 hours before moisture adjustment.

Each soil was brought to three different moisture

contents: saturated, 0.3 bar as an estimate of field capacity, and half-way between field capacity and wilting point (1/2 between 0.3 and 15 bar). The moisture contents of each soil are shown in Table 1. All of the samples were placed in a water incubator at 30 C. Duplicate samples of soil from each moisture content level were taken at intervals from zero time, 2, 4 days, 1, 2, 3, 4, 5, 6, 7, and 8 weeks respectively. The wet soil sample was mixed with an equal amount of anhydrous sodium sulfate to adsorb water before extraction as described above.

Effect of pH on the degradation of chlorpyrifos-methyl and propoxur in loamy sand from Thailand

The original pH of the loamy sand was 6.5. A sample of 500 grams was modified to a higher pH with calcium hydroxide powder one month before starting the experiment. The 500 grams of soil was spread in a very thin layer on aluminum foil. Calcium hydroxide powder at the rate of 0.1 ton/acre soil was spread uniformly on the soil, then mixed and the sample put in the Mason jar and mixed thoroughly in a roller mixer for 2 hours. The soil sample was then placed on aluminum foil again to adjust the moisture content to about two-third field capacity, mixed and kept in a Mason jar. The soil was allowed to stabilize and microbial activity was allowed to be established for one month at room temperature. The final pH was determined on 5 grams of soil mixed with 10 ml of

distilled water. The samples were allowed to stand for one hour with occasional stirring. The pH was measured with a PHM 64 Radiometer research pH meter. The modified soil had a pH of 7.3.

Two 200 gram samples of the soils, at pH 6.5 and at pH 7.3 were placed in one quart Mason jars. The soils in duplicate were incorporated with chlorpyrifos-methyl (1  $\mu\text{g}/\text{ml}$  hexane) to bring the concentration of 0.1 ppm in soil, or with with propoxur (10  $\mu\text{g}/\text{ml}$  hexane) to bring the concentration of 1 ppm in soil. Aliquots of each soil were put in 500 ml round bottom flasks to which excess hexane was added as a medium for the pesticides to disperse thoroughly in soil. These were allowed to stand for half an hour and the excess hexane evaporated in a Rotavapor. During this time soil was mixed thoroughly until the hexane was gone. The soil was placed in the Mason jar again, brought to half way between field capacity and wilting point moisture content, and incubated at 30 C. Aliquots in duplicate of the soils were taken at intervals from zero time 1, 3, 5, and 7 days for chlorpyrifos-methyl and further to 18 days for propoxur. The samples were analyzed for each chemical by gas chromatography as described above.

Effect of chlorpyrifos-methyl and propoxur on microbial activity in soils

Two soils, the silt loam soil from Oregon and the clay soil from Thailand were used in this study. A sample of ten grams of soil was placed in a two-arm flask and brought to field capacity one day before starting the experiment, and to a saturated condition at the day of starting the experiment. Chlorpyrifos-methyl or propoxur was incorporated in the soil at the rate of 100, 500, and 1,000 ppm in duplicate, with two duplicate control samples.

$^{14}\text{C}$ - glucose, uniformly labeled in all carbon positions with 0.5 mCi in 20 % ethanol, was mixed with 0.1 % non-labeled glucose to obtain 1  $\mu\text{Ci}$   $^{14}\text{C}$  / ml. The same concentration of  $^{14}\text{C}$ -glucose, 0.2  $\mu\text{Ci}$ , was added to each flask. The flasks with soil samples were placed in a water bath at 30 C. One arm of the flask was connected with the in-flow and the other with the out-flow air tube as shown in Figure A.5 of the Appendix. The flowing air, at a rate of 200 cc/min for each flask, was passed through 1 N sodium hydroxide to remove  $\text{CO}_2$  and then through water to obtain moist air to reduce soil water loss before passing through the flask. The  $^{14}\text{CO}_2$  released by metabolism was trapped in 50 ml 1N sodium hydroxide for 1, 2, 3, and 4 hour incubation periods. The  $^{14}\text{CO}_2$  in sodium hydroxide solution was reacted with 10 ml of 10 % barium

chloride and 1 ml of 2.5 % sodium carbonate to form barium carbonate. After a reaction time of one hour, the barium carbonate was filtered onto glass micropore filter paper, 2.4 cm in diameter, using vacuum. The barium carbonate filter cake was dried under a light bulb for two hours and weighed. Each sample was covered with another filter paper and put into a vial containing 3 ml Handifluor (Liquid Scintillation Counting Liquid). The  $^{14}\text{C}$  activity was counted in a Liquid Scintillation Counter (Packard-Tri-Carb model 3300).

Adsorption of chlorpyrifos-methyl on Thailand and Oregon soils

Clay soil from Thailand and silt loam soil from Oregon were used to study the adsorption of pesticides on soils. Eighteen 2 gram samples of each soil were weighed and put into 50 ml glass centrifuge tubes. Forty ml of a solution of chlorpyrifos-methyl at concentrations of 1, 5, 10, 20, and 40 ppm in water was put in triplicate tubes, with triplicate 40 ml of water used as a control. Each tube was covered with aluminum foil and the lid closed tightly. The samples were placed in the shaker and shaken for 4 hours at a temperature of 23 C, then centrifuged at 2,500 rpm for 45 minutes. Aliquots of 30 ml were removed and extracted for quantitative analysis as described.

### Evaporation of chlorpyrifos-methyl from the soil surface

Two 20 gram samples of the clay soil from Thailand and the silt loam soil from Oregon were placed in 5.9 cm diameter planchets. Soil in each planchet was incorporated with chlorpyrifos-methyl (20 mg/ml) to make a concentration of 1,000 ppm. Each soil was placed in separate closed chamber with air inflow and outflow tubes on top, and incubated in the water incubator at 32 C. The air outflow tube was connected to a flask filled with 20 ml ethylene glycol as trapping solution. The flask was connected to a vacuum to pull the vapor of chlorpyrifos-methyl into the trapping solution. The solution was collected for quantitative analysis and changed at 7 hours, 1, 2, 3, and 4 days of incubation. The experiment was repeated at field capacity moisture content. After the chemical was incorporated, the soil was brought to the field capacity moisture content before being placed in a closed chamber. The chemical was then collected in the trapping solution for quantitative analysis as described above.

### Vapor pressure of propoxur

Propoxur, technical grade from Mobay Chemical Corporation, was coated on silica sand. A large amount of propoxur was dissolved in acetone and poured into a round bottom flask containing silica sand. The acetone solution

completely covered the sand. The flask was allowed to stand for one day and then the acetone was evaporated to dryness using a Rotavapor. The coated sand was packed into a double-end tube (0.8 cm i.d. x 20 cm long). One end was connected to a water-free air inlet and the other end was connected with two solid-XAD-2-adsorbent-trap tubes (0.8 cm i.d. x 20 cm long). The water-free air flow passing through the packed tube was adjusted to 50, 75, 100, and 200 ml/min using a flow meter. The entire system was placed in an incubator room at 23 C or in a water incubator at 32 C. By timing the known volume of air passing through, the total air volume could be calculated and the amount of chemical trapped determined. The solid trap was analyzed by eluting with 200 ml of iso-octane, evaporated, and adjusted to volume for gas chromatography analysis. The vapor pressure of propoxur at these two temperatures has not been previously reported and it is important to know in assessing behavior which will help predict losses from evaporation at these temperatures.

#### Evaporation of propoxur from the soil surface

Fifty grams each of the clay and silt loam soils were placed in glass dishes (8.9 cm i.d. x 1 cm high). Soil was mixed with propoxur, 250 mg/ml, to make a concentration of 20,000 ppm and brought to field capacity moisture content. Each soil was placed in a separate closed chamber which had inflow and outflow tubes on top,



and incubated in the water incubator at 32 C with a plastic insulator covering the whole system. The outflow tube was connected to the two solid-trap tubes (0.5 cm i.d. x 12 cm long) packed with adsorbent XAD-2. The end of the second trapped tube was connected to a vacuum to pull the propoxur vapor into the solid trap. The vapor was collected for 7 hours, 1, 2, 3, 4, 5, 6, 7, and 8 day intervals for quantitative analysis.

Leaching of chlorpyrifos-methyl and propoxur from soil.

Two 50 gram samples of silt loam soil from Oregon were packed into open-end tubes which were 17 cm long and 2.6 cm in diameter. The lower end of each tube was plugged with glass wool. Soil was leached overnight with distilled water to ensure that it had attained field capacity. Chlorpyrifos-methyl and propoxur at concentrations of 50 µg and 1,000 µg respectively were applied together on the soil, then water was applied from a 500 ml separatory funnel which acted as a Marriott bottle to control the level of water at 1/2 - 3/4 inches above the soil surface. The leachate was collected every day for quantitative analysis.

Because of the low permeability of the clay soil from Thailand, it was necessary to use a vacuum to leach chlorpyrifos-methyl and propoxur through the soil using a known amount of water. Five grams of clay soil was packed in a Buchner funnel (2.6 cm i.d. x 2.5 cm long) with a

very-fine sintered glass bottom. This provided a 1.2 cm soil column. The soil was brought to field capacity and let stand one day. Duplicate columns were used. Each column received 50  $\mu\text{g}$  of chlorpyrifos-methyl and 1,000  $\mu\text{g}$  of propoxur on the surface. Water was added, and a vacuum was applied to leach the water and chemical through the column. The leachate was collected in 10 ml volumes and analyzed for chlorpyrifos-methyl and propoxur as mentioned before.

The particle density and percent porosity of these two soils is shown in Table 4.

Table 4. Particle density and porosity of soils in leaching columns.

Soil	Particle density(g/cm <sup>3</sup> )		% Porosity <sup>a</sup>
	1 <sup>b</sup>	2 <sup>c</sup>	
Clay	2.11	2.37	49.4
Loamy sand	2.66	2.46	51.2
Silt loam	2.18	2.57	53.3
Loam	2.30	2.45	51.0

a calculated from the equation;

$$\% \text{ Porosity} = 100 \left[ \frac{1 - \text{Bulk density}}{\text{Particle density}} \right]$$

using 1.2 g/cm<sup>3</sup> for bulk density and value of particle density from 2

b determined by measuring volume of solid soil in a graduated flask

c determined by Pycnometer bottle with organic matter removed and air removed under vacuum

## RESULTS AND DISCUSSION

Effect of temperature and moisture on the degradation of chlorpyrifos-methyl

The degradation of chlorpyrifos-methyl in soils as affected by temperature and moisture was determined by chemical analysis of residues. Results from this study are shown in Tables A.1 and A.2 of the Appendix and as percent lost during an 8 week period vs. temperature in Figure 1. Because of variability in the data in each soil and time interval, a rate constant (k) and half-life ( $t_{1/2}$ ) indicating the persistence of chlorpyrifos-methyl at each temperature and soil could not be calculated. The data are used only to show the trend of degradation.

