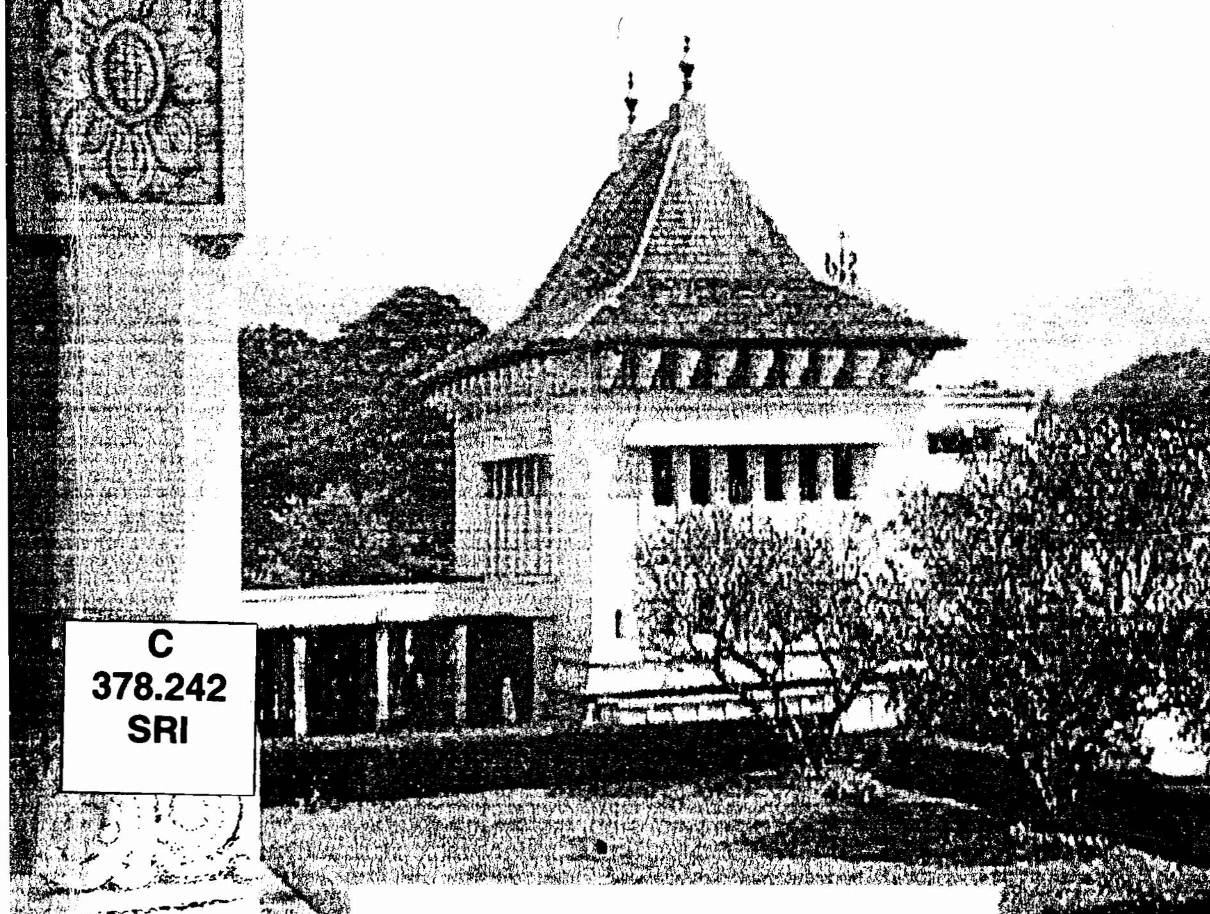
UNIVERSITY OF PERADENIYA
SRI LANKA

PROCEEDINGS
OF THE
ANNUAL RESEARCH SESSION
1997



NOVEMBER 22, 1997

ADSORPTION AND MOVEMENT OF CARBOFURAN IN SELECTED SOILS OF SRI LANKA

D. KUMARAGAMAGE, D.A.S. GAMAGE, M.M.S.S. SAMATHA AND J.I.L.B. RATNAYAKA

Department of Soil Science, Faculty of Agriculture
University of Peradeniya.

