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STUDY OF CARBOFURAN MOVEMENT IN SOILS.

I. INFLUENCE OF SOIL STRUCTURE, PERCOLATION SPEED, AND DOSE ON CARBOFURAN MOVEMENT AND LEACHING IN TWO TYPES OF SOIL

Under natural conditions, contamination of drained waters by a clay soil rich in organic matter was proved to be systematically higher than their contamination by a loamy clay soil. To elucidate this phenomenon, the role of soil structure, percolation speed, and product dose in carbofuran movement and leaching was studied in laboratory soil columns. Although these factors modify insecticide transfer, it has been observed that soil characterized by strong adsorption capacity does not retain all the product. Thus, the origin of this behaviour has been searched by a comparative study of adsorption-desorption phenomena. A conventional processing of experimental data for adsorption and desorption isotherms showed that organic clay soil is indeed the most adsorbing and suitable system for retaining the product. The processing of experimental data on the adsorption kinetics by means of different mathematical models provided an explanation of carbofuran behaviour in these two soils.

1. INTRODUCTION

Literature results tend to show that the movement of carbofuran in soils is relatively limited [1]–[3]. On the other hand, our own work carried out for over a two-year period with two types of soil (clay and loamy clay soil) sown with maize led to somewhat different results [4]. Indeed, the values obtained generally display both a maximum in the concentration of the product at the surface and significant leaching.

Furthermore, comparison of the results obtained for each soil showed that the kinetics of disappearance and the leaching of carbofuran was much lower for the

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loamy clay soil. The latter, less rich in organic matter, should theoretically have a lower significant adsorption capacity than the clay soil [5]–[7]. Carbofuran movement should be then facilitated, which was not in the case of our experiments.

The better understanding of the behaviour of this insecticide in two soils is possible due to 1) determination of the adsorption and desorption isotherms so as to verify the abilities of the soils to retain carbofuran, 2) carrying out a laboratory study with soil columns, taking into account the role of aggregate size, the applied dose, and the percolation speed of the water in the movement, as well as leaching of the product through the two soils.

2. MATERIALS AND METHODS

2.1. SOILS

The soils utilized were taken from the plough layer in fields which had been used for experimental purposes under natural conditions [4]. Their physicochemical characteristics are presented in tab. 1.

Table 1

Physicochemical characteristics of soils

Soil	pH (water)	Carbon (%)	Sand (%)	Loam (%)	Clay (%)
Clay	7.3	2.5	3.9	35.7	51.7
Loamy clay	6.4	1.6	20.3	39.4	24.2

2.2. ADSORPTION AND DESORPTION ISOTHERMS

For adsorption 9 replicates of 5 carbofuran concentrations, 0.82, 1.75, 3.60, 7.40 and 14.70 $\mu\text{g}/\text{cm}^3$, were used. To each of the 9 glass tubes containing 2 g of sieved soil (1 mm fraction) 5 cm^3 of aqueous solution of labeled ^{14}C -carbofuran was added. The mixture was shaken for 48 h at $20 \pm 1^\circ\text{C}$ and then centrifuged at 3 220 g for 20 min in a Beckman J2-21 centrifuge at $20 \pm 1^\circ\text{C}$. One cm^3 of the supernatant from each test in 10 cm^3 Instagel (Packard) was subsequently analysed by means of a Tri-Carb 460 Packard Liquid Scintillator. For desorption, after pipetting 1 cm^3 for adsorbed carbofuran quantification, another 2.5 cm^3 were taken from each of the 3 tubes for all concentrations tested and then 5 cm^3 of water were added to each sample. After 48 h shaking, the amount of carbofuran desorbed was determined in the same manner as for adsorption study.

2.3. SOIL COLUMNS

The air-dried soils were homogenized and sieved so as to obtain two kinds of samples in which the aggregate sizes were comprised between 0 and 2 mm or between 1 and 2 mm.

Columns of polyvinylchloride (PVC), 35 cm high and 4.3 cm in inner diameter, were then filled with 370 g of soil and lightly vibrated to obtain a height of 22 or 24 cm of earth according to the aggregate size. Treatment took place during the preparation of the columns, the product being applied in the form of CURATER[®] (5% carbofuran) at a depth of 3 cm. Two doses, equivalent to 12 or 36 kg of product/ha, were used. After treatment, the columns were saturated due to rising capillarity. Two regimes of percolation, free or controlled, were tested for a volume of water equivalent to 230 mm precipitation, being average in the Lorraine region in the period of mid April to late June.

