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Carbofuran Sorption Kinetics by Corn Crop Soils

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This work forms part of an ongoing program of research into the distribution and dynamics of pesticides in rural ecosystems. Basic to evaluation of the effectiveness and environmental risks posed by pesticides are the rates at which they are distributed among soil and water. The carbamate carbofuran is a versatile, broad-spectrum systemic insecticide-nematicide registered for use on a variety of crops. It is a particularly effective treatment for control of soil-insect pests (Mora et al. 1996). Normally, this chemical is applied directly to the soil. It is moderately persistent, generally retaining its biological activity from a single application throughout the crop season. Taking into account that this nematicide is applied into the soil 1 to 5 cm deep, as much as 11% of the applied carbofuran may be transported with surface waters in runoff events (Nicosia et al. 1991). Studies have been reported regarding carbofuran adsorption in soils from India (Singh et al. 1990), Kenya (Lalah and Wandiga 1996) and also from the UK, Turkey and Cyprus (Yazgan et al. 2005). In Galicia (NW Spain), soils are acid (Carballas et al. 1978). The dynamics of carbofuran in different agricultural soils from Galicia was studied, with emphasis on sorption kinetics. The purpose of this research was to evaluate factors affecting sorption kinetics of Carbofuran by corn crop soils.

MATERIALS AND METHODS

Carbofuran (2,3-dihydro-2-2-dimethyl-7-benzofuranyl-N-methylcarbamate) was obtained from Dr. Ehrenstorfer (Ausburg, Germany) with a listed purity of 99.5%. Soil samples were taken from the plough layer (0-20 cm) of four corn fields located in Galicia (NW Spain). Samples were air dried and sift through a 2 mm mesh. The main characteristics of the soils are shown in Table 1. The particle size fractions > 0.05 mm were determined by wet sieving and those < 0.05 mm by the International Pipette method (Gee and Bauder, 1998). Organic carbon content was determined by oxidation with potassium dichromate (Guitián and Carballas 1976). Total nitrogen and sulphur were determined by means of an autoanalyser. The cationic exchange capacity (CEC) was estimated by the addition of alkali elements (Na, K, Ca and Mg) extracted with ammonium chloride (Sumner and Miller 1996) plus the interchangeable-Al extracted with 1 M potassium chloride. Free Fe was extracted with sodium dithionite-citrate (Fe_d) (Holmgren 1967).

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Table 1. Physicochemical properties of soils.

Soil	Clay %	Silt %	Sand %	pH H_2O	pH KCl	C %	N %	S gKg^{-1}	CEC cmol©Kg^{-1}	Fe_d gKg^{-1}
1	26	36	38	5.1	4.6	6.6	0.8	0.8	6.8	52
2	28	38	34	5.1	4.5	6.8	0.6	0.3	5.5	44
3	10	16	74	4.4	3.7	3.0	0.2	0.1	4.4	2
4	9	10	81	4.1	3.6	3.3	0.3	0.4	4.3	4

C, N, S = Carbon, Nitrogen, Sulphur Content; CEC = Cationic Exchange Capacity; Fe_d = Dithionite Citrate Extractable Fe

All HPLC measurements were taken using a Thermo Separation Products (TSP) P2000 binary pump, equipped with a TSP AS1000 autosampler, a TSP SCM1000 vacuum membrane degasser and a Spectra-System UV2000 ultraviolet/visible detector. The optimized instrumental parameters for the chromatographic determination of carbofuran were as follows: injection loop, 100 μL; columns, A 5 cm x 4.6 mm i.d. stainless steel guard column packed with 40 μm Pelliguard LC-18 (Supelco), followed by a 15 cm x 4.6 mm i.d. stainless steel analytical column packed with 5 μm Symmetry C_{18} (Waters); elution conditions, isocratic elution at 50:50 acetonitrile/water at room temperature; flow rate, 1.5 mL/min; and UV detection operating at 278 nm.