ABSTRACT

Carbofuran is an insecticide, which is readily adsorbed to soil particles. Adsorption of carbofuran is a key parameter controlling the extent to which it will leach through the soil to ground water. The main objective of this study was to investigate the adsorption and movement of carbofuran in major soil types of Sri Lanka. Carbofuran adsorption was studied in soil samples collected from 20 locations by equilibrating with a carbofuran solution. After equilibration, the supernatant was analyzed for carbofuran and the amount adsorbed was calculated. Movement of surface-applied carbofuran was studied in disturbed (packed) and in undisturbed soil columns. Carbofuran was applied to the surface, after which columns were leached with water and leachate samples were analyzed for carbofuran. The relationship between the amount of carbofuran leached and soil properties was analyzed.

Carbofuran adsorption did not show a significant relationship with cation exchange capacity, pH and clay content. A significant quadratic relationship was observed between carbofuran adsorption and organic matter, but the linear relationship was not significant. When regression analysis was conducted separately for soils with pH less than 5.5, the relationship between organic matter and carbofuran adsorption improved. In soils with pH greater than 5.5, such a relationship was not observed. The percentage of carbofuran leached showed a significant negative relationship with soil organic matter content and a significant positive relationship with soil pH.

The results indicate that the adsorption of carbofuran is greater and leaching is less in strongly acidic soils with high organic matter contents. Thus, application of carbofuran to such soils, will reduce its effectiveness as a pesticide, but with less ground water pollution and therefore with less adverse effects on the environment.

INTRODUCTION

Pesticides are being extensively used in modern agriculture in order to control various insect pests, fungi, nematodes and weeds. The environmental impact of pesticides is highly influenced by the physical, chemical and biological processes that govern their persistence and movement in the soil. These processes, which include adsorption, degradation, volatilization and downward movement determine both the efficacy of pesticides in controlling target organisms as well as their potential adverse effects on non-target organisms.

Concern about the fate of these pesticides that are continuously introduced into the soil system over a long period of time, has intensified over the recent years. There is strong evidence indicating the potential of pesticides added to soil contaminating ground water (Jury, Focht and Farmer, 1987, Kookana, Di and Alymore, 1995, Di, Kookana and Alymore, 1995, Di and Alymore, 1997).

Carbofuran (2,3-dihydro-2,2- dimethyl - 7-benzofuranyl N-methyl carbomate) is a broad spectrum systemic insecticide commonly used in Sri Lanka to control soil dwelling and foliar feeding insects. Carbofuran is highly soluble in water and therefore highly mobile in soil. On addition to soil, carbofuran gets adsorbed to soil particles, thus, reducing its efficacy in controlling target organisms as well as reducing its mobility. Therefore, the capacity of a soil to adsorb or retain carbofuran is a key parameter controlling the extent to which it will leach through the soil to ground water. Investigations on adsorption reactions of various pesticides in soils have demonstrated that adsorption is related to soil properties such as clay content, clay mineralogy, cation exchange capacity (CEC) and organic matter content (Basile, Arienzo and Celerio, 1990, Singh and Sethunathan, 1991, Laird *et al.* 1992, Ratnayaka and Kumaragamage, 1996, Uckraiczyk and Ajwa, 1996, Rytwo, Nir and Marguilies, 1996, Celis *et al.* 1997).

In order to predict the fate of carbofuran in soils, it is essential to understand the various physical, chemical and biological processes that occur when the chemical is added to soils (Di and Alymore, 1997). Detailed studies of adsorption, degradation and movement of carbofuran in Sri Lankan soils will essentially help in improving the efficacy of this pesticide in controlling target organisms as well as in minimizing the adverse effects on non-target organisms.