For the controlled percolation, a peristaltic pump linked to the output of the columns ensuring a flow rate of 1 cm³/min was used. The water was poured in three 100 cm³ fractions and a fourth one of 30 cm³ was supplied to the tops of the columns every 12 hours. Three 100 cm³ fractions were obtained as well as a fourth one of 50 or 87 cm³, depending on the aggregate size.

As regards the free percolation, the same total volume of water was supplied in a continuous manner. Percolation lasted about two hours and a single fraction of water was obtained. Then, the soil columns were frozen at -18°C, and their content was divided into fractions corresponding to the depths: 0-5, 5-10, 10-15, 15-20, and 20-22 cm (or 24 cm, according to aggregate size). Each soil fraction was then dried at room temperature, homogenized, passed through a 2 mm mesh sieve, and finally stored, similarly as in the case of water fractions, at -18°C until analyzed.

For soil extraction, the method of CASSIL et al. [8], [9], as modified by ARCHER et al. [10], was adopted. Each soil sample was dried at room temperature, ground, and passed through a 2 mm mesh sieve. Fifty grams of soil was refluxed in a 250 cm³ flask with 100 cm³ of 0.25 M HCl for 1 h at 100°C. The resulting two-phase mixture was filtered under vacuum, and the soil residue was washed with 25 cm³ of hot 0.25 M HCl. Residues in the filtrate aqueous phase were extracted twice, in a separatory funnel, with 125 cm³ of dichloromethane. The extraction solvent was then evaporated at 35°C under vacuum and residues were recovered in 2 cm³ of methanol for gas chromatographic analysis. Under these conditions, extraction efficiency was 74 ± 4%.

For water, 200 cm³ of each sample were extracted twice with 200 cm³ dichloromethane in a separatory funnel, then the dried residues were recovered in 2 cm³ of methanol. Extraction efficiency was 85 ± 3%.

Derivatized carbofuran residues [11], [12] were quantified with a Varian 1400, using an AFID detector. The glass column (1.2 m × 3.2 mm) was packed with chromosorb GAW-DMCS (60-80 mesh) and with 10% UCON LB-500X + 0.5% of

KOH. The following conditions were created: column, injector, and detector temperatures of 120, 170, and 240°C, respectively, N₂ carrier gas at 20 cm³/min, and air and hydrogen, 170 and 3 cm³/min, respectively. 2 μdm³ of a mixture containing 950 dm³ of extract and 50 dm³ of 0.25 M NaOH in methanol was injected.

3. RESULTS AND DISCUSSION

The coefficients of linear regression (tab. 2) show that the L-type isotherms obtained are well described by the Freundlich equation. The adsorption constant *K* for the clay soil with the higher organic matter content (tab. 1) is greater than that for the loamy clay soil. This is in agreement with the relationship between the organic matter content of a soil and its adsorption capacity as shown by JAMET and PIEDALLU [5], MOREALE and Van BLADEL [6], and GARG and AGNIHOTRI [7], but in contradiction with our observations under natural conditions [4]. Indeed, leaching of the carbofuran through the clay soil was greater than that observed in the loamy clay one.

Table 2

Adsorption isotherms' constants of carbofuran in the two soils
(adjusted to the Freundlich equation $x/m = KC^{1/n}$; *K* and $1/n$ were estimated by
a linear regression of the logarithmic transformation of x/m and *C* mean values;
 $n = s$)

Soils	Adsorption			Desorption		
	<i>K</i>	$1/n$	<i>r</i> *	<i>K</i>	$1/n$	<i>r</i> *
Loamy clay	0.478	0.900	0.999	0.618	0.986	0.997
Clay	0.629	0.941	0.999	0.980	0.964	0.998

* $r = 0.917$; $df = 4$; $P < 0.01$.

Furthermore, the Freundlich desorption constants (tab. 2) were greater than those of the adsorption. On the other hand, the adsorption constant *K* for the clay soil was higher than that for the loamy clay one. This confirms a greater aptitude of the clay soil to retain the insecticide.