Chapman et al. (1986) have discussed the variability, which is the major difficulty faced by researchers in studying and describing the behavior of these heterogeneous systems. Since the variability might arise from volatility and from adsorption on the jar wall<sup>1</sup>, a trial was conducted to determine the effect of adsorption. Little volatility loss would be expected from a closed jar. It was found that about 60 % of chlorpyrifos-methyl was adsorbed on the jar wall from a solution. Thus some of the variability can be accounted for during mixing chlorpyrifos-methyl with soil; some chlorpyrifos-methyl

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1. From Dr. V.H. Freed

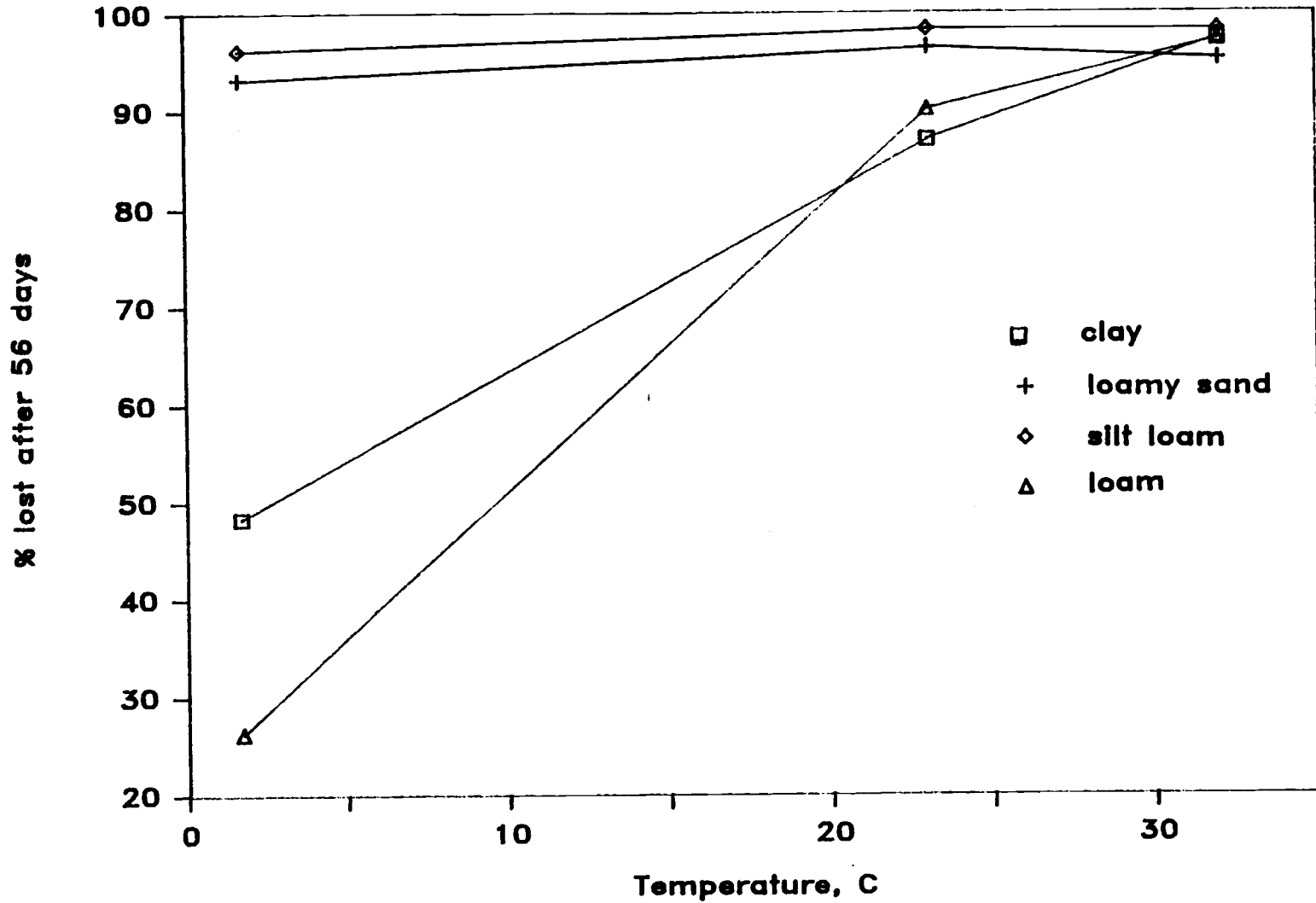


Figure 1. Chlorpyrifos-methyl degradation in soils as affected by temperature.

would be strongly adsorbed on the jar wall and some on the soil and could not disperse uniformly through the soil. This effect was overcome in the study on pH effect.

The temperature, Figure 1, was the most pronounced factor in degradation in all soils. Between 95-98 % of chlorpyrifos-methyl in all four soils had been lost during an 8 week period at 32 C. At 23 C the degradation loss was similar to that at 32 C, except in the clay and loam soil. The % lost after 56 days in loamy sand and silt loam at 1.7 C showed no substantial difference compared to the other two temperatures, but the clay (7 week period) and loam showed a large decrease at lower temperatures.

The amount of degradation in different soil as affected by temperature is evaluated in Table 5. The slope of the regression line plotted between the logarithm of concentration vs. time is  $32\text{ C} > 23\text{ C} > 1.7\text{ C}$  for all four soils, except the silt loam showed no difference and the loam soil showed an inverse trend between 23 C and 32 C, although the difference was small. This might indicate that a temperature of 32 C is approaching an optimum for microbial break down of chlorpyrifos-methyl in both Thailand and Oregon soils.

The effect of moisture on degradation of chlorpyrifos-methyl is shown in Table 6. These data show a significant trend at moisture levels midway between field capacity and wilting point in clay, loamy sand and

**Table 5.** Degradation of chlorpyrifos-methyl in air dry soils as affected by temperature.

Soil	Temperature (C)	Parameter	
		$r_1$	slope <sup>2</sup>
Clay	1.7	-0.30	-0.002
	23.0	-0.79	-0.011
	32.0	-0.97	-0.027
Loamy sand	1.7	-0.26	-0.007
	23.0	-0.62	-0.015
	32.0	-0.80	-0.024
Silt loam	1.7	-0.68	-0.013
	23.0	-0.86	-0.026
	32.0	-0.66	-0.022
Loam	1.7	-0.54	-0.008
	23.0	-0.67	-0.015
	32.0	-0.43	-0.014

- 1  $r$  = correlation coefficient as logarithm of concentration versus time  
 2 slope of the regression line

**Table 6.** Degradation of chlorpyrifos-methyl in soils as affected by moisture at 30 C temperature.

Soil	Moisture content	% of saturated moisture	Parameter	
			$r^1$	slope <sup>2</sup>
Clay	Saturated	100	-0.86	-0.017
	Field capacity	71	-0.61	-0.017
	1/2(FC and WP) <sup>3</sup>	53	-0.84	-0.021
Loamy sand	Saturated	100	-0.85	-0.031
	Field capacity	71	-0.98	-0.028
	1/2(FC and WP)	40	-0.99	-0.045
Silt loam	Saturated	100	-0.20	-0.002
	Field capacity	90	-0.17	-0.002
	1/2(FC and WP)	58	-0.60	-0.017
Loam	Saturated	100	+0.07	-0.001
	Field capacity	88	-0.70	-0.010
	1/2(FC and WP)	59	-0.41	-0.005

- 1  $r$  = correlation coefficient as logarithm of concentration versus time  
 2 slope of the regression line  
 3 FC = field capacity  
 WP = wilting point



silt loam soils. The loam soil on the other hand exhibits an inverse trend for midway between field capacity and wilting point and the field capacity condition. The decline of chlorpyrifos-methyl in the clay and silt loam was similar at saturated and field capacity moisture content.

It is apparent that the loamy sand had the highest decline of chlorpyrifos-methyl at all moisture contents when compared with the other three soils. This is in agreement with the study of Chapman and Harris (1980), who showed that 50 % of an initial chlorpyrifos application remained after 2 and 8 weeks in sand and muck. The high degradation rate in the loamy sand could occur from the low organic matter and low clay content (Helweg, 1981). The high organic matter in the other three soils would result in strong adsorption of chlorpyrifos-methyl in these soils (Szeto and Sundaram, 1982) and hence less availability for degradation. This study does not coincide with the study of Szeto and Sundaram (1982) which showed that chlorpyrifos-methyl was degraded rapidly in a flooded-anaerobic soil, and almost completely disappeared from the flooded soil in 90 days.

#### Effect of pH on the degradation of chlorpyrifos-methyl and propoxur

The effect of pH on degradation of chlorpyrifos-methyl and propoxur in loamy sand is shown in Table A.3 of

the Appendix. These data exhibit less variability between duplicates than some of the other degradation studies. Little variation in chlorpyrifos-methyl values between each time interval was observed but the propoxur data were not as closed. Even though the variation for each time interval of sampling had been reduced, still the adsorption on the jar wall of about 50-55 % of chlorpyrifos-methyl and 54-69 % of propoxur residues was found at the start of incubation (0 day).

The degradation of chlorpyrifos-methyl and propoxur (Table 7) showed a good correlation between the logarithm of concentration and time interval. The correlation coefficient for chlorpyrifos-methyl ranged from 0.94 to 0.95 and for propoxur from 0.85 to 0.99 for soil at pH 6.5 and 7.3 respectively.

The slope of the regression line indicates the rate at which each insecticide degraded as influenced by soil pH. At high pH, both insecticides showed slightly greater degradation than at low pH. This might result from increasing the rate of hydrolysis of the insecticides. Freed et al. (1979) showed the hydrolysis rates (half-life) of chlorpyrifos-methyl in a buffer solution pH 7.4, were 2.6 days at 37.5 C and 12.5 days at 20 C. The half-life of chlorpyrifos-methyl and propoxur in the loamy sand at pH 6.5 and 7.3 could not be accurately determined because of the effect of adsorption at the time of

**Table 7.** Degradation of chlorpyrifos-methyl and propoxur on loamy sand as affected by pH at 30 C temperature and moisture content between field capacity and wilting point.

Insecticide	pH	Parameter		
		$r^1$	slope <sup>2</sup>	% lost after 7 or 18 days
Chlorpyrifos-methyl	6.5	-0.94	-0.059	61
	7.3	-0.95	-0.07	65
Propoxur	6.5	-0.85	-0.015	49
	7.3	-0.99	-0.017	53

1 correlation coefficient as logarithm of concentration versus time

2 slope of the regression line

incubation. The percent loss after 7 days for chlorpyrifos-methyl and 18 days for propoxur is shown in Table 7. There was a slight increase in the percent of chlorpyrifos-methyl and propoxur lost with increasing pH in both soils. The results show that 61 and 65 % of chlorpyrifos-methyl apparently degraded and 49 and 53 % of propoxur was lost at soil pH 6.5 and 7.3 respectively. These were 6 and 8 % difference due to soil pH.

Effect of chlorpyrifos-methyl and propoxur on microbial activity in soils

Production of  $^{14}\text{CO}_2$  from respiration of microbial populations using  $^{14}\text{C}$ -glucose indicates the effect of chlorpyrifos-methyl and propoxur on microbial activity. The depression of  $^{14}\text{CO}_2$  production by the two insecticides is shown in Figures 2 and 4 and Tables A.4 and A.5 of the Appendix.

Figure 2 shows that  $^{14}\text{CO}_2$  evolution decreased as concentration of chlorpyrifos-methyl increased from 0 to 1,000 ppm on silt loam soil. The depression was much more pronounced during the one and two hour incubation periods, and recovered after three and four hours, but not quite reaching the level of the control. The amount of  $^{14}\text{CO}_2$  production increased from 46 and 34 % at two hours to 61 and 77 %, and 55 and 91 % at three and four hours for concentrations of 500 and 1,000 ppm chlorpyrifos-methyl respectively.

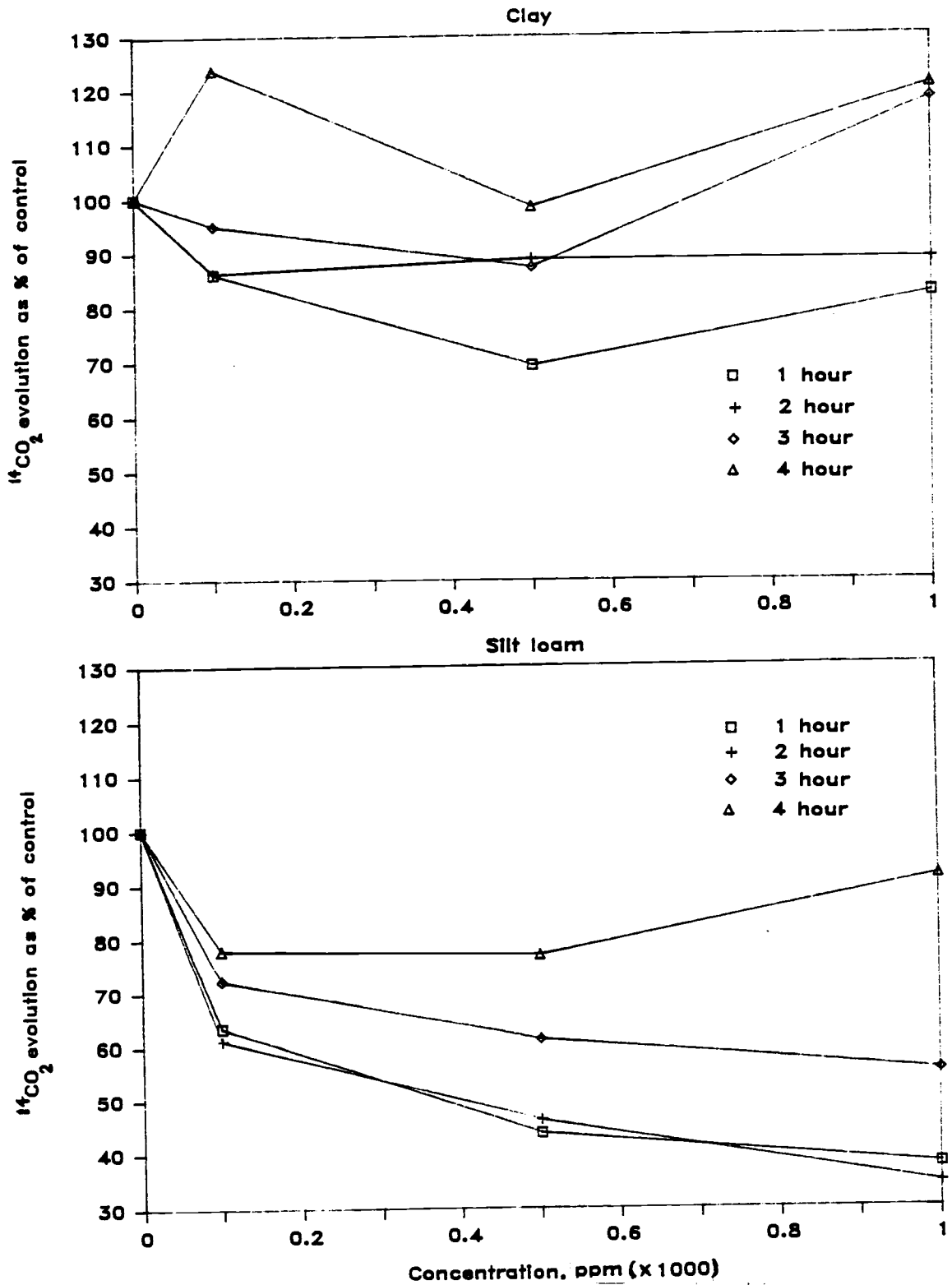


Figure 2. Effect of chlorpyrifos-methyl on microbial activity as indicated by  $^{14}\text{CO}_2$  production in saturated soils at 30 C.