In the above context, this study was conducted with the main objective of investigating the adsorption and movement of carbofuran in major soil types of Sri Lanka as related to soil properties such as clay content, CEC, pH and organic matter content.

MATERIALS AND METHODS

Carbofuran Adsorption in Soils

Surface soil samples (0-15 mm depth) of varying physical and chemical properties were collected from 20 different locations of Sri Lanka, to include Reddish Brown Earths (Rhodustalfs), Red Yellow Podsolic soils (Rhodudults), Noncalcic Brown soils (Haplustalfs), Reddish Brown Latasolic soils (Tropudults) and Immature Brown Loams (Dystropepts). These soil samples were collected from uncultivated lands in Mahallluppallama, Anuradhapura, Matale, Nilambe, Kamburugamuwa, Maradankadawala, Kegalle, Hettipola, Naula, Pussellawa, Girandurukotte, Wattegama, Gampola, Kuliyapitiya, Bingiriya, Mawathagama, Ranna, Yalegoda, Aralaganwila and Dodangolla. Soil Samples were air dried and sieved through a 2mm mesh before use.

Soil samples were analyzed for pH, CEC, organic matter content and texture in the laboratory. Soil pH was determined in a soil : 1N KCl suspension (1:2.5) using a pH meter (Hesse, 1971). To determine CEC, cations adsorbed to soil colloids were replaced with NH_4^+ and adsorbed NH_4^+ were determined using macro-Kjeldhal digestion method (Hesse, 1971). Organic matter content was determined by Walkey and Black titrimetric method (Walkey and Black, 1934) while soil texture was determined by hydrometer method (Gee and Bauder, 1986).

To compare adsorption of carbofuran in different soils, two replicate soil samples (5 g) were shaken with 25 ml of 25 mg l^{-1} carbofuran solution for 2 h using a mechanical shaker at 25 ± 1° C. Analytical grade carbofuran (100% purity) was used. After equilibrium was attained, the soil suspension was centrifuged at 22000 rpm for 20 min and the supernatant solution was removed and analyzed for carbofuran using a colorimetric method (Singh and Sethunathan, 1991). The amount of carbofuran adsorbed by the soil was calculated by the difference between the initial and the final concentrations of carbofuran, in mg carbofuran adsorbed per 100 g soil. The relationship between the amount of carbofuran adsorbed in different soils and soil properties was statistically analyzed using regression analysis.

Carbofuran Movement in Columns

Disturbed (packed) columns

Six soils, with varying physical and chemical properties, were selected for the leaching experiment with disturbed soil columns. Soils used were from Hettipola (Immature Brown Loams - Dystropepts), Naula (Reddish Brown Earths - Rhodudalfs), Pussellawa (Red Yellow Podsolic, Rhodudults), Maradankadawela (Reddish Brown Earths - Rhodustalfs), Ranna (Red yellow podsolic - Rhodudults) and Kuliyapitiya (Immature Brown Loams - Dystropepts).

Soils were packed into glass columns with a diameter of 3.4 cm and a height of 20 cm to obtain a bulk density of 1.2 g cm^{-3} and were saturated by adding de-ionized water. One ml of carbofuran solution (Analytical grade) with a concentration of 100 mg l^{-1} was applied to the surface. Soil columns were leached with de-ionized water and leachate fractions (10 ml) were analyzed for carbofuran colorimetrically. Leaching was continued until the concentration of carbofuran in leachate fractions was undetectable. The total amount of carbofuran leached in each soil (as a percentage of amount added) was calculated.

