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Journal of Hazardous Materials

Adsorption and desorption kinetics of carbofuran in acid soils

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ARTICLE INFO

ABSTRACT

Carbofuran adsorption and desorption were investigated in batch and stirred flow chamber (SFC) tests. The carbofuran adsorption capacity of the soils was found to be low and strongly dependent on their clay and organic carbon contents. Carbofuran sorption was due mainly (>80%) to fast adsorption processes governed by intraparticle diffusion. The adsorption kinetic constant for the pesticide ranged from 0.047 to 0.195 min^{-1} and was highly correlated with constant n in the Freundlich equation ($r = 0.965$, $P < 0.05$). Batch tests showed carbofuran desorption to be highly variable and negatively correlated with eCEC and the clay content. The SFC tests showed that soil organic carbon (C) plays a key role in the irreversibility of carbofuran adsorption. Carbofuran desorption increased rapidly at C contents below 4%. The desorption kinetic constant for the compound (0.086–0.195 min^{-1}) was generally higher than its adsorption kinetic constant; therefore, carbofuran is more rapidly desorbed than it is adsorbed in soil.

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1. Introduction

Pesticides are very intensively used against crop diseases in many agricultural areas [1,2]. In some, their use has increased markedly during the last few years [3] despite their well-known hazards for human health [4,5]. Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methylcarbamate) is a carbamate pesticide used against a wide range of insects adversely affecting a large number of crops such as potatoes, corn, rice, alfalfa, grapes and other foodstuffs. Carbofuran is directly sprayed onto soil and plants immediately after emergence in order to control beetles, nematodes and rootworms. According to EPA [6], there are considerable risks associated with carbofuran in food and drinking water, risks to pesticide applicators and risks to birds exposed in treated fields. Also, not all products containing carbofuran meet safety standards. This has led EPA to remind growers that carbofuran should not be used on any food crops since it was banned on December 31, 2009 [6].

Carbofuran is moderately persistent in soils [7], where it has a half-life of 30–117 days [8] depending on the particular agroenvironmental conditions (e.g. soil organic matter and moisture contents, and pH); also, it is highly mobile in soils and easily reaches waters by effect of its high solubility [8]. As a result, carbofuran has a high potential for contaminating groundwater in aquifers, which it may enter through leaching and runoff from treated fields. Monitoring pesticide trace levels in waters is important for human health protection and environmental control. The European Union has set a maximum allowed concentration of 0.5 μg/L for the combination of all pesticides, and 0.1 μg/L for individual compounds, in drinking water [9].
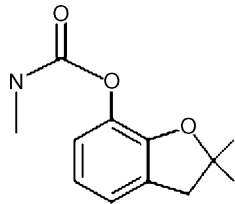
The fate of pesticides such as carbofuran in soil is influenced by a number of processes [8] specially prominent among which are adsorption and desorption by soil constituents (organic matter and clay, mainly) [10]. Adsorption in soil avoids the presence of pesticides in surface and ground waters, but hinders their volatilization and biodegradation; on the other hand, desorption into the soil solution facilitates runoff and leaching into water bodies, but makes the pesticide available to soil microorganisms and facilitates biodegradation as a result. The risk of carbofuran damages to plants and microorganisms, or its presence at high concentrations in nearby waters, depends on its concentration in the soil solution, which is in turn a function of the equilibrium governing its adsorption on, and desorption from, soil particles. A better understanding of the underlying mechanisms for this equilibrium should facilitate the evaluation of the potential adverse effects of carbofuran on agriculture and the environment.

The carbofuran adsorption and desorption capacity of different types of soils has been the subject of several studies [10–13] which have revealed that the two processes are governed mainly by the organic matter and clay contents of the soil in addition to its cation exchange capacity. By contrast, the adsorption and desorption kinetics of carbofuran in soils are less well-known. Adsorption/desorption kinetics can be examined by using various techniques [14]. Although many authors have studied carbofuran

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Table 1
Chemical structure and properties of carbofuran.

Common name	Carbofuran
Chemical structure	
Name	2,3-dihydro-2-2-dimethyl-7-benzofuranyl-N-methylcarbamate
CAS n°	1563-66-2
MW[a]	221
S[b] ($g L^{-1}$)	0.33
log P_{ow}[c]	1.7
K_{oc}[d]	209
Soil half-life[e]	50

Data were obtained from SciFinder® (https://scifinder.cas.org/).