The difference in recovery is also seen in the clay soil. The  $^{14}\text{CO}_2$  production was much higher at every concentration than in the silt loam soil, especially at 1,000 ppm where the  $^{14}\text{CO}_2$  production at three and four hours was even higher than in the control. The  $^{14}\text{CO}_2$  increased up to 118 and 120% for 1,000 ppm of chlorpyrifos-methyl.

This might be due to both physical properties of chlorpyrifos-methyl and to the different kinds and growth of microbial population in soils. This should be a fruitful study for the future. The measurements of adsorption of chlorpyrifos-methyl on these soils gave a distribution coefficient (Kd) on the clay and silt loam soil of 93.1 and 76.9 respectively. Chlorpyrifos-methyl adsorbed more readily on clay than on the silt loam soils, which reduced the amount of chlorpyrifos-methyl available for microbial activity, resulting in a greater  $^{14}\text{CO}_2$  production. Also the microbial population in the clay soil might be more resistant to chlorpyrifos-methyl, or may have recovered much faster. Also the carbon source from chlorpyrifos-methyl may have been used as a co-metabolite, with a greater  $^{14}\text{CO}_2$  production.

Figure 3 presents result for the clay soil incubated at 20 C. It did not show a significant difference in  $^{14}\text{CO}_2$  production when compared to the control. All concentrations of chlorpyrifos-methyl behaved in the same

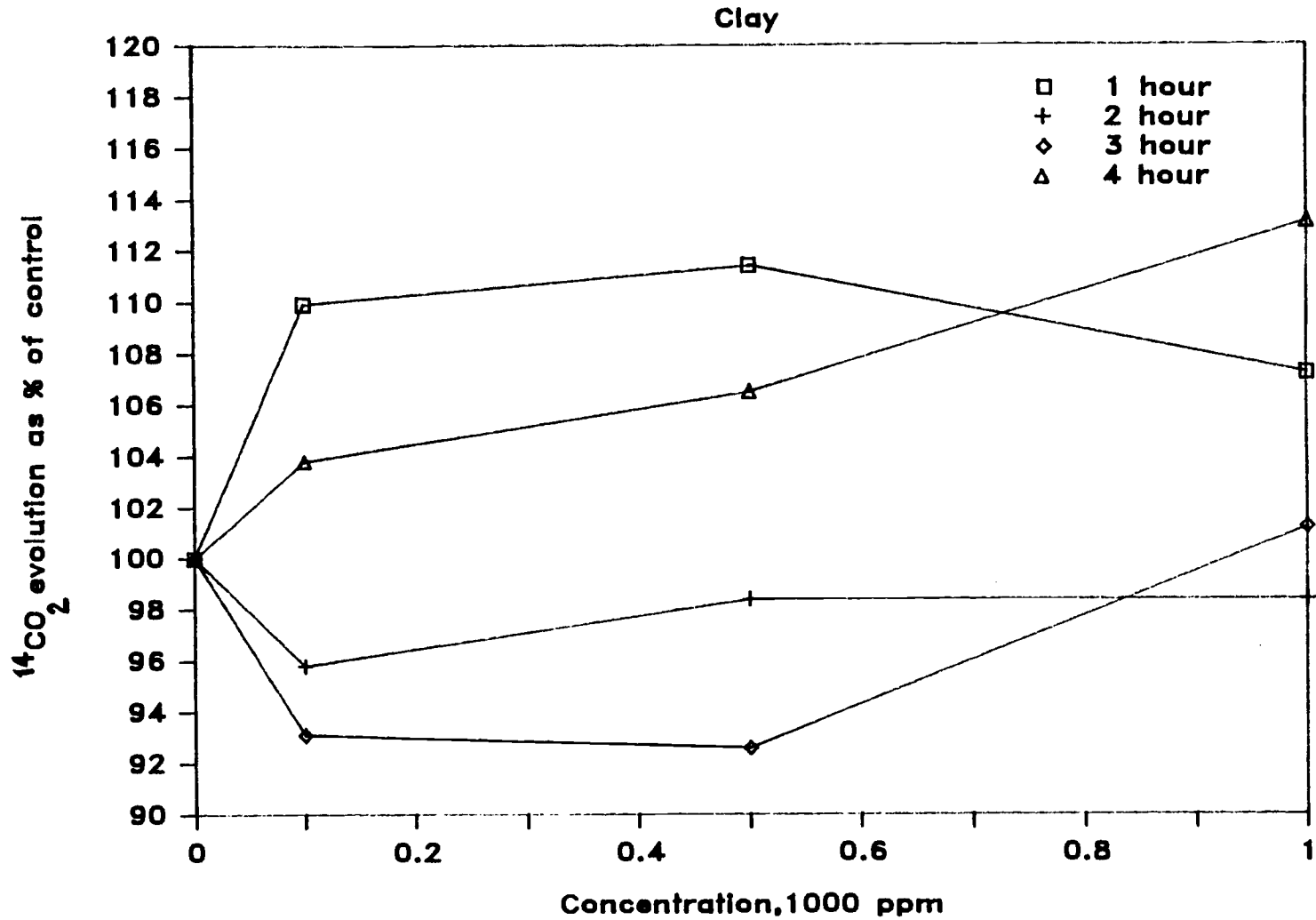


Figure 3. Effect of chlorpyrifos-methyl on microbial activity in clay soil at 20 C.

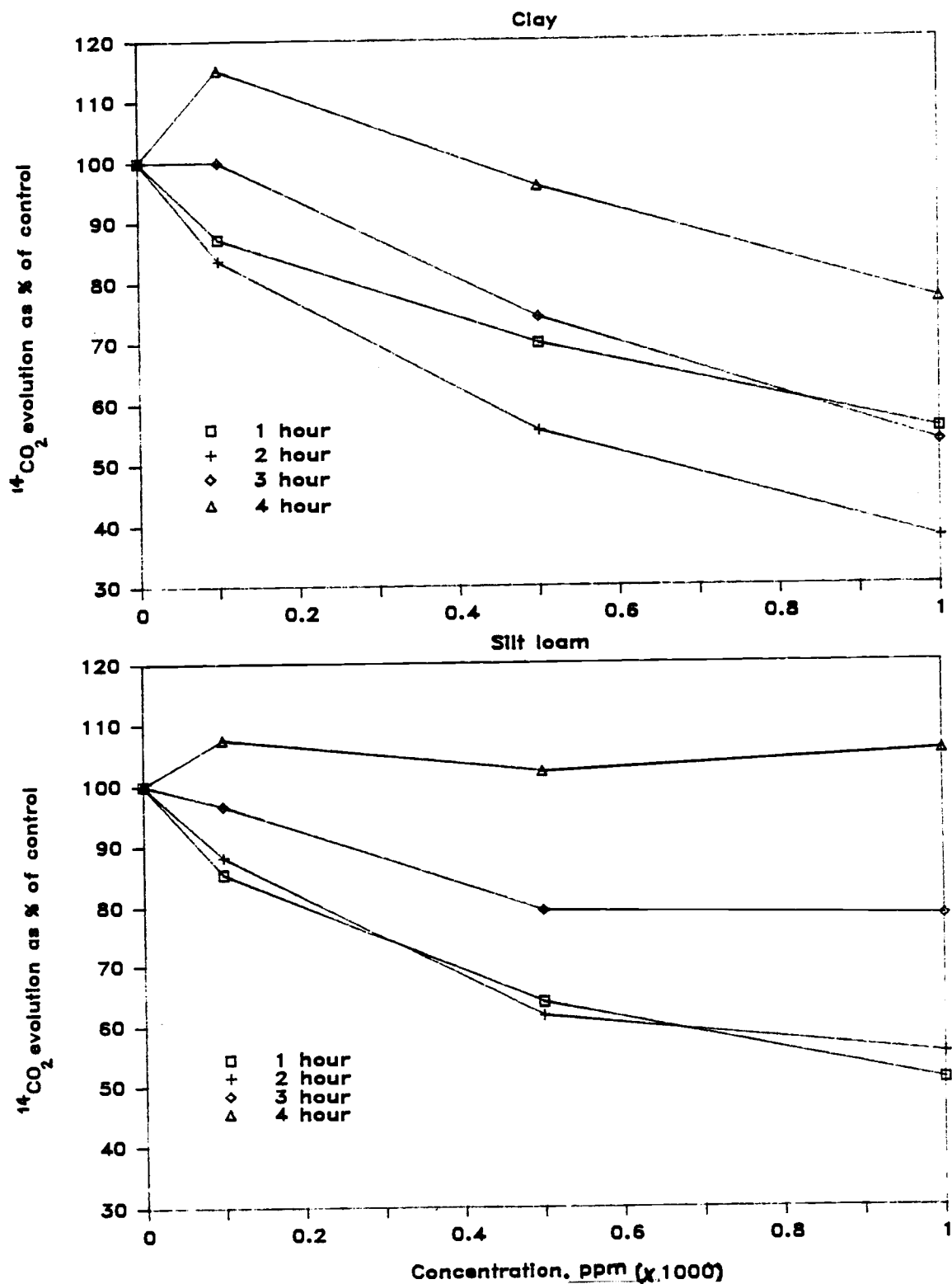


Figure 4. Effect of propoxur on microbial activity as indicated by  $^{14}\text{CO}_2$  production in saturated soils at 30 C.



manner. This might be the result of the low incubation temperature which could reduce 1) desorption of chlorpyrifos-methyl from soil and hence the amount available or, 2) the reduced amount of microbial activity. That temperature may not be suitable for illustrating differences in microbial activity or yield great differences in concentration of  $^{14}\text{CO}_2$  production.

The effect of propoxur on  $^{14}\text{CO}_2$  production (Figure 4) was the same as for chlorpyrifos-methyl. As the concentration of propoxur increased the  $^{14}\text{CO}_2$  production decreased. The exception occurred on the silt loam at four hours at all propoxur concentrations. Microbial activity recovered very well, and may have included co-metabolism of propoxur resulting in increasing the amount of  $^{14}\text{CO}_2$  produced to a level even higher than the control. This also occurred on clay soil at 1,000 ppm during the four hour period.

