

**MODELLING OF CARBOFURAN
MOVEMENT AND SORPTION
IN SOILS WITH VARYING
PHYSICO-CHEMICAL PROPERTIES**

By
MOOSSA, P. P.

THESIS
SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENT FOR THE DEGREE
MASTER OF SCIENCE IN AGRICULTURE
FACULTY OF AGRICULTURE
KERALA AGRICULTURAL UNIVERSITY

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY
COLLEGE OF AGRICULTURE
VELLAYANI — THIRUVANANTHAPURAM
1994

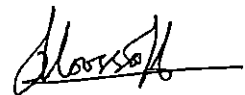
170693

631.4
N00/M0



DECLARATION

I hereby declare that this thesis, entitled "MODELLING OF CARBOFURAN MOVEMENT AND SORPTION IN SOILS WITH VARYING PHYSICO-CHEMICAL PROPERTIES" is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title, of any other University or Society.



College of Agriculture,
Vellayani.
18-1-1994.

MOOSSA, P.P.

CERTIFICATE

Certified that this thesis, entitled "MODELLING OF CARBOFURAN MOVEMENT AND SORPTION IN SOILS WITH VARYING PHYSICO-CHEMICAL PROPERTIES" is a record of research work done independently by Shri. MOOSSA P.P. under my guidance and supervision and that it has not previously formed the basis for the award of any degree, fellowship or associateship to him.



College of
Agriculture,
Vellayani
18-1-1994

Dr. P. RAJENDRAN
(Chairman, Advisory Committee)
Assistant Professor,
Department of Soil Science
and Agricultural Chemistry,
College of Agriculture,
Vellayani, Thiruvananthapuram.

ACKNOWLEDGEMENT

With immense pleasure, I wish to express my sincere and heartfelt gratitude to Dr. P. Rajendran, Assistant Professor, Department of Soil Science and Agricultural chemistry, Major Advisor and Chairman of my Advisory Committee for suggesting the problem, inspiring guidance, constant encouragement and unfailing patience throughout the course of the investigation. His keen interest, co-operation and help have been much beyond his formal obligation as the Chairman of the Advisory Committee, for which I am deeply indebted to him.

I express my sincere and deep sense of gratitude to Dr. (Mrs.) P. Padmaja, Professor and Head, Department of Soil Science and Agricultural Chemistry, Sri. Abdul Hameed, Professor, Department of Soil Science and Agricultural Chemistry and Dr. Thomas Biju Mathew, Assistant Professor, Department of Agricultural Entomology, members of my Advisory Committee for their constant encouragement, valuable suggestions and keen interest at all stages of the study.

I am extremely thankful to Dr. (Mrs.) P. Saraswathy, Associate Professor (H.G), and Head of the Department of Agricultural Statistics for her help in the statistical analyses of the data.

I am also indebted to Dr. A. Visalakshi, Professor, Agricultural Entomology for the sincere help rendered to me during the residue analysis.

I wish to express my sincere thanks to Dr. P.S. Mukherjee, Senior Scientist, RRL for his valuable help in X-ray analysis of clay samples.

My thanks are also due to C.E. AjithKumar, programmer for the help rendered in the analysis of the data.

I wish to express my sincere thanks to all members of the Department of Soil Science and Agricultural Chemistry for the help rendered through out the investigation.

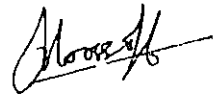
I take this opportunity to express my thanks to students of the Department of Soil Science and Agricultural Chemistry and all my friends especially Sanjeev, V., Louis

Joseph, Noushad, A., Chitra, V.G., Sreelatha, A.K., Geethakumari, V.S., Sreekumar, E.T. and Jacob John for their immense help and co-operation during the course of the investigation.

I am thankful to M/s. Athira Computers Kesavadasapuram for preparing this manuscript.

I am deeply indebted to members of my family for their unflinching inspiration and sincere encouragement in the pursuit and completion of the study.

Finally I express my gratitude to the I.C.A.R for awarding me the Junior fellowship which was quite helpful for the completion of my post graduation programme




Moossa, P.P.

APPROVED BY


CHAIRMAN

Dr. P. RAJENDRAN



19.3.94

MEMBERS

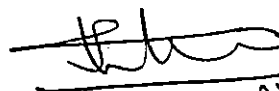
Dr. (Mrs.) P. PADMAJA


19/3/94

Prof. ABDUL HAMEED

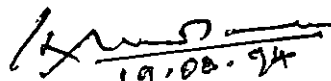

19-3-94

Dr. THOMAS BIJU MATHEW


19.3.94

EXTERNAL EXAMINER

Dr. K. VALSAGI .


19.03.94

CONTENTS

	Page No
INTRODUCTION	01 .. 04
REVIEW OF LITERATURE	05 .. 26
MATERIALS AND METHODS	27 .. 41
RESULTS	42 .. 75
DISCUSSION	76 .. 99
SUMMARY AND CONCLUSIONS	100 .. 103
REFERENCES	i .. xi
APPENDICES
ABSTRACT

No	Title	Page No.
11.	Direct and indirect effects of soil properties on carbofuran content (2 nd observation)	65
12.	Direct and indirect effects of soil properties on carbofuran content (3 rd observation)	66
13.	Direct and indirect effects of soil properties on carbofuran content (4 th observation)	67
14.	Direct and indirect effects of soil properties on carbofuran content (5 th observation)	68
15.	Direct and indirect effects of soil properties on carbofuran content (6 th observation)	69
16.	Mean values of carbofuran content in leachate	72
17.	Persistence and loss of carbofuran in soil	74

LIST OF FIGURES

No	Title	Between Pages
1.	Clay content - Depth wise	44 .. 45
2.	Water holding capacity of soils (mean)	45 .. 46
3.	Organic matter and CEC - Depth wise	46 .. 47
4.	Anion exchange capacity and sesquioxides - Depth wise	47 .. 48
5.	Hydraulic conductivity - Depth wise	48 .. 49
6.	X-ray diffractograms of the clay fraction - Inceptisol of Chengannur	50 .. 51
7.	X-ray diffractograms of the clay fraction - Ultisol of Malappuram	51 .. 52
8.	X-ray diffractograms of the clay fraction - Entisol of Kayamkulam	52 .. 53
9.	X-ray diffractograms of the clay fraction - Entisol of Kuttanad	53 .. 54
10.	X-ray diffractograms of the clay fraction - Mollisol of Nedumangad	54 .. 55
11.	Depth wise distribution of carbofuran at definite time intervals - Ultisol of Malappuram	56 .. 57

No	Title	Between Pages
12.	Depth wise distribution of carbofuran at definite time intervals - Inceptisol of Chengannur	56.. 57
13.	Depth wise distribution of carbofuran at definite time intervals - Entisol of Kayamkulam	57.. 58
14.	Depth wise distribution of carbofuran at definite time intervals - Mollisol of Nedumangad	57.. 58
15.	Depth wise distribution of carbofuran at definite time interval in the Entisol of Kuttanad	57.. 58
16.	Depth wise distribution of carbofuran during the first observation	58 .. 59
17.	Depth wise distribution of carbofuran during the second observation	58 .. 59
18.	Depth wise distribution of carbofuran during the third observation	58 .. 59
19.	Depth wise distribution of carbofuran during the fourth observation	58 .. 59
20.	Depth wise distribution of carbofuran during the fifth observation	58 .. 59
21.	Depth wise distribution of carbofuran during the sixth observation	58 .. 59
22.	Leachate concentration of carbofuran at different time intervals	72 .. 73

LIST OF APPENDICES

- I. Summary of analysis of variance of carbofuran
at different depth & intervals

- II. Anova table of carbofuran in leachate

INTRODUCTION

INTRODUCTION

The use of pesticides has become indispensable for modern strategy of crop production particularly under an intensive agricultural programme. Regardless of the method of application, large amounts of pesticides ultimately find their way into the soil, which finally acts as a reservoir for most of these chemicals. They are then acted upon by various physical, chemical and biological factors independently and/or in combination, thus leading to the formation of a wide variety of end products (Bailey and White, 1970).

Carbofuran is one of the widely used carbamate insecticides which was developed by FMC as a contact and systemic insecticide in 1969. It is being used as a broad spectrum insecticide for the control of sucking and chewing insect pests of rice, banana and many other crops. Carbofuran has a high acute toxicity but a rather low dermal toxicity. Hence it is most effective as a systemic insecticide when applied into the soil, in a granular form (IRRI, 1975). Owing to the low mammalian toxicity and persistence of carbamate pesticides, their use in pest control is getting

momentum now a days, as a substitute for the highly persistent chlorinated hydrocarbons.

Once the insecticide is applied to the soil, movement and degradation are the major processes that control its accumulation in the soil environment and plant uptake. Ground water contamination by leaching is another aspect of serious health concern with respect to the soil applied insecticides (Cohen et al., 1984; Hallbeg, 1989).

Another concern in respect of soil insecticide is the persistence which was used as a synonym to indicate the rate of transformation. According to IUPAC, persistence is the residence time of a chemical species in a specifically defined compartment of the environment (Green halgh, 1980). Hence not only transformation, but any process that affect the disappearance of the chemical from the plough layer (for instance, adsorption - desorption, movement, leaching etc.) can influence the persistence of a chemical in soil. (Jury et al., 1983; Pestmer et al., 1988). In agricultural lands, transport/movement of the chemical in the soil is also important since pesticide redistribution in the root zone enhances its efficiency.

With the introduction of high yielding varieties and the consequent adoption of better management practices, massive doses of carbofuran is being used extensively for pest control in rice, banana and vegetables in Kerala. Experiments on environmental fate studies of this chemical such as movement and distribution in soil, adsorption in soil system, persistence in the surface and subsoil and identification and bio-availability of residues are to be conducted in the major soils of Kerala with varying physico-chemical properties. Information generated on the above aspects will be useful in formulating efficient pest control strategies. Further, this will also help to reduce the hazardous effects to nontarget organisms of the soil and the environment.

Eventhough the major soils of Kerala show wide variation in physico-chemical properties, recommendation of carbofuran for a crop is the same in all the soils irrespective of its properties. As the fate determining process of carbofuran in a soil such as leaching, movement and distribution, persistence and degradation are highly dependent on soil properties such as pH, organic matter

content, CEC, clay content, hydraulic conductivity etc. (Helling, 1971; Rajukkannu, 1982; Neera Singh et al., 1990; Somasundaram, 1991), there is every possibility of getting differential response for carbofuran in Kerala soils.

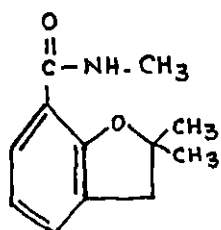
Keeping the aforementioned facts in view, the present study has been undertaken with the following objectives which are hitherto unstudied aspects of pesticide research in Kerala.

1. To study the movement and distribution pattern of carbofuran in soil columns.
2. To prepare a model for defining the influence of soil properties on carbofuran adsorption and movement in soil.
3. To study the leaching losses of carbofuran and its persistence in the major soils of Kerala.
4. To identify the degradation products or metabolites and their persistence in the major soils of Kerala.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Carbofuran (2,3-Dihydro-2,2-Dimethyl-7-Benzofuranyl Methyl carbamate) is an important soil insecticide grouped under carbamates with the molecular formula $C_{12}H_{15}NO_3$. The structural formula of Carbofuran is given below.



Carbofuran is considered to be less persistent in soil compared to organochlorine compounds. Persistence and bioavailability of carbofuran in soil is decided by processes like adsorption - desorption, movement and leaching, degradation and metabolism. A brief review of the research work done on the above aspects of carbofuran and its interaction with soil components is given below.

1. Adsorption - desorption

Hamaker et al. (1966) reported that there is stronger adsorption of picloram and 2,4,5-T by Fe and Al

oxides than clay minerals. They further stated that although crystallised and amorphous Fe and Al hydroxides are generally poor adsorbents, they are important in the sorption of weak acidic compounds. Adsorption mechanism of carbamate was reported to be through low energy ($< 80 \text{ kJ mol}^{-1}$) bonding and was considered to be due to hydrogen bonds (Bailey et al. 1968).

Helling et al. (1971) reported that organic matter, pH, clay, cation exchange capacity and field moisture capacity are the major factors that influence the behaviour of pesticides in soil.

Jamet and Piedallu (1975) found that the isotherm for the adsorption and desorption of labelled carbofuran in nine types of soils satisfied the Freundlich's equation and adsorption was reversible and increased with increasing organic matter content.

Felsot and Wilson (1980) has shown that carbofuran was very mobile in the agricultural soils and adsorption of carbofuran was positively correlated with organic matter content ($R^2 = 0.96$) and CEC ($R^2 = 0.83$). According to them

there appeared to be a direct relationship between adsorption of carbofuran and its mobility in soils.

Garg (1982) studied the adsorption, desorption and degradation of carbofuran and bendiocarb in soil and found that organic matter and clay content are the important factors that control the availability of carbofuran through adsorption - desorption mechanisms and in degradation.

Rajukkannu and Sree Ramulu (1982b) conducted a detailed study on the adsorption of carbofuran in red, alluvial, black and laterite soils. They found that the adsorption isotherm of carbofuran follows a Freundlich's adsorption equation $X/M = KC^{1/n}$ where X/M = Quantity of carbofuran adsorbed per unit weight of soil or clay, C = equilibrium concentration K = constant and n = constant which indicate energy of adsorption. The K value for red, black, alluvial and laterite soils were 9.09, 15.14, 0.56 and 70.79 respectively. The variation in clay content, organic matter and pH were attributed for this observation. In correlation studies, organic matter was highly correlated with K_d (ratio of the quantity of a compound adsorbed per unit weight of the adsorbent to the equilibrium concentration) values (0.98)

while pH and EC were found to be negatively correlated. Cation exchange capacity and sesquioxides had non significant relationship with Kd values. The Kd values were highest in laterite soil followed sequentially by black, alluvial and red soils.

Gārg and Agnihotri (1984) evaluated the adsorption of carbofuran and bendiocarb on alluvial soil, red soil, black soil and forest soils and in reference clays like bentonite, vermiculite and Kaolinite at pH 5, 7 and 9. They found that the amount adsorbed was related to the clay content and organic carbon and decreased in the order bentonite > vermiculite > Kaolinite. The adsorption increased with decreasing pH values. The infra red spectra showed shifting of bonds on adsorption of insecticides in 2920, 1745, 1225 cm^{-1} indicating that $-\text{CH}_2$, $\text{C}=\text{O}$ & $-\text{C}-\text{O}-\text{C}$ groups were involved in adsorption. Only about 18 to 43% of the adsorbed carbofuran could be desorbed.

Somasundaram et al. (1987) studied the effect of manuring on the persistence and degradation of carbofuran and found that in continuously manured soil, persistence of carbofuran was drastically increased. According to them

organic matter is a major adsorbent in the soil and the persistence of carbofuran was positively correlated with its content.

Kumari et al. (1988) studied the adsorption and movement of carbofuran using two Indian soils (clay loam & silt loam) of alluvial origin. Equilibrium adsorption coefficient (K) values measured using a batch - slurry technique followed the order clay loam > silt loam soil.

Singhal et al. (1988) evaluated the influence of particle size and other physico-chemical properties of the soils on the adsorption of carbofuran. The influence of the particle size on adsorption of carbofuran was investigated by mixing the insecticide with the soil sample at 50 µg/g. They observed that the recovery of carbofuran after 1 day, 7 days and 14 days was directly proportional to the particle size and inversely proportional to the duration of contact.

Adhikari and Ray (1990) observed that adsorption isotherm of carbaryl on a model soil was "S" shaped and followed the Freundlich's equation. The adsorption was mainly dependent on the availability of adsorbent surface and was found to be physical in nature.

Crepeion et al. (1990) has shown that the addition of coal to soil at 4:1 soil : coal ratio retained 94.7% of applied Carbofuran as compared to soil alone which have 48.5% retention. Moisture content of the coal was positively correlated with retention.

Neera singh et al. (1990) studied the sorption - desorption characteristics of carbofuran in 4 soils collected from rice growing areas in India. They reported organic matter as the most important factor which determined the rate of sorption - desorption of carbofuran. Freundlich's "K" and specific organic sorption of carbofuran in soil was less due to its low octanol - water partition coefficient (K_{ow}). The desorption rate was lesser with increase in the organic matter content of the soil.

Achik et al. (1991a) studied adsorption - desorption and movement of carbofuran in two soils viz. clay and clay loam and observed that adsorption in both the soils followed Freundlich's equation $X/M = KC^{1/n}$. The adsorption constant K for clay soil which had higher organic matter content was greater than that for loamy clay soil.

Achik et al. (1991b) found that carbofuran is a molecule which tended to desorb and remain in solution. The estimated values for desorption coefficient of carbofuran were always significantly higher than the estimated values for adsorption coefficient, irrespective of the soil. This indicates that carbofuran is not strongly adsorbed and shows a tendency to desorb whatever may be the soil type.

Kumari and Singh (1992) determined the adsorption of carbofuran on forest loam and black silt loam soils collected from India. The result showed that the amount of carbofuran adsorbed was high in forest loam soils which had a lower pH and higher organic matter content. The adsorption isotherm in these soils confined to Freundlich's adsorption model.

2. Movement and leaching

Many workers studying the movement of a wide variety of pesticides have reported that pesticides are leached to a greater degree in the light textured soils than in heavier textured soils. (Gantz, 1960; Harris, 1964;

Kearney et al., 1965 and Keys & Friesen, 1968). Changes in soil texture generally cause a resultant change in soil structure and therefore both soil texture and structure affect the movement and leachability of pesticides.

Hartley (1961) reported that percolating water is the principal means of movement of the relatively non volatile pesticides and found that diffusion in soil is important only for short distance movement of the chemicals.

Bowling (1970) studied the lateral movement of carbofuran and reported that carbofuran applied to flooded rice moved laterally at the rate of 22.5 cm in 48 hours in quantities toxic to leaf hopper.

Felsot and Wilson (1980) found that carbofuran was very mobile in agricultural soils studied and reported to have a direct relationship between adsorption of the insecticide and its mobility in soils.

According to Moreale and Bladen (1982) elution curves obtained by a method using undisturbed soil columns (1 m deep) showed the leaching characteristics of carbofuran

likely to contaminate the ground water and resulted in real contamination hazards.

Rajukkannu and Sree Ramulu (1982a) conducted a detailed investigation on leaching and movement of carbofuran in red, alluvial and black soils using TLC technique and soil column studies. From the Rf values of TLC, it was seen that carbofuran is highly mobile in red soil (Rf value 0.75 - 0.8) followed by black soil (0.73 - 0.75), alluvial soil (0.7 - 0.74) and the least in laterite soil (0.44 - 0.62). They attributed differences in organic matter content and clay to this effect. In the column study also the same trend was observed. In black, alluvial and red soils the movement of carbofuran was rapid and the effluent contained as much as 36.5, 41.59 and 55 per cent of added carbofuran respectively. But in laterite soil the effluent contained no carbofuran residue. In soil columns, depth wise distribution also showed wide variation. In laterite soil 63.9% of added carbofuran was retained in the top 0-10 cm layer and no carbofuran residue was detected below 30 cm. But in all other soils less than 35% of the added carbofuran was retained in the top layer and residues were detected in all the layers as well as in the effluent.

Dibakar Sahu and Agnihotri (1983) found that when 0.6 kg ai/ha of carbofuran was applied, no detectable residue was observed in sub soil samples at 15-30 cm. They suggested that carbofuran residues are rather tightly adsorbed on soil particles and are not available for leaching through percolating water.

Moreale and Bladen (1983) observed that due to increasing utilisation of carbofuran, relatively high water solubility, persistence in soils of low pH (less than 5.5) and low adsorption by soil colloids, the migration of this chemical to relatively deep water table can occur. Residual amounts were fairly high and the possibility of water table contamination depends primarily on the volume of water present (dilution effect).

Rajukkannu and Sree Ramulu (1984) conducted leachate studies of carbofuran in 5 types of soil using soil columns and classified carbofuran as mobile (class IV) in red, black and alluvial soils while in laterite soil it was ranked "moderately mobile" (Class III). The leaching of carbofuran was very rapid in red, black and alluvial soils and the leachate contained 55, 66.5 and 41.5% of the added

carbofuran. In laterite soil, a major portion of the added carbofuran was retained in the 1st column section (0- 10 cm) and the movement was not detected beyond the 3rd column section (20-30 cm).

Copin et al. (1985) in a field trial studied the leaching loss of carbofuran in corn field by soil analysis and observed that no residue was detected at > 10 cm depth. Residue of carbofuran in the top layer was smaller and decreased to undetectable limit within 3 months.

As a general rule, Rao et al. (1985) suggested that pesticides with solubilities > 10 mg l⁻¹ and half lives > 50 days show the highest potential for leaching and they included carbofuran under this category.

Kumari et al. (1988) studied the carbofuran movement in soil during water infiltration and found that larger amount of water was needed for leaching the carbofuran beyond 152 cm in clay loam soil than silt loam soil.

Radder et al. (1989) conducted an experiment to determine the leaching loss, movement and distribution of

carbofuran in soil columns and showed that leaching loss of carbofuran in black soil increased with time up to 72 h whereas in red and laterite soils the increase was only up to 48 h and then decreased. In saline alkali soil, there was no leaching until 12 h due to the dispersed condition of the soil, later the leaching increased till 72 h. The quantity of carbofuran lost by leaching during 72 h. period in 4 soils followed the order red soil > laterite soil > black soil > saline soil. The quantity of carbofuran retained in the soil decreased with increase in depth.

Lee et al. (1990) studied the fate of carbofuran in soil and found that carbofuran is highly mobile in soils and it moved to a depth of 70 cm under natural precipitation and evaporation conditions in 135 days after application and the concentration throughout the profile was $< 0.02 \text{ mg kg}^{-1}$ soil.

Naitan and Sukhani (1990) compared the vertical movement of carbofuran and isophenphos in soil columns and found that vertical movement of carbofuran in soil was faster than isophenphos and 24.9% of the applied carbofuran was recovered in 10-20 cm layer and 15.3% in 20-30 cm layer in the 14th day.

Somasundaram and Coats (1990) studied the mobility of pesticide using soil thin layer chromatography technique. They found that mobility of carbofuran was less in clay loam and silty clay loam compared to sandy loam and loamy sand. From the soil properties, they concluded that the low mobility in clay loam and silty loam soil was due to its low pH, high organic matter and high clay content compared to sandy loam and loamy sand soils.

Achik et al. (1991a) conducted an experiment on the movement of carbofuran in soils and influence of soil type and aggregate size on the movement of carbofuran. The result showed that carbofuran leaching in clay soil was greater than loamy clay and the product moved through the soil more rapidly and the total quantity exported by the percolating water was higher in clay soil than in loamy clay soil. The fine aggregate fraction retarded the movement of carbofuran and elimination of the fine aggregate fraction increased the movement of the product in the soil.

Kladivko et al. (1991) conducted an experiment with subsurface tile drains installed on a low organic matter and

poorly structured silt loam soil under typical agricultural management practices. They found that 0.8 to 14.1 g/ha or 0.05 to 0.94% of the soil applied carbofuran was lost in sub surface drain flow from the soil annually.

Somasundaram et al. (1991) conducted a detailed study of the mobility of carbofuran and its hydrolytic product - carbofuran phenol using soil TLC technique. From the result they have shown that carbofuran phenol is less mobile than carbofuran and soil pH doesn't has much influence on the mobility of carbofuran. But CEC, organic matter, clay content and water holding capacity has got an inverse relationship with mobility. Of the above factors organic matter and CEC were the best predictors for the mobility of carbofuran.

Daniel et al. (1992) conducted an experiment on dissolution rate of granular carbofuran and found that carbofuran concentration decreased rapidly as a function of distance, such that even after 72 hours there was only 1 mg ml⁻¹ of carbofuran at a distance of 2 cm from the surface of the granule applied. This data is indicative of the low molecular diffusion rate of carbofuran in soil and hence

could not be considered as a major factor in defining pesticide mobility.

3. Degradation and metabolism

Getzin (1973) reported that chemical hydrolysis in alkaline soil was the most important mechanism of carbofuran break down, but in acid and neutral soil both chemical and microbial process were involved.

Yu et al. (1974) studied the degradation of carbofuran in a model ecosystem and were able to detect the metabolites carbofuran phenol, 3 hydroxy carbofuran, 3 keto carbofuran, 3 hydroxy carbofuran phenol and N-hydroxy methyl carbofuran.