These experimental conditions, however, were far from those in the field. Thus, study of the leaching of the product, based on soil columns which at least partially imitate field conditions, appeared to be better adapted to these observations.

The different results presented here are expressed as percentages, and each of the values represents the mean value of five replicates.

3.1. SOIL EFFECT

In the first experiment, the influence of the type of soil on the movement of carbofuran was examined in soil columns containing aggregates of sizes ranging within 0 and 2 mm. The results obtained with a dose equivalent to 12 kg/ha (fig. 1a) show a better carbofuran leaching in the clay soil. Moreover, the elution curves (fig. 1b) prove that the product leaves this soil much more rapidly and that its overall

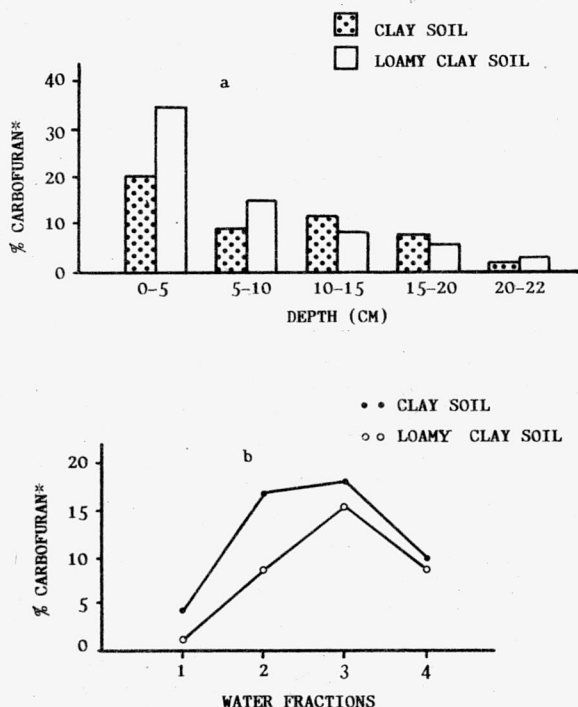


Fig. 1. Soil effect on migration and leaching of carbofuran

a) Distribution profile in columns. b) Elution in percolation water. * Carbofuran percent in total analyzed product

quantity transported by the percolation waters is higher. These results are in agreement with those observed in the field [4] but in contradiction with those reported by JAMET and PIEDALLU [5] who found a reduction in carbofuran mobility when the content of organic matter in soil increased. In our experiments, it can be hypothesized that during the percolation process the loamy clay soil fragile structure produces finer particles. This would increase the adsorption surface and hinder movement of the insecticide.

3.2. EFFECT OF AGGREGATE SIZE

Elimination of the fine aggregate fraction (0–1 mm) increased product movement in the soil (figs. 2a, 3a). A decreased concentration was observed at the surface of the column for the loamy clay soil as well as a concentration maximum which was displaced from the 0–5 cm level to the 15–20 cm one. There was a simultaneous increase in the quantities of product eluted by the percolation waters (figs. 2b, 3b). These results agree with those by HANCE [13] who showed that increasing the size of the aggregates reduced metribuzine retention in the soil.