Undisturbed columns

Undisturbed soil columns were collected using 60 cm PVC pipes with a diameter of 14 cm. Soil columns were taken from 4 locations, namely, Kiribathkumbura (Reddish Brown latasolic - Tropudults), Maha Illuppallama (Reddish Brown Earths - Rhodustalfs), Deltota (Immature Brown Loams -Dystropepets) and Meewatura (Alluvial soils - Quartzipsamments) with four replications. Soil columns were saturated with distilled water and 3 % granular carbofuran was added to the surface of columns at the rate of 120 mg per column. Columns were leached with water and 10 ml leachate fractions were collected and analyzed for carbofuran concentration. Leaching was continued until the concentration of carbofuran in leachates was undetectable. The total amount leached (as a percentage of the amount added) was calculated.

Soil samples were collected from the same four locations for the analysis of soil properties. The relationships between the amount of carbofuran leached in disturbed and undisturbed soil columns and soil properties were analyzed by simple and multiple regression analysis using all replicates.

RESULTS AND DISCUSSION

Carbofuran Adsorption in Soils

Selected soils were weakly acidic to very strongly acidic in reaction, with CEC values ranging from 7.4 to 28.8 cmol(+) kg^{-1}. Organic matter content (OM) varied from 0.65 and 2.99 % while the textural class of soils ranged from sandy loam to clay (Table I).

Amount of carbofuran adsorbed in different soils ranged from 1.7 to 6.9 mg per 100 g soil. Generally, soils with high organic matter contents, such as soils from Gampola and Pussellawa, had a higher capacity to adsorb carbofuran. Soils with low organic matter contents, such as soils from Aralaganwila and Dodangolla, had a lower capacity to adsorb carbofuran (Table I). When all soils were considered, none of the soil properties tested had a significant relationship with carbofuran adsorption for the simple linear model. However, soil organic matter content showed a significant positive relationship with carbofuran adsorption ($r^2 = 0.50$, $p=0.01$) for the quadratic model (Figure 1a). The results therefore indicate that the most important colloidal fraction responsible for the adsorption of carbofuran is the organic matter, and not clay. Similar results were reported by Singh and Sethunathan (1991). CEC was not significantly related to carbofuran adsorption, which indicates that either cation exchange sites are not limiting in these soils for adsorption of carbofuran at the rate applied, or carbofuran is not necessarily adsorbed as a cation.

Although there was no significant relationship between adsorption of carbofuran and soil pH, it was noted that soils with low pH values generally had a higher adsorption of carbofuran (Table I). Therefore, the experimental soils were categorized according to the pH values and the relationships between carbofuran adsorption and soil properties were analyzed separately, for strongly acidic ($pH < 5.5$) and moderately

Table I. **Characteristics of the soils used in the study and amount of carbofuran adsorption**

Location	Texture			CEC cmol(+)/kg	pH	OM %	Amount Adsorbed mg/100g
	Sand%	Silt %	Clay%				
Maha Illuppallama	6.7	54.2	39.1	17.1	5.0	1.83	5.6
Anuradhapura	26.3	17.4	56.3	15.9	5.1	0.94	4.6
Matale	54.4	29.1	16.5	14.9	5.5	0.94	3.0
Nilambe	11.1	22.5	66.4	17.5	3.8	1.21	4.1
Kamburugamuwa	55.2	35.6	9.2	16.7	6.6	2.99	4.1
Maradankadawala	06.4	68.0	25.6	7.4	5.1	1.37	4.4
Kegalle	46.7	13.2	40.1	24.7	3.9	1.95	4.3
Hettipola	76.6	8.3	15.1	20.0	5.7	1.25	2.4
Naula	42.8	22.9	34.3	17.7	5.4	1.50	4.6
Pussellawa	34.7	4.1	61.2	16.1	5.0	2.88	5.7
Girandurukotte	36.3	53.1	10.6	14.8	5.3	0.94	3.1
Wattegama	45.4	11.8	42.8	21.6	5.6	2.19	6.0
Gampola	41.4	41.5	17.1	18.6	5.1	2.48	6.9
Kuliyapitiya	72.5	15.6	11.9	14.3	5.8	0.84	2.6
Bingiriya	49.0	32.3	18.7	11.3	5.9	1.27	3.9
Mawathagama	48.7	29.6	21.7	15.3	4.9	1.32	4.5
Ranna	36.8	13.5	49.7	25.1	5.8	0.71	4.9
Yalegoda	28.3	51.7	20.0	21.3	5.7	2.92	4.8
Aralaganwila	58.4	32.1	9.5	14.5	4.9	0.65	1.8
Dodangolla	19.0	36.1	44.9	28.8	5.0	0.87	1.7