Williams et al. (1976) through a study have reported that the microbial degradation rate of carbofuran was 40 times greater in nonsterile soils compared to sterile soils.

Kandaswamy et al. (1977) studied a Helminthosporium sp which would degrade greater than 70% of a

20 ppm amount of carbofuran within 14 days. Strains of Aspergillus niger and Trichoderma viridae were less active in degradation. All the 3 isolates formed hydroxy carbofuran as an intermediate.

Green halgh and Relangur (1981) observed that when carbofuran was applied to a humic mesisol, 3 OH carbofuran and 3 Keto carbofuran were detected as transformation products. Three hydroxy carbofuran reached maximum concentration in 1-7 days and 3 Keto carbofuran attained maximum value in 16-36 days.

Rajukkannu and Sree Ramulu (1981) studied the degradation of carbofuran in 4 soils under field capacity and flooded moisture levels and found that there was an exponential decrease in the concentration of carbofuran whose dose at initial application was 100 ppm and the process of disappearance obeyed the first order kinetics. The data showed the reaction as $C = C_0 e^{-kt}$, where C = concentration of carbofuran (ppm) remaining at time "t" (days), C_0 = initial concentration added and K = degradation reaction rate (day^{-1}). K value was low in soil maintained at field capacity than in flooded condition and also in laterite soil than in

red, alluvial and black soils, indicating the slower and faster degradation of carbofuran in the respective group of soils. Faster degradation according to them was due to the result of high pH and low organic matter content of black, alluvial and red soils.

Garg and Agnihotri (1984) studied the degradation rate of carbofuran in 5 soils and observed that half life period of carbofuran showed wide variation between different soils. In the case of laterite soil, half life period was 69 days compared to 8 days in black soil.

Brahmaprakash and Sethunathan (1985) reported that degradation of carbofuran occurred in soils mainly by hydrolysis and 3 OH carbofuran was found to be the chief metabolite in soil.

Pestemer et al. (1989) conducted an experiment under field as well as laboratory condition to study the degradation of carbofuran and found that DT 50's (Disappearance time) under laboratory conditions varied from 2 to 15 days. Similar results were obtained under outdoor condition too by the same authors.

Rouchand et al. (1989) observed 3 Keto carbofuran, carbofuran phenol and 3-Keto carbofuran phenol as the chief metabolites of degradation of soil applied carbofuran.

Soudamini Panda and Sethunathan (1989) studied the influence of soil salinity on the degradation of soil applied carbofuran. They tried 3 levels of salt concentration ie. 4, 8 and 10 dS m⁻¹ (EC) and found that degradation of carbofuran was little affected by the presence of added salt.

Arunachalam and Lekshmanan (1990) studied the decomposition of labelled carbofuran under 4 condition viz. Sterile flooded (CF), sterile non flooded (SNF), non sterile flooded (NSF) and non sterile non flooded (NSNF) and observed that in SF and SNF soil, more than 75% of the added carbofuran was recovered as residue after 60 days. In NSF and NSNF Soil, more than 75% of the added carbofuran was metabolised during the same period with 3 Keto carbofuran and carbofuran 7 phenol as major metabolites during incubation.

Jae-Koo Lee et al. (1991) found that after the application of carbofuran in the soil, 3 Keto carbofuran phenol was the major metabolite and carbofuran phenol, 3

hydroxy carbofuran and 3 hydroxy carbofuran phenol were found as minor metabolites.

4. Persistence

In a sandy loam soil Harris (1969), employing bioassay techniques, found that the carbofuran was detectable up to 16 weeks after the application. He also noticed the persistence of this carbamate insecticide for a longer period in muck soil compared to sandy loam soil.

Gupta and Devan (1974) under Indian conditions observed much shorter persistence for carbofuran in soils. The residue persisted only for 35 days when 0.4 to 1.33 kg ai/ha was applied to soil.

Das et al. (1975) found a high persistence for carbofuran in laterite and black soils of Kerala as shown by the mortality of Aphis craccivora released on cowpea Vigna unguiculata grown in the treated soils.

Rajukkannu et al. (1977) conducted an experiment in rice with carbofuran 3 G applied at the rate of 1.25 kg ai/ha

as 2 equal doses i.e. 15 days after transplanting and 30 days thereafter. On the first day after application the residue in soil was 8.26 ppm which reduced to 1.9 ppm during 30th day. On the 31st day when the second dose was applied, the residue became 10.35 ppm which declined to 2.1 ppm on the 60th day. These results showed that carbofuran persisted in soil for more than 30 days after application.

Green halgh and Relangur (1981) observed the half life of carbofuran to be 15-30 days when applied to a humic mesisol at the rate of 2.24 and 4.48 kg ai/ha.

Rajukkannu and Sree Ramulu (1981) studied the persistence of carbofuran and found that it persisted for a long period in soils at field capacity moisture level than under flooded condition. Laterite soils recorded a longer persistence while the black soils registered the least. The half life value of carbofuran at field capacity ranged from 22 to 47 days and were highest in laterite soils followed sequentially by alluvial, red and black soils.

Gordan et al. (1982) in field and lab studies on the persistence of soil applied carbofuran identified soil

moisture as the most important factor in carbofuran persistence. He observed no carbofuran residue at a depth of more than 7.5 cm, 22 weeks after application.

Sahu and Agnihotri (1983) in a study carried out in Delhi, in the Kharif seasons of 1975 and 1976 showed that granular formulation of carbofuran applied as a side dressing @ 0.6 kg a.i./ha to the maize crop persisted in the soil for about 30 days in 1975 and 45 days in 1976.

Copin et al. (1985) found the residue of the surface applied carbofuran in the top soil layer to be very small and became undetectable within 3 months.

Getzin and Shanks (1990) measured the persistence of C¹⁴ carbonyl carbofuran in pacific north west soils. The half life was > 2 weeks in all cases and > 15 weeks in 5 soils. The carbofuran decay curve always possessed an initial lag phase where soil mixing enhanced insecticide decline.

Rouchand et al. (1992) studied the persistence of carbofuran in soils. It was applied to plots in cauliflower fields, in which pig slurry, cow manure, city refuse or

mushroom compost had been incorporated. Persistence of the insecticide was greater (2.4 times) in compost treated plots than in those without organic fertilizers and the insecticide protection efficiency was correspondingly better. The result suggested that the increase in soil persistence due to manuring corresponded to greater adsorption of the insecticide on to soil organic matter, thus protecting them against microbial activity and degradation.

MATERIALS AND METHODS

MATERIALS AND METHODS

The present study was conducted in the Department of Soil Science and Agricultural Chemistry at the College of Agriculture, Vellayani during 1992-93. Undisturbed vertical and horizontal soil columns of five different soil types were used to study the movement, adsorption and persistence of carbofuran within the soil matrix having varying physico-chemical properties. This study was undertaken with a view to define the adsorption and thereby the movement of carbofuran taking in to consideration the physico-chemical properties of these soils. Analysis of soils at different depth, distance and time intervals were carried out to estimate the concentration of carbofuran and its metabolites in selected soil columns. The methodologies employed in the present investigation are summarised hereunder.

1. Materials used

1.1 Carbofuran technical

Technical grade carbofuran supplied by M/s F.M.C corporation, Middleport, New York was used for the

preparation of standard solutions. A full description of the chemical used for the study is given below:

Chemical name	: 2,3- Dihydro-2, 2- Dimethyl -7 Benzofuranyl methyl carbamate (C ₁₂ H ₁₅ NO ₃)
Common name	: Carbofuran
Molecular weight	: 221.15
Appearance	: White crystalline Solid
Odour	: None
Specific gravity	: 1.18 at 20/20°C
Vapour pressure	: 2x10 ⁻⁵ mm Hg at 33°C
Flamability	: Non-flamable, support combustion when ignited
Stability	: Unstable in alkaline media and prone to degradation at temperature in excess of 130°C
Solubility in water	: 250-700 ppm at 25°C
Toxicity (Acute)	

Oral

L D 50 Rat :- 8.2 - 14.1 mg kg⁻¹

Dermal

L D 50 Rabbit :- 10200 mg kg⁻¹

1.2 Carbofuran commercial grade

Furadan 3G, granular formulation of carbofuran (Rallis India Limited, Bombay) containing 3% active ingredient was used for the study.

2. Collection of soil samples and columns

Five locations, to represent four major soil orders namely Entisol - (Onattukara region of Kayamkulam - $76^{\circ} 31'$ E longitude & $9^{\circ} 11'$ N latitude and Kari lands of Kuttanad - $76^{\circ} 28'$ E longitude $9^{\circ} 26'$ N latitude), Inceptisol - (Riverine alluvium of Chengannur - $76^{\circ} 39'$ E longitude $9^{\circ} 17'$ N latitude), Mollisol - (Hilly regions of Nedumangad - $77^{\circ} 2'$ E longitude $8^{\circ} 43'$ N latitude), and Ultisol - (Malappuram - $75^{\circ} 59'$ E longitude $10^{\circ} 51'$ N latitude) were selected for the study. Banana growing fields of these tracts were located for collecting soil samples and columns since the chemical is used extensively for the control of banana aphids in these areas. From each of the above 5 locations, 12 vertical columns of 50 cm length and 7.5 cm diameter and 5 horizontal columns of 40 x 10 x 8 cm were collected using p.v.c. pipes

of appropriate size in the former case and wooden boxes of suitable size in the latter. Soil samples were also collected separately from distinct layers of the profile at 10 cm intervals up to a depth of 50 cm to study the physico-chemical properties.

2.1 Vertical columns

Undisturbed vertical columns were collected by the method as described by Smelt et al. (1981) with slight modification using p.v.c tubes of 55 cm length and 7.5 cm inner diameter. The tubes were hammered into the soil to a depth of 50 cm. Soil surrounding the p.v.c. tube was then removed up to a depth of 50 cm and the tube with the soil inside was lifted up after closing the lower end of the tube with a thick cotton cloth and sealed either side with high density polythene sheet to prevent moisture and soil loss while in transport.

2.2 Horizontal columns

Wooden boxes of size 40 x 10 x 8 cm with open top and bottom were used for collecting soils. The boxes were

placed horizontally and pressed in to the soil. Soil outside the column was removed carefully and a perforated base was pushed in to the lower side of the box, simultaneously lifting the column up, supporting the perforated base with the right hand. The horizontal column of soil contained in the box was covered at first with thick cotton cloths and sealed with high density polythene sheet to avoid soil and moisture loss. The above columns were then transported to the laboratory for setting up the experiment.

3 Laboratory analyses of soil

The bulk samples collected from the different layers of the profile representing the various soil orders were air dried in shade, gravel and roots were removed and the samples were gently powdered with a wooden plank, passed through 2 mm sieve and stored in 1 kg plastic containers with screw cap for analysis. Analytical methods employed for different physico-chemical characteristics of the samples are outlined below.

3.1 Mechanical analysis

The mechanical composition of the soil was determined by the International pipette method (Gupta & Dakshinamoorthi, 1980).

3.2 Soil reaction (pH)

Soil reaction was measured in a 1:2.5 soil water suspension using a pH meter (Elico-model L1.120)

3.3 Electrical conductivity (EC)

Electrical conductivity was determined in a 1:2.5 soil water suspension using a conductivity bridge (Model. Elico. CM: 84)

3.4 Single value constants

Bulk density (B.D), particle density (P.D) and maximum water holding capacity (W.H.C) of the soils were determined by the Keen - Raczkowski box method (Gupta & Dakshinamoorthi, 1980)

3.5 Organic matter (OM)

Organic carbon was estimated by Walkely and Black's rapid titration method as detailed by Jackson (1971)

and converted into organic matter by multiplying with the factor 1.724.

3.6 Cation Exchange Capacity (CEC)

Cation Exchange Capacity was determined using N ammonium acetate (pH 7) as per method outlined by Jackson (1971).

3.7 Anion exchange capacity (AEC)

Anion exchange capacity was determined by phosphate retention method as detailed by Hesse (1971).

3.8 Total sesquioxides (R_2O_3)

Sesquioxides in the HCl extract of the samples was estimated by employing the method described by Chopra & Kanwar (1976).

3.9 Hydraulic conductivity

Using Jodpur constant head permeameter, hydraulic conductivity of the samples were determined (Gupta & Dakshinamoorthi, 1980).

3.10 Clay minerals

Fine clay of the samples were separated by gravity sedimentation and were subjected to X-ray diffraction using Phillips X-ray diffractometer (Model PW 1130/00/60) with Cu - K α radiation. Identification of the clay minerals present in the samples were made by calculating the characteristic d-spacing.

4. Preparation and treatment of the columns

Vertical columns were supported on a wooden frame after removing the plastic seal and kept in a vertical position. At the base of the column a plastic tube was fitted to collect the leachate. Columns were maintained at its field capacity by adding adequate quantity of water and allowing free drainage. To this columns 10 g of commercial grade carbofuran was added and thoroughly mixed with the surface soil up to a depth of almost 5 cm. On alternate days 50 ml of water was added to this columns through the open end with minimum disturbance to the surface soil matrix. The leachate collected at the bottom was taken for analysis of carbofuran.

Soil Columns collected in wooden boxes were kept in a horizontal position and maintained at field capacity after removing the plastic covering. At the centre of the column a small hole was made to a depth of 5 cm and 5 g of commercial grade carbofuran was added. The columns were maintained at its field capacity by adding 150 ml water in alternate days.

5. Estimation of carbofuran

5.1 Collection of soil samples from soil columns

At 6 time intervals after carbofuran application viz., 1st day, 5th day, 10th day, 20th day, 40th day and 80th day, two vertical columns from each soil type were taken for analysis. These soil columns were cut in to 5 segments of 10 cm length. Soil in each segment was mixed thoroughly and 25 g of soil was taken for the analysis of carbofuran residue. Leachate was also collected and analysed at intervals of 5, 10, 15, 20, 30, 40, 50, 60, 70 and 80 days after application from the columns representing the last time interval (Corresponding to 80th day after application)

In the case of horizontal columns, collection of samples were done at 5 time intervals after the application of carbofuran viz. 2nd day 5th day, 10th day, 15th day and 20th day. On these days, one column from each of the 5 locations were taken out and soil samples at 4 distances viz. 0,3,5 and 10 cm from the point of application were taken for analysis. On either side of the point of application, two samples representing the above horizontal distance were taken for analysis using a test tube with an internal diameter of 15 mm. The samples were thoroughly mixed and 25 g soil was taken for the analysis of carbofuran. Carbofuran in soil and leachate was determined colorimetrically following the procedure developed by Gupta & Dewan (1973). The method is based on the hydrolysis of carbofuran and allowing the resulting carbofuran phenol to complex with P-nitrobenzene diazonium tetra fluoborate and measuring the resulting colour complex at 550 nm using a spectrophotometer (Spectronic - 2000).

5.2 Extraction and determination

Extraction of carbofuran from the soil was done by acid hydrolysis and solvent partitioning. Twenty five gram

of the soil was taken in a 500 ml conical flask and 250 ml 0.25 N HCl was added (Cook et al. 1969). An air condenser was fitted on to the flask and the mixture was refluxed in a water bath for 2 hours. Then the contents were filtered through Whatman No. 42 filter paper and the volume was made up to 250 ml using hot 0.25 N HCl. The extract was transferred to a 500 ml separating funnel and shaken with 45 ml of dichloromethane and 10 drops of 4% solution of sodium lauryl sulphate for 2 minutes. The lower layer consisting the dichloromethane was transferred through anhydrous sodium sulphate placed over a plug of cotton taken in a funnel. This extraction with dichloromethane was repeated thrice for each sample and the extracts obtained were combined.

From the above combined extract 10 ml was taken and evaporated to almost dryness. The side of the test tube was rinsed down with 3 ml methanol and 7 ml freshly prepared coagulating solution (0.5 g ammonium chloride mixed with 200 ml glass distilled water and one ml H_3PO_4) was added to it. This was allowed to stand for 10 minutes with occasional shaking and filtered through whatman No. 42 filter paper to separate the precipitate formed if any. Five ml. of this solution was pipetted out to separate test tubes and placed

in an ice bath. Two ml. of 1.5 N methanolic KOH was added to the solution, mixed well and allowed to stand for 5 minutes. Then 1 ml of cold chromogenic reagent (prepared by saturating a cold mixture of 25 mg P-nitro benzene diazonium tetra fluoborate in 25 ml ethanol and 2 ml glacial acetic acid, filtered through Whatman No. 42 filter paper and kept below 4°C) was added, shaken well and kept in an ice - bath for 2 minutes. Then the pink colour developed was read at 550 nm using a spectrophotometer (Spectronic - 2000).

The concentration of carbofuran was calculated from the absorbance value obtained with the help of a standard curve and expressed as $\mu\text{g } 25 \text{ g}^{-1}$ soil.

5.3 Preparation of the standard curve

From a primary stock solution of 1000 ppm carbofuran, secondary stock solution of 50 ppm was prepared. From this 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5 and 3 ml. were taken in separate test tubes. The volume was made up to 3 ml. using methanol. Seven ml. of freshly prepared coagulating solution was added to each test tube and allowed to stand for 10 minutes with occasional shaking.

Five ml. each of these solutions were pipetted out to separate test tubes and placed in an ice-bath. Colour was developed and the absorbance read against a blank solution as detailed above. Using these absorbance values, a calibration curve for carbofuran was prepared to find out the concentration of carbofuran in the samples.

5.4 Estimation of carbofuran in leachate

Water samples collected was filtered through a whatman No. 1 filter paper, transferred to a 500 ml separating funnel and shaken with 45 ml of dichloromethane with 10 drops of 4% solution of sodium lauryl sulphate for 2 minutes. The lower layer consisting of dichloromethane was transferred through anhydrous sodium sulphate. This extraction procedure was repeated 3 times and the combined extract after further processing was used for the estimation of carbofuran as described above.

5.5 Determination of metabolites of Carbofuran

Dichloromethane extract of the surface soil collected from the columns were used for the identification

and determination of the metabolites of carbofuran. Appropriate quantity of the above dichloromethane extract was taken for each sample so as to get approximately 150 ug of carbofuran or metabolites and evaporated to almost dryness. The residue was dissolved in 3 ml of the reactant solution (obtained by dissolving 1.0 g of 1 fluoro 2, 4-dinitrobenzene in 100 ml of acetone) and transferred quantitatively into stoppered 25 X 190 mm test tube. Added 15 ml of the buffer solution (obtained by dissolving 2.3 g of Na_2HPO_4 in 250 ml distilled water containing 2 ml of 1 M NaOH solution, mixed well and kept in a water bath maintained at 50°C for 30 minutes. After cooling the mixture, it was transferred to a 100 ml separating funnel. The solution was extracted twice with 3 x 25 ml portions of n-hexane, collecting the organic layer and pooled the hexane extract. Evaporated the pooled extract so as to get a final volume of 10 ml. Five 5 μl of this solution was injected into a gas chromatograph (model - chemito 3865). The peaks for carbofuran, 3-OH carbofuran or 3 keto carbofuran was identified based on its retention time and the peak area was measured. The content of carbofuran or its metabolites was determined by comparing the response for known standards.

6. Statistical analysis

Ten important soil properties which influence the movement and adsorption of carbofuran either directly or indirectly as evidenced by carbofuran content of the samples were subjected to correlation and path analysis to study the interrelationship, direct and indirect influences of these factors in the adsorption and movement of carbofuran. Analysis of variance was done to study the effect of soil variation, depth of sampling and time intervals of sampling on carbofuran concentration. The data from leachate analysis were also subjected to analysis of variance to study the influence of soil and time intervals on carbofuran concentration.

RESULTS

RESULTS

The results of the study conducted to assess the physico-chemical properties of the five soil types and the data on the movement/adsorption of carbofuran as influenced by the above properties in these soils are presented in the following pages.

1. Laboratory analysis of soils

Soil samples collected from the different layers of each soil were subjected to physico-chemical analysis and the data obtained are presented in Table 1.

1.1 Mechanical analysis

A close scrutiny of the data given in the Table 1 shows a clear increase in clay content with depth in the case of the Ultisol taken from Malappuram. The surface soil recorded the lowest value of 40%, and the highest observed value was 55 % for the 5th layer (Fig. 1). However this

Table 1. Physico-chemical properties of soils used for the study

Sample/ location	Depth (cm)	pH	OM (%)	CEC (C mol (p ⁺) Kg ⁻¹)	Clay (%)	B.D. (g cm ⁻³)	P.D. (g cm ⁻³)	WHC (%)	A.E.C (C mol (e ⁻) Kg ⁻¹)	R ₂ O ₃ (%)	Hydraulic Conductivity (cm hr ⁻¹)
Ultisol Malappuram	0-10	5.09	2.50	9.75	40.00	1.24	2.34	39.30	3.54	24.00	10.73
	11-20	5.25	1.32	7.95	47.50	1.32	2.53	35.88	3.84	26.25	14.00
	21-30	5.39	1.08	7.92	50.00	1.35	2.45	35.79	3.29	25.25	9.33
	31-40	5.38	0.83	8.30	55.00	1.30	2.55	38.38	2.22	29.75	11.79
	41-50	5.48	0.91	7.90	55.00	1.21	2.21	40.39	3.15	24.50	14.79
Inceptisol (Chengannur)	0-10	5.09	0.62	2.37	20.00	1.66	2.42	21.42	1.29	3.75	15.37
	11-20	4.66	0.56	3.22	30.00	1.48	2.31	27.54	1.39	5.25	20.17
	21-30	4.70	0.48	3.65	25.00	1.66	2.57	23.59	1.24	6.25	9.16
	31-40	4.85	0.49	3.70	27.50	1.55	2.49	27.44	1.34	6.50	12.97
	41-50	4.04	0.44	4.25	30.00	1.46	2.42	29.60	1.67	6.75	14.00
Entisol (Kayamkulam)	0-10	5.35	0.5	2.17	10.00	1.67	2.53	22.30	0.92	2.75	66.60
	11-20	5.41	0.31	1.85	12.50	1.59	2.48	24.92	0.85	2.50	70.76
	21-30	5.28	0.43	2.12	13.75	1.72	2.73	24.24	1.17	2.75	47.91
	31-40	5.29	0.31	1.90	12.50	1.66	2.84	26.03	1.06	2.75	66.39
	41-50	5.29	0.21	1.75	12.50	1.62	2.56	24.95	1.15	2.00	75.97
Mollisol (Nedunangad)	0-10	4.38	2.35	4.97	42.50	1.37	2.32	32.85	2.42	8.75	16.83
	11-20	4.81	1.86	4.50	42.50	1.47	2.55	30.87	2.30	7.00	22.07
	21-30	4.92	1.88	3.50	45.00	1.51	2.37	27.11	1.82	4.75	15.57
	31-40	4.98	1.21	3.02	37.50	1.56	2.49	27.93	1.57	5.50	16.97
	41-50	4.57	1.92	3.42	37.50	1.48	2.34	27.46	1.74	4.00	18.99
Entisol (Kuttanad)	0-10	4.87	1.81	5.77	25.00	1.51	2.39	28.87	2.28	11.00	5.99
	11-20	4.57	1.57	6.07	25.00	1.40	2.48	32.13	2.08	12.25	12.78
	21-30	4.69	1.11	5.25	27.50	1.60	2.69	28.57	2.08	12.00	12.56
	31-40	4.79	0.34	2.62	20.00	1.61	2.66	26.98	1.95	6.75	16.93
	41-50	4.90	0.31	2.87	22.50	1.49	2.35	28.67	1.75	6.75	21.55
CO Soil		0.43	0.23	0.58	8.69	0.08	0.17	2.21	0.27	3.10	12.8
depth		0.18	0.18	0.49	2.98	0.09	0.22	1.90	0.23	1.80	4.90
Interaction		0.40	0.41	1.09	6.67	0.21	0.49	4.26	0.51	4.10	10.95

increasing trend was not uniformly observed for other soils. Increase in clay content was marginal for the Inceptisol from Chengannur, the highest value observed being 30% in the 2nd and 5th layer. Very low clay content of 10% was observed in the surface samples of the Entisol from Kayamkulam which increased to 13.75% at the 3rd layer and decreased subsequently to 12.5% towards the lowest layer. A decreasing trend in clay content with depth was observed in the forest soil of Nedumangad except for the 3rd layer which recorded the maximum clay content of 45%. Profile samples of the Entisol of Kuttanad representing riverine alluvium showed moderate values for clay content which decreased with depth after the 3rd layer with the maximum value of 27.5%.