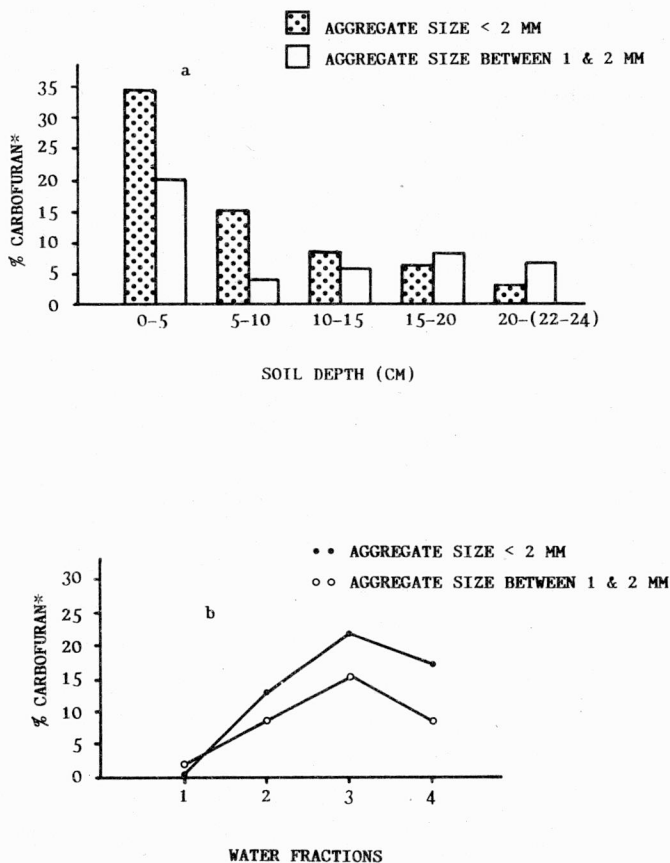


Fig. 2. Aggregate size effect of loamy clay soil on migration and leaching of carbofuran
 a) Distribution profile in columns. b) Elution in percolation water. * Carbofuran percent in total analyzed product

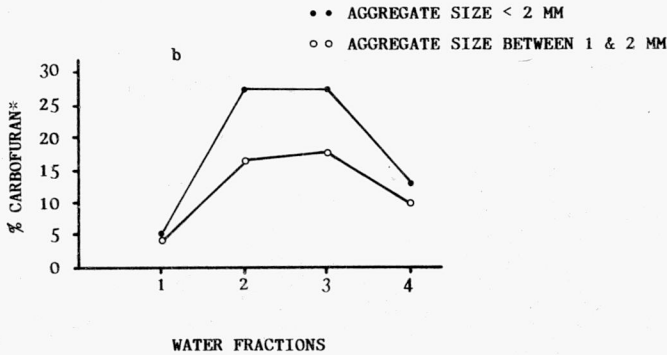
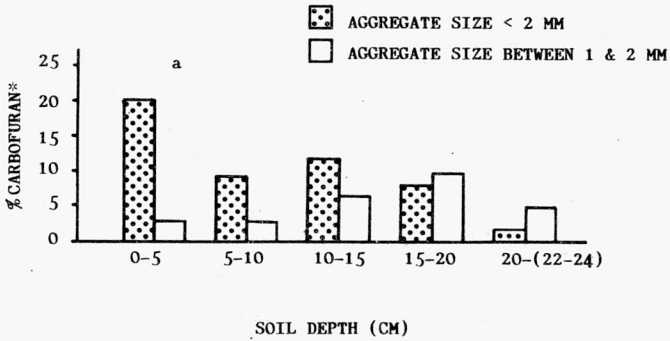


Fig. 3. Aggregate size effect of clay soil on migration and leaching of carbofuran. a) Distribution profile in columns. b) Elution in percolation water. * Carbofuran percent in total analyzed product

3.3. EFFECT OF THE DOSE

In soil columns constituted of 1 to 2 mm aggregates, increasing the dose from an equivalent of 12 kg/ha to 36 kg/ha leads to a proportional increase of the product, neither in the profile of the column (figs. 4a, 5a), nor in the percolation waters (figs. 4b, 5b). In the case of such a high dose, a considerable quantity of the product remained simply at the surface of the column (0-5 cm level).

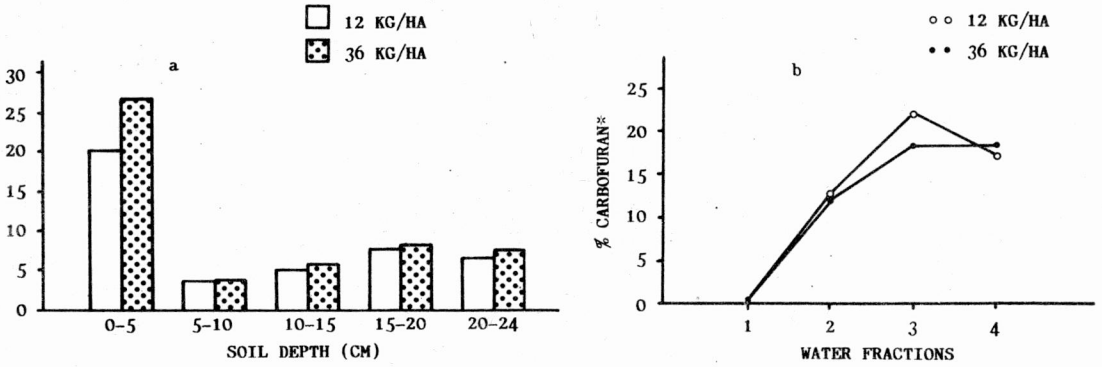


Fig. 4. Dose effect on migration and leaching of carbofuran in loamy clay soil
 a) Distribution profile in columns. b) Elution in percolation water. * Carbofuran percent in total analyzed product