CEC - Cation exchange capacity   OM - Organic matter

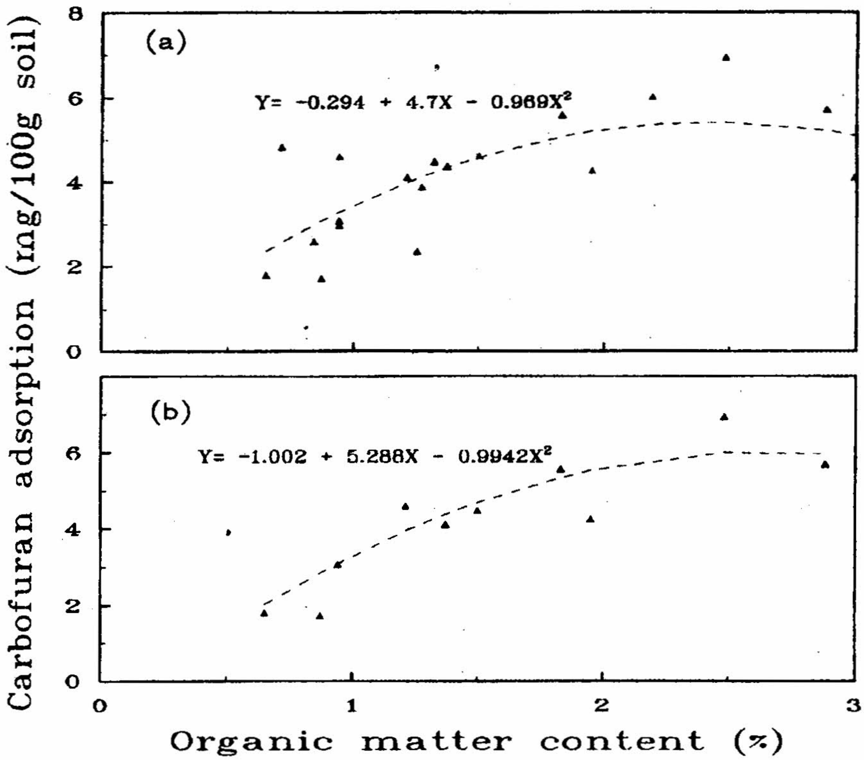


Figure 1. **Relationship between carbofuran adsorption and soil organic matter content (a) for all soils (b) for soils with pH <5.5.**

to slightly acidic (pH > 5.5) soils. When only strongly acidic soils were considered, the relationship between organic matter and carbofuran adsorption improved both for the linear (r^2=0.66, p=0.05) and quadratic (r^2=0.76, p= 0.001) models (Figure 1b). However, for soils with pH values greater than 5.5, there was no significant relationship between organic matter and carbofuran adsorption. The results therefore indicate that carbofuran adsorption is pH dependent, and in strongly acidic soils adsorption is favoured.

Under strongly acidic conditions, carbofuran yields to carbofuran phenol, which is strongly bound to soil by forming a complex with organic matter (Getzin, 1973; Singh *et al.*, 1990). In addition, soil acidity may convert carbofuran from negatively charged anions to uncharged molecules or even to positively charged cations, and thus dramatically increase their adsorption (Getzin, 1973). The results of this study also revealed that strongly acidic soils with comparatively higher organic matter contents, had a higher capacity to adsorb carbofuran.