Statistical analysis of the data showed significant difference in clay content between soils, between depth within a soil and interaction effect of soil with depth. Among the soils studied samples taken from Malappuram representing the Ultisol showed the highest clay content of 49.5% while Kayamkulam representing the Entisol gave the lowest value of 12.25%.

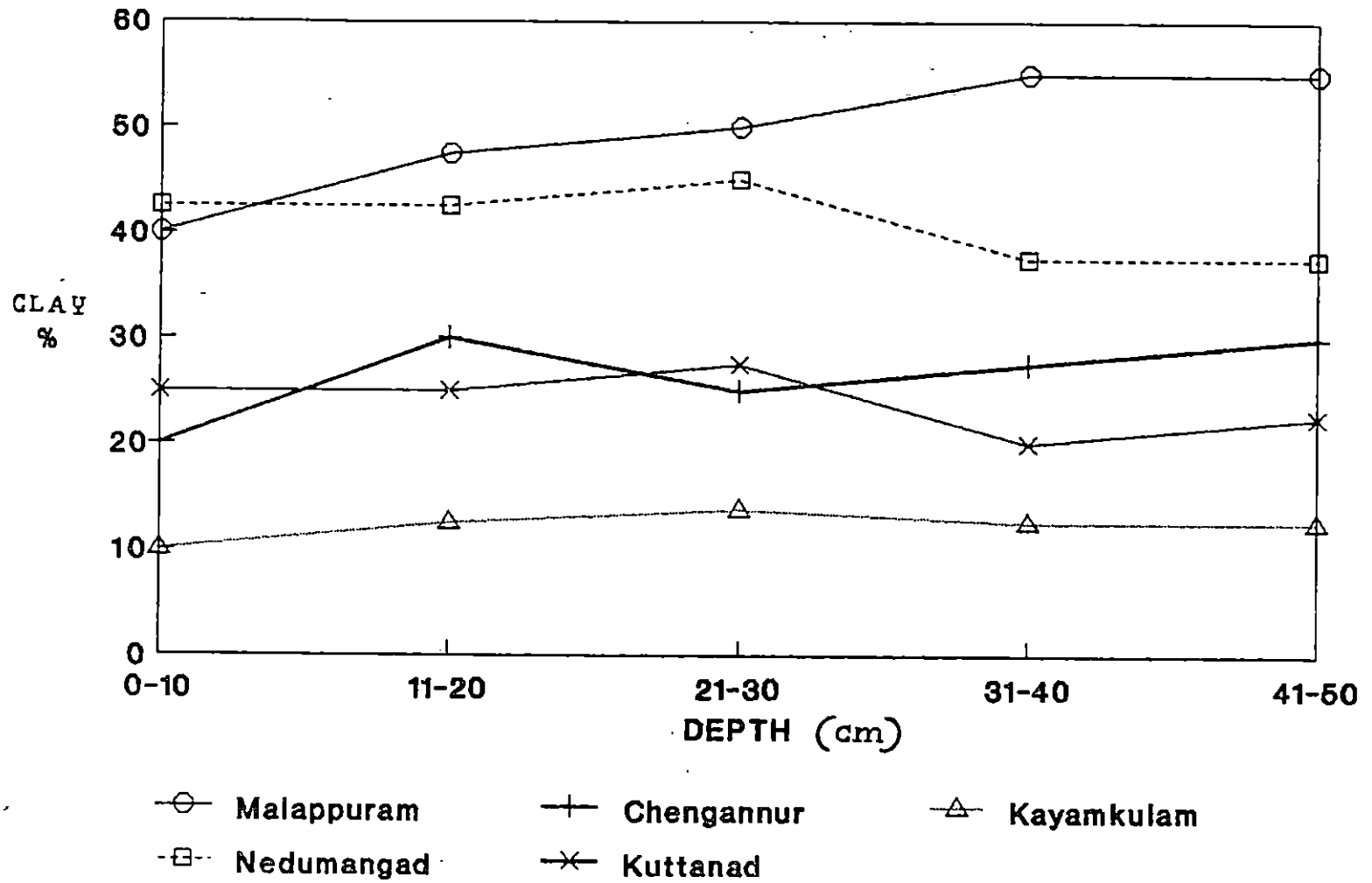


Fig. 1. Clay content - Depth wise

1.2 Soil reaction (pH)

All the soils studied were acidic in reaction showing a range of values from 5.09 to 5.48 in the case of Ultisol, 4.66 to 5.09 in the case of Inceptisol of Chengannur, 5.29 to 5.41 in the case of Entisol of Kayamkulam, 4.38 to 4.98 for the forest soil of Nedumangad and 4.57 to 4.90 for the Entisol of Kuttanad. Statistical analysis revealed significant differences among soil types.

1.3 Electrical conductivity (EC)

Electrical conductivity of all the samples were below 0.05 dS m^{-1} and hence was beyond the resolution of the instrument used.

1.4 Single value constants

Samples taken from the Ultisol of Malappuram recorded the lowest bulk density of 1.29 g cm^{-3} (mean) followed by the forest soils of Nedumangad (1.47), Entisol of Kuttanadu (1.52), Inceptisol of Chengannur (1.56) and the

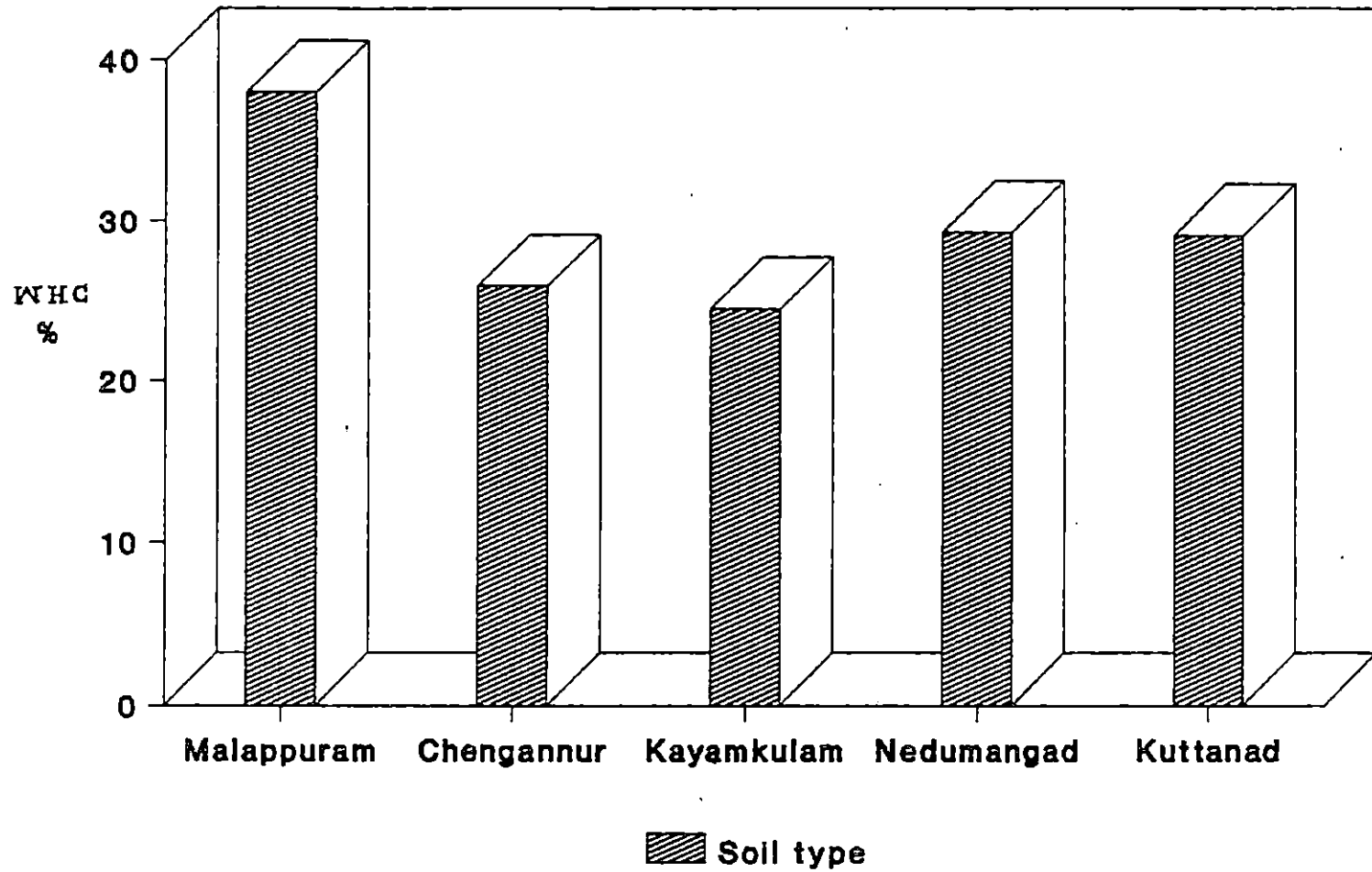


Fig. 2. Water holding capacity of soils (Mean)

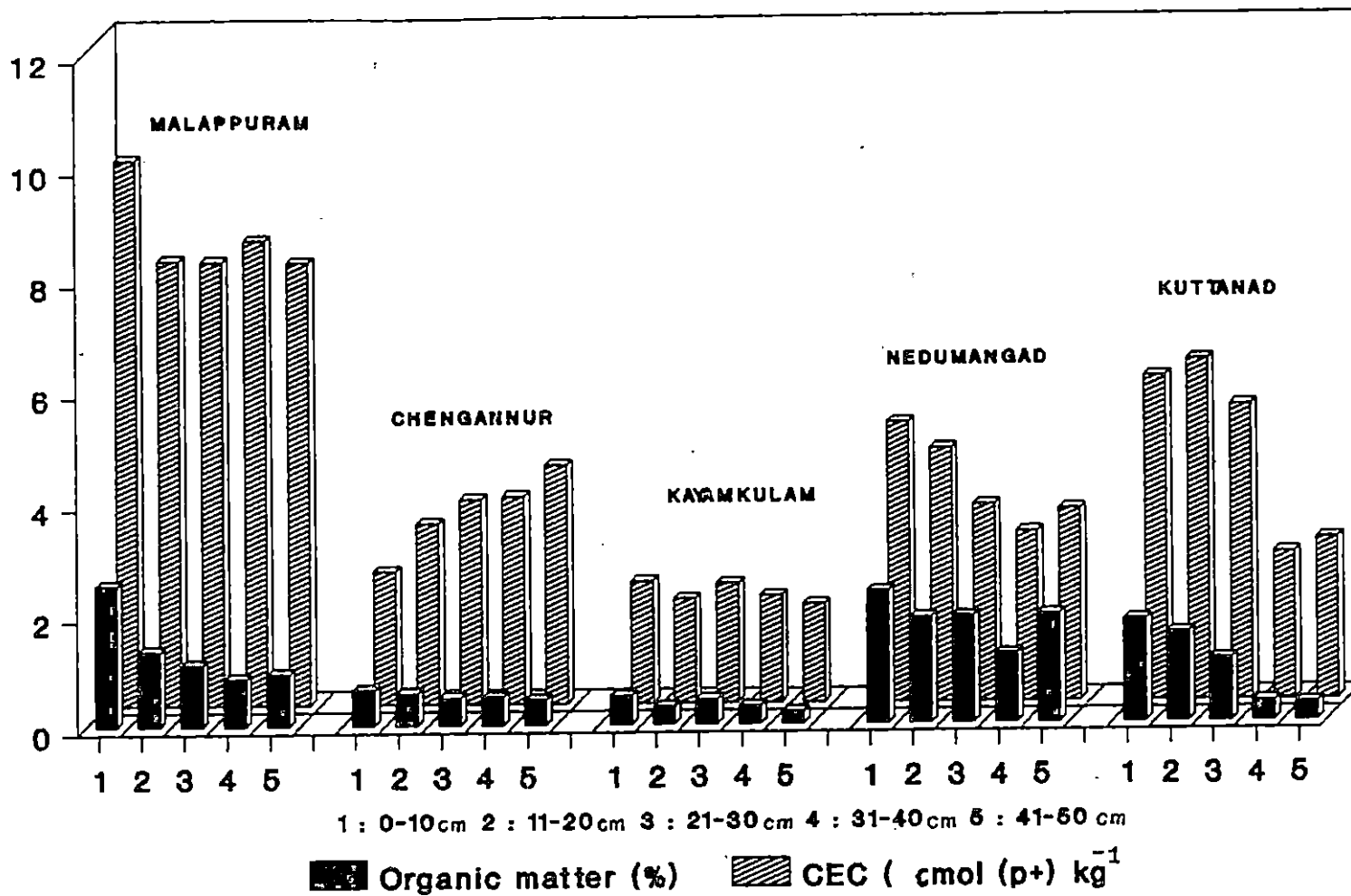
Entisol of Kayamkulam (1.65). Statistical analysis showed significant difference in bulk density between soils.

Particle density had comparatively higher values. Mean values observed were 2.41, 2.41, 2.44, 2.51 and 2.63 g cm⁻³ for the Ultisol of Malappuram, Mollisol of Nedumangad, and Inceptisol of Chengannur, Entisol of Kuttanad and the Entisol of Kayamkulam respectively. No significant difference could be observed between soils or between samples within a soil.

In respect of water holding capacity (Fig. 2), the Ultisol of Malappuram with a mean value of 37.99% showed the maximum value followed by the Mollisol of Nedumangad (29.24%), Entisol of Kuttanad (29.04%), Inceptisol of Chengannur (25.92%) and the least for the Entisol of Kayamkulam (24.49%). Significant difference in WHC could be observed only between soils.

1.5 Organic matter (O.M)

All the soils studied showed a general decrease in organic matter content with depth from the surface. However



**Fig. 3. Organic matter and CEC -
Depth wise**

in the case of the Mollisol of Nedumangad an increase in organic matter content was observed in the 5th layer. Organic matter content of the surface soils studied decreased in the order Ultisol of Malappuram (2.50%), Mollisol of Nedumangad (2.35%), Entisol of Kuttanad (1.01%) Inceptisol of Chengannur (0.62%) and Entisol of Kayamkulam (0.05%) (Fig. 3) Statistical analysis of the data on organic matter revealed significant difference between soil types, between samples within a profile and for interaction effects.

1.6 Cation exchange capacity (CEC)

Perusal of the data on CEC of the soil types studied indicated the highest mean CEC value for the Ultisol of Malappuram ($8.36 \text{ cmol (P}^+) \text{ kg}^{-1}$) followed by the Entisol of Kuttanad ($4.54 \text{ cmol (P}^+) \text{ kg}^{-1}$), the Mollisol of Nedumangad ($3.88 \text{ cmol (P}^+) \text{ kg}^{-1}$), the Inceptisol of Chengannur ($3.44 \text{ cmol (P}^+) \text{ kg}^{-1}$) and the Entisol of Kayamkulam ($1.92 \text{ cmol (P}^+) \text{ kg}^{-1}$). Depth wise decrease in CEC were observed in most of the soil types studied. Cation exchange capacity values generally followed the trend observed in the case of organic matter (Fig. 3). Statistical analysis revealed a similar trend as observed in the case of organic matter with respect to CEC also.

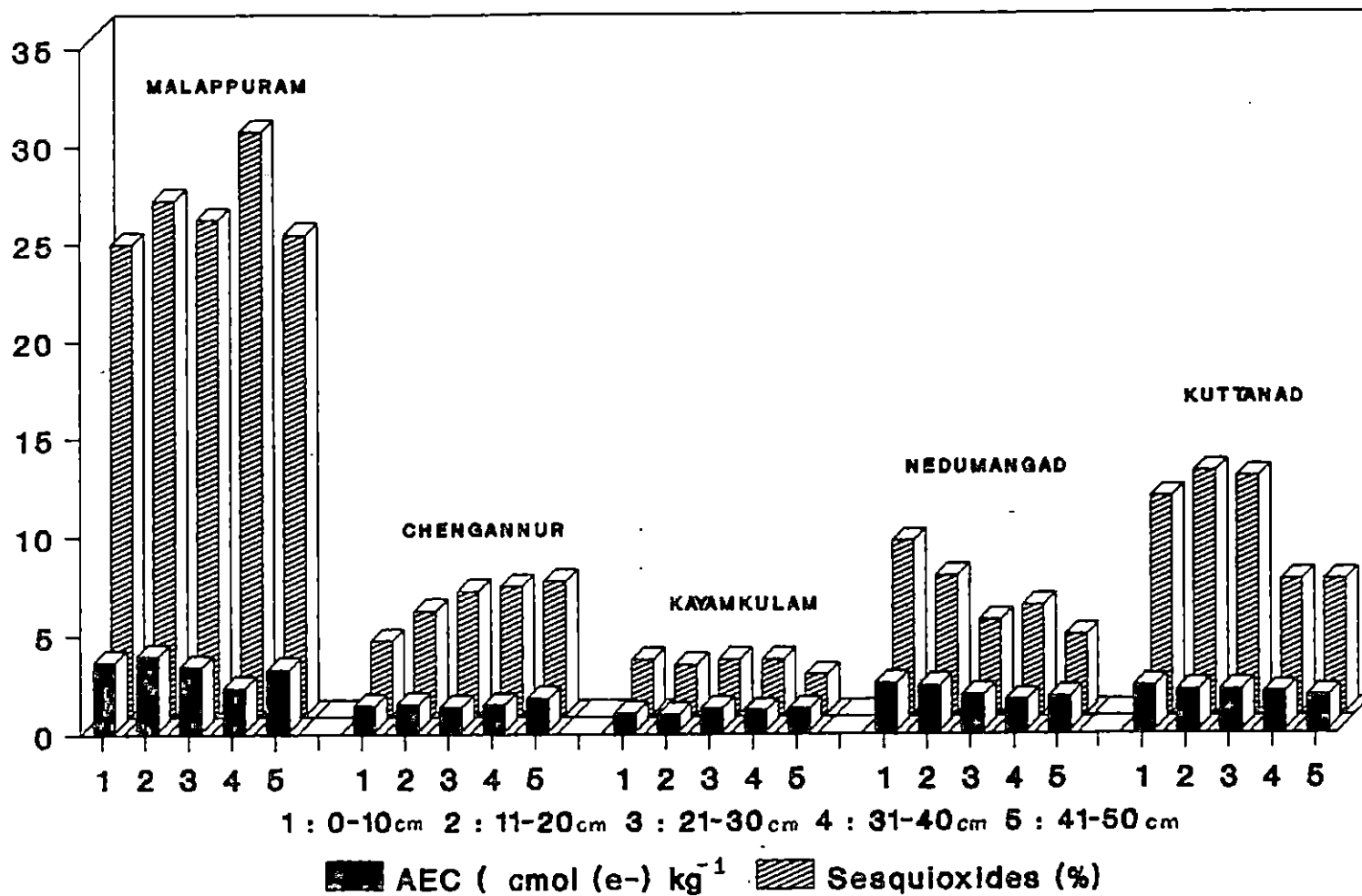


Fig. 4. Anion Exchange Capacity and sesquioxides - Depth wise

1.7 Anion exchange capacity (AEC)

Data on AEC showed maximum values for samples taken from the Ultisol of Malappuram. Maximum AEC value of 3.54 cmol (e⁻) kg⁻¹ was reported in the case of the surface layer of the Ultisol of Malappuram. Mean AEC values decreased in the order of, Ultisol of Malappuram (3.41 cmol (e⁻) kg⁻¹), Entisol of Kuttanad (2.11 cmol (e⁻) kg⁻¹), Mollisol of Nedumangad (1.97 cmol (e⁻) kg⁻¹), Inceptisol of Chengannur (1.38 cmol (e⁻) kg⁻¹) and Entisol of Kayamkulam (1.03 cmol (e⁻) kg⁻¹). (Fig. 4). Statistical analysis of the data on AEC revealed significant difference between soils and also between samples within a soil type.

1.8 Total sesquioxides (R₂ O₃)

A close examination of the values of the sesquioxide content (Fig. 4) revealed that the Ultisol of Malappuram recorded the maximum mean value of 25.95% followed by the Entisol of Kuttanad (9.75%), Mollisol of Nedumangad (6%), Inceptisol of Chengannur (5.7%) and the Entisol of Kayamkulam (2.55%). Significant difference in the sesquioxide content was observed between soil types, however

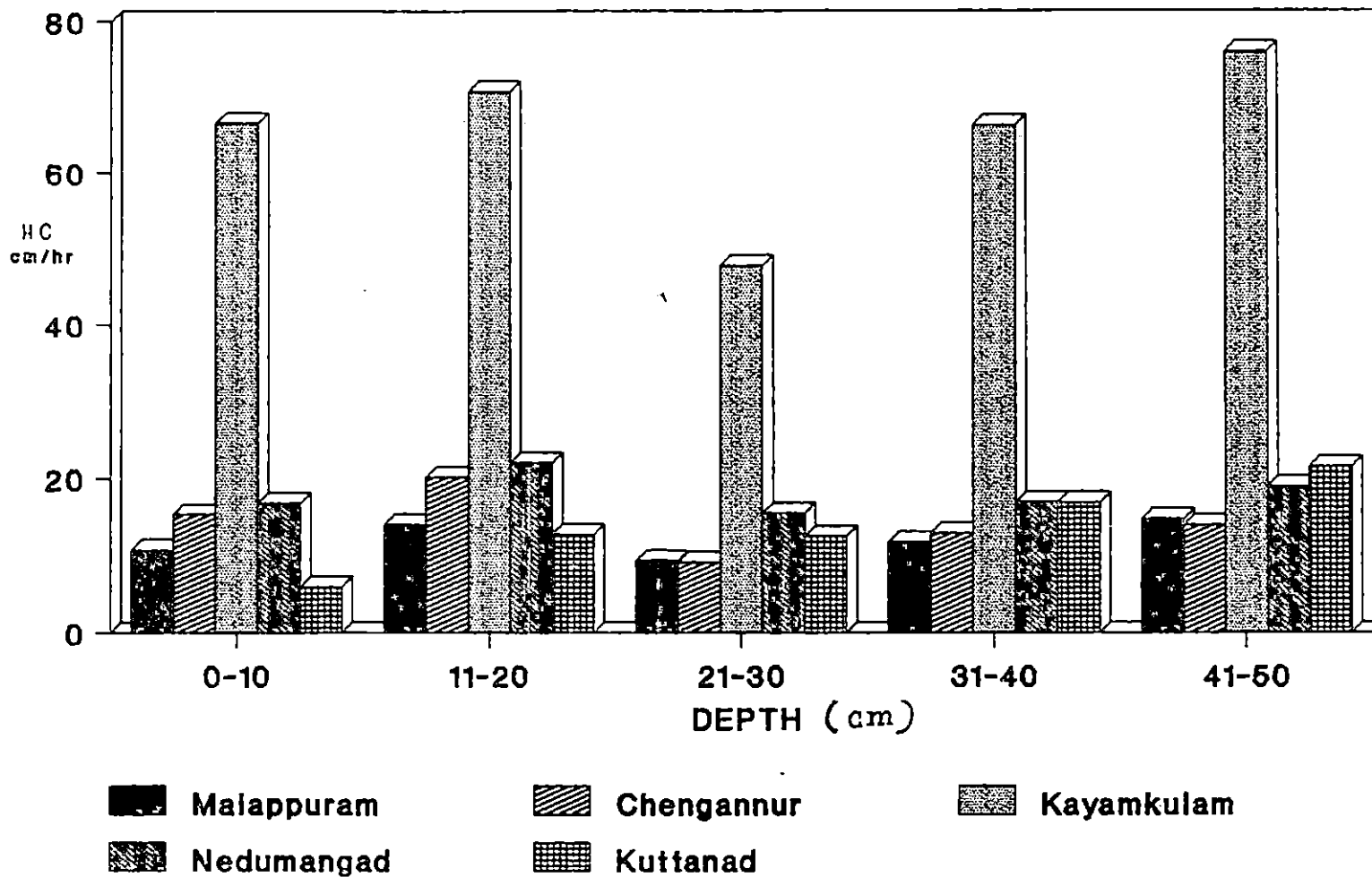


Fig. 5. Hydraulic conductivity -
Depth wise

interaction effects and variation between samples within a soil type was not significant statistically.