The comparison between the effects of chlorpyrifos-methyl and propoxur in the two soils is shown in Figure 5 and 6. Microbial activity showed different relationships for the clay and silt loam soils. At 100 ppm the effect was quite similar for both insecticides on clay soil but different in the silt loam soil. Chlorpyrifos-methyl had a more pronounced inhibiting effect in the silt loam soil. At concentrations of 500 and 1,000 ppm chlorpyrifos-methyl had a greater effect on the silt loam than on the clay

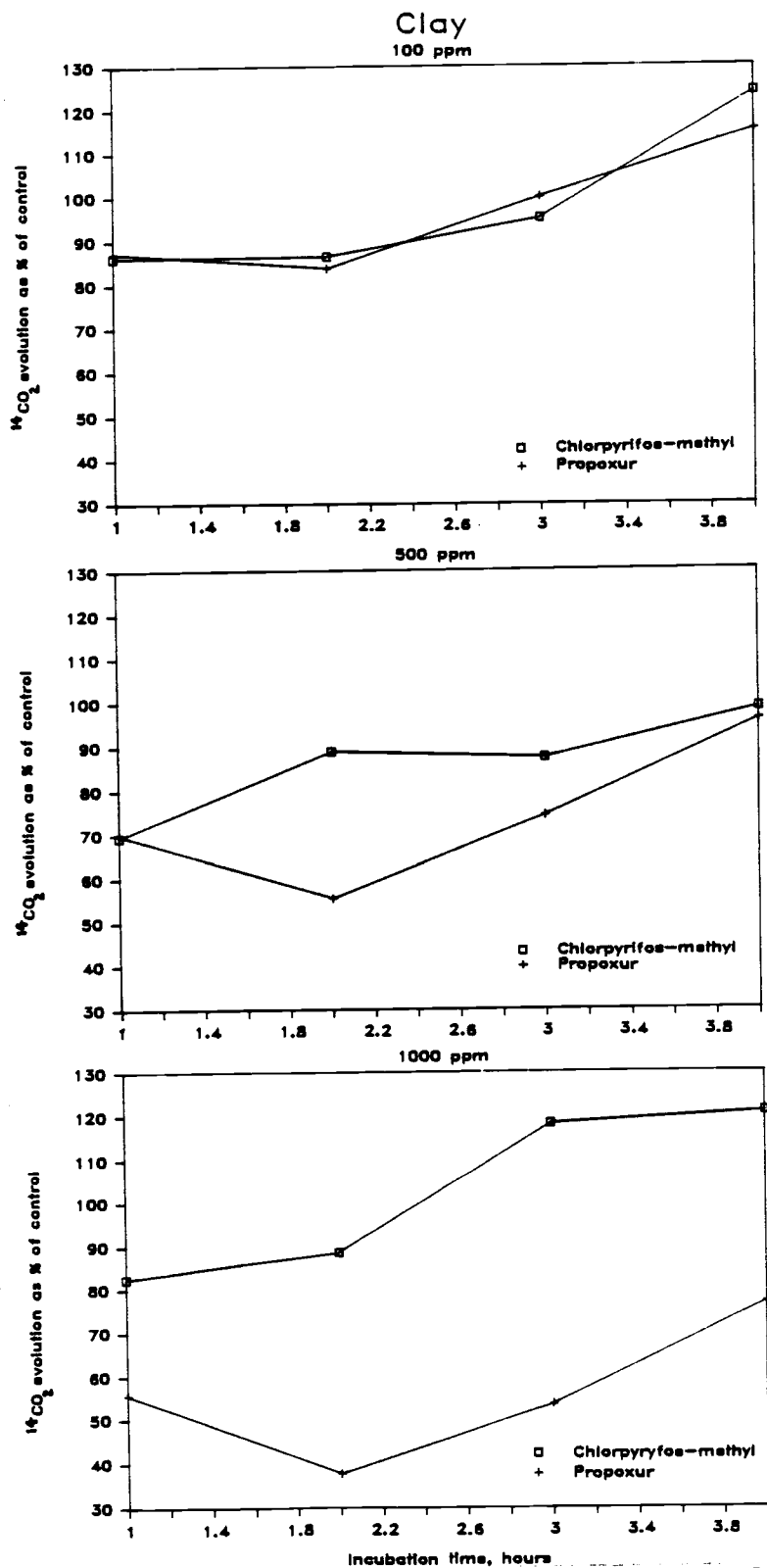


Figure 5. Comparison of the effect of different concentrations of chlorpyrifos-methyl and propoxur on microbial activity in the clay soil.

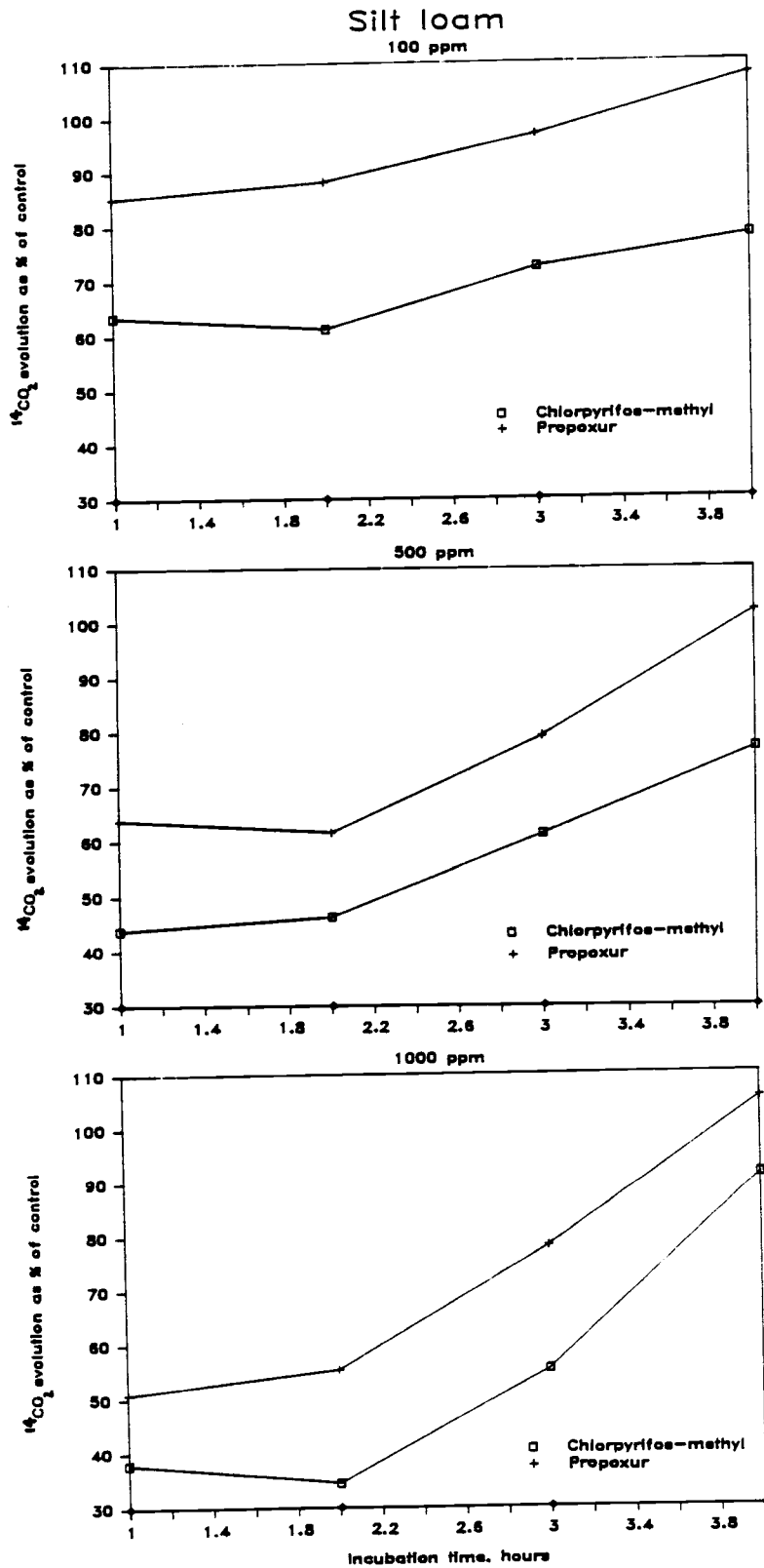


Figure 6. Comparison of the effect of different concentrations of chlorpyrifos-methyl and propoxur on microbial activity in the silt loam soil.

soil, but propoxur had a more pronounced effect on the clay soil. This might be due to physical properties of propoxur and resistance of microbial populations to different amounts of chemical in each soil. Anderson (1973) and Ashworth et al. (1980) reported a solubility of propoxur of about 0.2 % at 20 C. Propoxur dissolved in water would be available for microbial activity in clay soil. A more precise explanation might be possible if the  $K_d$  value of propoxur was known. Kuseske et al. (1974) studied the effect of propoxur in soil and found that propoxur at field rate applications (5 ppm) did not greatly influence the microbial populations in the soil. At a concentration of 500 ppm the fungal and actinomycete populations showed a marked increase in response to propoxur. This could explain the resistance of microbial populations that resulted in tolerance, and the different effect of propoxur in clay and silt loam soils.

#### Adsorption of chlorpyrifos-methyl on Thailand and Oregon soils

Chlorpyrifos-methyl adsorption on a clay soil from Thailand and a silt loam soil from Oregon were expressed as the distribution between the soil phase and water phase. The results were fitted to a Freundlich isotherm (Table 8);  $x/m = KC^n$  where  $x/m$  = amount sorbed per mass of soil,  $C$  = equilibrium concentration of insecticide in solution,  $K$  = adsorption coefficient and  $n$  = a constant

Table 8. Distribution coefficient of chlorpyrifos-methyl at 23 C as related to physical properties of soils.

Soil	$r^1$	$n^2$	$Kd^3$	%OM <sup>4</sup>	% clay	CEC <sup>5</sup>	pH
Clay	0.95	1.0	93.1	2.72	66.0	29.0	7.8
Silt loam	0.82	1.2	76.9	2.88	25.4	12.4	5.6

- 
- 1 correlation coefficient of linear isotherm
  - 2 a constant describing the nature of the adsorption
  - 3 distribution coefficient between two phases
  - 4 organic matter content
  - 5 cation exchange capacity, meq/100g

describing the nature of the adsorption (Hamaker and Thompson, 1972). The constant,  $n$ , was one for the clay soil and greater than one for the silt loam soil. This indicated that there was no limit to the amount sorbed on soils at concentration found in the environment (Tinsley, 1979). If the isotherm is linear; i.e  $n = 1$ , the constant,  $K$ , is identical with  $K_d$  (distribution coefficient). If  $n$  is greater than one the adsorption is usually referred to as S or concave type (Freed and Haque, 1973).

The distribution coefficient for the clay soil was about 17 % higher than for the silt loam soil. The organic matter contents were not significantly different, so it was difficult to tell whether there was a correlation with  $K_d$  values. The study on adsorption of carbofuran and dieldrin on soil by Felsot and Wilson (1980) found a positive correlation. There was a high positive correlation with clay content and cation exchange capacity. High clay content and organic matter in soil would contribute to total exchange capacity, which results in greater adsorption of chlorpyrifos-methyl on the clay soil than on the silt loam soil.

The correlation of the  $K_d$  value with pH of the solution or the soil would depend upon whether the ionic pesticides were acidic or basic. Freed and Haque (1973) cited the work of Weber, showing maximum adsorption of

prometone, a basic methoxy s triazine herbicide, which occurred in the vicinity of its pK value. But as chlorpyrifos-methyl is a non-ionic insecticide, the pH might not exert much effect on adsorption. The difference in adsorption on these two soils might arise from other physical properties.

#### Evaporation of chlorpyrifos-methyl from soils

The evaporation rate of chlorpyrifos-methyl is given in Table A.6 of the Appendix and Figure 7. The wet soils at field capacity for both clay and silt loam soils showed higher rates of evaporation than air dry soils. This is ascribed to the "wick effect", where water moving upward to the surface also transports chlorpyrifos-methyl to replenish the soil surface, allowing more chlorpyrifos-methyl to evaporate (Spencer et al., 1969; Spencer and Cliath, 1973). This effect occurred until most of the water was lost from the soil and the surface became dry. Then the evaporation behaved similar to air dry soil. In air dry soil, the evaporation depended only on the diffusion, controlled by the concentration gradient of chlorpyrifos-methyl from the soil surface to the atmosphere. Also adsorption may be greater in dry than in wet soil since water competes for adsorption sites with chlorpyrifos-methyl. This would allow more evaporation loss.