[a] Molecular weight.
[b] Solubility in water at 25 °C.
[c] Octanol/water partition coefficient at 25 °C.
[d] Partition coefficient normalized to organic carbon content ($mL g_{oc}^{-1}$ or $L kg_{oc}^{-1}$).
[e] Aerobic soil half-life (Avg, days).

sorption kinetics in soils and other materials with batch techniques [15–17], batch tests are subject to a number of shortcomings [14] that are efficiently circumvented by the stirred flow chamber technique [18], which combines the best features of batch and flow methods while avoiding or lessening many of their limitations [19]. However, carbofuran sorption kinetics has seemingly never to date been studied with the stirred flow chamber technique. In this work, we used this technique for the first time to investigate carbofuran adsorption/desorption kinetics.

Acid soils are present in large areas of Western Europe where intensive agriculture relying on fertilizer and pesticide application has been practiced since the second half of the 20th century. This led us undertake a study of the carbofuran adsorption and desorption characteristics in acid soils with the aims of (a) providing a detailed description of carbofuran adsorption/desorption on acid soils; (b) relating the sorptive behaviour of carbofuran to soil characteristics; (c) examining the adsorption and desorption kinetics of carbofuran in acid soils; and (d) identifying the principal factors governing them in acid soils. To this end, we used batch tests in order to establish the effect of the concentration of carbofuran at equilibrium on its adsorption characteristics and stirred flow chamber tests to examine the carbofuran adsorption/desorption kinetics. Wherever possible, the results obtained with the two methods were compared.

2. Materials and methods

2.1. Chemicals

Carbofuran (2,3-dihydro-2-2-dimethyl-7-benzofuranyl-N-methylcarbamate) was obtained from Dr. Ehrenstorfer Lab. (Augsburg, Germany) in 99.5% purity. Table 1 shows the chemical structure and properties of carbofuran. Ultrapure water was obtained from a Milli-Ro water purification system. Acetonitrile was supplied in analytical reagent grade from Merck (Darmstadt, Germany) and all other chemicals were purchased from Panreac (Barcelona, Spain). All aqueous solutions were homogenized by vortex agitation.

2.2. Soil sampling

Soil sampling was carried out in a former lake area which was intensively drained for agricultural purposes in the mid-20th century. Because of its present flat relief, a shallow groundwater table can be seen during the rainy season in some areas. For the past 50 years, these soils have been intensively managed to grow potatoes and wheat, mainly, under a crop rotation scheme.

A total of 16 soil samples were collected from a soil depth of 0–20 cm by using an Edelman probe (Giesbeck, The Netherlands) in sixteen crop stands; care was exercised to span as wide as possible a range of organic matter contents. According to the IUSS Working Group-WRB 2006 [20], the soils were mostly Phaeozems and Umbrisols. Phaeozems can be classified as Haplic Phaeozems (Anthric) or Stagnic Phaeozems (Anthric) when they exhibit signs of hydromorphy. When base saturation is less than 50% at any soil depth, soils are classified as Mollic Umbrisols (Anthric) or Stagnic Umbrisols (Anthric) depending on the presence or absence of reductive conditions at any time during the year.

After field collection, soil samples were air-dried and sieved through a 2 mm mesh, homogenized and stored in polypropylene bottles prior to analysis.

2.3. Soil characteristics

The proportions of sand (2–0.05 mm), silt (0.05–0.002 mm) and clay (<0.002 mm) of the soils were determined by wet sieving for the size fractions greater than 0.05 mm and with the international pipette method for all others [21]. Total carbon content was determined on a ThermoFinnigan 1112 Series NC elemental analyser (Waltham, MA, USA). pH was measured at a soil/water ratio of 1:2.5, using a combined glass electrode 10 min after mixing [21]. The cation exchange capacity at soil pH (eCEC) was estimated as the combination of exchangeable base cations extracted by 0.2 M NH_4Cl [22] and exchangeable Al extracted by 1 M KCl [23]. Available phosphorus was determined with the Bray II assay [24]. Al oxyhydroxides were quantified by selective extraction with 0.5 M NaOH [25] and Fe oxyhydroxides by dithionite-citrate extraction [26]. The contents in Ca, Mg, Al and Fe were determined by flame atomic absorption spectrometry, and those in Na and K by flame atomic emission spectrometry.