Kinetics of carbofuran-soil interactions were examined by using the stirred batch incubation and extraction method. Five grams of air-dried soil were placed in 50 mL-Pyrex glass centrifuge tubes. The soil was wetted with 25 mL of 0.02 M NaCl containing 45 or 4.5 μM of carbofuran at a fixed pH of 5.0. The tubes were then placed on a rotary shaker for 1, 2, 4, 8, 16, 24 and 48 h incubation times and shaked at 200 rpm at room temperature (20 ± 2°C). After incubating the soil for the desired time, the samples were centrifuged (30 min, 4000 rpm) and the carbofuran concentrations in the clear supernatants were determined by HPLC-UV. Since samples were analyzed directly without any pre-analytical step, such as extraction, clean-up or concentration, recoveries were kept at about hundred percent. The quantity of carbofuran adsorbed by the soil samples was calculated as the difference between the initial concentration of carbofuran in the solution and the concentration remaining in the solution after contact with soil. All assays were carried out by triplicate. The effect of carbofuran concentration on adsorption at equilibrium after 48 h contact with soil was monitorized in the same way with concentrations ranging between 0.5 and 5.0 μM at a fixed pH of 5.0. All assays were carried out in triplicate. To evaluate the effect of pH, the adsorption experiments were carried out at different pH values (2, 5 and 8) and at a constant concentration of carbofuran (1.8 μM). Experimental procedure was as described above. The effect of Cu and Zn (added as nitrates with a purity > 99 %) on carbofuran adsorption was measured at an carbofuran concentration of 1.8 μM, while Cu and Zn concentrations were at 1.6 mM in different experiments. The copper and zinc contents of supernatants were determined by flame atomic absorption spectrophotometry using a Thermo Solar M series spectrometer.

RESULTS AND DISCUSSION

To interpret experimental data on carbofuran kinetics in the batch experiments, three consecutive steps were considered. The first is related to carbofuran transport across the boundary layer to the exterior of active soil surfaces (i.e., where adsorption or degradation occurs). Then, the carbofuran is transported within the pores to the inner active surfaces. Finally, chemical o physical binding, or degradation on surface occurs.

Table 2. Equations tested to describe the dynamics of carbofuran.

Kinetic equation	**Parameters**
First order: $\ln X^* = \mathrm{Ln}\, X - k_1 t$	k_1 min^{-1}
Second order: $1 / X^* = 1 / X + k_2 t$	k_2 (kg mg^{-1} min^{-1})
Simplified Elovich: $X^* = \mathrm{a} + \mathrm{b}\, \mathrm{Ln}\, t$	a (mg kg^{-1}), b (mg kg^{-1})
Parabolic diffusion: $X^* = X + D t^{1/2}$	D (mg kg^{-1} min$^{-1/2}$)
Power law: $X^* = k t^b$	b, k (mg kg^{-1} min^{-b})

X: equilibrium adsorbed concentration (mg kg^{-1}) in soil
X^*: non equilibrium adsorbed concentration (mg kg^{-1}) in soil.

In most cases, the dynamic processes in soils are limited by diffusion. Several models were used in order to identify the mechanism controlling adsorption. Therefore, first order, Elovich, power-function and parabolic diffusion models were tested. Model equations are listed in Table 2. The best results were obtained for Elovich model. This model describes a number of reaction mechanisms that include bulk and surface diffusion. A linear relationship by plotting transient adsorbed concentration (X^*) versus Ln(t) was obtained (Figure 1). The fitting of results for an initial concentration of carbofuran in suspension of 45.0 μM to simplified Elovich model shows that kinetic rates are quite similar for all soils (Table 3). Also, note that X^* increases at incubation times of 48 h, suggesting that diffusion is still the limiting step at late stages of the process.

Table 3. Simplified Elovich kinetic model*.

Soil	b	a	r^2
		$C = 45.0$ μM	
1	0.60	7.79	0.9641
2	0.69	6.30	0.9351
3	0.77	0.85	0.9786
4	0.78	3.41	0.9623
		$C = 4.5$ μM	
1	0.19	0.73	0.9657
2	0.14	0.48	0.9919
3	0.14	0.30	0.9999
4	0.14	0.70	0.9890

$X^* = \mathrm{a} + \mathrm{b}\, \mathrm{Ln}\, t$ (a (mg kg^{-1}), b (mg kg^{-1}))