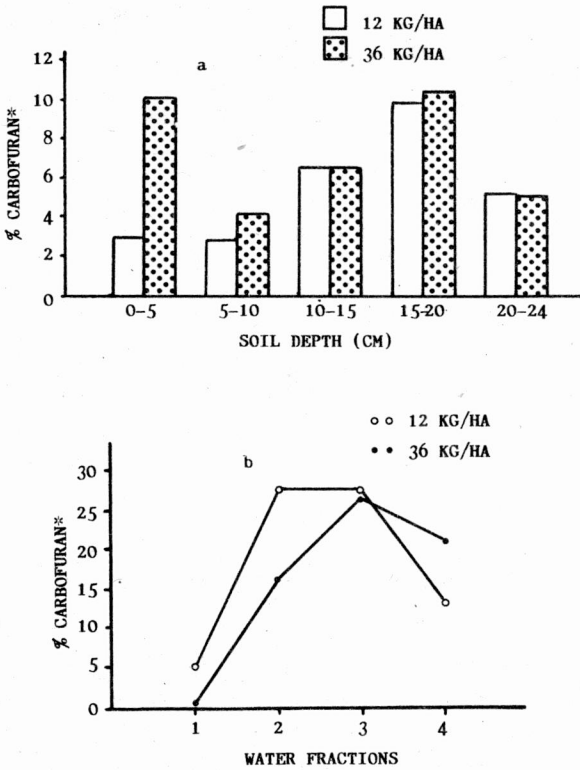


Fig. 5. Dose effect on migration and leaching of carbofuran in clay soil
 a) Distribution profile in columns. b) Elution in percolation water. * Carbofuran percent in total analyzed product

3.4. EFFECT OF PERCOLATION SPEED

All the above examinations were carried out at a $1 \text{ cm}^3/\text{min}$ flow rate. By analogy with natural conditions, another possibility was to allow the water to flow freely through the columns. The equivalent of 230 mm of precipitation was supplied in a continuous fashion to the surface of the soil column composed of particles between 0 and 2 mm. In this case percolation required 2 hours, in other words, the speed was about three times greater than in the previous cases. These experimental conditions cause the shortening of the contact time between the carbofuran and the humid soil by 36 hours.

The results obtained showed that the distribution of the product was almost identical for the two soils. The maximum insecticide concentration was found at the surface of the column in both cases (figs. 6, 7). However, the concentration observed

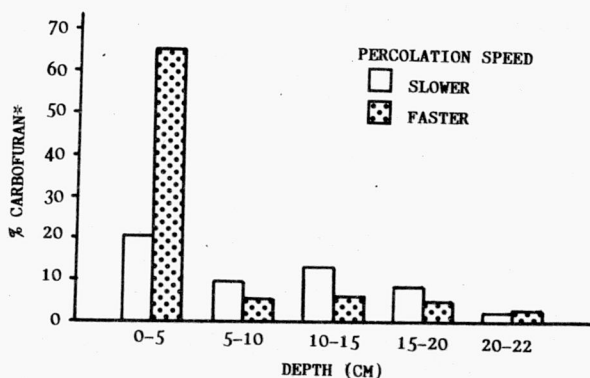


Fig. 6. Water percolation speed effect on carbofuran migration in loamy clay soil