2.4. Carbofuran adsorption and desorption

2.4.1. Batch tests

Before the effect of the concentration of carbofuran on its adsorption characteristics was studied, four soil samples (no. 2, 5, 14 and 15) were used to calculate the time needed to reach the equilibrium. To this end, an amount of soil of 1 g was shaken at different times with 10 mL of a 2.3 μM carbofuran solution containing 0.005 M $CaCl_2$ as background electrolyte for a variable length of time (0.5, 1, 4, 8, 16, 24 and 48 h). After incubation, the soil suspensions were centrifuged at 2000 rpm and passed through a polyester filter of 0.45 μm pore size from Macherey-Nagel (Düren, Germany). Previous tests revealed that these filters adsorb no carbofuran. The resulting supernatant was used to determine the pesticide by HPLC-UV. The amount of soil sorbed carbofuran was calculated by subtracting that of carbofuran in solution from the amount added. All tests were carried out in triplicate. Fig. 1 shows the amount of carbofuran adsorbed as function of time. Equilibrium was always reached after 8–16 h of incubation. Also, adsorption was negligible after 24 h of contact in all samples.

Soil adsorption batch tests with carbofuran were performed as follows: an amount of 1 g of soil was mixed with 10 mL of carbofuran aqueous solutions at concentrations ranging from 2 to 18 μM, all containing 0.005 M $CaCl_2$ as background electrolyte. After 24 h of
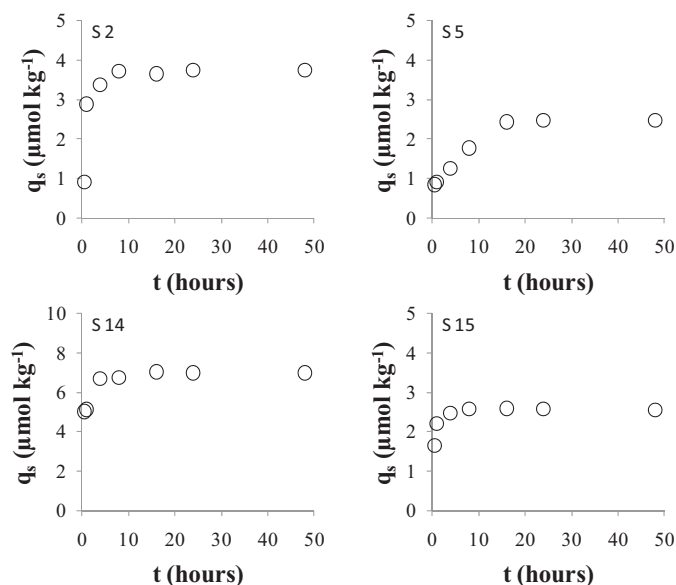
Fig. 1. Carbofuran adsorption kinetics in batch test.

shaking (long enough time as previously), the soil suspensions were centrifuged at 2000 rpm and passed through a filter of 0.45 μm pore size, the resulting supernatant being used to determine carbofuran by HPLC-UV. The amount of pesticide sorbed by the soil was calculated by subtracting that present in solution after 24 h of equilibrium from the amount initially added. Dissolved organic matter was determined from the absorbance at 400 nm [27]. Adsorption tests were carried out in triplicate. The limit of quantitation for carbofuran was 0.04 μmol kg⁻¹. The results were modeled by fitting to the equations of Freundlich (Eq. (1)) and Langmuir (Eq. (2)):

$$X = K_F C^n \tag{1}$$

$$X = \frac{K_L X_m C}{1 + K_L C} \tag{2}$$

where X is the concentration of carbofuran sorbed at equilibrium (μmol kg^{-1}); C is the concentration of carbofuran in the aqueous phase equilibrium after 24 h (μM); K_F (L^n, kg^{-1} μmol$^{(1-n)}$) and n (dimensionless) are the Freundlich coefficients; K_L (L, μmol^{-1}) is a Langmuir constant related to the energy of adsorption and X_m (μmol kg^{-1}) is the maximum adsorption capacity of the sample. The optimum parameter values for these equations were determined by non-linear regression analysis.