Carbofuran Movement in Columns

Disturbed (packed) columns

The quantity of carbofuran leached varied from 7.5 to 37.6 %. The quantity leached showed a significant negative relationship with organic matter content and a significant positive relationship with soil pH. This again, confirms that adsorption is greater in strongly acidic soils with high organic matter contents, which makes carbofuran less mobile. According to the regression analysis, the quadratic model gave a better fit than the linear model with r^2 of 0.96 (p=0.01) and 0.85 (p=0.05) for organic matter content and soil pH, respectively (Figure 2). Cation exchange capacity

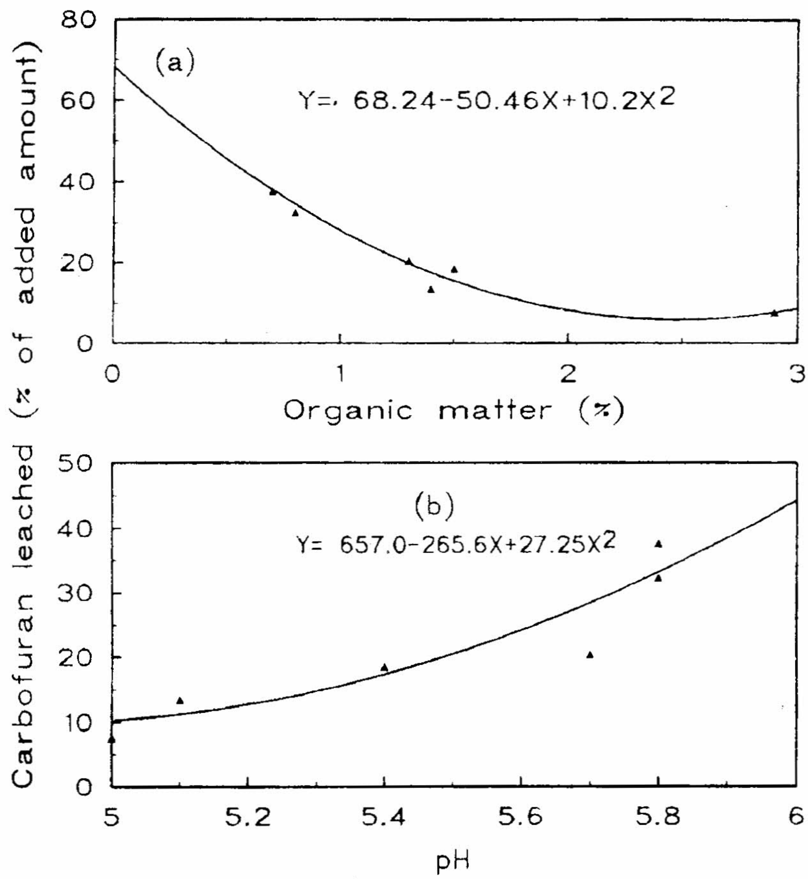


Figure 2. Relationship between carbofuran leached in disturbed columns and soil properties a) organic matter b) pH.

and clay content, however, did not show a significant relationship with the amount of carbofuran leached, indicating that these properties do not have much effect on adsorption and movement of carbofuran in soils.

Multiple regression analysis indicated a highly significant (R^2 = 0.87, p=0.05) combined effect of soil organic matter content and pH on leaching of carbofuran through packed soil columns. The regression equation was

$$Y = -76.91 - 5.26\ OM + 19.4\ pH$$

where Y is the carbofuran leached as a percentage of amount added.

Undisturbed columns

The texture of soils used were sandy loam to loam. Soils were moderately acidic to very strongly acidic reaction. CEC values ranged from 7.8 to 12.4 cmol(+) kg^{-1} and organic matter content ranged between 0.15 and 3.18 % (Table II).