* Carbofuran percent in total analyzed product

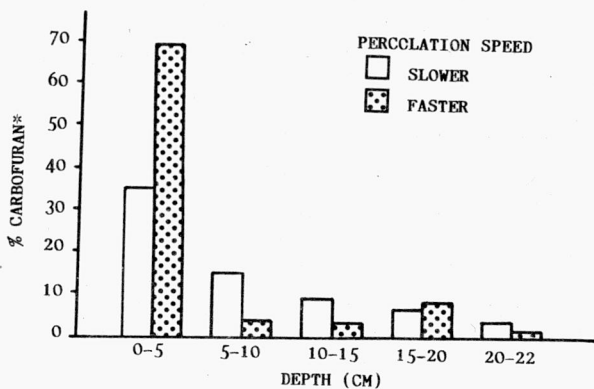


Fig. 7. Water percolation speed effect on carbofuran migration in clay soil

* Carbofuran percent in total analyzed product

at this level (70% of the applied product) was too high with respect to the values stated in the previous experiments due to the insolubilization of the carbofuran microgranular formulation (CURATER®). The reduction in contact time in the product-water-soil system suggests a similar movement of carbofuran in the two soils.

4. CONCLUSIONS

As shown by the results obtained following the modification of certain experimental parameters, such as the aggregate size or the percolation speed, carbofuran movement can be significantly modified, and the adsorbing power of the soil suppressed.

The difference in behaviour of the insecticide under natural conditions in the loamy clay soil and the clay soil may be due to structural differences.

Heavy soils are always more difficult to prepare for seeding. However, the insecticide adsorption kinetics on the two soils should also be considered, since it can also modify the movement of the product, after its solubilization from its microgranular formulation (CURATER®).

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BADANIA MIGRACJI WĘGLOFURANU W GLEBACH

I. WPŁYW STRUKTURY GLEBY, PRĘDKOŚCI PRZESĄCZANIA I DAWKI NA MIGRACJĘ I WYPŁUKIWANIE WĘGLOFURANU W DWÓCH RODZAJACH GLEBY

W naturalnych warunkach zanieczyszczenie wód drenażowych glebą gliniastą bogatą w substancje organiczne jest znacznie większe niż zanieczyszczenie glebą piaszczysto-gliniastą. Aby wyjaśnić to zjawisko zbadano w laboratoryjnych kolumnach z glebą wpływ struktury gleby, prędkości przesączania

i dawki produktu na migrację i wypłukiwanie węglofuranu. Te parametry modyfikują przenoszenie środka owadobójczego, jakkolwiek zaobserwowano, że gleba o teoretycznie większej pojemności adsorpcyjnej nie zatrzymuje produktu w całości. Porównawcze badania zjawisk adsorpcji-desorpcji pozwoliły wyjaśnić to zjawisko. Konwencjonalne przetworzenie danych doświadczalnych dla izoterm adsorpcji i desorpcji wykazało, że istotnie gleba gliniasta jest systemem najlepiej adsorbującym produkt. Zjawisko migracji węglofuranu w tych dwóch glebach zostało wyjaśnione dzięki przetworzeniu danych doświadczalnych, dotyczących kinetyki adsorpcji za pomocą różnych modeli matematycznych.

ИССЛЕДОВАНИЯ МИГРАЦИИ КАРБОФУРАНА В ПОЧВАХ.

I. ВЛИЯНИЕ СТРУКТУРЫ ПОЧВЫ, БЫСТРОТЫ ФИЛЬТРИРОВАНИЯ И ДОЗЫ НА МИГРАЦИЮ И ВЫМЫВАНИЕ КАРБОФУРАНА В ДВУХ ВИДАХ ПОЧВЫ

В натуральных условиях загрязнение дренажных вод глинистой почвой, богатой органическими веществами, является значительно большим, чем загрязнение суглинистой почвой. Чтобы выяснить это явление в лабораторных колоннах с почвой исследовано влияние структуры почвы, быстроты фильтрования и дозы продукта на миграцию и вымывание карбофурана. Вышеперечисленные параметры модифицируют перемещение инсектицида, хотя наблюдали, что почва теоретически большего адсорбционного объема не задерживает продукта в целом. Сравнительные исследования явлений адсорбции-десорбции позволили выяснить это явление. Конвенциональная обработка экспериментальных данных для изотерм адсорбции и десорбции обнаружила, что действительно глинистая почва является системой адсорбирующей продукт лучше всего. Явление миграции карбофурана в этих двух почвах было выяснено благодаря обработке экспериментальных данных, касающихся кинетики адсорбции при помощи разных математических моделей.