The trend in evaporation rates can be seen more

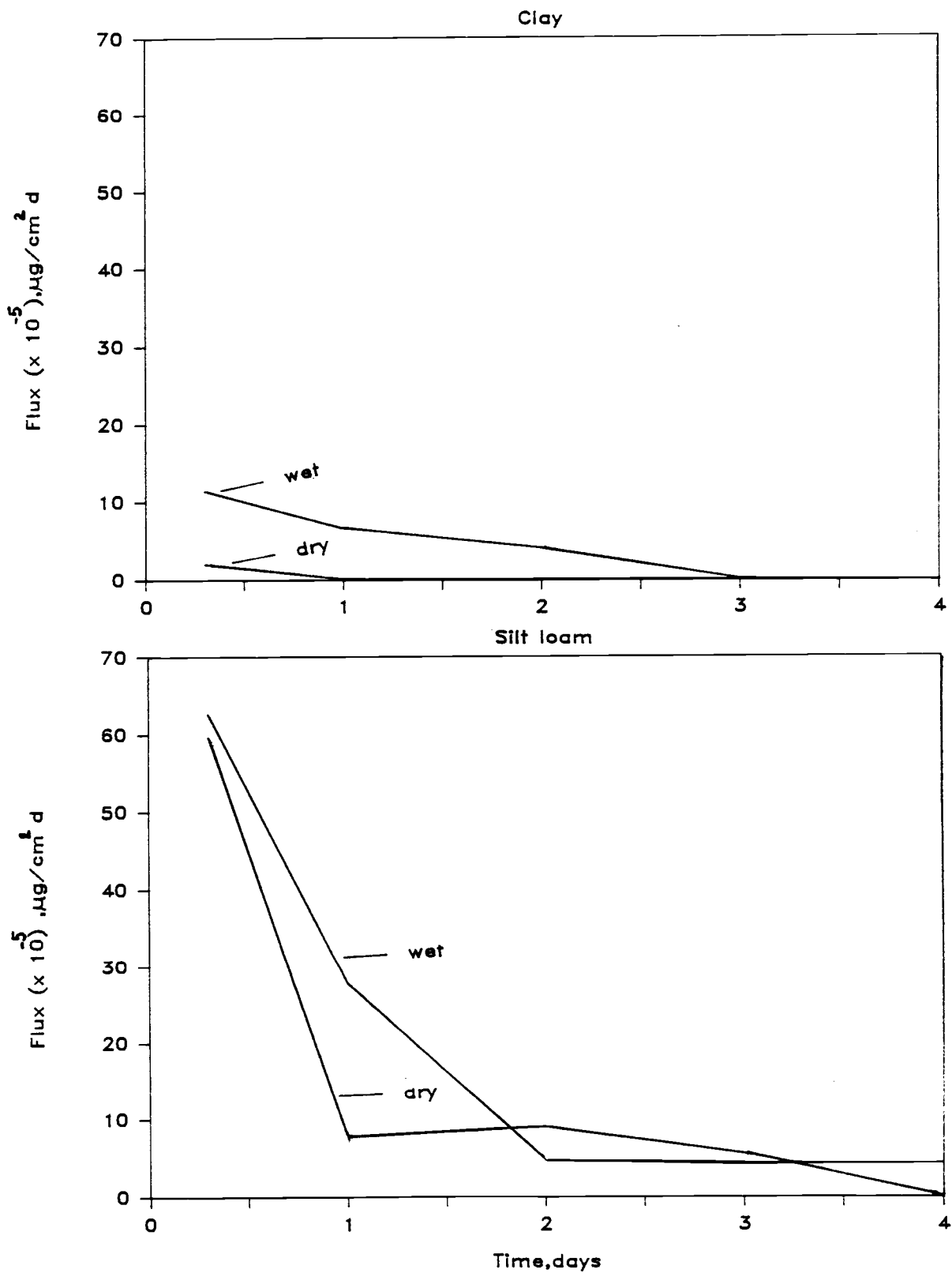


Figure 7. Chlorpyrifos-methyl evaporation rate at 32 C as affected by moisture content; air dry and field capacity.



clearly in the silt loam as compared to the clay soil (Figure 7) due, no doubt to lower adsorption of chlorpyrifos-methyl in silt loam soil (Table 8). The evaporation rate at 7 hours from air dry soil was 18 % of wet soil in clay and 95 % in silt loam soil. Comparing the two soils, evaporation from air dry clay soil was about 4 % of that from air dry silt loam, and the wet clay soil was 18 % of wet silt loam soil at 7 hours incubation. This revealed that the factor of adsorption on soil, which depends on the type of soil, would be of great importance in the evaporation of the chemical from different soils.

#### Vapor pressure of propoxur

The determined vapor pressure at 23 C and 32 C and the latent heat of evaporation of pure propoxur is shown in Table 9. Vapor pressure of propoxur at 32 C, was about four fold greater than at 23 C, which corresponds to the findings of Spencer and Farmer (1980) for other chemicals. The vapor pressure at 120 C was calculated from the vapor pressure of the two lower temperatures. It was  $6.8 \times 10^{-1}$  mm Hg, which was about 68 times the value of  $1 \times 10^{-2}$  mm Hg compiled by Anderson (1973) and Spencer (1981).

The latent heat of evaporation calculated from the vapor pressure at two different temperatures was 29 kcal / mole. This figure might be high, due to the adsorption of propoxur on silica sand since some energy would be required to release it from sand to the atmosphere.

Table 9. Vapor pressure of propoxur and latent heat of evaporation ( $\Delta H$ ).

Temperature (C)	Vapor pressure (mm Hg)	$\Delta H$ (kcal/mole)
23	$(3.5 \pm 0.5) \times 10^{-6}$	29
32	$(1.5 \pm 0.4) \times 10^{-5}$	29
120 <sup>a</sup>	$6.8 \times 10^{-1b}$	-

a vapor pressure compiled from Anderson (1973) and Spencer (1981) at 120 C =  $10^{-2}$  mm Hg

b calculated from the equation;

$$\log \frac{P_1}{P_2} = \frac{\Delta H}{2.303R} \left[ \frac{\Delta T}{T_1 T_2} \right]$$

Nevertheless, these values will be useful in predicting the vapor losses of propoxur from surface deposits, to predict their partitioning between soil, water and air, in order to predict volatility from water solutions and from wet soils, and to calculate atmospheric residence times of propoxur in droplets and aerosols (Spencer and Farmer, 1980).

#### Evaporation of propoxur from soils

The evaporation rate of propoxur on clay and silt loam soils at field capacity moisture content is presented in Table A.7 of the Appendix and Figure 8. The evaporation rate from silt loam is higher than from the clay soil. This corresponds to the evaporation of chlorpyrifos-methyl as described before. The rate in the clay soil was highest at 1 and 2 days of incubation and decreased to a constant rate after 4 to 7 days. The evaporation rate of propoxur from silt loam soil showed a different pattern. The rate moved up and down with each time interval, and the trend appeared to be increasing evaporation with time. This might reflect the influence of the interaction of adsorption, desorption, and solubility of propoxur in silt loam soil. It may be possible to explain this phenomenon from further study of these factors in the field.

#### Leaching of chlorpyrifos-methyl and propoxur from soils

The amount of leaching of chlorpyrifos-methyl and

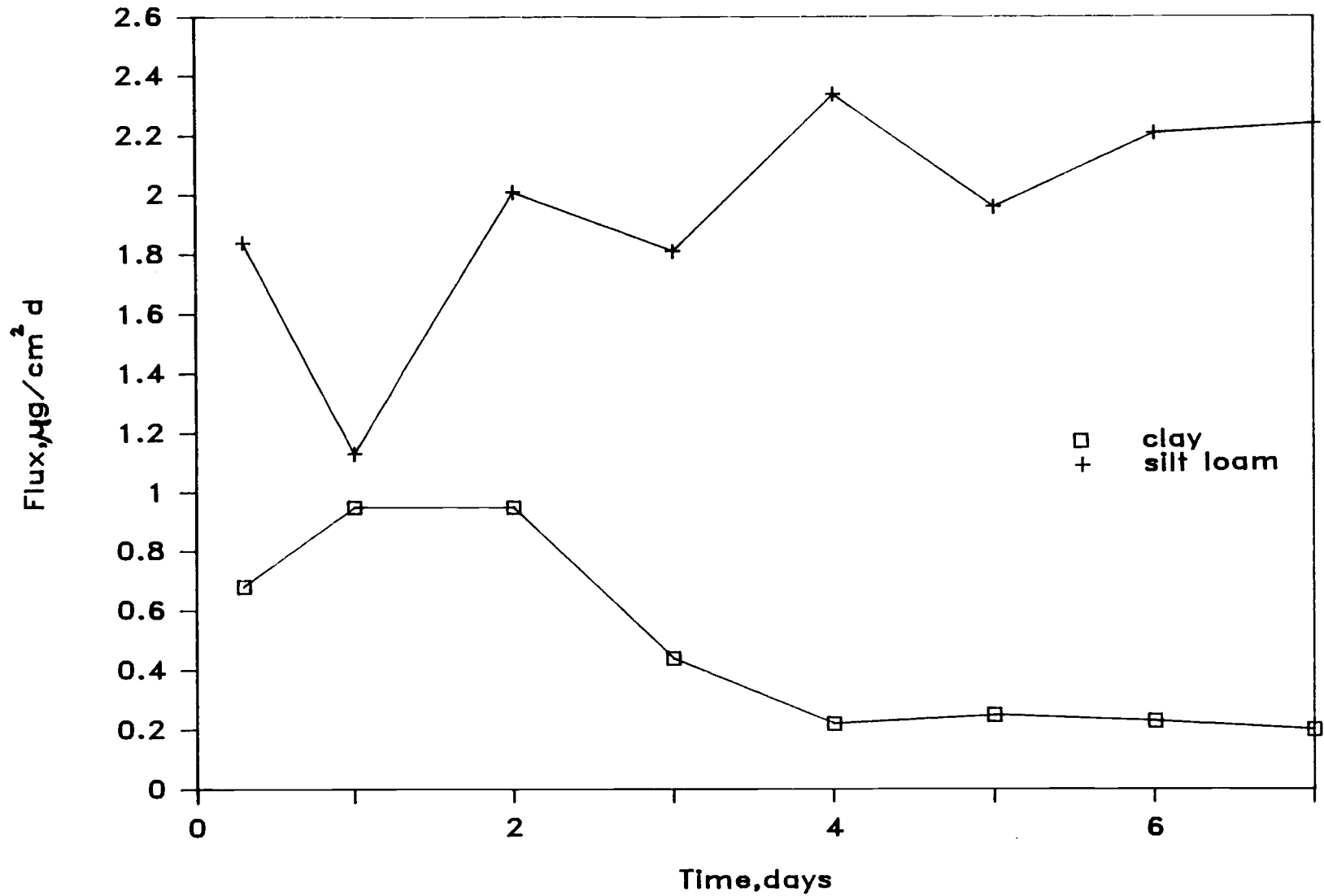


Figure 8. Propoxur evaporation rate at 32 C from soils at field capacity.

propoxur through columns of clay and silt loam soils is presented in Tables A.8 and A.9 of the Appendix and Figures 9 and 10. The amount of chlorpyrifos-methyl leached was too low to show on the figures. The results are presented as the percent of the initial amount applied on the soil surface.

Chlorpyrifos-methyl showed stronger adsorption on both soils than propoxur, which resulted in very small amounts of chlorpyrifos-methyl being leached out of the soil. The total leachate of chlorpyrifos-methyl was less than 0.5 % of the initial amount in the silt loam soil and less than 0.1 % in the clay soil. The clay soil from Thailand exhibited a high degree of swelling of clay particles when wet, so much so as to restrict movement of water. Leaching was achieved with suction. The chlorpyrifos-methyl leaching data in the silt loam and clay soils correspond to the distribution coefficient ( $K_d$ ) of chlorpyrifos-methyl in clay soil and silt loam soil as shown in Table 10, and reflect the reduced mobility in the clay soil.

Propoxur leaching was much greater than chlorpyrifos-methyl on both soils, with the total leachate being 56 % for the clay and 60 % for the silt loam soil. This showed the greater affinity of propoxur for clay soil, even though pressure was applied to facilitate leaching. Propoxur moved very quickly during 2 and 3 days in silt