For the desorption tests, immediately following adsorption of carbofuran in the soils, the centrifuged residues were weighed to determine the amount of occluded solution and re-suspended in 10 mL of a 0.005 M CaCl₂ solution containing no carbofuran which was allowed to equilibrate for 24 h. Then, the samples were centrifuged at 2000 rpm to remove the supernatant. Occluded carbofuran was calculated as the difference between the final and initial weights, and desorbed carbofuran was then estimated and expressed in μmol kg⁻¹.

2.4.2. Stirred flow chamber (SFC) tests

Four soil samples (no. 2, 5, 14 and 15) were used to study carbofuran adsorption/desorption in an SFC-based reactor. The reactor used was one previously employed by the authors [28], albeit with slight modifications. The SFC reactor was made of polypropylene and had an inlet side port at the bottom and a cover with an outlet port at the top. Two polytetrafluoroethylene (PTFE) filters 10 mm in diameter and 0.45 μm in pore size were fitted immediately below the outlet port and over the inlet port to retain soil samples in the

chamber. The chamber volume was 1.5 cm³. Both the influent and effluent were carried through 0.5 mm i.d. PTFE tubing connected to a Gilson Minipuls 3 peristaltic pump (Gilson S.A.S., Villiers Le Bel, France). The temperature was kept at 25 ± 0.1 °C by placing the reactor chamber in a thermostated cabinet. The optimum flow rate (0.2 mL min⁻¹) was monitored throughout and found to oscillate by <3%. Stirring was provided by a PTFE-coated magnetic bar (3 mm × 1 mm) that was spun at 400 rpm to provide a constant flow. Effluent fractions were collected into 2 mL polypropylene Eppendorf vials by using a Gilson FC 203 G automatic fraction collector (Gilson S.A.S., Villiers Le Bel, France).

An amount of about 0.2 g of soil (<2 mm) was placed together with a magnetic stirring bar in the reaction chamber. A 4.5 μM carbofuran solution was circulated at the selected flow rate with CaCl₂ as background electrolyte (0.005 M). In total, 60 subsamples of 0.2 mL were collected in different vials (all filled in 1 min each). Immediately after carbofuran sorption, desorption tests were performed by circulating the background electrolyte (0.005 M CaCl₂). Then, 20 subsamples of 0.2 mL were collected in different vials (all filled in 1 min each). The subsamples from the adsorption and desorption runs were used to determine carbofuran by HPLC-UV

2.4.3. Carbofuran determination

Liquid chromatography (LC) analyses were carried out on a Dionex Corporation liquid chromatograph (Sunnyvale, USA) equipped with a P680 quaternary pump, an ASI-100 autosampler, a TCC-100 thermostated column compartment and a UVD170U detector. Chromatographic separations were done on a Symmetry C18 column (150 mm long, 4.60 mm i.d., 5 μm particle size) obtained from Waters (Milford, MA, USA) and a C18 guard column (4 mm long, 2 mm i.d., 5 μm particle size) packed with the same material. Elution conditions: isocratic elution with 30:70 acetonitrile/water at room temperature. The flow rate was 1 mL/min⁻¹ and UV detection performed at 278 nm.

2.5. Statistical analysis

Pearson correlation coefficients were determined and a stepwise multiple regression analysis was conducted in order relate adsorption/desorption variables to soil characteristics. Also, a paired two-sample test was used to compare carbofuran desorption at variable added concentrations. The results of these analyses were considered significant at a probability level of $P < 0.05$. All statistical processing was done with the Statistical Package for the Social Sciences (SPSS), version 17.0, for Windows.

3. Results and discussion

3.1. General soil characteristics

The general properties of the studied soils are summarized in Table 2. Most of the samples were loam or sandy loam in texture, and had an organic carbon content in the range 1.4–17%. Also, they were acid (pH 4.3–5.7) and exhibited a low cation exchange capacity (1.92–10.24 cmol$_{(c)}$ kg^{-1}). Their phosphorus contents were high and highly variable (15–703 mg kg^{-1}). Finally, their contents in Al oxyhydroxides ranged from 1.34 to 7.97 mg g^{-1} and those in Fe oxyhydroxides from 1.89 to 9.26 mg g^{-1}.