1.9 Hydraulic conductivity (H.C)

Data on Hydraulic conductivity of samples (Fig. 5) of various soil types studied showed the highest mean value for the Entisol of Kayamkulam ($65.5\% \text{ cm h}^{-1}$) followed by the Mollisol of Nedumangad (18.09 cm h^{-1}), Inceptisol of Chengannur (14.33 cm h^{-1}), Entisol of Kuttanad (13.96 cm h^{-1}) and the Ultisol of Malappuram (12.12 cm h^{-1}). Statistical treatment of the data also revealed significant effect due to soil type and depth. However interaction effects were non significant statistically.

1.10 Clay minerals

X-ray analysis of the fine clay fraction of all the five soils showed the occurrence of kaolinite as the dominant clay mineral (Fig. 6 to 10 and Table 2-6). However presence of smectites was also indicated in a few samples.

Table 2. X RD - data of fine clay fractions of the Inceptisol of Chengannur

d-value (Ang)	Angle (deg)	Width (deg)	Signif- icance	Minerals
13.681	6.45	0.56	1.19	Vermiculite, chlorite
7.078	12.49	0.12	1.06	Kaolinite
4.828	18.36	0.64	0.96	Chlorite, Gibbsite
4.440	19.98	0.24	1.99	Illite, Muscovite
3.565	24.95	0.40	2.46	Kaolinite
3.326	26.77	0.10	2.40	Quartz
3.151	28.29	0.14	1.15	-----
3.551	35.15	0.32	2.05	Kaolinite
2.484	36.13	0.24	1.09	-----
2.330	38.60	0.40	0.95	-----

Fig. 6. X-ray diffractogram of the clay fraction
Inceptisol of Chengannur

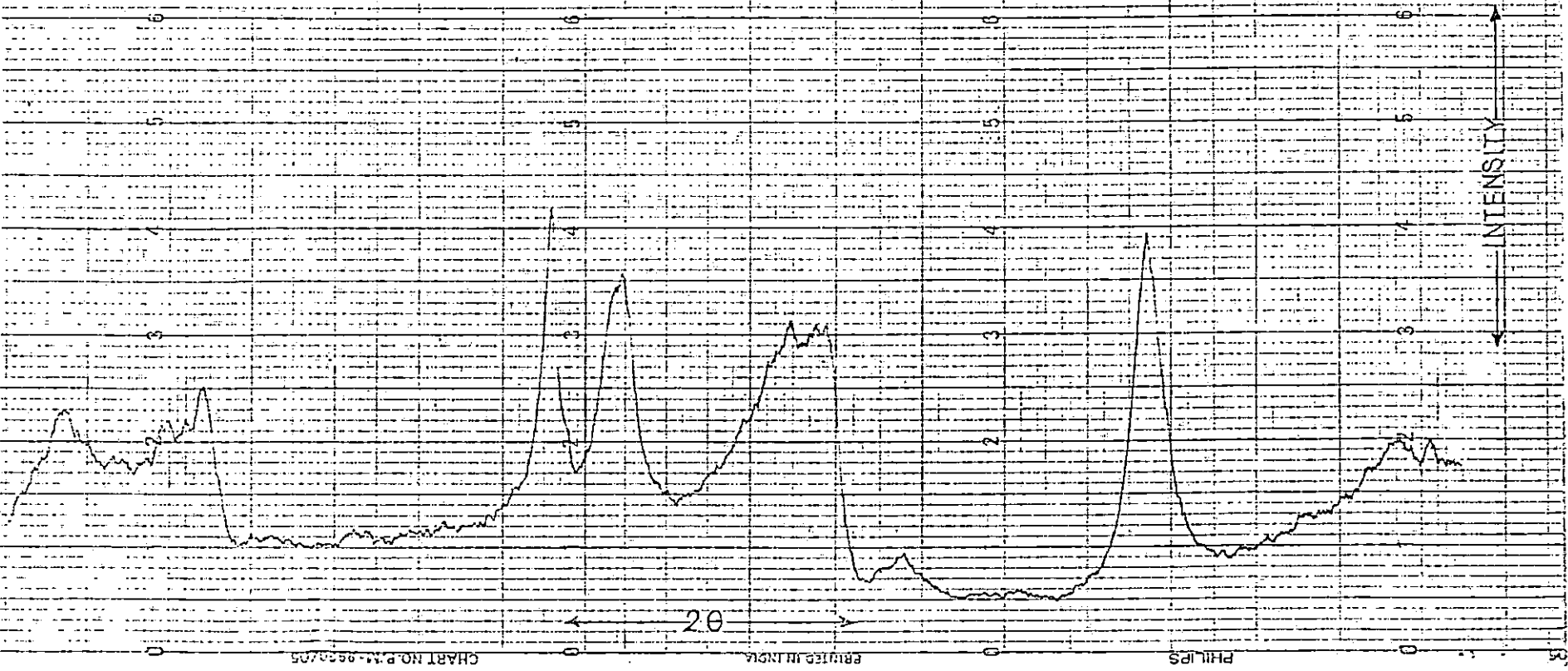


CHART NO. P.M.-986705

PHILIPS

PHILIPS

Table 3. X RD - data of fine clay fractions of the Ultisol of Malappuram

d-value (Ang)	Angle (deg)	Width (deg)	Signif- icance	Minerals
7.115	12.43	0.16	1.09	Kaolinite
4.831	18.35	0.12	3.51	Chlorite, Gibbsite
4.468	19.85	0.24	1.33	Kaolinite
4.142	21.43	0.32	1.25	Dickite
3.581	24.84	0.28	2.44	Kaolinite
3.338	26.68	0.10	0.94	Gibbsite
3.299	27.00	0.16	1.28	Lepidocrocite
3.197	27.88	0.48	0.76	-----
2.695	33.20	0.32	0.86	-----
2.564	34.96	0.32	1.18	-----
2.503	35.84	0.40	1.00	-----
2.344	38.37	0.24	0.99	-----



Fig. 7. X-ray diffractogram of the clay fraction

Ultisol of Malappuram

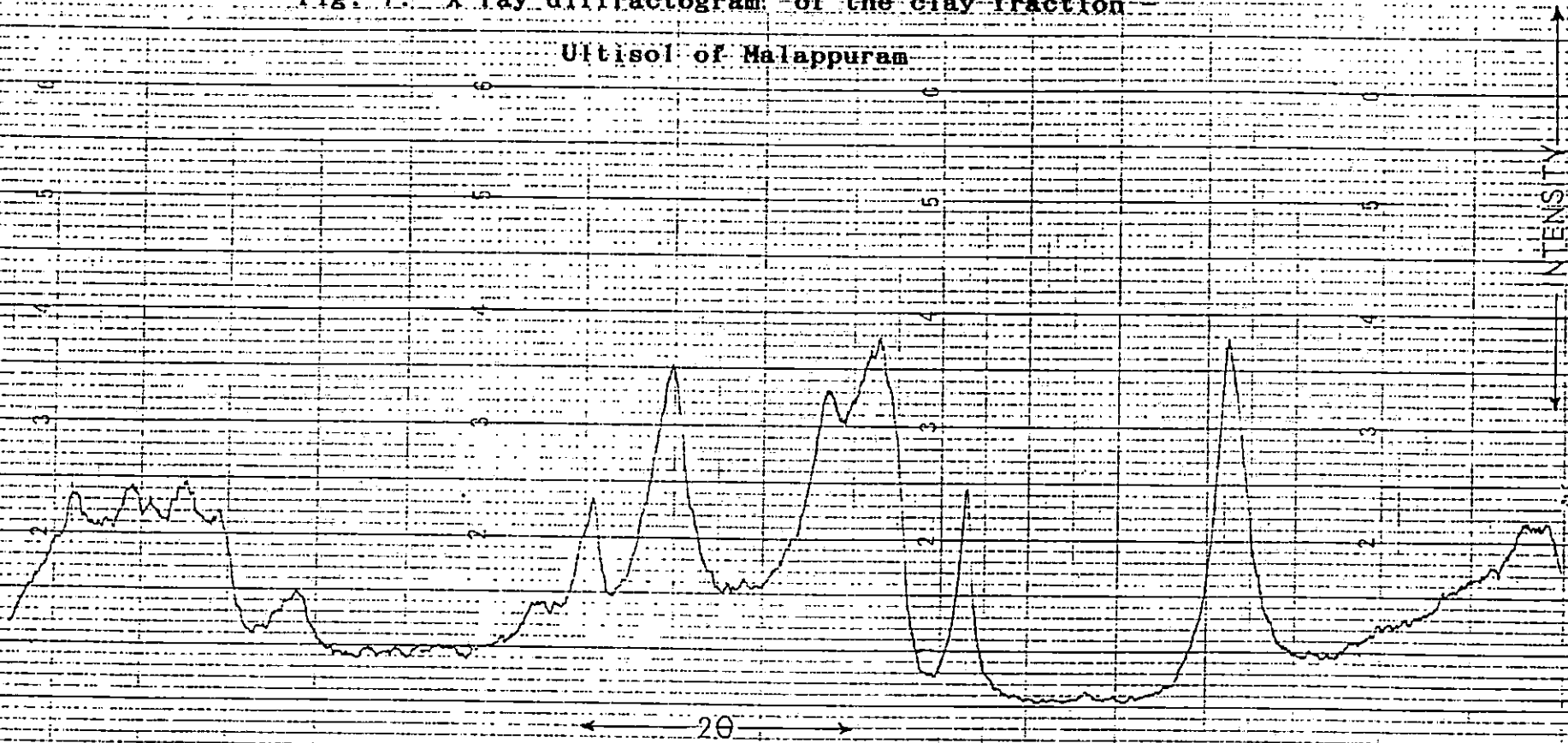


Table 4. X RD - data of fine clay fractions of the Entisol of Kayamkulam

d-value (Ang)	Angle (deg)	Width (deg)	Significance	Minerals
14.718	6.00	0.80	0.91	Vermiculite
7.254	12.19	0.48	1.08	Kaolinite
4.357	20.36	1.60	2.42	Quartz
3.550	25.06	0.96	0.87	Kaolinite
3.342	26.64	0.24	1.55	Kaolinite
2.746	32.58	0.12	0.84	-----
2.541	35.20	1.12	1.04	-----

Fig. 8. X-ray diffractogram of the clay fraction -
Entisol of Kayankulam

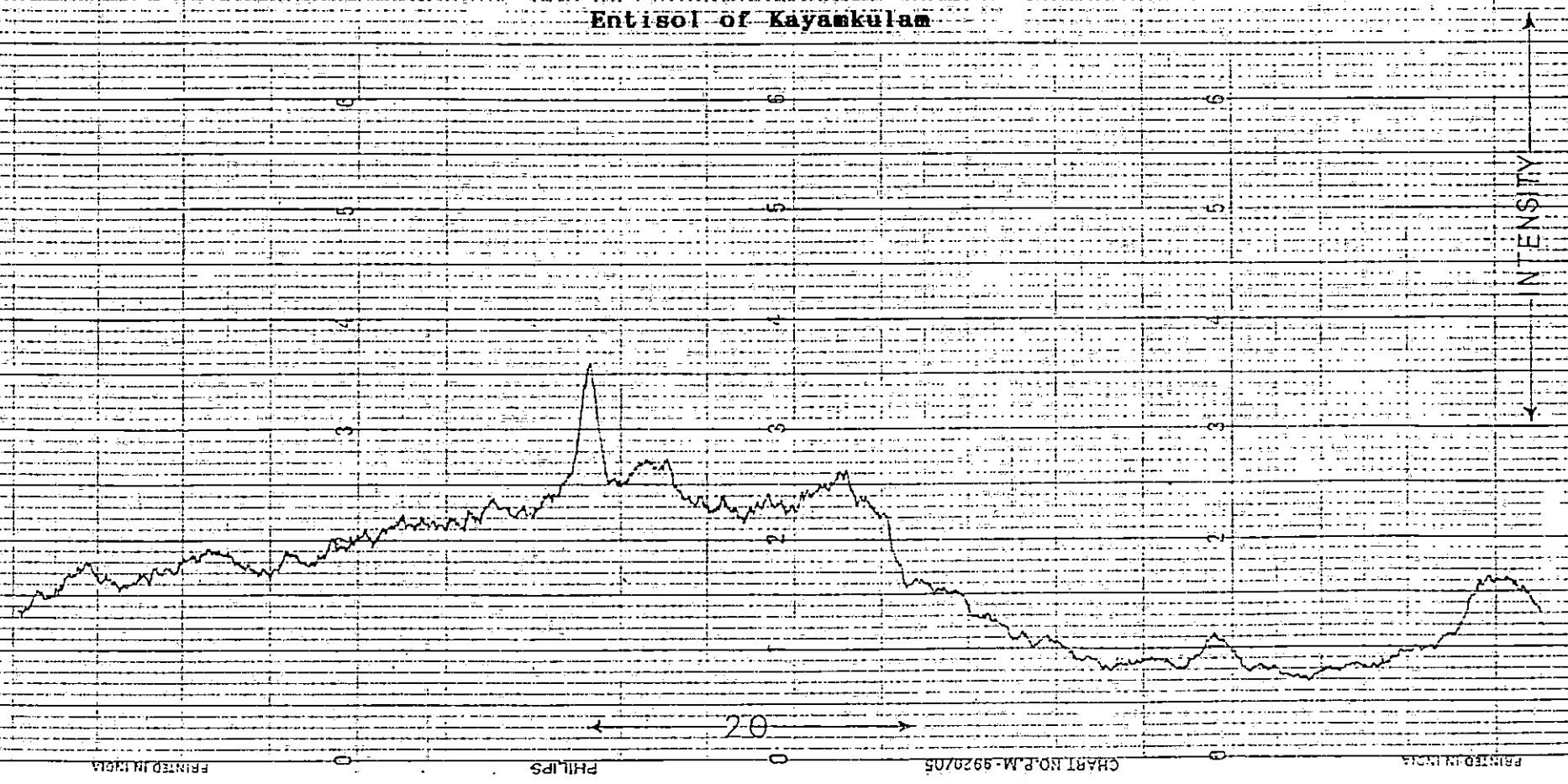


Table 5. X RD - data of fine clay fractions of the Entisol of Kuttanad

d-value (Ang)	Angle (deg)	Width (deg)	Signif- icance	Minerals
7.129	12.40	0.28	1.64	Kaolinite
4.808	18.43	0.10	1.49	Chlorite, Gibbsite
4.448	19.89	0.24	1.54	Illite/Muscovite
4.167	21.30	0.48	0.92	Dickite
3.568	24.93	0.40	0.97	Kaolanite
3.331	26.73	0.20	4.20	Kaolinite
2.561	35.00	0.24	0.98	-----
2.377	37.00	0.48	0.90	-----

Table 6. X RD - data of fine clay fractions of the Mollisol of Nedumangad

d-value (Ang)	Angle (deg)	Width (deg)	Signif- icance	Minerals
7.161	12.35	0.40	3.09	Kaolinite
4.891	18.39	0.20	1.39	Chlorite, Gibbsite
4.439	19.89	0.32	1.65	Nacrite
4.172	21.28	0.12	1.23	Kaolinite
3.577	24.87	0.32	1.33	Kaolinite
3.337	26.68	0.16	1.20	Kaolinite
2.781	32.16	0.48	1.03	-----
2.560	35.02	0.32	1.15	-----
2.338	38.46	0.48	2.35	-----

2. Movement and distribution of carbofuran in vertical soil columns

In all the soil types studied, as the time advanced from the date of application, carbofuran content decreased drastically towards the last day of observation (Table 7). Soil to soil variation was also observed for this trend. In the case of the Ultisol of Malappuram, initial concentration of 6200, $\mu\text{g } 25 \text{ g}^{-1}$ soil has decreased to 1000 $\mu\text{g } 25 \text{ g}^{-1}$ towards the 80th day corresponding to the 6th observation. One day after application the movement was restricted to the 3rd layer in this soil and even traces were not detected in the 4th and 5th depths. However in the 2nd observation corresponding to the 5th day of application, the chemical was distributed in all the layers with maximum concentration in the surface. At the 3rd observation on the 10th day after the addition, concentration at the surface was decreased drastically and the lower layer showed greater accumulation towards the 4th, 5th and 6th observations. The concentration at the surface layer decreased further with an enrichment in the concentration of the chemical downwards in the profile. In the Ultisol of Malappuram the highest concentration observed in the 5th depth was 420 $\mu\text{g } 25 \text{ g}^{-1}$ after the 6th

Table 7. Mean values of carbofuran in vertical soil columns ($\mu\text{g}/25\text{ g soil}$)

Sample/ location	Depth (cm)	1 st day	5 th day	10 th day	20 th day	40 th day	80 th day
Ultisol Malappuram	0-10	6200.0	4490.0	3500.0	2700.0	1600.0	1000.0
	11-20	137.0	270.0	410.0	730.0	622.5	430.0
	21-30	67.0	95.0	240.0	430.0	532.5	380.0
	31-40	0.0	97.0	150.0	225.0	425.0	385.0
	41-50	0.0	110.0	140.0	190.0	332.5	420.0
Inceptisol (Chengannur)	0-10	5100.0	3875.0	2760.0	1885.0	1015.0	475.0
	11-20	125.0	385.0	680.0	590.0	582.5	227.5
	21-30	90.0	320.0	695.0	480.0	492.5	170.0
	31-40	0.0	180.0	280.0	600.0	387.5	235.0
	41-50	0.0	77.0	155.0	300.0	412.5	205.0
Entisol (Kayamkulam)	0-10	4500.0	3500.0	2600.0	1660.0	1040.0	485.0
	11-20	275.0	407.5	445.0	335.0	287.5	170.0
	21-30	170.0	237.5	390.0	447.5	347.5	195.0
	31-40	100.0	120.0	332.5	225.0	357.5	220.0
	41-50	0.0	62.5	332.5	255.0	357.5	220.0
Mollisol (Nedumangad)	0-10	4200.0	3225.0	2220.0	1880.0	1300.0	750.0
	11-20	260.0	417.5	800.0	770.0	667.5	395.0
	21-30	120.0	202.5	375.0	457.0	457.5	390.0
	31-40	30.0	130.0	260.0	305.0	285.0	295.0
	41-50	0.0	110.0	165.0	235.0	340.0	370.0
Entisol (Kuttanad)	0-10	4700.0	3735.0	2850.0	2060.0	1740.0	920.0
	11-20	175.0	347.5	750.0	970.0	948.0	550.0
	21-30	110.0	225.0	500.0	655.0	575.0	505.0
	31-40	75.0	190.0	252.0	555.0	290.0	210.0
	41-50	0.0	135.0	160.0	235.0	290.0	210.0
CD Soil		149.26	199.79	122.49	253.47	136.33	49.09
Depth		120.28	145.49	171.42	101.41	78.44	42.85
Interaction		268.95	325.33	383.22	226.78	175.41	95.81

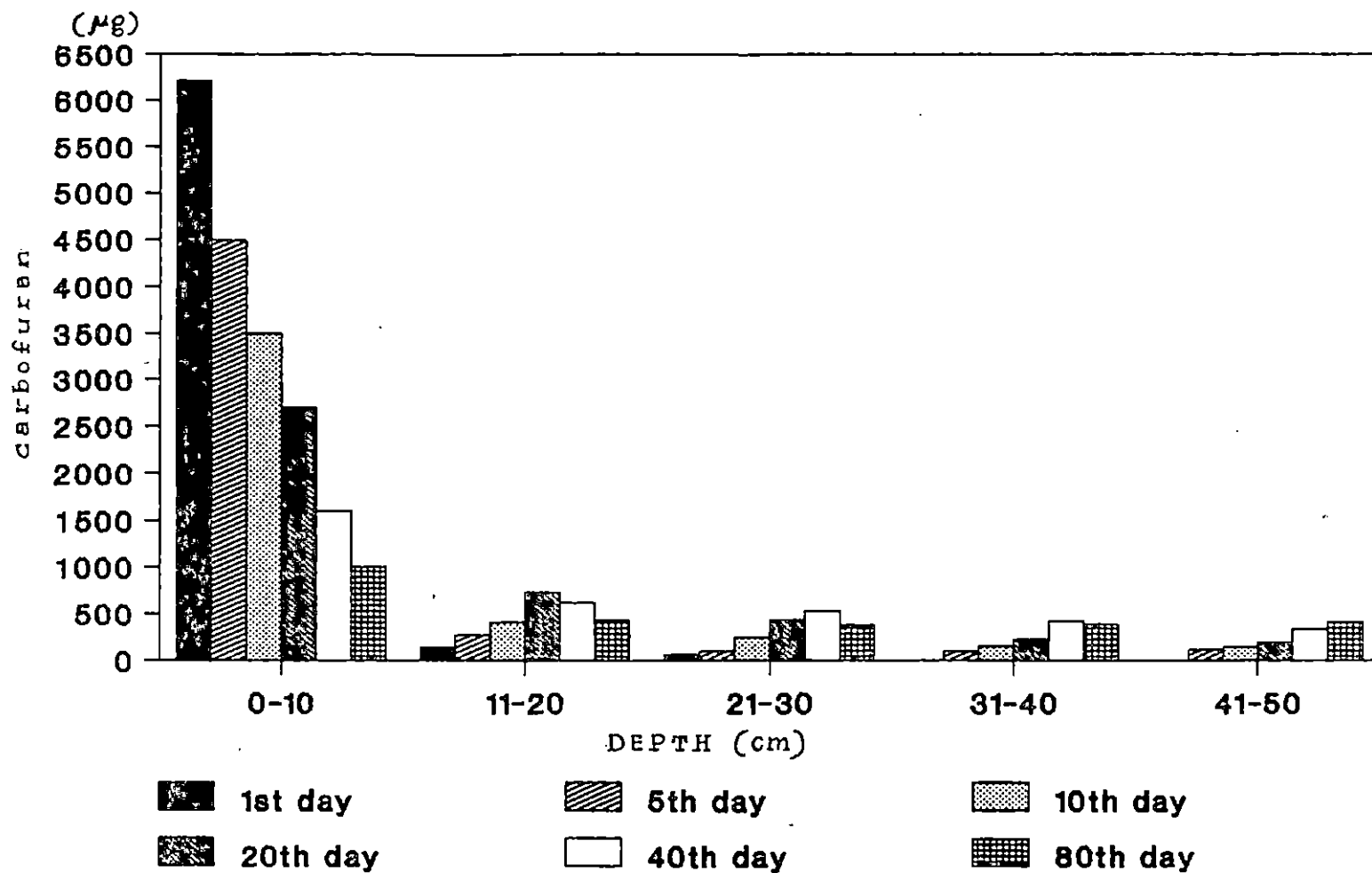


Fig. 11. Depth-wise distribution of carbofuran at definite time intervals - Ultisol of Malappuram

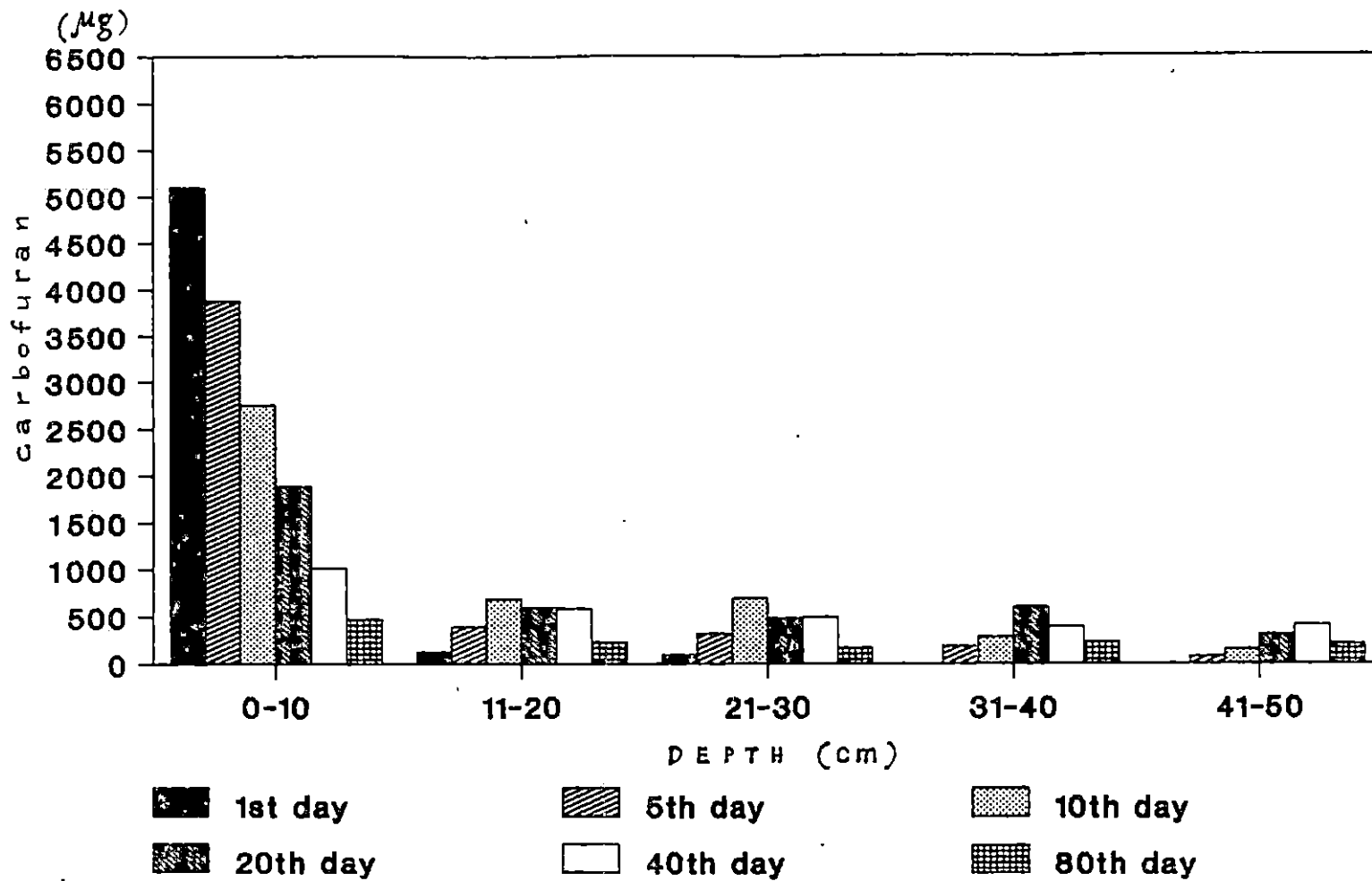


Fig. 12. Depth-wise distribution of carbofuran at definite time intervals - Insectisol of Chengannur

observation followed by $332.5 \mu\text{g } 25 \text{ g}^{-1}$ soil for the 5th, $190 \mu\text{g } 25 \text{ g}^{-1}$ soil for the 4th, $140 \mu\text{g } 25 \text{ g}^{-1}$ soil for the 3rd and $110 \mu\text{g } 25 \text{ g}^{-1}$ soil for the 2nd observations. In all the depths, as time advanced concentration of the chemical was found to be increasing (Fig. 11). It is clear from the table - 7 that a substantial amount of the chemical has been lost through leaching and degradation, with advancement in time interval between application and sampling.