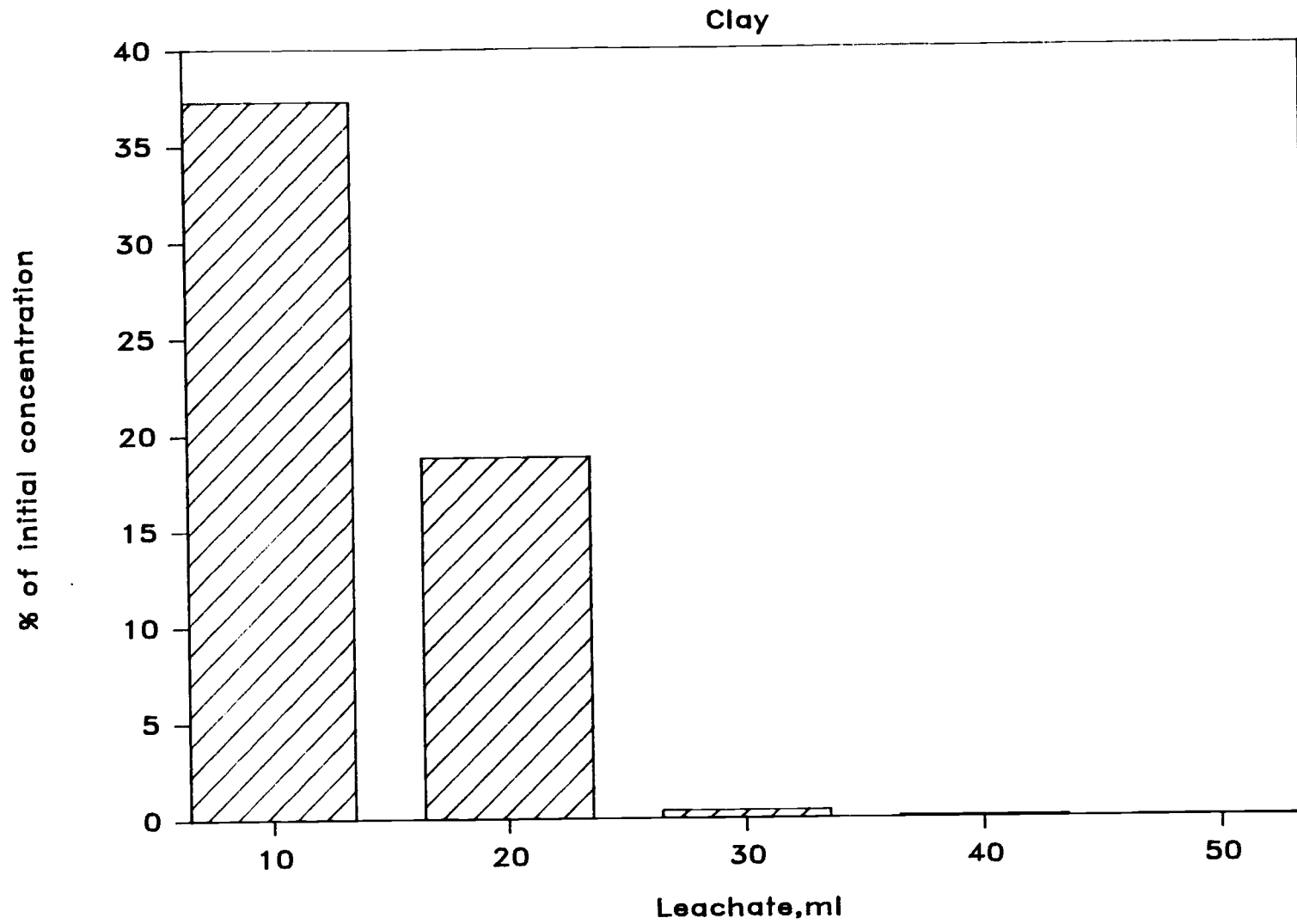


Figure 9. The leaching of propoxur from the clay soil.

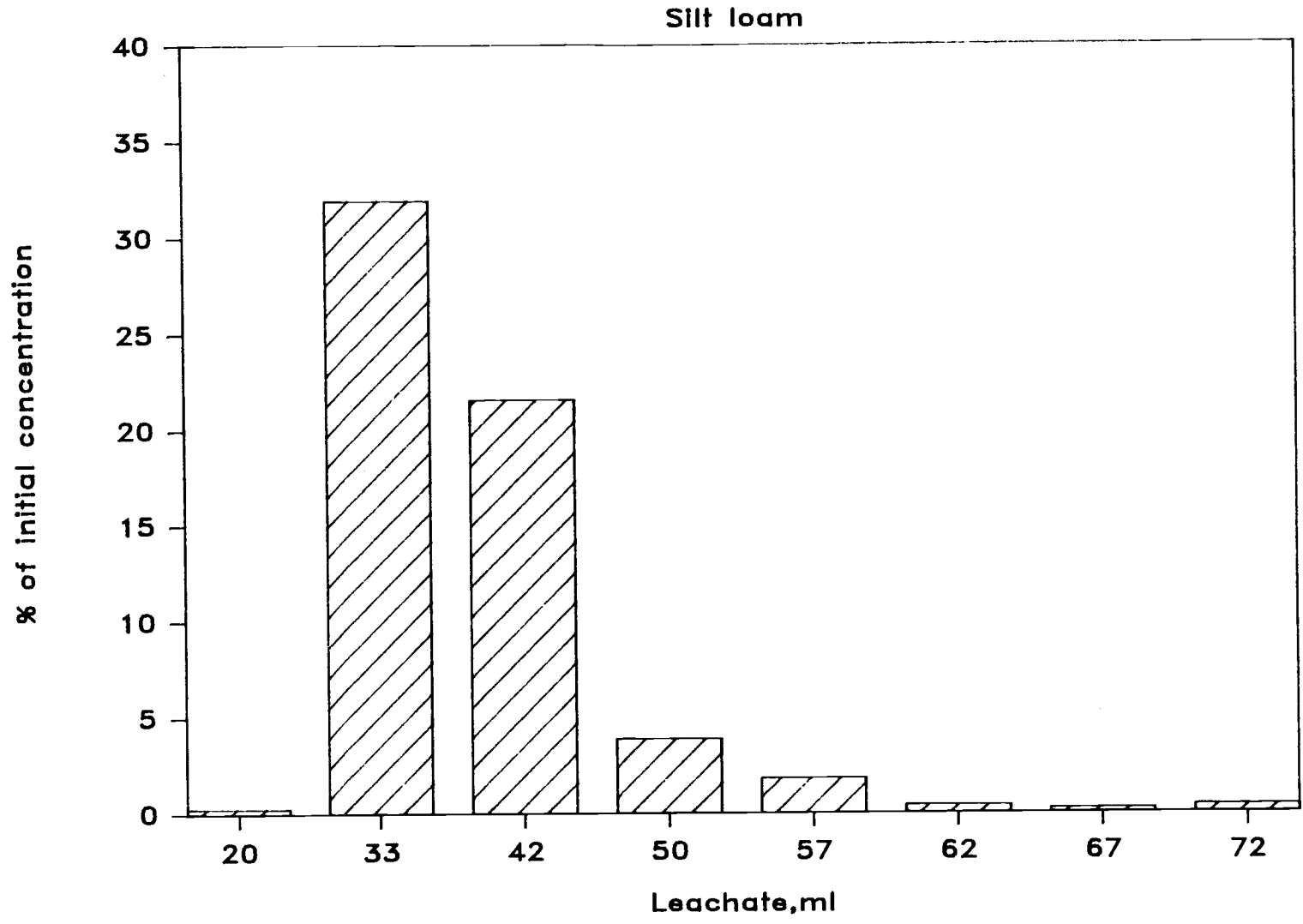


Figure 10. The leaching of propoxur from the silt loam soil.

Table 10. Compilation of factors affecting leaching in soils.

Parameter	Result
Kd <sup>a</sup>	.93.1 (clay-chlorpyrifos-methyl)
	76.9 (siltloam-chlorpyrifos-methyl)
% organic carbon	1.57 (clay)
	1.67 (silt loam)
Koc <sup>b</sup>	5915 (clay-chlorpyrifos-methyl)
	4614 (silt loam-chlorpyrifos-methyl)
Bulk density (Mg/m <sup>3</sup> )	1.23 (clay)
	1.35 (silt loam)
Solubility in water (ppm)	4.76 <sup>c</sup> (chlorpyrifos-methyl)
	2x10 <sup>3d</sup> (propoxur)
Partition coefficient	20,200 <sup>e</sup> (chlorpyrifos-methyl)
	28 <sup>f</sup> (propoxur)

a distribution coefficient

b calculated from  $Koc = \frac{Kd \times 100}{\% \text{ organic carbon}}$  ;  $OC = \frac{OM}{1.728}$

c from Freed et al. (1979)

d from Anderson (1973)

e from Freed et al. (1979)

f calculated from the equation;

$$\log P = 5 - 0.67 \log S$$

(Freed et al., 1979)



loam soil, with cumulative leachate of 53 % and 88 % of the total chemical.

Table 10 presents factors of both soil and pesticide which influence the degree of leaching through soil. McCall et al. (1981) indicated that as organic carbon increased, the mobility of a chemical decreased. This could not be seen in this study because the difference in organic carbon between soils was not great. Koc values, which are higher for clay than silt loam soil, might explain the difference in leaching rate. This could be used as an indicator to predict the mobility of chlorpyrifos-methyl on these two soils, which supports the contention of McCall et al. (1981) that a single Koc value could be used as a good indicator to represent the sorption tendency of a chemical for any soil in order to compare different chemicals.

The factors that clearly show the difference between chlorpyrifos-methyl and propoxur were solubility and partition coefficient. Solubility of propoxur was about 420 times that of chlorpyrifos-methyl, which played the major role in increasing leaching of propoxur through soil, especially in the silt loam soil. The partition coefficient is another parameter to use to compare chlorpyrifos-methyl to propoxur. The greater partition coefficient of chlorpyrifos-methyl would result in a decrease in mobility of this chemical.

## CONCLUSIONS

The studies of degradation and behavior of chlorpyrifos-methyl and propoxur in clay and loamy sand from Thailand and silt loam and loam soils from Oregon lead to the following conclusions:

1. Rate of chlorpyrifos-methyl degradation in soil as affected by temperature is in the order  $32\text{ C} > 23\text{ C} > 1.7\text{ C}$  in all four soils, except the silt loam and loam soils, where  $23\text{ C}$  and  $32\text{ C}$  are reversed but with only a slight difference.
2. The effect of moisture on the degradation of chlorpyrifos-methyl generally shows the highest rate at a moisture content midway between field capacity and wilting point and little change in rate between saturation and field capacity. The ranking for degradation rate in soils is sand  $>$  clay  $>$  silt loam  $>$  loam soil.
3. Chlorpyrifos-methyl and propoxur show slightly greater degradation in soils at pH 7.3 than at pH 6.5. The difference in percent of chlorpyrifos-methyl and propoxur degraded is 6 % and 8 % respectively.
4. Microbial activity was shown to be depressed by chlorpyrifos-methyl and propoxur. The activity depends on the concentration of pesticide, with the effects in the ascending order of 100 ppm  $>$  500 ppm  $>$  1000 ppm at 1 - 3 hours incubation periods. The activity higher than the control after 4 hours. The effect of pesticide on

microbial activity is chlorpyrifos-methyl > propoxur on silt loam soil and propoxur > chlorpyrifos-methyl on clay soil.

5. The distribution coefficients (Kd) of chlorpyrifos-methyl are 93.1 on the clay soil and 76.9 on the silt loam soil.

6. The evaporation rate of chlorpyrifos-methyl in a soil at field capacity is larger than in air dry soil for both clay and silt loam soils. Silt loam soil shows a higher rate of evaporation than clay soil on both wet and air dry soil with chlorpyrifos-methyl and wet soil with propoxur.

The vapor pressure of pure propoxur was determined to be  $3.5 \times 10^{-6}$  mm Hg at 23 C and  $1.5 \times 10^{-5}$  mm Hg at 32 C. The latent heat of evaporation of propoxur is 29 Kcal/mole.

7. Chlorpyrifos-methyl is nearly immobile on clay and silt loam soils. The leaching is less than 0.1 % of the initial concentration for the clay soil and less than 0.5 % for the silt loam soil. Propoxur is much more mobile than chlorpyrifos-methyl. The total leached is 56 % and 60 % on clay and silt loam soil respectively.

These findings have implications for place and manner of use of these chemicals in Thailand. These results show that under the higher soil temperature and apparent different microbial activity in Thai soils, they would have shorter persistence. Further, the higher temperature would result in more rapid evaporation from surfaces

whether soil (chlorpyrifos-methyl) or in home (propoxur).

The data also indicate that surface erosion with water is more likely with the clay soil which could result in water contamination.

The greater adsorption of chlorpyrifos-methyl would probably reduce its biological availability as compared to the more soluble propoxur.

Therefore, places and methods of uses of these chemicals should be considered in light of their properties and their environmental behavior.

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## APPENDIX

Table A.1 Chlorpyrifos-methyl residues found at different times as affected by temperature (Duplicate values).