3.2. Carbofuran adsorption

3.2.1. Batch tests

Fig. 2 shows the carbofuran adsorption results for the 16 samples studied in the batch tests. Most of the carbofuran adsorption curves were of the L type, with a slope decreasing with increas-

Table 2
General soil characteristics.

| Sample	Sand	Silt	Clay	C	pH	eCEC	P (Bray-II)	Al_n	Fe_d
	%					$cmol_{(c)} kg^{-1}$	$mg kg^{-1}$	$mg g^{-1}$	$mg g^{-1}$
1	48	20	32	4.9	4.3	4.38	282	4.52	2.01
2	56	22	22	4.3	5.0	4.29	15	3.61	2.18
3	58	23	19	2.0	5.4	3.17	129	2.75	3.34
4	77	11	12	1.6	5.4	1.92	119	2.58	2.48
5	72	15	13	1.4	4.8	2.49	280	1.34	2.26
6	74	13	13	1.7	5.0	2.35	455	2.50	3.11
7	67	20	13	1.8	4.9	2.40	278	2.37	3.18
8	59	25	16	1.6	4.7	3.04	170	2.30	6.21
9	71	17	12	2.0	4.8	3.26	133	3.18	7.66
10	58	26	16	1.4	4.3	2.84	703	6.05	7.17
11	48	30	22	2.7	5.5	6.96	360	2.75	7.83
12	58	20	22	2.1	4.9	4.81	387	3.91	6.13
13	77	8	15	6.5	5.7	6.18	224	2.50	1.89
14	21	35	44	17.1	5.4	10.24	280	7.97	5.28
15	42	31	27	4.0	4.9	4.95	331	7.46	9.26
16	54	20	26	3.0	5.0	3.35	45	4.73	3.88
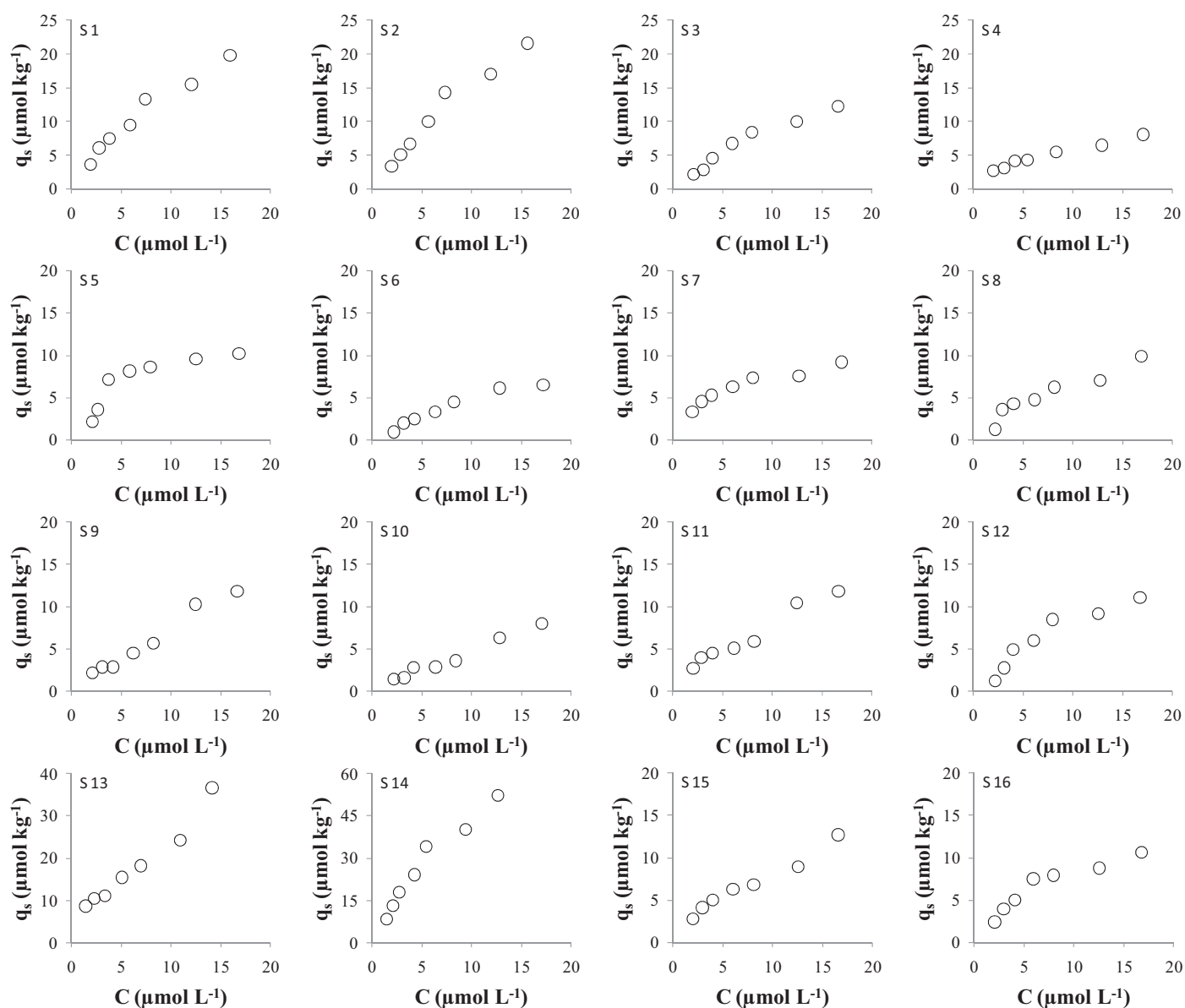
Fig. 2. Carbofuran adsorption equilibria in the 16 soil samples studied. The data shown are the means of triplicate determinations. Coefficients of variation were less than 10% in all cases.