In the case of the inceptisol of Chengannur (Fig. 12), decrease in concentration in the surface layer in all the 6 observations was more when compared to the ultisol. The concentration of the chemical in other lower layers was also found to be higher. The final concentration in the last observation for all the depth were much lower for this soil compared to corresponding values in the ultisol.

More or less the same trend was observed for the Entisol of Kayamkulam which showed a greater distribution of the chemical downwards right from the 1st observation onwards (Fig. 13). This is further substantiated by the high concentration of the chemical in the leachate collected in all the observations.

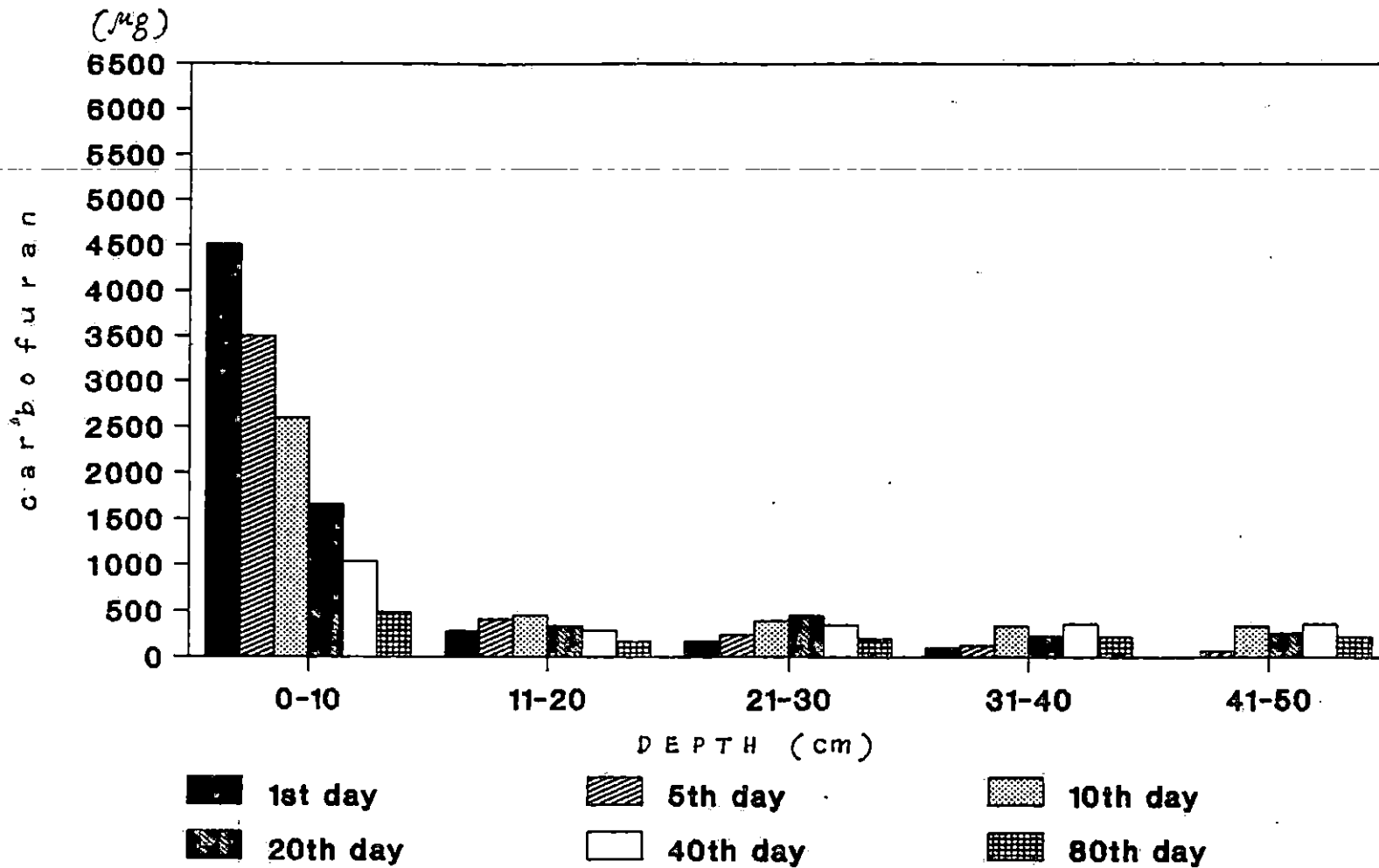


Fig. 13. Depth-wise distribution of carbofuran at definite time intervals - Entisol of Kayamkulam

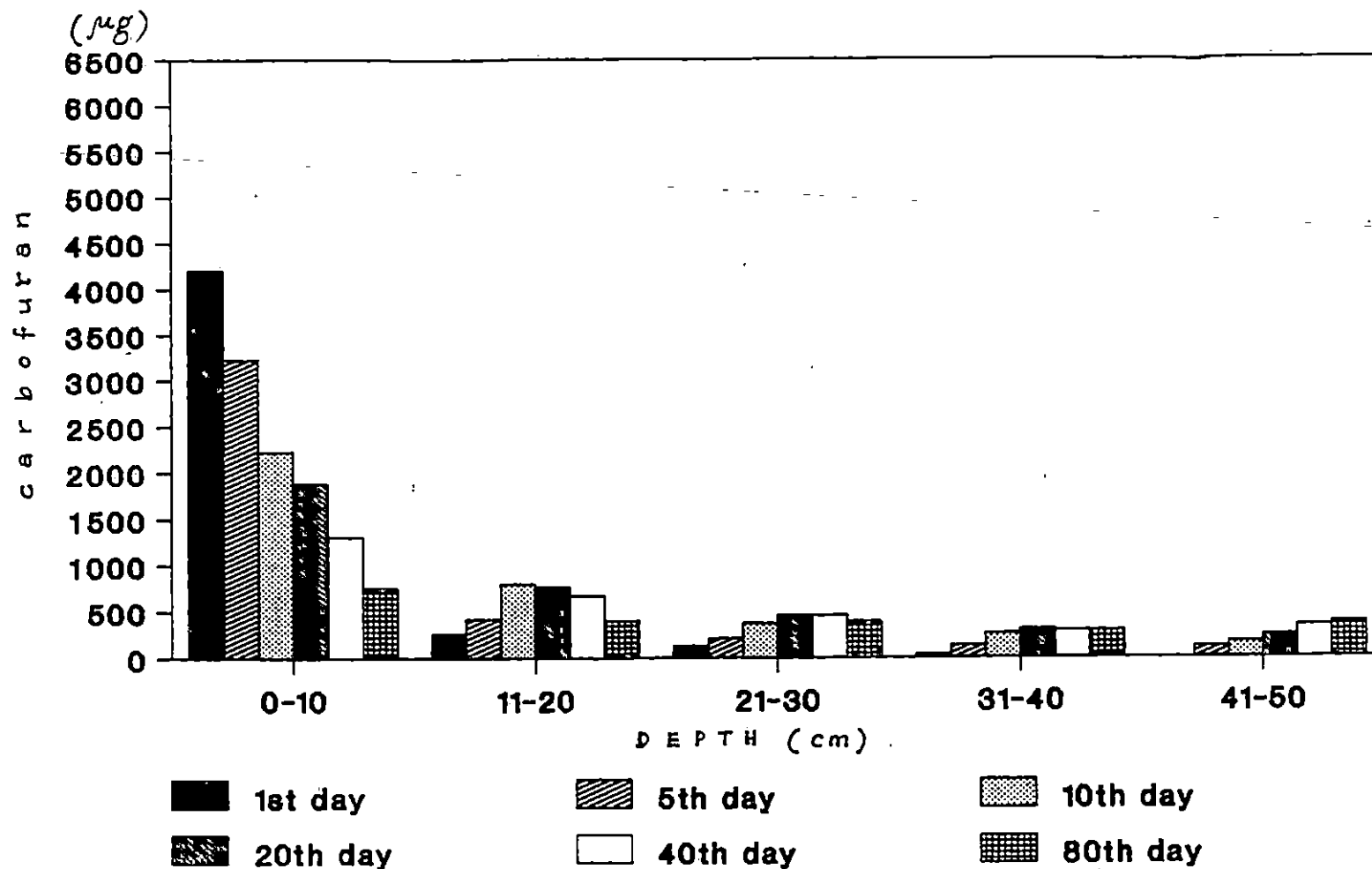


Fig. 14. Depth-wise distribution of carbofuran at definite time intervals - Mollisol of Nedumangad

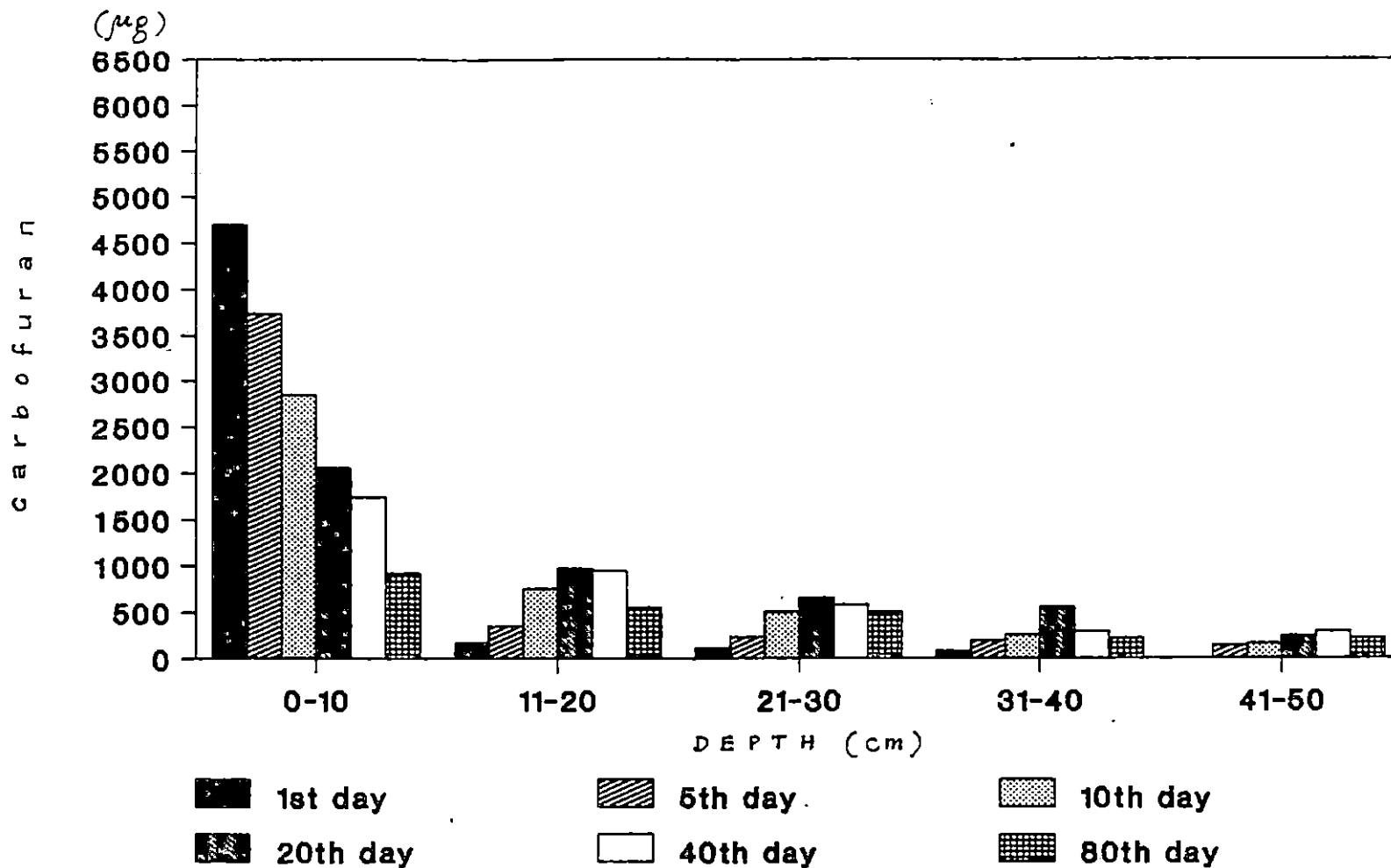


Fig. 15. Depth-wise distribution of carbofuran at definite time intervals - Entisol of Kuttanad

The Mollisol of Nedumangad (Fig. 14) has given comparatively higher concentration of the chemical even after the 6th observation in all the layers, next only to the Ultisol of Malappuram and Entisol of Kuttanad.

A critical evaluation of the data for the Entisol of Kuttanad reveals that the concentration of the chemical distributed in the lower layers are more when compared to the Entisol of Kayamkulam, Inceptisol of Chengannur and Mollisol of Nedumangad (Fig. 15). However the distribution was found to be uniform in the lower layers when compared to the Ultisol of Malappuram.

Analysis of variance (Appendix I) revealed significant difference in the distribution of the chemical in all the soils during the 1st observation corresponding to 24 hours after the application (Fig. 16). Significant difference was also observed in the distribution with depth as well as for interaction effects. However soil to soil variation gave significant difference only for the 1st layer. Concentration of the chemical at the surface layer in the 1st observation was 6200, 5100, 4500, 4200 and 4700 $\mu\text{g } 25 \text{ g}^{-1}$ for the Ultisol of Malappuram, Inceptisol of Chengannur, Entisol of

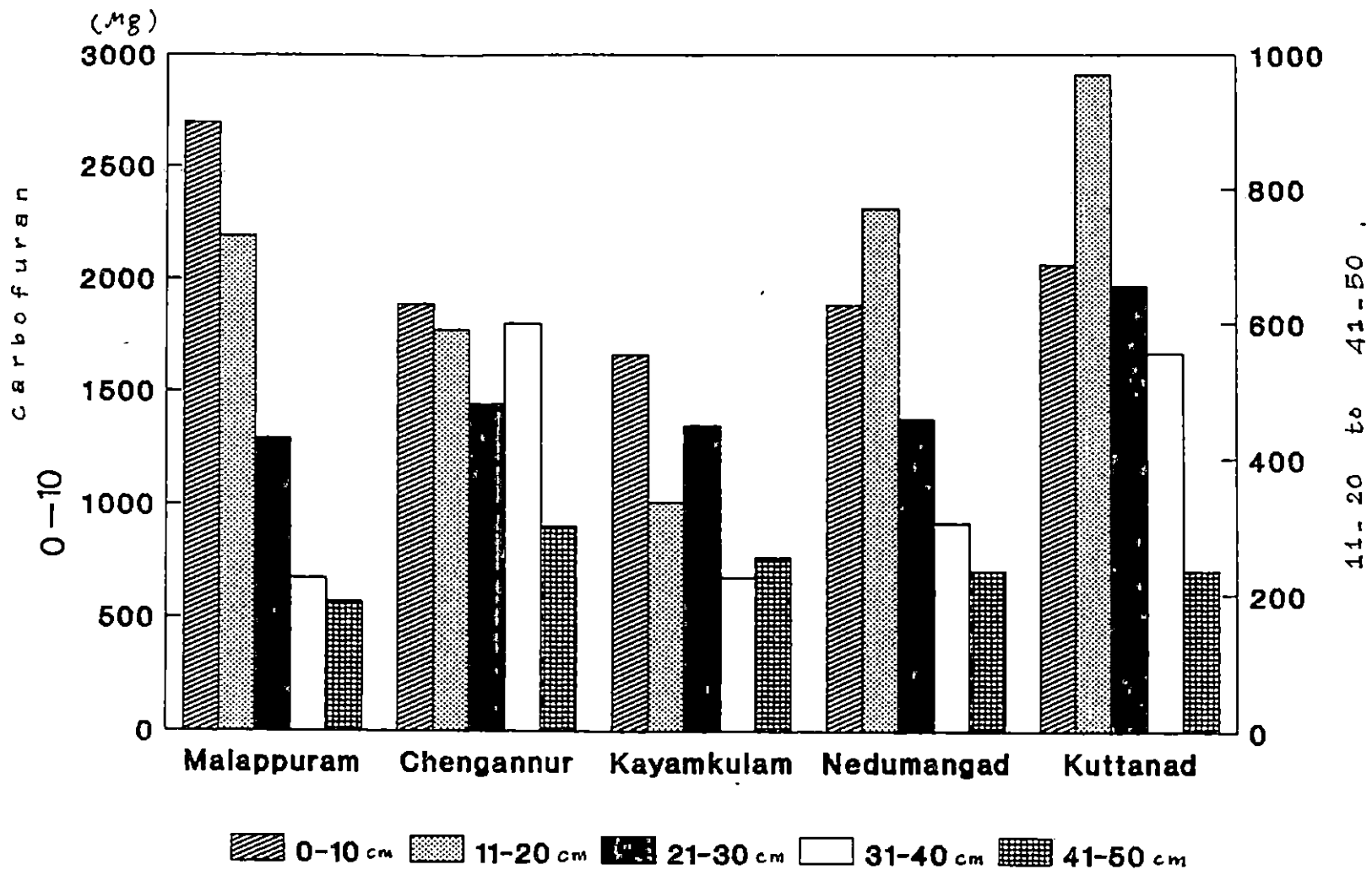


Fig. 19. Depth-wise distribution of carbofuran during the fourth observation

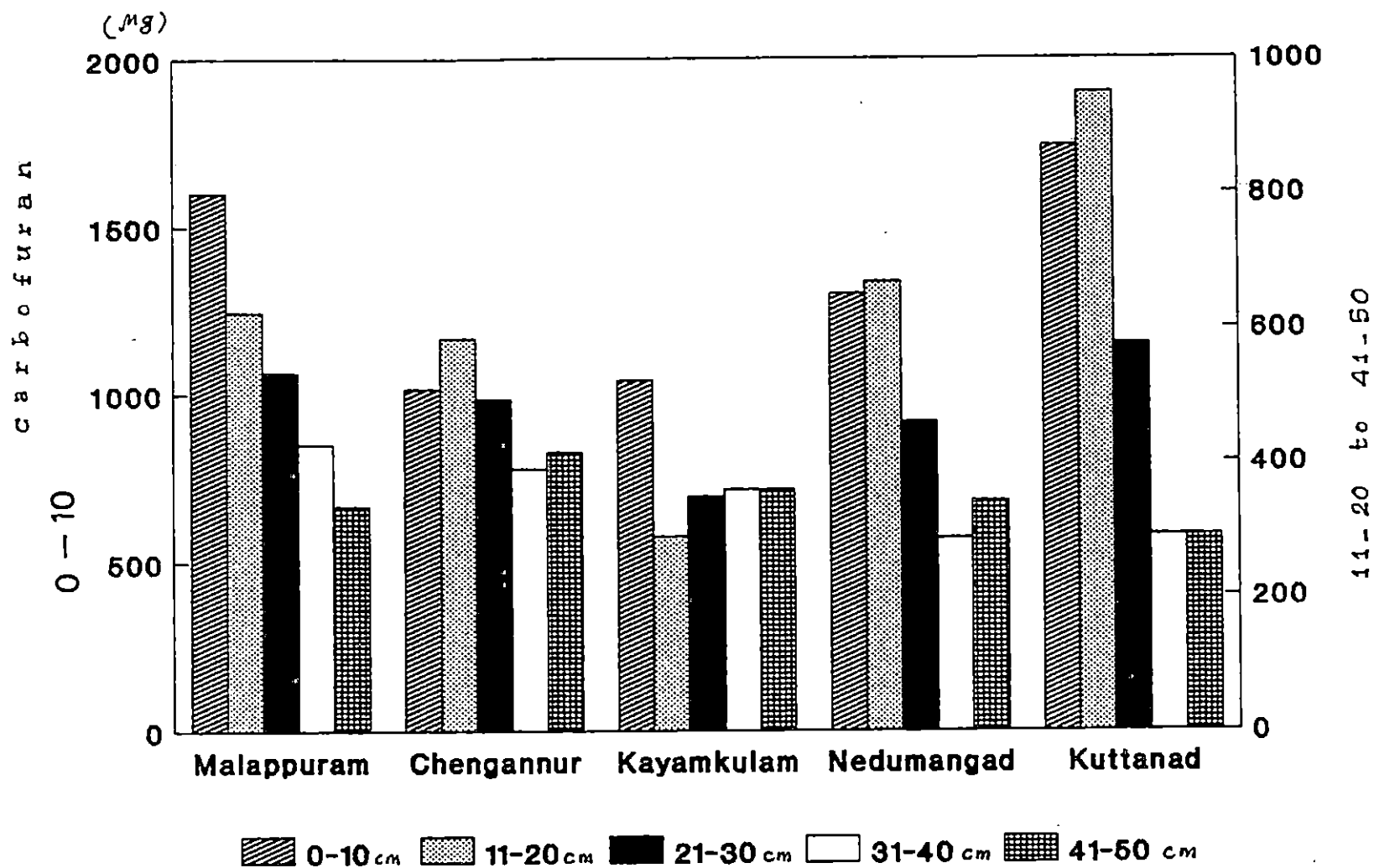


Fig. 20. Depth-wise distribution of carbofuran during the fifth observation

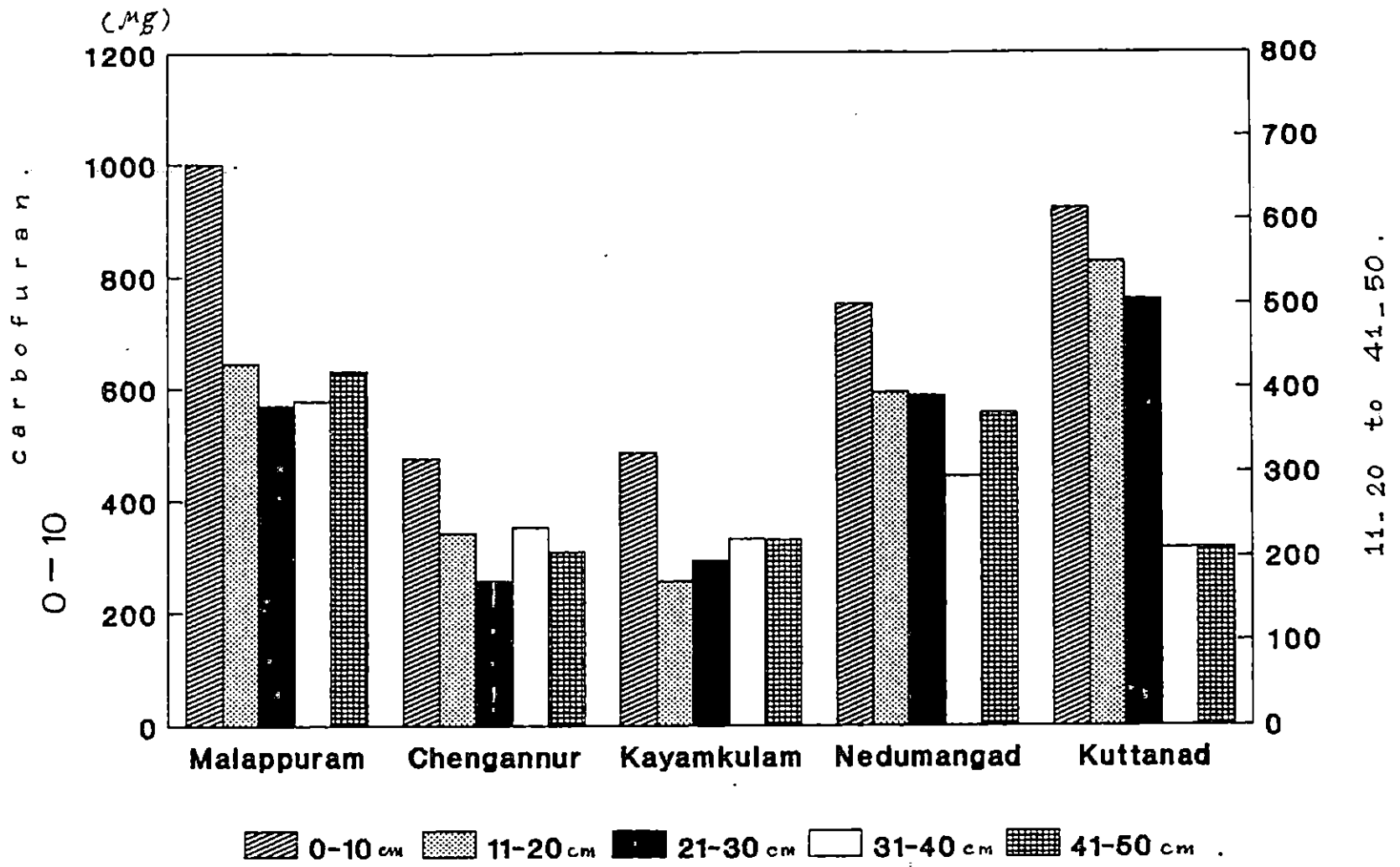


Fig. 21. Depth-wise distribution of carbofuran during the sixth observation

Kayamkulam, Mollisol of Nedumangad and the Entisol of Kuttanad respectively. During the 1st observation, the chemical was not moved into the last two depths in the Ultisol of Malappuram and the inceptisol of Chengannur whereas in the case of the Entisol of Kayamkulam, the mollisol of Nedumangadu and the Entisol of Kuttanad only the last depth was free of carbofuran.