Time (day)	Chlorpyrifos-methyl(ppb) <sup>1</sup>											
	Clay (TH)			Loamy sand (TL)			Silt loam (OH)			Loam (OL)		
	T1 <sup>2</sup>	T2 <sup>3</sup>	T3 <sup>4</sup>	T1	T2	T3	T1	T2	T3	T1	T2	T3
0	68,51	53,54	36,48	23,25	12,24	15,21	24,39	39,8	35,31	23,25	12,24	15,21
2	42,51	56,31	45,33	21,27	13,17	13,8	23,6	3,14	4,3	20,27	13,17	13,8
4	33,48	54,25	50,44	23,22	7,7	6,5	9,4	8,13	6,8	23,22	7,7	6,5
7	58,49	53,35	43,39	10,11	6,5	1,0.4	6,18	1,2	0.3,0.4	10,11	6,5	1,0.4
14	33,51	66,56	3,34	10,13	1,2	tr <sup>5</sup> ,0.2	23,21	3,0.1	tr, tr	10,13	1,2	tr,0.2
21	43,31	9,19	13,14	8,16	1,1	0.1,0.2	4,7	1, tr	ND, ND	8,16	1,1	0.1,0.2
28	61,20	28,27	10,6	7,10	2,1	0.7, tr	13,8	2.5, ND <sup>6</sup>	ND, ND	7,10	2,1	1, tr
35	60,24	26,17	8,5	20,13	2,2	2,1	20,15	tr, 1	0.2, tr	20,13	2,2	2,1
42	21,30	25,21	6,11	0.3,18	2,2	2,1	17,1	0.3, tr	ND, ND	0.3,18	2,2	2,1
49	46,15	27,21	2,1	0.5,4	2,2	1,2	4,4	ND, 1	0.6,0.6	0.5,4	2,2	1,2
56	63,68	1,13	2,0.4	16,18	1,2	0.5,0.5	1,2	0.3,0.5	0.6,0.5	16,18	1,2	0.5,0.5
% lost after 56 days	48 <sup>7</sup>	87	97	93	96	95	96	98	98	26	90	97

- 1 parts per billion (ng/g)
- 2 T1 = incubation temperature of 1.7 C (35 F)
- 3 T2 = incubation temperature of 23 C (70 F)
- 4 T3 = incubation temperature of 32 C (89.6 F)
- 5 tr = trace; residue found less than 0.1 ppb
- 6 ND = non detectable
- 7 calculated after 49 days

**Table A.2** Chlorpyrifos-methyl residues found at different times as affected by moisture (Duplicate values).

Time (day)	Chlorpyrifos-methyl(ppb)											
	Clay (TH)			Loamy sand (TL)			Silt loam (OH)			Loam (OL)		
	W1 <sup>1</sup>	W2 <sup>2</sup>	W3 <sup>3</sup>	W1	W2	W3	W1	W2	W3	W1	W2	W3
0	-	-	-	37,44	32,62	40,49	17,28	33,29	27,32	-	-	-
2	-,45	24,30	15,18	59,41	45,63	24,39	5,39	11,12	5,4	35,24	30,-	9,12
4	33,50	21,19	18,17	21,17	53,57	25,30	38,52	15,19	23,25	18,14	24,26	-,18
7	24,30	12,10	9,9	37,42	41,42	26,31	19,18	26,24	33,17	6,10	24,25	6,13
14	24,10	6,7	14,tr	48,21	25,26	10,12	7,36	24,31	16,13	16,14	1,19	7,7
21	43,24	ND,3	8,12	-,14	22,14	5,5	34,16	25,6	13,11	33,9	7,20	7,7
28	5,22	6,4	3,4	14,14	tr,12	3,tr	23,24	22,20	5,8	19,30	23,11	13,12
35	10,11	7,14	ND,ND	2,2	5,5	1,tr	25,18	12,19	5,3	14,15	13,12	9,6
% lost after 77 35 days		63	100	96	90	98	4	49	88	51	58	26

- 1 W1 = saturated moisture content
- 2 W2 = field capacity moisture content
- 3 W3 = midway between field capacity and wilting point moisture content

**Table A.3** Chlorpyrifos-methyl and propoxur residues as a function of time and pH on the loamy sand (Duplicate values).

Time (day)	Chlorpyrifos-methyl (ppb)		Propoxur (ppb)	
	pH 6.5	pH 7.3	pH 6.5	pH 7.3
0	50, 49	53, 55	689, 675	536, 661
1	46, 47	47, 50	531, 531	546, 546
3	44, 46	47, 44	632, 488	460, 517
5	29, 29	22, 23	546, 474	373, 474
7	19, 19	19, 19	302, 421	402, 402
18	-, -	-, -	359, 330	273, 287
% lost after 7 or 18 days	61	65	49	53

**Table A.4** Microbial activity on clay soil from Thailand as affected by chlorpyrifos-methyl and propoxur at 30 C and saturated moisture condition.

Pesticide	Concentration (ppm)	<sup>14</sup> C counts per minute				% of control			
		1hr	2hr	3hr	4hr	1hr	2hr	3hr	4hr
Chlorpyrifos-methyl	0	2396	4798	5496	3521	100	100	100	100
	100	2064	4145	5221	4360	86.1	86.4	95.0	123.8
	500	1660	4263	4797	3466	69.3	88.9	87.3	98.4
	1,000	1973	4251	6490	4253	82.4	88.6	118.1	120.8
propoxur	0	1768	4521	5740	4615	100	100	100	100
	100	1542	3783	5736	5311	87.2	83.7	99.9	115.1
	500	1235	2508	4259	4421	69.9	55.5	74.2	95.8
	1,000	983	1704	3066	3550	55.6	37.7	53.4	76.9

**Table A.5** Microbial activity on silt loam soil from Oregon as affected by chlorpyrifos-methyl and propoxur at 30 C and saturated moisture condition.

Pesticide	Concentration (ppm)	<sup>14</sup> C counts per minute				% of control			
		1 hr	2 hr	3 hr	4hr	1hr	2hr	3hr	4hr
Chlorpyrifos- methyl	0	4409	8099	9620	7234	100	100	100	100
	100	2801	4951	6954	5642	63.5	61.1	72.3	78
	500	1931	3747	5894	5570	43.8	46.3	61.3	77
	1000	1673	2786	5321	6602	37.9	34.4	55.3	91.3
Propoxur	0	4382	8752	9179	7118	100	100	100	100
	100	3736	7710	8863	7655	85.3	88.1	96.6	107.5
	500	2800	5394	7270	7265	63.9	61.6	79.2	102.1
	1000	2230	4843	7178	7500	50.9	55.3	78.2	105.4

**Table A.6** The evaporation rate (flux) of chlorpyrifos-methyl from clay and silt loam soils as affected by moisture content.

Time	flux x 10 <sup>-5</sup> (µg/cm <sup>2</sup> d)			
	clay		silt loam	
	air dry	wet soil <sup>1</sup>	air dry	wet soil
0-7 hr	2.1	11.5	59.7	62.7
7hr-1d	<0.2	6.7	7.8	27.8
1d-2d	<0.2	4.1	9.1	4.6
2d-3d	<0.2	<0.2	5.5	4.1
3d-4d	ND <sup>2</sup>	ND	<0.2	4.3

1 at field capacity  
2 non detectable

Table A.7 The evaporation rate (flux) of propoxur from clay and silt loam soils at field capacity.

Time	flux ( $\mu\text{g}/\text{cm}^2\text{d}$ )	
	clay	silt loam
0-7hr	0.68	1.84
7hr-1d	0.95	1.13
1d-2d	0.95	2.01
2d-3d	0.44	1.81
3d-4d	0.22	2.34
4d-5d	0.25	1.96
5d-6d	0.23	2.21
6d-7d	0.20	2.24



Table A.8 The comparison of leaching of chlorpyrifos-methyl and propoxur from the clay soil.

Leachate (ml)	Chlorpyrifos-methyl		Propoxur	
	amt. found (µg)	% of initial	amt. found (µg)	% of initial
10	ND <sup>1</sup>	-	373.33	37.3
20	ND	-	187.5	18.8
30	tr <sup>2</sup>	< 1 x 10 <sup>-3</sup>	4.19	0.4
40	tr	< 1 x 10 <sup>-3</sup>	0.92	0.09
50	tr	< 1 X 10 <sup>-3</sup>	0.52	0.05
60	tr	< 1 x 10 <sup>-3</sup>	-	-

1 non detectable

2 trace; amount found less than 0.0005 µg

Table A.9 The comparison of leaching of chlorpyrifos-methyl and propoxur from the silt loam soil.

Time (day)	Leachate (ml)	Chlorpyrifos-methyl		Propoxur	
		amt. found ( $\mu\text{g}$ )	% of initial	amt. found ( $\mu\text{g}$ )	% of initial
1	20	0.12	0.24	2.8	0.28
2	33	$1.56 \times 10^{-3}$	$3.12 \times 10^{-3}$	319.0	31.90
3	42	$6.25 \times 10^{-4}$	$1.25 \times 10^{-3}$	215.6	21.56
4	50	$4.50 \times 10^{-3}$	$9.00 \times 10^{-3}$	38.9	3.89
5	57	tr <sup>1</sup>	$< 1 \times 10^{-3}$	18.1	1.81
6	62	tr	$< 1 \times 10^{-3}$	4.0	0.40
7	67	tr	$< 1 \times 10^{-3}$	2.2	0.22
8	72	ND <sup>2</sup>	-	4.1	0.41

<sup>1</sup> trace; amount found less than 0.0005  $\mu\text{g}$   
<sup>2</sup> non detectable

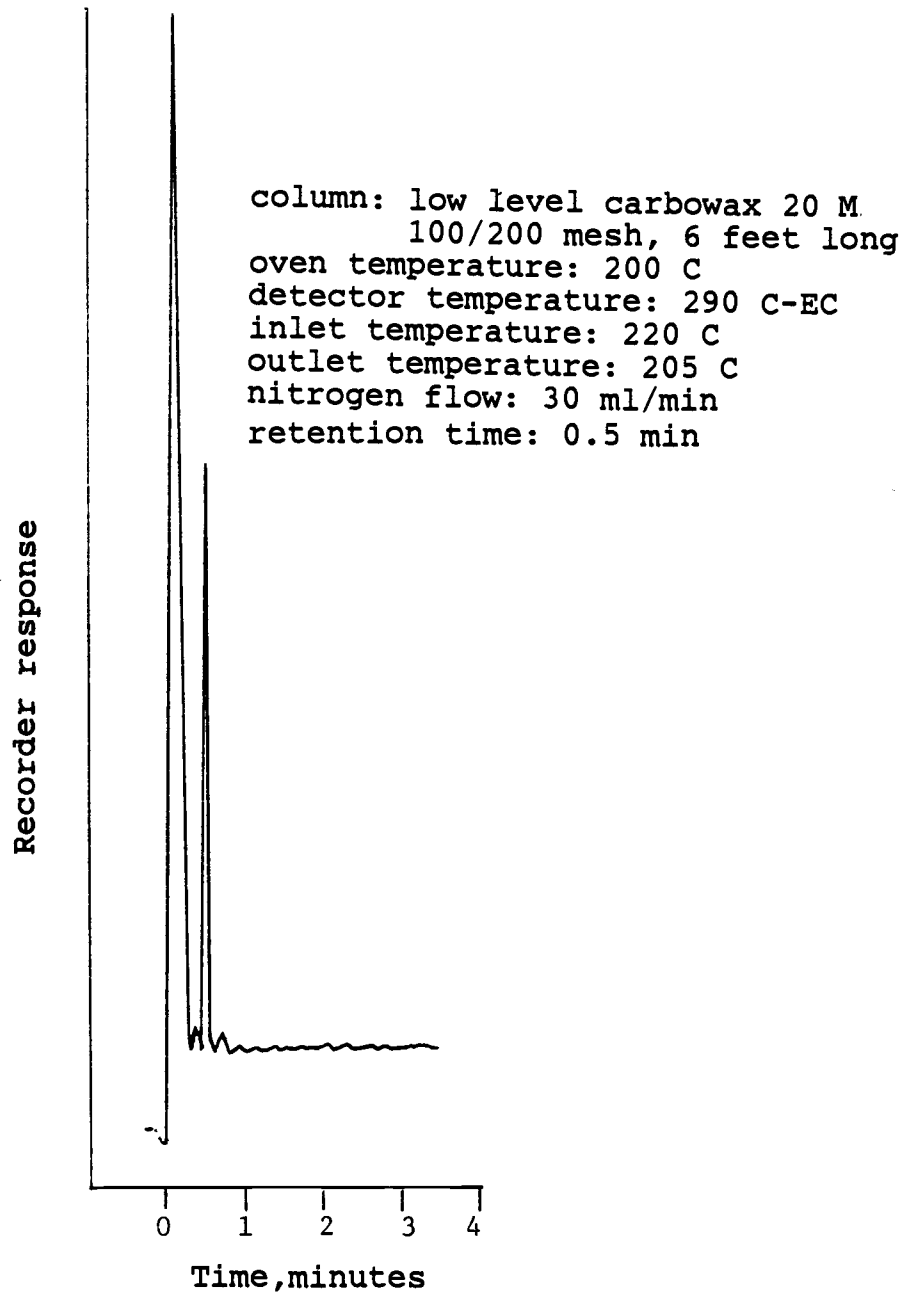


Figure A.1 Chromatogram of chlorpyrifos-methyl.