Table II. Characteristics of soils and the amount of carbofuran leached in undisturbed columns

Location	Sand %	Silt %	Clay %	CEC cmol(+)/kg	pH	OM	Amount leached (%)
Kiribath-kumbura	59.8	24.8	15.4	12.1	4.0	3.18	1.4
Meewathura	39.0	35.9	25.1	10.8	4.5	2.18	2.1
Maha Illuppallama	32.2	48.7	19.1	7.8	5.7	0.95	2.4
Deltota	67.3	20.7	12.0	12.4	6.0	0.15	3.1

CEC - Cation exchange capacity OM- Organic matter

The total amount of carbofuran leached through undisturbed soil columns were very low ranging from 1.4 to 3.1% of the amount added. This indicates that carbofuran is very persistent in these soils. However, the concentration of carbofuran in leachates during the initial stages of leaching, was higher than 0.2 mg l^{-1} in all the soils. Thus, the concentration of carbofuran in leachates was much greater than the upper limit of carbofuran allowed in drinking water which is 0.04 mg l^{-1} (USEPA, 1990).

The quantity of carbofuran leached (Figure 3) showed a highly significant negative relationship with organic matter content (r^2 0.92, p=0.001) and a highly significant positive relationship with soil pH (r^2 = 0.86, p=0.001). Again, CEC and clay content did not show a significant relationship with the amount of carbofuran leached.

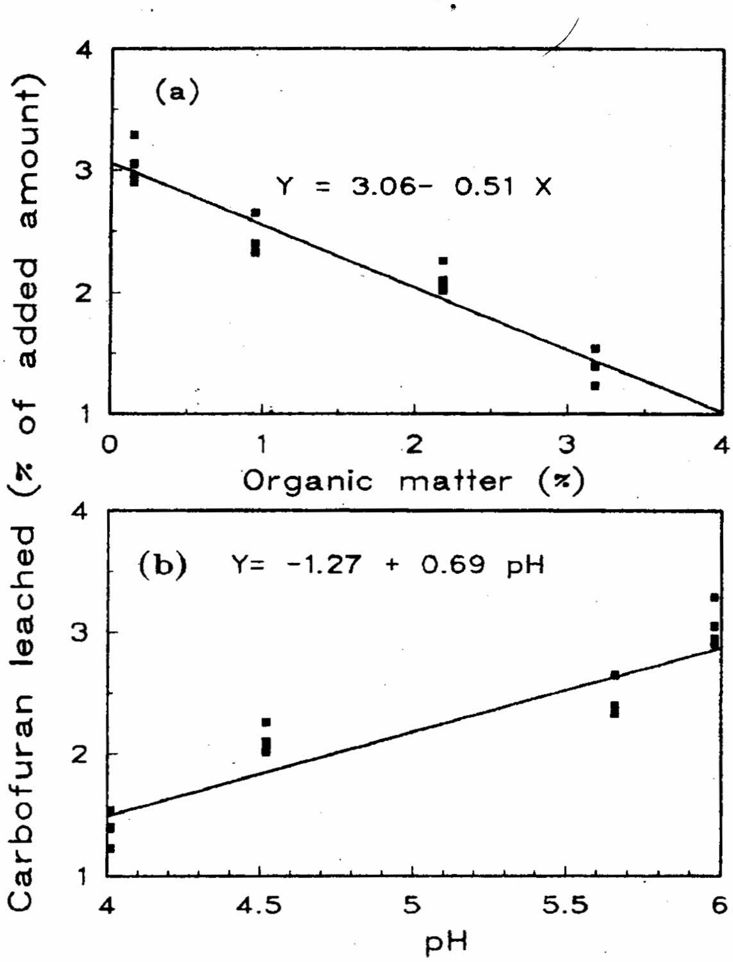


Figure 3. Relationship between carbofuran leached in undisturbed columns and soil properties a) organic matter b) pH.

Results of these experiments, therefore, consistently indicate that adsorption of carbofuran is greater in strongly acidic soils with high organic matter contents, which reduces the mobility of carbofuran in such soils, thus controlling the extent to which it will leach through the soil.