During the 2nd, 3rd and 4th observations no significant variation in the distribution of the chemical was observed for the soil types studied (Fig. 17, 18 and 19). However depth wise distribution and interaction effects were found to be highly significant.

During the last two observations corresponding to 40th and 80th day of application of the chemical (Fig. 20 and 21) significant difference in the distribution of carbofuran was found between soils, between depths within a soil and also for interaction effects.

3. Movement and distribution of carbofuran in horizontal columns

Table 8 summerises data on concentration of carbofuran at different distances in horizontal columns at

Table 8. Mean values of carbofuran in horizontal soil columns
($\mu\text{g} / 25 \text{ g soil}$)

Distance(cm)	2nd day	5th day	10th day	15th day	20th day
Utisol (Malappuram)					
0	25300	24100	22600	18600	13750
3	0	100	230	280	320
5	0	0	60	100	100
10	0	0	0	0	0
Inceptisol (Chengannur)					
0	26000	23000	18000	14600	11025
3	0	40	100	120	160
5	0	0	0	20	40
10	0	0	0	0	0
(Entisol) (Kayamkulam)					
0	25000	22600	20500	15200	12750
3	0	0	80	100	120
5	0	0	0	20	20
10	0	0	0	0	0
(Mollisol) (Nedumangad)					
0	24200	21800	19600	16225	14500
3	0	60	140	180	210
5	0	0	40	60	60
10	0	0	0	0	0
Entisol (Kuttanad)					
0	27000	24800	23100	17300	12325
3	0	60	240	325	425
5	0	0	30	100	100
10	0	0	0	0	0

different time intervals. It is clear from the data that the horizontal movement is very poor when compared to vertical movement. Though all the three horizontal distances had given no values for carbofuran content during the 1st observation, as time advanced the chemical was distributed horizontally also in the soil giving values for 2nd and 3rd horizontal distances. It is pertinent to note that the maximum radial distance for horizontal movement of carbofuran was 5 cm. Concentration in the 2nd and 3rd distances in all the soils during all the intervals were negligible when compared to the site of application. It is also clear from the data that the concentration decreased drastically at the point of application with progress in time. The decrease was from 25300 μg to 13750 μg 25 g^{-1} of soil in the case of the Ultisol of Malappuram, 26000 to 11025 μg 25 g^{-1} in Inceptisol of Chengannur, 25000 to 12750 μg 25 g^{-1} in the Entisol of Kayamkulam, 24200 to 14500 μg 25 g^{-1} in Mollisol of Nedumangad and 27000 to 12325 μg 25 g^{-1} soil for the Entisol of Kuttanad. With progress in time after application, 2nd and 3rd horizontal distances had shown increasing values

for the chemical. Thus last observations had invariably given the highest values for 2nd and 3rd horizontal distances.

4. Influence of soil properties on carbofuran concentration in soil columns

In order to study the influence of soil properties on carbofuran concentration, multiple regression analysis of the various physico-chemical properties of the soils on carbofuran concentration at 6 time intervals were carried out. The data on the regression coefficients are presented in table - 9.

Out of the 10 soil properties compared, only organic matter and clay content were found to have significant regression coefficients. The regression coefficient of organic matter had a range of values from 1954.74 during the first observation to 270.99 towards the 6th observation, while clay content had a range between -82.2 for first observation to -10.15 for the last.

Path coefficient analysis conducted to study the direct and indirect effects of soil properties on carbofuran

Table 9. Multiple regressions between soil properties and carbofuran content

Soil Parameters	Regression coefficient at different intervals					
	1 st day y=	5 th day y=	10 th day y=	20 th day y=	40 th day y=	80 th day y=
pH	707.36	417.00	326.70	226.70	13.54	4.36
OM	1954.74**	1392.40**	1005.10**	710.38**	415.05**	270.99**
CEC	439.12	338.99	321.70	189.59	114.67	26.15
Clay	-82.20*	-60.28*	-47.31**	-39.00**	-24.38**	-10.15**
BD	12652.30	8903.80	3822.80	1452.30	825.30	1322.33
PD	-5583.78	-4085.70	-2036.50	-884.90	-520.87	-481.51*
WHC	115.91	65.29	-7.00	-10.53	1.64	29.50
AEC	-483.34	-361.67	-323.40	-69.97	-49.29	-21.05
R ₂ O ₃	67.36	49.50	23.14	8.57	7.46	9.31
HC	2.05	0.91	0.35	-3.63	-2.29	-0.85
Constant unit	-12179.90	-7171.70	-1839.60	-260.10	-468.94	-1395.56
F 10, 39	3.58**	3.59**	4.57**	6.02**	7.83**	15.61**
R ²	0.478	0.479	0.539	0.607	0.667	0.800

* Significant at 5% level

** Significant at 1% level

Table 10. Direct and indirect effects of soil properties on carbofuran content (1st observation)

	pH	OM	CEC	Clay	BD	PD	WHC	AEC	R ₂ O ₃	HC	Y
pH	<u>0.128</u>	-0.261	0.04	0.034	-0.089	0.008	0.043	-0.016	0.075	0.010	-0.038
OM 6	-0.048	<u>0.697</u>	0.287	-0.318	-0.488	0.166	0.147	-0.117	0.092	0.011	0.408
CEC 6	0.001	0.384	<u>0.521</u>	-0.438	-0.778	0.138	0.279	-0.196	0.269	0.013	0.175
Clay3	-0.008	0.381	0.392	<u>-0.582</u>	-0.722	0.163	0.244	-0.162	0.209	0.014	-0.098
BD 8	-0.011	-0.343	0.409	-0.423	<u>-0.993</u>	-0.394	-0.285	0.166	-0.209	+0.009	-0.058
PD 3	+0.002	-0.193	-0.120	+0.157	0.649	<u>-0.602</u>	-0.098	0.048	-0.041	-0.005	-0.192
WHC 4	0.017	0.326	0.465	-0.453	-0.903	0.188	<u>0.313</u>	0.186	0.246	-0.01	0.005
AEC 7	0.010	0.385	0.485	-0.448	-0.781	0.138	0.276	<u>-0.211</u>	+0.263	-0.011	0.104
R ₂ O ₃ 8	0.033	0.219	0.478	-0.416	-0.707	0.084	0.264	-0.19	<u>0.293</u>	-0.001	0.046
HC 1	0.054	-0.322	-0.298	0.361	0.408	-0.122	-0.136	0.116	-0.141	<u>0.023</u>	-0.058

Residue = 0.7221

Table 11. Direct and indirect effects of soil properties on carbofuran content (2nd observation)

	pH	OM	CEC	Clay	BD	PD	WHC	AEC	R ₂ O ₃	HC	Y
pH	<u>0.103</u>	-0.253	0.043	0.036	-0.085	-0.001	0.033	-0.017	0.077	0.006	-0.059
OM	0.038	<u>0.678</u>	0.303	-0.318	-0.468	0.166	0.112	-0.119	0.093	0.006	0.401
CEC	0.008	0.373	<u>0.549</u>	-0.438	-0.746	0.137	0.213	-0.201	0.272	0.008	0.160
Clay	-0.006	0.369	0.413	<u>-0.583</u>	-0.691	0.162	0.186	-0.166	0.212	0.008	-0.110
BD	-0.009	-0.330	0.430	-0.423	<u>-0.951</u>	-0.392	-0.217	0.170	-0.211	0.005	-0.044
PD	0.001	-0.187	-0.126	0.157	0.622	<u>-0.600</u>	-0.075	0.049	-0.041	0.003	-0.197
WHC	0.014	0.317	0.490	-0.453	-0.864	0.187	<u>0.239</u>	-0.1907	0.250	-0.006	0.016
AEC	0.007	0.374	0.511	-0.448	-0.748	0.138	0.210	<u>-0.216</u>	0.267	-0.007	0.088
R ₂ O ₃	0.026	0.213	0.504	-0.416	-0.677	0.083	0.201	-0.195	<u>0.297</u>	-0.006	0.030
HC	0.043	-0.313	-0.314	0.361	0.391	-0.1219	-0.103	0.118	-0.143	<u>0.013</u>	-0.068

Residue = 0.721

Table 12 Direct and indirect effects of soil properties on carbofuran content (3rd observation)

	pH	OM	CEC	Clay	BD	PD	WHC	AEC	R ₂ O ₃	HC	Y
pH	<u>0.115</u>	-0.261	0.057	0.040	-0.052	-0.006	-0.005	-0.021	0.050	0.003	-0.073
OM	-0.043	<u>0.698</u>	0.411	-0.356	-0.286	0.118	-0.019	-0.153	0.061	-0.003	0.428
CEC	0.009	0.348	<u>0.746</u>	-0.492	-0.456	0.097	-0.036	-0.257	0.179	-0.004	0.172
Clay	-0.007	0.381	0.562	<u>-0.653</u>	-0.422	0.115	-0.031	-0.213	0.140	-0.005	-0.133
BD	-0.010	-0.343	-0.583	0.475	<u>0.581</u>	-0.279	0.036	0.218	-0.139	0.003	-0.043
PD	0.001	-0.193	-0.170	0.176	0.380	<u>-0.427</u>	0.012	0.063	-0.027	0.002	-0.182
WHC	0.016	0.327	0.666	-0.509	-0.528	0.133	<u>-0.040</u>	-0.243	0.164	-0.003	-0.018
AEC	0.008	0.385	0.693	-0.502	-0.457	0.098	-0.035	<u>-0.276</u>	0.176	-0.004	-0.086
R ₂ O ₃	0.029	0.219	0.684	-0.467	-0.414	0.059	-0.034	-0.250	<u>0.196</u>	-0.003	0.021
HC	0.049	-0.323	-0.426	0.404	0.238	-0.087	0.017	0.151	0.942	<u>-0.007</u>	-0.061

Residue = 0.678

Table 13 Direct and indirect effects of soil properties on carbofuran content (4th observation)

	pH	OM	CEC	Clay	BD	PD	WHC	AEC	R ₂ O ₃	HC	Y
pH	<u>0.117</u>	-0.272	0.050	0.048	-0.029	-0.004	-0.011	-0.006	0.027	-0.048	-0.124
OM	-0.043	<u>0.727</u>	0.356	-0.433	-0.160	0.075	-0.039	-0.049	0.034	0.053	0.521
CEC	0.009	0.400	<u>0.647</u>	-0.596	-0.255	0.062	-0.074	-0.082	0.098	0.065	0.274
Clay	-0.007	0.397	0.487	<u>-0.793</u>	-0.236	0.074	-0.065	-0.068	0.077	0.071	-0.064
BD	-0.010	-0.357	-0.507	0.576	<u>0.325</u>	-0.178	0.076	0.069	-0.076	-0.047	-0.130
PD	0.0002	-0.201	-0.148	0.214	0.213	<u>-0.273</u>	0.026	0.020	-0.015	-0.023	-0.186
WHC	0.016	0.340	0.577	-0.617	-0.296	0.085	<u>-0.084</u>	-0.078	0.090	0.049	0.084
AEC	0.009	0.401	0.601	-0.609	-0.256	0.063	-0.074	<u>-0.088</u>	0.096	0.063	0.206
R ₂ O ₃	0.030	0.228	0.293	-0.567	-0.232	0.038	-0.070	-0.079	<u>0.107</u>	0.055	0.104
HC	0.049 _a	-0.336	-0.369	0.469	0.133	-0.055	0.036	0.048	-0.051	<u>-0.115</u>	-0.168

Residue = 0.626

Table 14 Direct and indirect effects of soil properties on carbofuran content (5th observation)

	pH	OM	CEC	Clay	BD	PD	WHC	AEC	B ₂ O ₃	HC	O
pH	<u>0.012</u>	-0.265	0.051	0.051	-0.027	-0.003	0.002	-0.008	0.040	-0.051	-0.196
OM	-0.004	<u>0.709</u>	0.360	-0.451	-0.150	0.073	0.008	-0.057	0.049	0.056	0.592
CEC	0.001	0.390	<u>0.654</u>	-0.623	-0.239	0.061	-0.015	-0.096	0.142	0.069	0.375
Clay	-0.001	0.387	0.492	<u>-0.827</u>	-0.221	0.072	-0.014	-0.079	0.111	0.075	0.021
BD	-0.010	-0.348	-0.512	0.601	<u>0.305</u>	-0.175	-0.016	0.081	-0.110	-0.049	-0.225
PD	0.000	-0.195	-0.149	0.223	0.199	<u>-0.267</u>	-0.005	0.023	-0.021	-0.024	-0.217
WHC	0.002	0.332	0.583	-0.644	-0.277	0.083	<u>0.017</u>	-0.091	0.131	0.052	0.188
AEC	0.001	0.391	0.607	-0.636	-0.240	0.061	-0.016	<u>-0.103</u>	0.139	0.006	0.306
B ₂ O ₃	0.003	0.223	0.599	-0.591	-0.217	0.037	-0.015	-0.093	<u>0.155</u>	0.058	0.189
HC	0.005	-0.327	-0.373	0.512	0.125	-0.054	-0.007	0.056	-0.075	<u>-0.121</u>	-0.259

Residue = 0.5764

Table 15 Direct and indirect effects of soil properties on carbofuran content (6th observation)

	pH	OM	CEC	Clay	BD	PD	WHC	AEC	R ₂ O ₃	HC	Y
pH	<u>0.0072</u>	-0.3201	0.0214	0.0392	-0.0823	-0.006	0.0964	-0.0062	0.0925	-0.035	-0.7876
OM	-0.0027	<u>0.8564</u>	0.152	-0.3477	-0.4513	0.1269	0.3304	-0.0449	0.1130	0.0381	0.7704
CEC	0.0006	0.4716	<u>0.2764</u>	-0.4742	-0.7195	0.1050	0.6292	-0.0756	0.3294	0.0471	0.5850
Clay	-0.0004	0.4676	0.2080	<u>-0.6368</u>	-0.6690	0.1242	0.5494	-0.0625	0.2569	0.0510	0.2905
BD	-0.0006	-0.4210	-0.2166	0.4625	<u>0.9180</u>	-0.3005	-0.6412	0.0640	-0.2559	-0.0339	-0.4250
PD	0.000	-0.2365	-0.0632	0.1721	0.6004	<u>-0.4591</u>	-0.2201	0.0187	-0.0500	-0.0167	-0.2548
WHC	0.001	0.4011	0.2465	-0.4959	-0.8343	0.1483	<u>0.7055</u>	-0.0716	0.3023	0.0356	0.4335
AEC	0.0005	0.4729	0.2568	-0.4895	0.7221	0.1054	0.6210	<u>-0.0814</u>	0.3232	0.0451	0.5320
R ₂ O ₃	0.0018	0.2693	0.2533	-0.4551	-0.6536	0.0640	-0.5935	-0.0732	<u>0.3594</u>	0.0396	0.3990
HC	0.0030	-0.3958	-0.1579	0.3944	0.3769	-0.0933	-0.3049	0.0445	-0.1727	<u>-0.0824</u>	-0.3882

Residue = 0.4472

concentration at 6 time intervals are given in table Nos. 10 to 15.

Among the 10 soil properties subjected to path coefficient analysis, pH, Bulk density, particle density and hydraulic conductivity had negative influences on carbofuran content at all the 6 intervals. Clay content influenced the carbofuran concentration negatively in the 1st, 2nd, 3rd and 4th observations and towards the 5th and 6th observation clay showed a positive effect. Similarly WHC showed positive influence at the 1st, 4th, 5th and 6th observations on carbofuran content while at the 2nd and 3rd observations it negatively influenced the concentration. Organic matter, cation exchange capacity, anion exchange capacity and sesquioxides are seen to exert positive influence in all the observations. Out of the 10 soil properties studied only organic matter and clay content showed significant influence on carbofuran concentration in the soils at all the intervals. Organic matter had a direct effect of 0.697 at 1st observation to 0.856 at the 6th observation and the total effect for the same was 0.408 and 0.770 respectively. Direct effect of clay content was -0.582 at the 1st observation and -0.636 at the 6th observation. The total effect of clay for the above observations were -0.0983 and 0.290 respectively.

5. Concentration of carbofuran in the leachate

Data on the concentration of carbofuran in the leachate collected at definite time intervals from the different soil types are presented in table 16. It is observed from the table that in all the soils carbofuran content increased in the leachate gradually giving maximum values and then showed a decline except for the Entisol of Kuttanad where the maximum concentration was obtained for the last observation (Fig. 22). Remaining 4 soils showed maximum concentration in the leachate towards the 7th (in Kayamkulam soil), 8th (in Chengannur and Nedumangadu soil) and 9th (in Ultisol of Malappuram) observation.

It is very clear from the data that the Entisol of Kayamkulam (33260 μg) and Inceptisol of Chengannur (31240 μg) gave maximum concentration of carbofuran in the leachate. The lowest value observed was in the case of the Ultisol of Malappuram (26880 μg).

Statistical treatment of the data (Appendix 2) showed highly significant effect due to soil variation and variation in the time interval.

Table 16. Mean values of carbofuran content in leachate (μg)

Intervals (days)	Soil type				
	Malappuram	Kayamkulam	Chengannur	Kuttanad	Nedumangad
5	1100	1720	1530	1205	1415
10	1250	1960	1730	1355	1680
15	1520	2235	2040	1625	1810
20	1600	2775	2250	1850	1965
30	2315	3835	3330	2650	2715
40	2600	4230	4050	2915	3205
50	3260	5010	4190	3495	4100
60	4300	4725	4755	4055	4695
70	4550	3510	3970	4330	4385
80	4385	3260	3395	4485	4060

CD

Soil	96.77
Intervals	55.75
Interaction	124.60

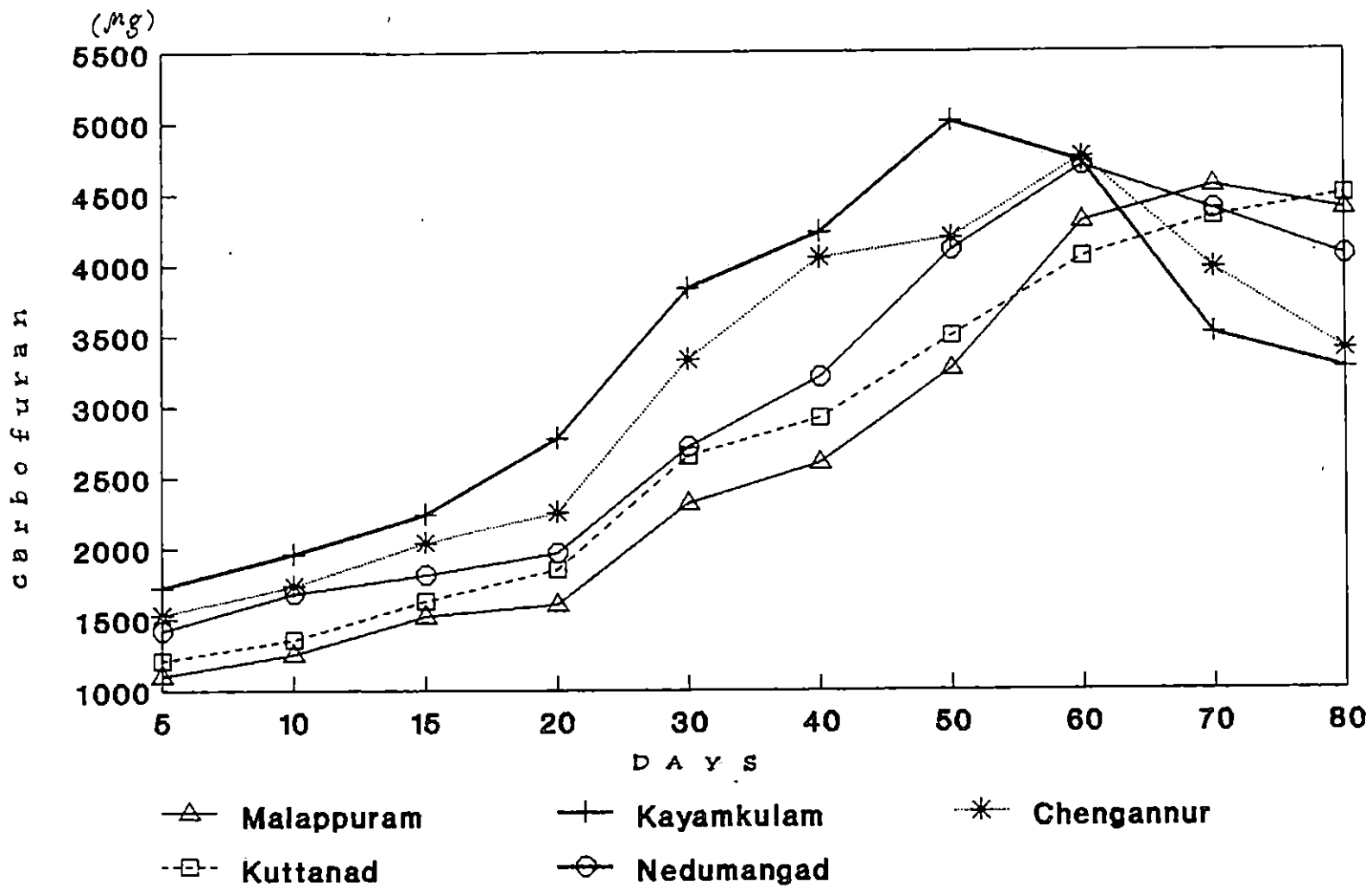


Fig. 22. Leachate concentration of carbofuran at different time intervals

6. Degradation and persistence

Data on the concentration of carbofuran in soils at different days after application (Table 7) showed that carbofuran persisted in soil even after 80 days and the maximum value (mean) observed was in the Entisol of Kuttanad 490 (48.4%) followed by Mollisol of Nedumangad 440 ug (47.7%) and the Ultisol of Malappuram 523 ug (40.8%). But the Entisol of Kayamkulam and Inceptisol of Chengannur showed the minimum persistence of 242 (23.6%) and 262 (24.6%) respectively. Hence it is clear that an average of 48% of the initial quantity of carbofuran persisted in the soil matrix up to a depth of 50 cm in Nedumangad and Kuttanad soils under the experimental condition.