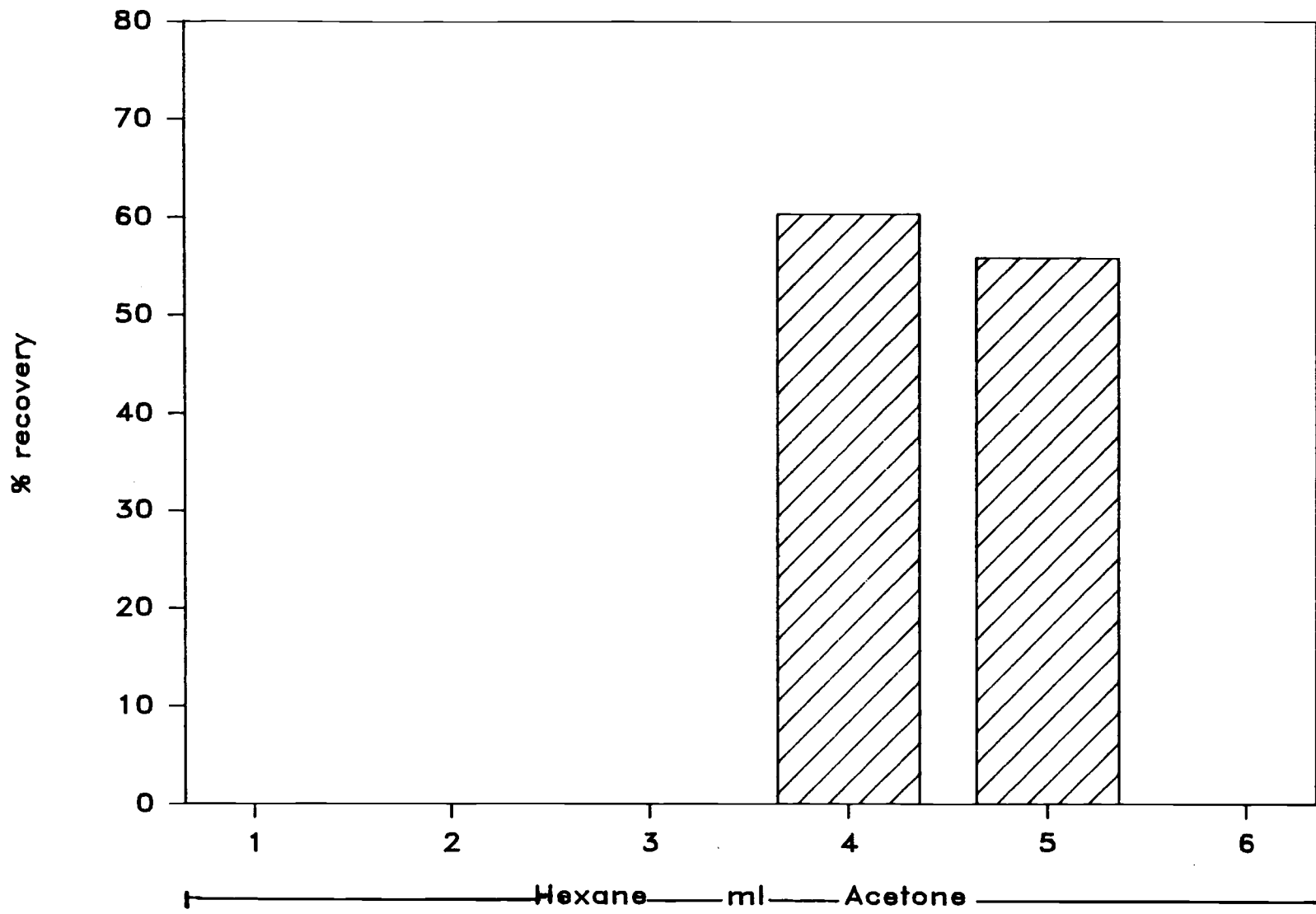


Figure A.2 Elution pattern of chlorpyrifos-methyl.

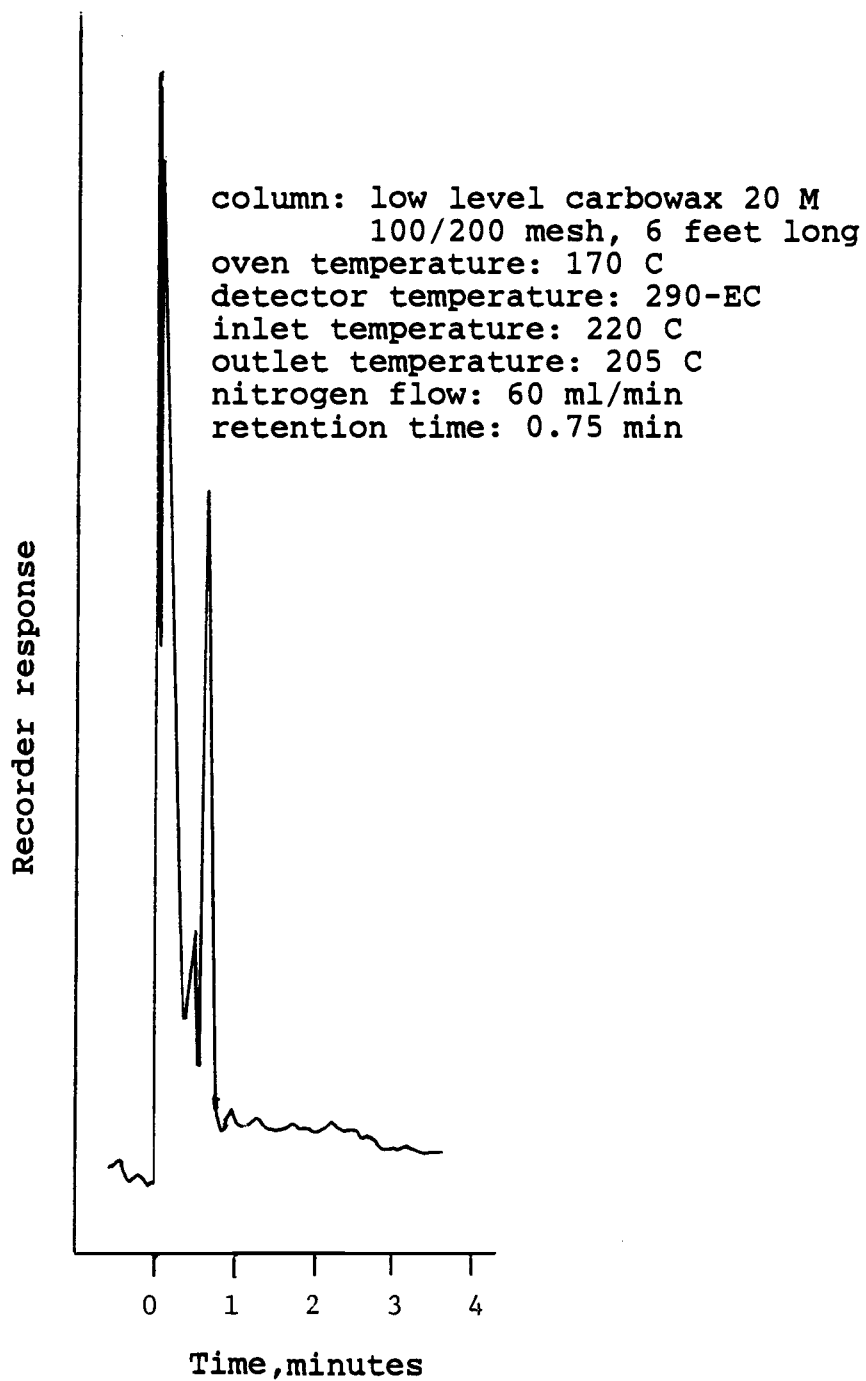


Figure A.3 Chromatogram of propoxur.

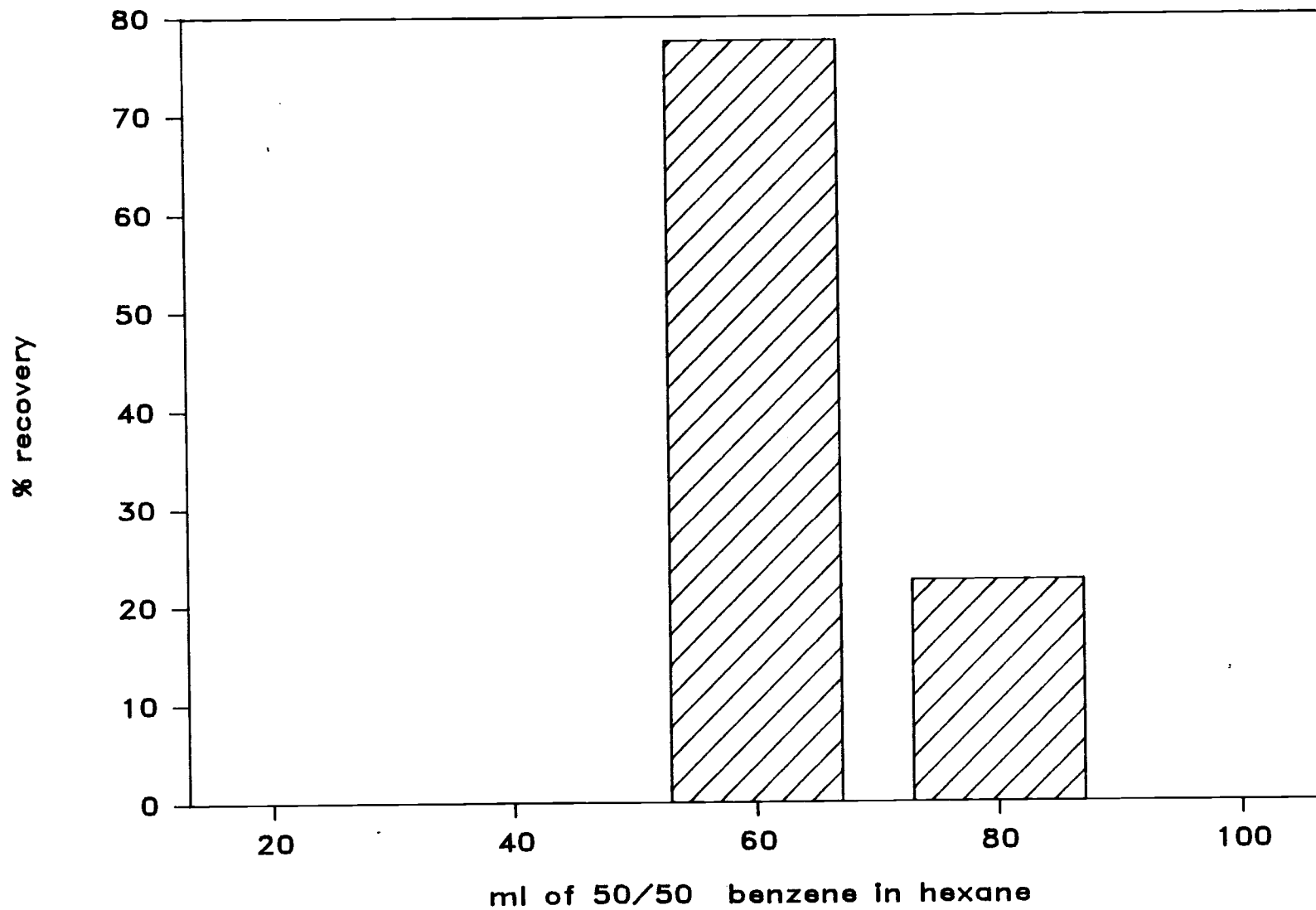


Figure A.4 Elution pattern of propoxur.

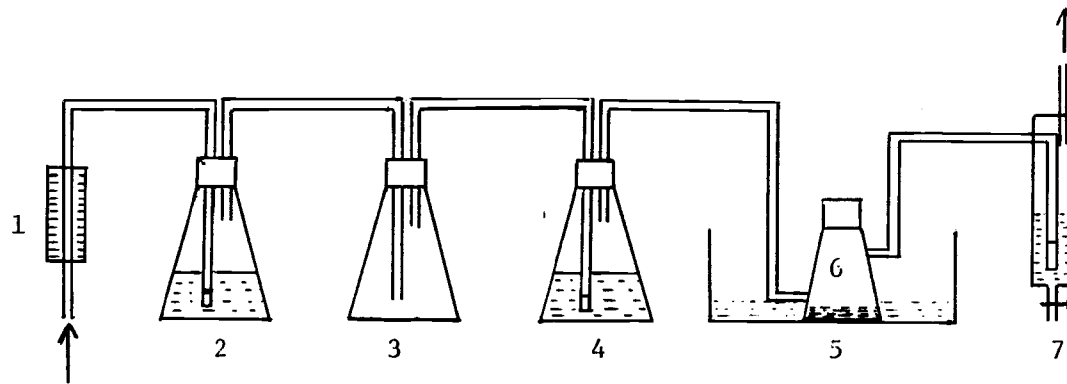


Figure A.5 Microbial activity study equipment, 1. flow meter, 2. NaOH, 3. empty flask, 4. water, 5. water bath, 6. soil metabolism flask, and 7. NaOH.