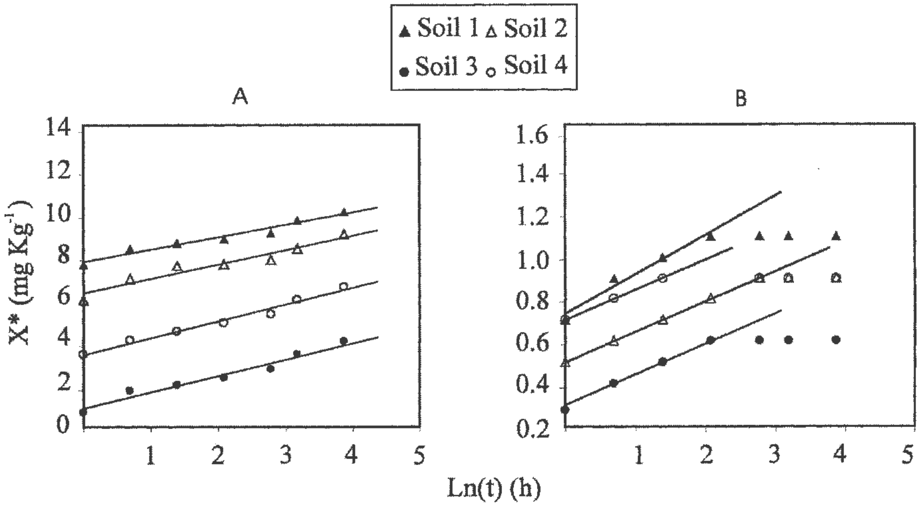

Figure 1. Linealized layout of the adsorption kinetic data for an initial concentration of carbofuran of 45.0 µM (A) and of 4.5 µM (B). Linear regression lines were calculated for the straight relationship occurring in < 16 h of incubation. Standard deviation lower than 3%. Fitting results in Table 3.

The kinetics with 4.5 µM carbofuran can also be described by Elovich model, however, at late stages the adsorption rate decreased. This behavior suggests that at low concentrations in solution diffusion decreases, as expected from the low concentration gradient between the bulk solution and water nearby the binding soil surface. The average kinetic constant rate (a) of Elovich model for 45.0 µM carbofuran was about 4.7 times higher than in the lower concentration. Experimental data at equilibrium were fitted to Freundlich equation:

$$X = K_F C^{1/n} \qquad \text{Eq. 1}$$

where X ($\mu g\ g^{-1}$) is the amount adsorbed per unit mass, and C ($\mu g\ L^{-1}$) is the equilibrium concentration, while K_F($L\ g^{-1}$) and 1/n (dimensionless) are constants. Fitting was done by the Levenberg-Marquardt least-squares algorithm.

The fits of experimental data for carbofuran adsorption (X *vs.* C) to eq. 1 are shown in Table 4. The equations provided significant r^2 values (higher than 0.95). K_f and 1/n were in the same order for all soils, even though soils 1 and 2 have larger contents of Fe_d, clay and organic matter than soils 3 and 4 (Table 1).

Table 4. Freundlich equation parameters for carbofuran adsorption.

Soil	K_F	1/n	r^2
1	0.43	0.75	0.951
2	0.46	0.68	0.994
3	0.36	0.69	0.955
4	0.52	0.61	0.986

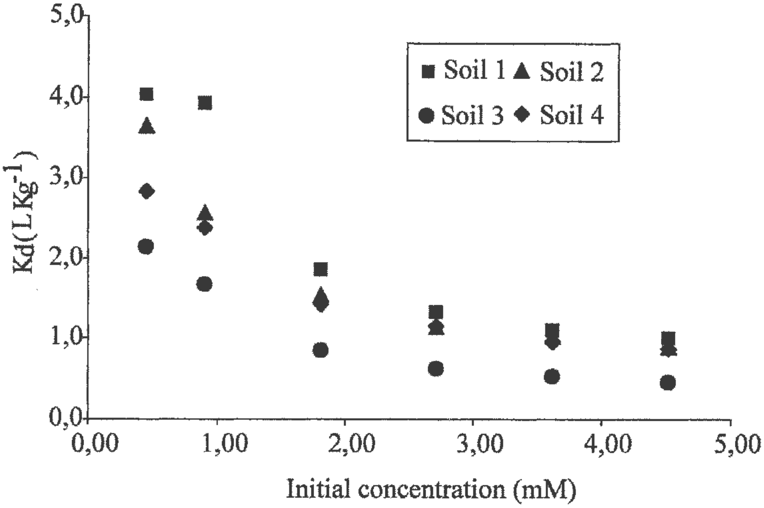

Figure 2. Relation between the carbofuran distribution coefficient (K_d) and carbofuran input concentrations. .