Table 3
Fitting of the results of the batch tests to the experimental Freundlich equation (mean ± SE).

Sample	K_F ($\mu mol^{(1-n)} L^n kg^{-1}$)	n (dimensionless)	R^2
1	2.9 ± 0.4	0.69 ± 0.06	0.975
2	2.5 ± 0.4	0.79 ± 0.07	0.973
3	1.7 ± 0.3	0.72 ± 0.07	0.965
4	1.9 ± 0.1	0.51 ± 0.03	0.986
5	3.0 ± 0.8	0.46 ± 0.12	0.797
6	0.9 ± 0.2	0.74 ± 0.08	0.962
7	2.9 ± 0.3	0.40 ± 0.04	0.957
8	1.4 ± 0.3	0.67 ± 0.09	0.929
9	0.8 ± 0.2	0.95 ± 0.08	0.975
10	0.6 ± 0.1	0.92 ± 0.08	0.975
11	1.5 ± 0.3	0.74 ± 0.08	0.957
12	1.6 ± 0.4	0.70 ± 0.11	0.914
13	4.8 ± 1.0	0.74 ± 0.09	0.941
14	8.7 ± 1.2	0.71 ± 0.06	0.970
15	1.8 ± 0.3	0.67 ± 0.06	0.965
16	2.4 ± 0.4	0.54 ± 0.08	0.925

Table 4
Significant correlation coefficients between K_F in the Freundlich equation and general soil characteristics.

Soil characteristics	r	P
Organic carbon (C)	0.927	0.000
Sand	−0.500	0.049
Clay	0.658	0.006
eCEC	0.746	0.001

ing equilibrium concentration of the pesticide. In some cases, the adsorption curve was near-linear and hence of the C type. Judging by its low content (<0.3% in all samples), dissolved organic matter contributed very little to carbofuran adsorption. The experimental data obtained were modeled by fitting to the Langmuir and Freundlich equations. Fits to the Langmuir equation were discarded either because R^2 was not statistically significant or because the estimated parameters had large associated errors. By contrast, the Freundlich equation provided reasonably good fits in all cases ($R^2 = 0.797$–0.975). This equation is an empirical relation where K_F can be interpreted as the amount sorbed with $C = 1$ and n is a measure of heterogeneity in sorption sites [29]. In this work, n ranged from 0.40 to 0.95 (Table 3) and exceeded 0.5 in most samples (mean = 0.68), which is suggestive of low heterogeneity in the sorption sites [29]. Constant n exhibited no significant correlation with any of the soil variables measured. On the other hand, K_F ranged from 0.6 to 8.7 and was significantly correlated with various soil characteristics (Table 4), but especially with soil organic carbon ($r = 0.927$, $P < 0.05$). These results are consistent with previously reported values and confirm the substantial influence of organic matter on carbofuran sorption in soil [15,30,31]. A multiple regression analysis revealed that 96% of the variance in K_F was explained by the soil characteristics C and Fe_d through the following equation:

$$K_F = 1.68 + 0.46C - 0.20\,Fe_d$$

with $R^2 = 0.959$ and $F = 74.1$ ($P < 0.001$).