CONCLUSIONS

Chemical properties of soils determine the fate of carbofuran to a considerable extent. Organic matter was the most important single factor responsible for adsorption of carbofuran. Carbofuran adsorption was pH dependant and was favoured in soils with pH less than 5.5. Therefore, application of carbofuran to strongly acidic soils with high organic matter contents may reduce its efficacy in controlling target organisms, at the same time, reducing the potential of ground water pollution through leaching. Further research on the fate of carbofuran in different soils would be very valuable in predicting ground water pollution resulting from carbofuran application.

ACKNOWLEDGEMENT

Authors acknowledge the International Foundation for Science, Sweden, for the financial support.

REFERENCES

Basile, G., Arienzo, M. and Celerio, G. (1990). Sorption of pesticides by soils of Compania (Italy). *Agrochimica*, **34**,181-192.

Celis, R., Cornejo, J., Hermosin, M.C. and Koskinen, W.C. (1997). Sorption-desorption of atrazine and simazine by model soil colloidal components. *Soil Sci. Soc. Am. J.*, **61(2)**,436-443.

Di, H.J. and Alymore, L.A.G. (1997). Modelling of probabilities of ground water contamination by pesticides. *Soil Sci. Soc. Am. J.*, **61**, 17-23.

Di, H.J., Kookana, R.S. and Alymore, L.A.G. (1995). Application of a simple modelto assess ground water contamination potential of pesticides. *Aust. J. Soil Res.*, **33**, 1031-1040.

Gee, G.W. and Bauder J.W. (1986). Particle size analysis. Method of Soil Analysis Part 1, Physical and Mineralogical Methods, 2 nd Ed., American Soc. of Agronomy, Inc. Publisher Madison, Wisconsin, USA. pp 404-491.

Getzin, L.W. (1973). Persistent and degradation of carbofuran in soil. *Environ. Entomology*, **2**, 461-467.

Hesse, P.R. (1971). Textbook of Soil Chemical Analysis, John Murray (Publishers) Ltd., London. 103-105.

Jury, W.A., Focht, D.D. and Farmer, W.J. (1987). Evaluation of pesticide groundwater pollution from standard indices of soil chemical adsorption and biodegradation. *J. Environ. Qual.*, **16**, 422-428.

Kookana, R.S., Di, H.J. and Alymore, L.A.G. (1995). A field study on leaching and degradation of nine pesticides in a sandy soil. *Aust. J. Soil Res.*, **33**, 1019-1030.

Laird, D.A., Barriuso, E., Dowdy, R.H. and Koskinen, W.C. (1992). Adsorption of atrazine on smectites. *Soil Sci. Soc. Am. J.*, **36**, 62-67.

Ratnayaka, J.I.L.B. and Kumaragamage, D. (1996). Adsorption of paraquat in selected Sri Lankan soils. *Trop. Agric. Res.*, **8**, 78-88.

Rytwo, G., Nir, S. and Margulies, L. (1996). Adsorption and interactions of diquat and paraquat with montmorillonite. *Soil Sci. Soc. Am. J.*, **60**, 601-610.

Singh, N. and Sethunathan, N. (1991). Degradation of soil-sorbed carbofuran by an enrichment culture from carbofuran- re treated azolla plot. *J. Agric. Food Chem.*, **40**, 1062-1065.

Singh, N., Wahid, P.A., Murty M.V.R. and Sethunathan N. (1990). Sorption desorption of methyl parathion, fenitrothion and carbofuran in soils, *J. Environ. Sci. Health*, **25(6)**, 713 - 728.

Uckrainczyk, L. and Ajwa, H.A. (1996). Primisulfuron sorption on minerals and soils. *Soil Sci. Soc. Am. J.*, **60**, 460-467.

United States Environment Protection Agency (USEPA), (1990). In Environmental Handbook. Tenessy Valley Authority, USA.

Walkey, A. and Black, I.A. (1934). An examination of the Detjareft method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.*, **37**, 29-38.