It is possible to describe the adsorption process by focusing on K_d, the carbofuran distribution coefficient, which reflects a balance between carbofuran levels bound to the solid phase and dissolved into the liquid phase (μg kg^{-1}/μg L^{-1}). A large K_d value represents high soil affinity by carbofuran. As it can be seen in Figure 2 the K_d decreased while increasing initial carbofuran concentration, but also when CEC and pH (KCl) levels in soils are lower (Table 1). The decrease in K_d with the increase in the initial concentration of carbofuran might be related to the adsorption of carbofuran to high-affinity sites at low concentrations (specific adsorption) and to low-affinity sites at high concentrations (non-specific adsorption). The rate of decrease of K_d is small (from 4.0 to 0.5 L kg^{-1}), suggesting that this behavior is preferentially due to the adsorption taking place via electrostatic interactions This hypothesis was formulated for soil adsorption of cations such as Cu, Pb, Zn and Ni (Basta and Tabatabai 1992); carbofuran under acid media has a positive charge and can behave in the same way. Previous studies using data obtained with surface or near-surface soils have established that carbofuran sorption is proportional to their organic matter content (Singh et al. 1990; Jana and Das 1998). The clearest correlation we found is that of CEC on carbofuran adsorption.

The influence of pH upon the adsorption process was checked at an initial concentration of 1.8 μM carbofuran. The experiments were carried out at pH 2, 5 and 8 (Table 5). Carbofuran adsorption to the soils was higher when the pH is lower. At pHs 5 and 8 the cationic carbofuran percentage was lower than at pH 2, which reduces electrostatic interactions with the negative charge of the soil. An increase of pH can also produce the dissolution of some organic matter (Lee and Farmer 1989; Kookana et al. 1998) and reduce carbofuran adsorption because of the decrease in adsorption sites.

Table 5. Carbofuran adsorption in μg g^{-1} (adsorption percentages in brackets) *vs.* pH.

	pH		
Soil	2	5	8
1	0.6 (30)	0.5 (25)	0.5 (25)
2	0.6 (30)	0.5 (25)	0.4 (20)
3	0.4 (20)	0.3 (15)	0.3 (15)
4	0.5 (25)	0.4 (20)	0.4 (20)

Carbofuran input level= 1.8 μM.Standard deviation lower than 3%.

Table 6. Influence of Copper and Zinc on carbofuran adsorption (μg g^{-1}).

	Adsorbed carbofuran (μg g^{-1})		
Soil	Alone	Cu	Zn
1	0.54 ± 0.01	0.55 ± 0.01	0.52 ± 0.02
2	0.47 ± 0.01	0.50 ± 0.03	0.45 ± 0.01
3	0.29 ± 0.01	0.37 ± 0.01	0.27 ± 0.01
4	0.44 ± 0.04	0.47 ± 0.01	0.41 ± 0.01

Carbofuran input level= 1.8 μM., Cu and Zn at 1.6 mM.

Carbofuran adsorption at different pHs was higher for soils 1 and 2 (with larger contents of Fe_d, clay and organic matter) than for 3 and 4 (Table 1). It is also observed that the change in the adsorption percentage of carbofuran for all soils at different pHs is small (about 5%). The effect of Cu and Zn on carbofuran adsorption was studied at constant concentration of carbofuran and metals keeping the initial pH at 5.0. Both Cu and Zn can coexist together with carbofuran in soils because of agricultural practices. Cupper slightly enhanced carbofuran adsorption in sample 3. Zinc produced no effect on carbofuran adsorption (Table 6). The adsorption of Cu, but especially of Zn, was severely reduced by the presence of carbofuran in the soils (Table 7). This can be attributed to the formation of metal-pesticide complexes reducing metal affinity by sorption sites, which is reminiscent of Mortland's finding (1970) that desorption of the herbicide 3-aminotriazole from clay was greatest when the dominant exchangeable cation was calcium, presumably due to the coordination of the herbicide to the cation being weakest for this metal.

Table 7. Influence of carbofuran on Copper and Zinc adsorption (μg g^{-1}).

Sample	Carbofuran Concentration (μM)	Cu adsorption	Zn adsorption
1	0.0	0.8	0.7
	1.8	0.2	<0.1
2	0.0	0.8	0.5
	1.8	0.2	<0.1
3	0.0	0.5	0.4
	1.8	0.1	<0.1
4	0.0	0.5	0.4
	1.8	0.1	<0.1

Cu and Zn input levels= 1.6 mM.

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