Absolute quantities of carbofuran in soil matrix at the 1st observation, last observation and in leachate (Table 17) clearly indicated that maximum persistence of carbofuran was in the Entisol of Kuttanad and Mollisol of Nedumangad (49%) followed by the Ultisol of Malappuram (43%), Inceptisol of Chengannur (24%) and the Entisol of Kayamkulam (24%).

Table 17. Persistence and loss of carbofuran in soil

Soil type	Soil matrix		Quantity in the leachate (μg)	% loss
	Initial quantity (μg)	Final quantity (μg)		
Malappuram	158845	69381 (43%)	26880 (17%)	40
Chengannur	158144	38027 (24%)	31240 (19%)	57
Kayamkulam	153000	36824 (24%)	33260 (22%)	54
Kuttanad	139218	68220 (49%)	27960 (20%)	31
Nedumangad	120582	59774 (49%)	30030 (24%)	27

In order to identify the degradation products and metabolites, the extracts from top layers of each soil at all the intervals were subjected to gas chromatographic analysis. The results showed that in the Entisol of Kuttanad, Inseptisol of Chengannur and the Entisol of Kayamkulam, carbofuran was present even after 80 days while in the Ultisol of Malappuram and Mollisol of Nedumangadu, 3 Keto carbofuran was also detected in addition. No metabolite was found in any of the soil type upto 40 days.

DISCUSSION

DISCUSSION

There has been considerable interest in the study of carbofuran as a broad spectrum systemic insecticide in pest control and its related effects in residual toxicity and biodegradability in the plant and animal systems. However, the use of this chemical in the soil has posed serious problems of soil pollution consequent to residual accumulation. A detailed investigation of the movement of this chemical in the soil, interaction with soil components, persistence, degradation and various losses in relation to the physico-chemical properties of the soil has not been systematically attempted so far. The above aspects were not given much attention, rather was ignored till recently. Recent reports highlighting the insecticidal efficiency and its dependence on soil properties (Getzin 1973, Rao and Davidson 1980, Rajukkannu and Sree Ramulu 1982, Radder et al., 1989, Somasundaram et al. 1991, Kumari and Singh 1992) have further necessitated investigations on these aspects. It is now realised that a better understanding of the processes which operate in soil and the variation from soil to soil which contributed to the retention of this chemical is needed, to institute better management procedures, and

time and method of application which will allow maximum efficiency of the applied chemical in these soils with minimum environmental hazard. In order to have a deeper insight into the above aspects, studies in undisturbed soil columns have been conducted in the laboratory. Simultaneously determination of the important physico-chemical and electrochemical parameters of these soils also have been undertaken.

Salient features of the result thus obtained are discussed hereunder.

1. Laboratory analyses of soils (Table 1)

Laboratory investigation of the 5 soil types collected from the most important Banana growing tracts of the state revealed a clear increase in clay content with depth in all the soils, except the forest soils of Nedumangadu, in the 1st 3 layers (Fig. 1). In the case of the Ultisol of Malappuram a steady increase in clay content was noticed towards the last depth of sampling which is obviously due to uniform clay migration to lower levels consequent to high rainfall. The soil is less influenced by

lateral movement or alluviation from the nearby areas and hence a well developed soil profile is believed to have formed. Sandy tracts of the Kayamkulam region showed very low clay content with a maximum value of 13.73%. This soil is inherently poor in clay and hence subjected to severe leaching of the fine particles. Forest soil of Nedumangad (Mollisol) and the Entisol of Kuttanad showed moderate values for clay which decreased with depth. This might be due to variation in the hydrological situation leading to deposition of soil materials from the adjoining areas by horizontal movement through definite cycles of rainfall. Thus the transported finer materials tends to accumulate at the surface layer leading to a decrease in clay content downwards. The drastic variation observed between soils with respect to clay content (Fig. 1) has been explained through the data obtained from statistical analysis. There was significant difference in clay content among soils, between depth within a soil and interaction effects of soil with depth. Thus based on the percentage of textural separates these soils could be grouped under clayey, sandy clay loam, loamy sand, sandy clay and sandy clay loam for the Ultisol of Malappuram, Inceptisol of Chengannur, Entisol of Kayamkulam, Mollisol of Nedumangad and Entisol of Kuttanad respectively.

All the above soils studied were moderately acidic in reaction, more or less depleted of bases and rich in Fe and Al oxides and hydroxides. Entisol of Kayamkulam with the lowest clay, organic matter and sesquioxide contents had given the highest observed pH of 5.38 (mean) (Fig. 2). Moderately high clay content and highest mean organic matter content have contributed to the lowest mean pH value (4.73) of the forest soil (Mollisol) of Nedumangad. Further the distribution of organic matter also was more or less uniform through out the profile when compared to other soils (Fig. 4). Thus the role of organic matter in converting the potential acidity to active acidity during the estimation of pH is clearly brought out here. The influence was amply substantiated with the statistical analysis too, which revealed significant differences among soil types with respect to pH.

As all the soils were more or less depleted of bases, EC values recorded were very low below the readable range of the instrument used. The Entisol of Kuttanad and the Inceptisol of Chengannur which had been subjected to alluviation for years also have given the same trend. This is

obviously due to the removal of bases from the alluviated material through leaching and run off.

Single value constants like bulk density, particle density and water holding capacity are generally influenced by the organic matter content and the differences in the clay/sand ratio. Soils with high organic matter and clay content had shown low values for the bulk density, while high sand content with low organic matter increased the particle density. Thus the Ultisol of Malappuram and the Mollisol of Nedumangad had shown the minimum values for bulk density (1.29 and 1.49 g cm^{-3} respectively) and the Entisol of Kayamkulam and Kuttanad had given the highest values for particle density (2.63 and 2.51 cm^{-3} respectively). Water holding capacity of the soil followed the absolute content of clay and organic matter (Fig. 3).

Data on the organic matter and CEC of the soils studied indicated a depth wise decrease in two major soils namely the Ultisol of Malappuram and the Mollisol of Nedumangad. The values for these two parameters further indicated that these soils are low in CEC and poor in organic matter. This is particularly true for subsurface layers which

had given much lower values in many cases. The range of values for CEC varied from 7.9 to 9.75 cmol (p⁺) kg⁻¹ in the Ultisol and 3.02 to 4.97 cmol (p⁺) kg⁻¹ in the Mollisol. Corresponding values for organic matter is 0.83 to 2.5% in the Ultisol and 1.21 to 2.35% in the Mollisol. In these two soils clay and organic matter content was found to influence the CEC significantly. In the case of the Inceptisol of Chengannur, increase in clay content with depth was much more important in controlling the CEC than the marginal increase in organic matter content. In all the other soils a general decrease in organic matter and CEC was observed with depth. Thus the role of organic matter and clay content in deciding the charge behaviour of the soil is clearly brought out (Fig. 4).

Anion exchange capacity and sesquioxide content of the soils studied are found to have a direct relationship as the former increased with an increase in the latter (Fig. 5). A generalisation in the depth wise distribution of sesquioxides could not be made in any of the soils studied and hence variation in AEC values followed the same trend with depth. In general, clay distribution in the profile had influenced the sesquioxide content to the maximum. This

is mainly due to the distribution of the major sesquioxides like Fe and Al oxides in the clay fractions. However the influence of organic matter in reducing the sesquioxide content in the case of the Mollisol of Nedumangad is an exception for the above general statement. This is further evidenced from the X-ray diffractograms (Fig. 7) obtained with well defined Fe and Al oxide peaks along with kaolinite peaks in the case of the Ultisol and well ordered Kaolinite peaks alone for the Mollisol of Nedumangad. Statistical analysis also showed significant variation in both AEC and sesquioxide content between soils.

Data on hydraulic conductivity showed the highest mean value (65.52 cm h^{-1}) for the Entisol of Kayamkulam followed by the Mollisol of Nedumangad (18.09 cm h^{-1}), the Inceptisol of Chengannur (14.33 cm h^{-1}), the Entisol of Kuttanad (13.96 cm h^{-1}) and the lowest for the Ultisol of Malappuram (12.12 cm h^{-1}). There was no significant difference in hydraulic conductivity among Mollisol of Nedumangad, Inceptisol of Chengannur, Entisol of Kuttanad and Ultisol of Malappuram (Fig. 5). This clearly indicate the importance of clay content in deciding the hydraulic conductivity. This is further explained by the highest bulk

density observed for the Entisol of Kayamkulam.

Details of the X-ray diffractograms obtained for the clay fractions of the various soils are presented in Fig. 6-10 and Tables 2-6. Major clay mineral present was Kaolinite as indicated by the peaks at 7.2 and 3.57 A° units. Sharpness of the peak suggest well formed crystals. Appreciable amounts of chlorite and vermiculite with traces of mica was also observed in many soils. Entisol of Kayamkulam showed appreciable amounts of quartz. The Ultisol of Malappuram had given very sharp goethite peaks even after the removal of Fe oxides during pretreatment of the samples. Trace quantities of feldspars, gibbsite and lepidocrosite were also observed. The result of the mineralogical analyses show that Kaolinite is the most dominant clay mineral with lesser amounts of smectite, quartz and gibbsite. This observation clearly suggests that all these soils have been developed from highly weathered parent materials.

Physico-chemical analyses of the soil revealed that the Ultisol of Malappuram is a clayey soil, acidic in reaction with high organic matter, CEC, WHC, AEC, sesquioxides and low in bulk density, particle density and

Hydraulic conductivity. Inceptisol of Chengannur is texturally sandy clay loam with acidic reaction having low organic matter, CEC, AEC, sesquioxide, hydraulic conductivity and high in bulk density and particle density. The Entisol of Kayamkulam is texturally loamy sand with acidic reaction, having the lowest organic matter, CEC, WHC, AEC, sesquioxides and highest bulk density, particle density and hydraulic conductivity. The Mollisol of Nedumangad is sandy clay, acidic in reaction with high organic matter and CEC, moderate in WHC, AEC, sesquioxides, hydraulic conductivity, and low with respect to bulk density and particle density. The Entisol of Kuttanad is sandy clay loam with acidic soil reaction, having, low organic matter, hydraulic conductivity, moderate in CEC, AEC, WHC, sesquioxides and high in bulk density and particle density. Kaolinite is the dominant clay mineral present in all the soils studied.

2. Movement and distribution of carbofuran in vertical soil columns

The result presented in Table 7 revealed that the movement of carbofuran was faster downwards as time advanced, in all the soil types studied. Higher quantities of

carbofuran was retained in the upper layer (0-10 cm) in all soils during the 1st observation. In all the observations same trend was followed in the 1st layer at various intervals. In the case of the Ultisol of Malappuram, in the second layer, maximum concentration was observed during the 4th observation while it is in the 5th observation for the 3rd layer, 5th for the 4th layer and in the 6th observation for the 5th layer (Fig. 11). A totally different distribution pattern was observed for the Inceptisol of Chengannur which showed the maximum accumulation of the chemical in the 3rd observation for 2nd and 3rd depths (10-20 and 20-30 cm), in the 4th and 5th observation for the 4th and 5th layer respectively (Fig. 12). This could be explained by the faster movement of the chemical in the Inceptisol when compared to the Ultisol of Malappuram. High clay and organic matter contents of the Ultisol when compared to the Inceptisol would have restricted the movement of the chemical in the former case. In the Entisol of Kayamkulam maximum concentrations in soil segments was reached in the 3rd, 4th, 3rd and 5th intervals for the 2nd, 3rd, 4th and 5th depths respectively (Fig.13). However the absolute values observed were very low when compared to other soils. The drastic decrease in the concentration of carbofuran retained may be due to intense

leaching of the chemical subjected to because of the very low clay and organic matter content. This observation is in conformity with the reports of Rajukkannu and Sree Ramulu (1982) and Radder et al. (1989). The main mechanism of retention here is mostly molecular adsorption. This is further evidenced from the comparatively higher values recorded for the other soils in the 1st observation. Thus the vertical movement of the chemical appears to be maximum in the case of the Entisol of Kayamkulam. This is obvious from the high concentration of carbofuran obtained in the leachate. The Mollisol of Nedumangad and Entisol of Kuttanad showed more or less the same pattern with respect to the distribution of carbofuran (Fig. 14 and 15) except for the 2nd and 5th layer. These two layers show maximum concentration of carbofuran in the 3rd and 6th interval for the 2nd and 5th depth respectively for the Mollisol and 4th and 5th intervals for the 2nd and 5th depth respectively for the Entisol. Distribution of the chemical within each segment for different intervals also appears to be more or less the same in these two soils. Leachate concentration of carbofuran (Table 16) is also giving a similar pattern in both cases.

A close scrutiny of the data given in table 7

reveals that during the 1st observation, humus poor non clayey soils like the Entisol of Kayamkulam and the Inceptisol of Chengannur could give higher values of carbofuran when compared to other soils rich in clay and organic matter (Fig. 16). For subsequent depths of sampling also the same trend was followed. However for subsequent observation after the 4th interval this trend was clearly reversed and clayey soils rich in organic matter had given the maximum concentration (Fig. 20 and 21). Hence during the last observation, the Ultisol of Malappuram retained the maximum concentration followed by the Entisol of Kuttanad, the Mollisol of Nedumangad, the Inceptisol of Chengannur and the Entisol of Kayamkulam for the surface samples. The Inceptisol of Chengannur and the Entisol of Kayamkulam had shown invariably lower values for all the depths (Fig. 21).

Thus during the initial stages of the vertical movement, mobility of the chemical was faster in the Entisol and Inceptisol and hence the deeper layers could reach higher concentrations much earlier than in the Ultisol and mollisol. As time advanced the chemical has moved down further without much adsorption and hence equal depths of Ultisol and Mollisol have shown higher values than the Entisol and

Inceptisol. This is due to the high retention capacity of the Ultisol and Mollisol having high CEC, organic matter and clay content.

Once the water has moved down the column, subsequent addition of water was responsible for the re-distribution of the chemical from the upper segments to lower segments and this re-distribution was dependent on the soil properties, chiefly clay content, organic matter content and CEC. Thus once the equilibrium is attained the accumulation of the chemical in different segments was decided by the above factors. Attainment of the equilibrium could be located from the leachate concentration of the chemical. In all the soils except the Entisol of Kuttanad equilibrium was attained before the last observation as evidenced by a decline in concentration at a particular stage (Table 16). Soils poor in clay and organic matter had shown the attainment of this equilibrium at an earlier date than the other soils. However the Entisol of Kuttanad continued to give an increase in concentration of the chemical in the leachate even at the last observation. (Fig. 22). This is probably due to a comparatively lower movement of the chemical consequent to

lesser adsorption. Total quantity of carbofuran lost by leaching during the entire period of observation in 5 soils studied, followed the order Entisol of Kayamkulam > Inceptisol of Chengannur > Mollisol of Nedumangad > Entisol of Kuttanad > Ultisol of Malappuram, the percentages retained being 43, 24, 24, 49 and 49 for the Ultisol, Inceptisol, Entisol of Kayamkulam, Mollisol and Entisol of Kuttanad respectively.

Analysis of variance revealed significant difference in the distribution of the chemical in all the soils during the 1st observation. During 2nd, 3rd and 4th observations no significant variation in the distribution of the chemical was observed. However the depth wise distribution and interaction effects were found to be highly significant. In the last two observations significant difference in carbofuran distribution was found between soils, between depths and for interaction effects.

The significant difference in the distribution of carbofuran during the 1st observation may be due to the variation in movement consequent to the differences in soil properties. During the 2nd, 3rd and 4th observations, the

quantity of carbofuran added was mainly restricted to the top layers and its movement and distribution to deeper layers had not been fully achieved and hence depthwise distribution could give significant difference. But during the 5th and 6th observation, sufficient time had elapsed for the vertical movement and distribution of the chemical and to stabilise according to variation in soil properties (between soils and within soils at different depths). Thus significant difference in the distribution of the chemical was observed between soils, between depths and also for the interaction.

3. Horizontal movement and distribution of carbofuran

The horizontal movement of the chemical in all the soils studied was restricted to 5 cm of radial distance from the point of application. Fourth radial distance of 10 cm from the point of application had given no values for carbofuran even after 20 days. The 2nd and 3rd distance had given very low values compared to the concentration at the point of application. There was considerable differences in the carbofuran content observed in the 2nd and 3rd distances among soils studied. Entisol of Kuttanad, Ultisol of Malappuram and Mollisol of Nedumangad with comparatively

higher organic matter content and CEC had given higher values for the 2nd and 3rd distances in all the intervals. This observation clearly indicate very low lateral movement of the chemical since the diffusion rate is very low. This observation is in accordance with the reports of Daniel et al. (1992). Further the enhanced vertical mobility of the chemical along with water under the influence of gravitational force might be another reason for the very low horizontal movement. However the effect of major soil parameters in influencing the retention and mobility of the chemical in soil has been reflected here also, though the gradation of values obtained is negligible.

4. Influence of soil properties on carbofuran concentration in soil columns

To investigate the contribution of the various soil factors studied to the adsorption and movement of carbofuran in 5 selected soils, multiple regression analysis has been made. The results indicating the regression equation of the soil factors on carbofuran content are presented in Table 9. Out of the 10 factors studied, the influence of organic matter and clay was found to be significant at all the

intervals as evidenced from the highly significant regression coefficient. However the effect of CEC on the content of carbofuran was not significant. This may be due to the highly significant negative effect of clay content. Significant positive effect of organic matter in influencing the CEC was made nonsignificant by the negative effect of clay. Combined effect of all the soil properties was significant with respect to all the observations. Almost 48% of the carbofuran content was attributed to the combined effect of these factors in the 1st and 2nd observation. In 3rd, 4th, 5th and 6th observations, nearly 54%, 61%, 67% and 80% respectively of the carbofuran content were explained by the soil factors studied, the percentage variability accounted in the increasing order from the first to the last observation. The lower percentage variability that is accounted for the 1st and 2nd observation might be due to the non uniform distribution of the chemical owing to the non expression of the full effect of all the soil parameters. As time advanced the carbofuran content and vertical distribution could be better explained by the soil parameters because of the expression of the fullest effect of all the soil properties, thus giving higher values for the coefficient of determination.

Correlation matrix between different soil properties as obtained in the path coefficient analysis showing the direct and indirect effects of these soil parameters on carbofuran content is given in table 10-15. From the path coefficient analysis it was observed that the maximum positive direct effect on carbofuran content with significant positive correlation was recorded in the case of organic matter (0.697, 0.678, 0.698, 0.727, 0.709 and 0.856). Clay content clearly indicated a negative direct effect (-0.582, -0.583, -0.653, -0.794, -0.827 and -0.636). This trend was observed at all the intervals. The effect of organic matter on carbofuran retention is direct and as expected, contributed from the various functional groups like $-CH_2$, $C=O$, $-C-O-C$, through specific adsorption mechanism. This observation is in conformity with the reports of Garg and Agnihotri (1984) who studied such adsorption mechanism by organic matter for carbofuran. Highly significant positive correlation of organic matter on carbofuran adsorption was also reported by Felsot et al. (1980) ($r^2 = 0.96$), Rajukkannu and Sree Ramulu (1982) ($r^2 = 0.98$) and Somasundaram et al. (1991) ($r^2 = 0.78$). The highly significant negative correlation with clay content obviously indicate the presence

of appreciable amounts of sesquioxides having very low CEC in the clay fraction. X - ray analysis of the clay fraction also revealed the occurrence of kaolinite as the dominant clay mineral with poor exchange capacity. Further, kaolinite has got a very low binding ability for organic molecules especially of carbofuran (Garg and Agnihotri (1984)). Thus the dilution effect caused by sesquioxides and low CEC minerals present in the clay fraction on organic matter would have modified the exchange complex to give very low adsorption of applied carbofuran. The total effect of organic matter observed was smaller (0.408, 0.401, 0.428; 0.521, 0.592 and 0.770) (table 10 - 15) compared to direct effect because of the negative indirect influence of organic matter through pH and AEC. However indirect positive effects of organic matter through CEC and sesquioxide were also positive which added to the direct positive effect. In the case of clay content, though the direct effect is highly negative, the total effect is slightly negative to positive (-0.098, -0.11, -0.133, -0.064, 0.02 and 0.29) in all the observations. This is mainly due to the indirect positive effect of clay content through organic matter, CEC and sesquioxides in all the observations. But the indirect and negative effect of clay through pH and AEC along with direct negative effect has

modified the total effect as negative and significant.

4. Concentration of carbofuran in the leachate

Statistical treatment of the data on carbofuran content of the leachate shows highly significant effects due to soil variation and variation due to time intervals. Leachate concentration of carbofuran increased progressively, reached the maximum and then decreased to lower values (Fig. 22). This observation is in conformity with the reports made by Radder et al. (1989). The plateau maximum was attained in the 7th observation (5010 μg) with respect to the Entisol of Kayamkulam which decreased drastically (3260 μg) towards the last observation. The same pattern was observed for the Inceptisol of Chengannur and the Mollisol of Nedumangad with the maximum concentration of carbofuran (4755 and 4695 μg respectively) attained in the 8th observation. The Ultisol of Malappuram showed the maximum leachate concentration of carbofuran (4385 μg) in the 9th observation, whereas the Entisol of Kuttanad continued to give increasing concentration even at the last observation. It is inferred from the data that soils which are generally poor in organic matter, clay and low in CEC attains equilibrium at an early

date when compared to soils rich in organic matter, clay and with high CEC. Mobility of the chemical in the Ultisol, Mollisol and Entisol of Kuttanad is very slow and hence take more time for the movement to deeper layers; Many workers reported slow movement of carbofuran in soils with low pH, high organic matter, clay content and CEC (Rajukannu and Sree Ramulu, 1984; Raddar et al., 1989 and Somasundaram et al., 1990). Owing to greater adsorption and slow movement, time taken for the leachate concentration to attain maximum value is more in these soils. On the other hand the Entisol of Kayamkulam and the Inceptisol of Chengannur with low CEC, clay and organic matter content showed very poor adsorption and faster movement of the chemical. This is further evident from the value of the total quantity of carbofuran present in the leachate which is maximum for the Entisol of Kayamkulam (33260 µg) followed by the Inceptisol of Chengannur (31240 ug), Mollisol of Nedumangad (30030 µg), Entisol of Kuttanad (27960 µg) and the Ultisol of Malappuram (26880 µg).

5. Degradation and persistence

Data presented in Table 7-15 and Figures 9 to 14 explain the distribution of the chemical in the soil matrix

as well as in the leachate collected. A critical study of the data showed persistence of carbofuran in all the soils even after 80 days. The percentage retention over the initial observed concentration (1st day) was 41.0, 24.0, 23.0, 47.0 and 48.0% for the Ultisol of Malappuram, Inceptisol of Chengannur, Entisol of Kayamkulam, Mollisol of Nedumangad and Entisol of Kuttanad respectively. Thus when all the depths were considered, the Mollisol of Nedumangad and the Entisol of Kuttanad with a more uniform distribution of clay and organic matter showed maximum percentage retention of the chemical though the absolute content of carbofuran retained was more in Malappuram. Similar results have been reported by many workers (Harris, 1969; Rajukkannu and Sree Ramulu, 1981 and Radder et al., 1991).

When the loss through leaching also was accounted, it appears from the table - 18 that the loss of the chemical through microbial degradation, volatilization, in bound residues and through other mechanisms are maximum in the Inceptisol of Chengannur (57%) followed by the Entisol of Kayamkulam (54%) Ultisol of Malappuram (40%), Entisol of Kuttanad (31%) and the Mollisol of Nedumangad (24%). In order to have a clear understanding of the adsorption mechanisms

and losses involved, separate experiments are to be undertaken, and hence generalisations become difficult from the present study.

As the study was conducted without the involvement of any plant systems, transformations of the chemical to give derivatives were possible mainly through microbial activity (Rajagopal et al., 1984; Karns et al., 1986 and Choudhry and Ali, 1988). Thus for all the soils, the surface samples with maximum microbial activity was subjected to the analysis of carbofuran derivatives at all the intervals using gas chromatographic techniques. Carbofuran derivatives were obtained only for 2 soils viz. the Mollisol of Nedumangad and the Ultisol of Malappuram, and that too only at the last observation. Out of the 5 major metabolites identified in soil, (Jae-Koo Lee et al., 1991) only 3 Keto carbofuran was obtained in the present study. This observation also is corroborated by the study of Arunachalam et al. (1990) who identified 3-keto carbofuran as the chief metabolite in soil. Thus it can be inferred that the process of degradation through microbial action is very slow in soils presently investigated, though the microbial activity is very high. The exact reason for the slow degradation of the chemical is to

be investigated separately by further experimentation.

Based on the investigation conducted, it is felt that the following aspects are to be further investigated, through future work.

1. Interaction of the chemical with different fractions of the organic matter and the stability of the organic complex formed.
2. The effect of varying flow rates of water on the distribution of the chemical is to be standardised.
3. Influence of plant systems and the role of microorganisms of the rhizosphere in the rate of degradation and in the nature of products formed.
4. Effect of concentration of carbofuran on the population of microorganisms in the soil including those involved in the degradation of carbofuran.

SUMMARY AND CONCLUSIONS.

SUMMARY AND CONCLUSIONS

An investigation was conducted at the college of Agriculture, Vellayani, during 1992-93' using undisturbed soil columns to study the movement and sorption of carbofuran in soils with varying physico-chemical properties. From five locations representing farmer's field cropped to banana. Vertical and horizontal soil columns along with bulk samples at different depths were collected to study the movement, distribution, leaching loss, persistence and transformations of carbofuran in soils. The important observations and conclusions drawn from the investigations conducted are summarised below.

Soil types selected for the study were having wide variation in physico-chemical properties. The Ultisol of Malappuram was clayey, acidic in reaction, high in organic matter, CEC, water holding capacity, AEC, sesquioxides and was low with respect to bulk density, particle density and hydraulic conductivity. Inceptisol of Chengannur was sandy clay loam, acidic in reaction, low in organic matter CEC, AEC sesquioxides, hydraulic conductivity and high in bulk density and particle density. Entisol of Kayamkulam was loamy sand,

acidic in pH, low in organic matter, CEC, water holding capacity, AEC, sesquioxides and high with respect to bulk density, particle density and hydraulic conductivity. Mollisol of Nedumangad was sandy clay, acidic in reaction with high organic matter, CEC, moderate in water holding capacity, AEC, sesquioxides, hydraulic conductivity and low in bulk density and particle density. Entisol of Kuttanad was sandy clay loam, acidic in reaction, with low organic matter, hydraulic conductivity, moderate in CEC, water holding capacity, AEC, sesquioxides and high in bulk density and particle density; Dominant clay minerals present in all the soils were kaolinite, with appreciable amounts of smectites and quartz.

Distribution of carbofuran in vertical columns at six time intervals of upto 80 days showed significant difference with depth, but between soils, difference were observed only at the first, fifth and sixth observations. Initial distribution of carbofuran was high in the Entisol of Kayamkulam and the Inceptisol of Chengannur but in later observations the Entisol of Kuttanad, the Mollisol of Nedumangad and the Ultisol of Malappuram recorded higher values than the first two, probably due to higher adsorption and poor mobility.

Horizontal distribution of carbofuran was very low in all the soil types studied. At a distance of 10 cm from the point of application, the content of carbofuran was zero, even twenty days after the application. Between soil types there was difference in the horizontal distribution of carbofuran. Maximum horizontal movement was for the Entisol of Kuttanad, followed by the Ultisol of Malappuram, Mollisol of Nedumangad, Inceptisol of Chengannur and was least for the Entisol of Kayamkulam.

Regression model of soil properties on the carbofuran content at all the intervals showed significant regression co-efficient only for organic matter and clay content. Organic matter expressed a positive influence while clay content had a negative effect. Path co-efficient analysis of soil properties revealed maximum positive effect on carbofuran content for organic matter, through its direct effect and indirect positive effect via. CEC, particle density and sesquioxides, while indirect negative effect observed where through pH, clay content bulk density and AEC. Clay content had a negative direct effect on carbofuran content while its indirect effects were negative via. pH,

bulk density and AEC and positive via. organic matter, CEC and sesquioxides.

Leaching loss of carbofuran in soils showed wide variation among the soil types studied. Maximum leaching loss was observed in the Entisol of Kayamkulam, followed by the Inceptisol of Chengannur and the Mollisol of Nedumangad. As time advanced, concentration in leachate increased upto a stage and then decreased in all the soils except for the Entisol of Kuttanad.

Persistence of carbofuran in five soils studied showed wide variation. Eighty days after the application, maximum persistence of carbofuran in soil matrix was observed in the Mollisol of Nedumangad, followed by the Entisol of Kuttanad, Ultisol of Malappuram, Inceptisol of Chengannur and the Entisol of Kayamkulam. The only transformation product observed was 3 - Keto carbofuran, identified in the Ultisol of Malappuram and in the Mollisol of Nedumangad during the sixth sampling after eighty days.

REFERENCES

REFERENCES

- Achik, J., Schiavon, M. and Janet, P. (1991a). Study of carbofuran movement in soils. Part I - soil structure. Environmental International., 17: 73-79.
- Achik, J., Schiavon, M. and Janet, P. (1991b). Study carbofuran movement in soils. Part II - soil structure. Environmental International., 17: 81-88.
- Adhikari, M. and Ray, A. (1990). Studies on adsorption of carbaryl and atrazine on model soils and an agronomic soil. Clay Research., 6(2): 101-106.
- Arunachalam, K.D. and Lakshmanan, M. (1990). Decomposition of c^{14} labelled carbofuran in a black tropical soil under laboratory condition. Soil biol. biochem., 22(3): 407-412.
- Bailey, G.W. and White, J.I. (1970). Factors influencing the adsorption and movement of pesticides in soil Residue Reviews., 32: 29-92.
- Bailey, G.W., White, J.L. and Rotbbert, T. (1968). Adsorption of organic herbicides by montmorillonite, role of pH and chemical character of adsorbate. Proc. Soil Sci. Soc. Am., 32: 222-234.

- Bowling, C.C. (1970). Lateral movement, uptake and retention of carbofuran applied to flooded rice plants. J. Econ. Ent., 63: 239-242.
- Brahmaprakash, G.P. and Sethunathan, M. (1985). Mineralization of carbaryl and carbofuran in soil planted to rice. Rice Research News Letter., CRRRI 5(314): 2.
- *Choudhry, G.R., Ali, A.N. (1988). Bacterial metabolism of carbofuran. Appl. Environ. Microbiol., 54: 1414-1419.
- Chopra, S.L. and Kanwar, J.S. (1976). Analytical Agricultural Chemistry., Kalyani publishers, Ludhiana - New Delhi.
- *Cohen, S.Z., Creeger, S.M., Carsel, R.F. and Enfield, C.G. (1984). Potential pesticide contamination of ground water from agricultural uses. In treatment and disposal of pesticide wastes. ACS Symp. Ser., 259: 297-325.
- Cook, R.F., Stanovick, R.P. and Cassil, C.C. (1969). Determination of carbofuran and its carbonate metabolite residues in corn using a nitrogen-specific Gas Chromatographic Detector. J. Agric. Food Chem., 17(2): 277-282.
- *Copin, A., Deleum, R., Salembier, J.F. and Belien, J.M. (1985). Study of movement of three pesticides of different solubility in soil under natural condition., INRA. Belgium. 47-56.

- *Crepeion, K.L., Walker, G. and Winterlun, W. (1990). Use of coal to retreat pesticide movement in soils. J. Environ. Sci. Health., 26 (5-6): 529-545.
- Daniel, R. Shelton., Ali, M. Sodeghi. and Allen, R. Isensea. (1992). Estimation of granular carbofuran dissolution rates in soil. J. Agric. Food Chem., 41(7): 412-416.
- Das, N.M., Dale, D. and Pillai, K.S. (1975). Persistence of some systemic insecticides in cowpea, when applied as granules in different soil types of kerala. Agric. Res. J. Kerala., 13(2): 175-178.
- Dibakar Sahu. and Agnihotri, N.P. (1983). Persistence and metabolism of carbofuran in soil and maize crop Indian J. Ent., 45(1): 38-44.
- Felsot, A. and Wilson; J. (1980). Adsorption of carbofuran and movement on soil thin layers. Bull. Environ. Contam. Toxicol., 25(5): 778-782.
- *Gantz, R.C. (1960). Persistence and movement of CDAA and CDEC in soils and tolerance of corn seedlings to these herbicides. Weeds., 8: 599.
- Garg, P.K. (1982). Adsorption, desorption and degradation of carbofuran and bendiocarb in soil. Ph.D Thesis., IARI.
- Garg, P.K. and Agnihotri, N.P. (1984). Adsorption and desorption of carbofuran and bendiocarb on soils and clay minerals. Clay Research., 3(1): 17-22.

- Getzin, L.W. (1973). Persistence and degradation of carbofuran in soils. Environ. Entomol., 2: 461-467.
- Getzin, L.W. and Shanks, C.H.C. (1990). Enhanced degradation of carbofuran in pacific north west soils. J. Environ. Sci. Health., 25(4): 433-446.
- Gorden, G.W., Dahun, P.A. and Tollefson, J.J. (1982). Carbofuran persistence in cornfield soils. J. Eco. Ent., 75(4): 637-642.
- *Green halgh, R. (1980). Definition of persistence in pesticide chemistry. Pure. Appl. Chem., 52: 2563-2566.
- Green halgh, R. and Relangur, A. (1981). Persistence and uptake of carbofuran in a humic mesisol and the effect of drying and storing soil samples on residue level. J. Agric. Food chem., 29(2): 231-253.
- Gupta, R.P. and Dakshinamoorthi, C. (1980). Procedures for physical analysis of soil and collection of Agrometeorological data. ICAR.
- Gupta, R.C. and Dewan, R.S. (1973). A raipd colorimetyric method for the estimation of carbofuran residues. Proc. Symposium on Progress and Problems in Pesticide Residue Analysis, Ludhiana pp. 208-214.
- Gupta, R.C. and Dewan, R.S. (1974). Residues and metabolism of carbofuran in soil. Pesticides., 8: (12): 36-39.

- *Hallberg, G.R. (1989). Pesticide pollution of ground water in the humid united states. Agric. Ecosyst. Environ., 26: 299-367.
- *Hamaker, J.W., Goring, C.A.I. and Youngson, C.R. (1966). Soption and leaching of 4-amino-3-4-6-trichloropicolinic acid in soils. In Gould, F. (ed.). Organic Pesticides in the Environment., 23-27. Advances in Chemistry, Series 60., American Chemistry Society.
- *Harris, C.I. (1964). Movement of dicamba & diphanamide in soils. Weeds., 12: 112.
- Harris, C.R. (1969). Laboratory studies on the persistence of biological activities of some insecticides in soil. J. Econ. Ent., 62: 1437-1441.
- Hartley, C.S. (1961). Physico-chemical aspects of the availability of herbicides in soil. In K.K. Woodford and G.R. Sagar (eds.). Herbicides in soils., New York.
- Helling, C.S. (1971). Pesticides mobility in soils. III. influence of properties. Soil Sci. Soc. Am. Proc., 35: 743-748.
- Helling, C.S., Kearney, P.C. and Alexander, M. (1971). Behaviour of pesticides in soils. Advances in Agronomy., 23: 147-240.
- Hesse, P.R. (1971). A text book of soil chemical analysis. John Murray (Publishers) Ltd., London. pp. 105, 271-277.

International Rice Research Institute. (1975). Control and management of Insects., Annual Report. 1974.

Jackson, M.L. (1971). Soil chemical analysis., Asia publishing house, Bombay - New Delhi.

Jae - Koo Lee., Kee - Sung Kyung. and Willis, B. Wheeler. (1991). Rice plant uptake of fresh and aged residues of carbofuran from soil. J. Agric. Food Chem., 39: 588-593.

*Jamet, P. and Piedallu, N.A. (1975). (The movement of carbofuran in different types of soils - The adsorption and desorption of carbofuran) Phytiatrie - phytopharmacie., 24(4): 279-295.

*Jury, W.A., Spencer, W.F. and Farmer. W.J. (1983). Behaviour assessment model for trace organics in soil: I Model description. J. Environ. Qual., 12: 588-564.

Kandaswamy, D., Chandrayan, K., Rajukkannu, K. and Balasubramanian, K. (1977). Current Science., 46: 280.

*Karns, J.S., Mulbry, W.W., Nelson, J.O. and Kearney, P.C. (1986). Metabolism of carbofuran by a pure bacterial culture. Pestic. Biochem. Physiol., 25: 211-217.

*Kearney, P.C., Harris, C.I., Kaufman, D.D. and Sheets, T.J. (1965). Behaviour and fate of chlorinated aliphatic acids in soils. Adv. Pes. Cont. Research., 6: 1.

- *Keys, C.H. and Friesen, H.A. (1968). Persistence of picloram activity in soil. Weeds., 16: 341.
- *Kladivko, E.J., Scoyoc, G.E. Ven., Monke, E.J. and Oates, K.M. (1991). Pesticides and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. J. Environ. Quality., 20(1): 264-270.
- Kumari, K. and Singh, R.P. (1992). Adsorption thermodynamics of carbofuran on forest and black soils. Pesticide Research Journal., 4(1): 43-46.
- Kumari, K. Singh, R.P. and Sexena, S.K. (1988). Movement of carbofuran in soil columns. Ecotoxicology and environmental safety., 16: 34-44.
- Lee, D.Y., Chen, C.T. and Houng, K.H. (1990). Behaviour assesment of eight major pesticides used in Taiwan in soil by mechanistic model. Soil & Fertilizers in Taiwan., 33-50. Graduate institute of Agric chem. National Taiwan University.
- *Moreale, A. and Bladen, R. Van. (1982). (Mobility and dispersion of some pesticides in undisturbed soil columns). Mededelingen Van de Faculteit Landbouwwetenschappen., 47(1): 381-394.
- *Moreale, A. and Bladen, R. Van. (1983). (Movement of insecticide carbofuran towards the water table). Mededelingen Van de Faculteit Landbouwwetenschappen. 48(4): 895-995.

- Naitan, N.R. and Sukhani, T.R. (1990). Leaching of carbofuran and isophenphose in soil. Indian J. Ent., 52(3): 514-516.
- Neera singh., Wahid, P.A. and Murty, M.V.R. (1990). Sorption - desorption of methyl parathion, fenitrothion and carbofuran in soils. J. Environ. Sci. Health., 25: 713-728.
- *Pestemer, W., Bunte, D. and Guenther, P. (1988). Persistence; The main factor influencing the behaviour and activity of herbicides in the soil. pp. 281-288. In Proceedings. EWRS symp. "Factors affecting herbicidal activity and selectivity".
- *Pestemer, W., Peter, G. and Hammer, M. (1989). Degradation of carbofuran and chlorfenviphos in soil after single and repeated application under field condition. Nachrichtenblatt des Duetchen Pflanzenschutzdienstec., 41(6): 81-85.
- Radder, B.M., Parama, V.R.R. and Siddaramappa, R. (1991). Degradation of carbofuran fenitrothion and carbendazin under flooded and non flooded conditions in selected soils from karnataka. Pesticide Research Journal., 3(2): 123-128.
- Radder, B.M., Ramakrishnan, V.R. and Siddaramappa, R. (1989). Leaching loss, Movement and Distribution of Carbofuran and Fenitrothion in Different Soil Columns. Pesticide Research Journal., 1(2): 59-62.
- Rajagopal, B.S., BrahmaPrakash, G.P., Reddy, B.R., Singh, V.D. and Senthunatan, M. (1984). Effect and persistence of selected carbamate pesticides in soils. Residue Reviews., 93: 1-199.

- Rajukkannu, K., Raguraj, R. and Krishnamurthy, K.K. (1977). Persistence of phorate and carbofuran in flooded soils. Pesticides., 1: 14-15.
- Rajukkannu, K. and Sree Ramulu, U.S. (1981). Degradation and persistence of carbofuran in soils. Madras Agric. J., 68(10): 668-671.
- Rajukkannu, K. and Sree Ramulu, U.S. (1982a). Leaching and movement of carbofuran in soils. Madras Agric J., 69(8): 501-506.
- Rajukkannu, K. and Sree Ramulu, U.S. (1982b). Influence of soil properties on the adsorption of carbofuran in soil. Madras Agric J., 69(9): 580-584.
- Rajukkannu, K. and Sree Ramulu, U.S. (1984). Mobility of carbofuran in soils. In "Pesticide and Environment" (eds.) Ragupathy, A., Rajukkannu, K. and Chellaih, S. TNAU., 101-104.
- *Rao, P.S.C. and Davidson, J.M. (1980). Estimation of pesticide retention and transformation parameters required in nonpoint source pollution model. In Environmental impact of non point source pollution. (eds.) Overcash, M.R. and Davidson, J.M., 23-67.
- *Rao, P.S.C., Hornsby, A.G. and Jessup, R.E. (1985). Indices for ranking the potential for pesticide contamination of ground water. Soil and Crop Science Society of Florida Proceedings., 44: 1-8.

- *Rouchand, J., Gustin, F. and Steene, F. (1989). Plant and soil metabolism of carbofuran in cauliflower, bressels sprouts and sugar beet crops. Mededelingen Van de Faculteit Landbouwwetenschappen., 54(1): 263-266.
- *Rouchard, J., Gustin, F., Steene, F. Van De., Palevents, C., Gillet, J., Benoit, F., Cuestermans, N., Vanporgs, C., Proft, M.De. and Seutin, E. (1992). Organic fertilizers, soil organic matter and insecticides. Soil biodegradation and efficiencies. Revue de l'Agriculture., 45(3): 575-589.
- Sahu, D. and Agnihotri, N.P. (1983). Persistence and metabolism of carbofuran in soil and maize crop. Zea maize. Indian J. Ent., 45(1): 38-44.
- Singhal, K.C., Quedri, S.K., Varshney, R.P. Saini, K. and Varshney, S. (1988). Influence of particle size and other physico-chemical properties of the soils on the adsorption of carbofuran. Pesticides., 22(11): 38-40.
- Smelt, J.H., Leistra, M., Dekker, A. and Schut, C.J. (1981). Movement and conversion of ethoprophos in soil in winter: Measured concentration patterns and conversion rates. Soil Science., 131(4): 242-248.
- Somasundaram, L. and Joel, R. Coats. (1990). Influence of pesticide metabolites on the development of enhanced biodegradation. Journal paper No. J - 13794 of the Iowa Agriculture and Home Economics Experiment Station. Ames, IA. Project No. 2306., pp. 128-140.

Somasundaran, L., Racke, K.D. and Coats, .R. (1987). Effect of manuring on the persistence and degradation of soil insecticides. Bull. Environ. Contam. Toxicol., 39: 579-586.

Somasundaran, L., Joel, R. Coats and Kenneth, D., Racke. (1991). Mobility of pesticides and their hydrolysis metabolites in soil. Environ. Toxicol. Chemistry., 10: 185-194.

Soudamini panda and Sethunathan, N. (1989). Persistence and Degradation of carbofuran in soil and in microbial cultures without and with added salts. Pesticide Research Journal., 1(1): 1-6.

*Williams, I.H., Pepin, H.S. and Brown, M.J. (1976). Degradation of carbofuran by microorganisms. Bull. Environ. Contam. Toxicol., 15: 244.

Yu, C.C., Booth, V.M., Hansen, D.J. and Lassen, J.R. (1974). Fate of carbofuran in model ecosystem. J. Agric. Food. Chem., 22: 431-434.

* Originals not seen

APPENDICES

Appendix - 1

Abstract of anova table of concentration of carbofuran (ug/25 g soil) at different depth & intervals

Mean sum of squares and F values

Source	DF	1st day		5th day		10th day		20th day		40th day		80th day	
		MSS	F	MSS	F	MSS	F	MSS	F	MSS	F	MSS	F
Soils	4	181914	10.8*	61358	2.03	39467	3.47	130526	2.6	153187	10.8*	170845	93.73**
Error I	5	16853.6		30195		1349.6		48509.6		14059.2		1822.6	
Depth	4	4.7x10 ⁷	2837*	2.5x10 ⁷	1044**	1.19x10 ⁷	353.5**	5259.82	444**	1707161	241.4**	362225	171.67**
Soilxdepth	16	260176	15.65*	103645	4.26**	146416.3	4.33**	926.67	7.8**	49503.25	7.00**	178075	8.40**
Error II	20	16624		24324		33768		11819.2		7071.7		2110	

* Significant at 5% level

** Significant at 1% level

Appendix - 2

Anova table of carbofuran in the leachate

Source	DF	MSS	F
Soil	4	1298192	91.61**
E ₁	5	14169.2	
Intervals	9	1.369x10 ⁷	3577.50**
Interaction	36	380792.90	99.45**
E ₂	45	3828.62	

* Significant at 5% level

**MODELLING OF CARBOFURAN
MOVEMENT AND SORPTION
IN SOILS WITH VARYING
PHYSICO-CHEMICAL PROPERTIES**

By
MOOSSA, P. P.

**ABSTRACT OF THE THESIS
SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENT FOR THE DEGREE
MASTER OF SCIENCE IN AGRICULTURE
FACULTY OF AGRICULTURE
KERALA AGRICULTURAL UNIVERSITY**

**DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY
COLLEGE OF AGRICULTURE
VELLAYANI — THIRUVANANTHAPURAM
1994**

ABSTRACT

An experiment was conducted at the College of Agriculture, Vellayani, during 1992-93 for modelling carbofuran movement and sorption in soils with varying physico-chemical properties. Undisturbed vertical and horizontal soil columns were used for the study.

Five major locations of the state cropped to banana were selected for the study viz. Malappuram (Ultisol), Chengannur (Inceptisol), Kayamkulam (Entisol), Nedumangad (Mollisol) and Kuttanad (Entisol). The soils exhibited wide variation in the major physico-chemical properties such as texture, water holding capacity, bulk density, particle density, hydraulic conductivity, CEC, AEC and organic matter. The mineralogy of the clay samples had revealed the occurrence of kaolinite, quartz and smectite as major minerals in these soils.

Distribution of carbofuran in the vertical soil columns showed high concentration of carbofuran at lower depths in the first observation for the Inceptisol of

Chengannur and the Entisol of Kayamkulam. While in the 6th observation, the Ultisol of Malappuram, Entisol of Kuttanad and the Mollisol of Nedumangad showed higher concentrations in the lower layers due to higher adsorption.

Horizontal distribution of carbofuran was very low though significant differences were observed between soils. Maximum horizontal distribution was observed in the Entisol of Kuttanad and the least for the Entisol of Kayamkulam.

Regression equation of soil properties on carbofuran content indicated significant influence for organic matter and clay content. Path coefficient analysis of soil properties revealed significant direct positive effect for organic matter and significant direct negative effect for clay content. Indirect negative effects expressed through pH, clay content, Bulk density and AEC with respect to organic matter was not strong enough to counteract the direct positive effect. Similarly the indirect positive effect contributed by clay through organic matter, CEC and sesquioxide was also not sufficient to overcome the direct negative effect.

Concentration of carbofuran in the leachate showed highest values for the Inceptisol of Chengannur followed by the Entisol of Kayamkulam, both having low CEC, organic matter and clay content. The Ultisol of Malappuram with high organic matter, CEC and clay had given the lowest value for carbofuran in the leachate.

Persistence of carbofuran was maximum in the Mollisol of Nedumangad with high organic matter, clay content and CEC. Persistence was poor in the Inceptisol of Chengannur and the Entisol of Kayamkulam which are low in organic matter, clay content and CEC. The only transformation product identified was 3 - keto carbofuran observed in the surface soil of Ultisol of Malappuram and Mollisol of Nedumangad in the last observation made at 80 days after application.