If an increased value of K_F resulted in increased carbofuran adsorption, then soil organic matter clearly facilitated carbofuran adsorption, whereas iron oxides extracted by dithionite-citrate had the opposite effect. This suggests that carbofuran adsorption is influenced by negative charge present in soil colloids. In these acid soils, organic matter has largely negative charge, whereas iron oxides have mainly positive charge.
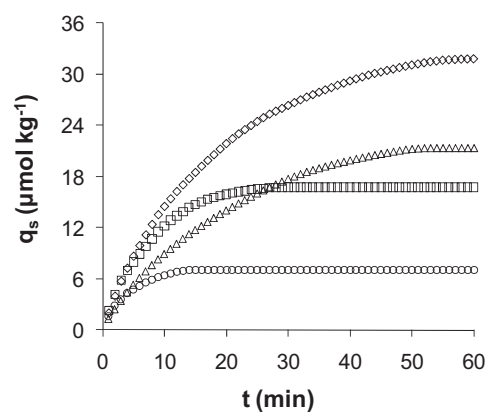

Fig. 3. Cumulative carbofuran adsorption (q_s) as function of time (t) in samples no. 2 (triangles), 5 (circles), 14 (diamonds) and 15 (squares).

3.2.2. Stirred flow chamber tests

The results of carbofuran adsorption obtained with the SFC-based reactor are shown in Fig. 3. The amount of carbofuran retained was always small (7.1–31.9 $\mu mol\,kg^{-1}$). These data are in the same magnitude order than those from the batch tests. This is consistent with the known low capacity of soils to adsorb this pesticide, which is widely assumed to have a low affinity for soil components [32,33]. Such a low capacity resulted in very fast adsorption of carbofuran by the soils. Thus, more than 50% was sorbed within 13 min, and 95% of the maximum adsorption reached within 45 min. The carbofuran adsorption kinetics was much faster in the SFC tests than in the batch tests. Thus, on batch tests at identical starting concentration than in SFC test, 1 h is needed to reach 77, 37, 73 and 86% of carbofuran adsorbed at equilibrium in samples no. 2, 5, 14 and 15, respectively, and they need more than 8 h to reach the equlibrium.

Generally, sorption in the SFC-based reactor occurred in two steps, namely: rapid adsorption during the first few minutes followed by slow adsorption afterwards [34]. Both types of reactions, fast and slow, could be separated. Fast adsorption reactions are usually diffusion–controlled [35,36]. The relationship among relative adsorption (q_s/q_{max}) and the square root of time ($t^{1/2}$) allows one to discriminate diffusion–controlled processes (i.e., rapid adsorption) from processes controlled by other factors (i.e., slow adsorption). Fig. 4 shows the q/q_{max} vs. $t^{1/2}$ curves for the four selected samples. As can be seen, they were largely linear and only bent at high q/q_{max} values. The linear portion of the curves corresponds to diffusion–controlled adsorption and their curved portion to slow adsorption reactions. Also, carbofuran adsorption occurred largely (>80%) via fast adsorption reactions.

Krishna and Philip [10] found a highly linear relationship between relative adsorption and the square root of time in carbofuran batch sorption tests. However, they only obtained 5 experimental data and were unable to discriminate diffusion–controlled and other processes. This was also the case with our batch tests (Fig. 5). Therefore, SFC tests are advantageous here since they allow samples to be collected at 1 min intervals, which is utterly impossible with classical batch techniques. In order to facilitate the analysis of the carbofuran retention kinetics, the experimental data were fitted to a first-order mathematical model considering one adsorption site (Eq. (3)).

$$\frac{d_{qs}}{d_t} = k_s(q_{max} - q_s) \tag{3}$$

where d_{qs}/d_t ($\mu mol\,kg^{-1}\,min^{-1}$) is the carbofuran adsorption rate, k_s a kinetic constant (min^{-1}), q_{max} ($\mu mol\,kg^{-1}$) the maximum carbofuran adsorption capacity under the experimental conditions
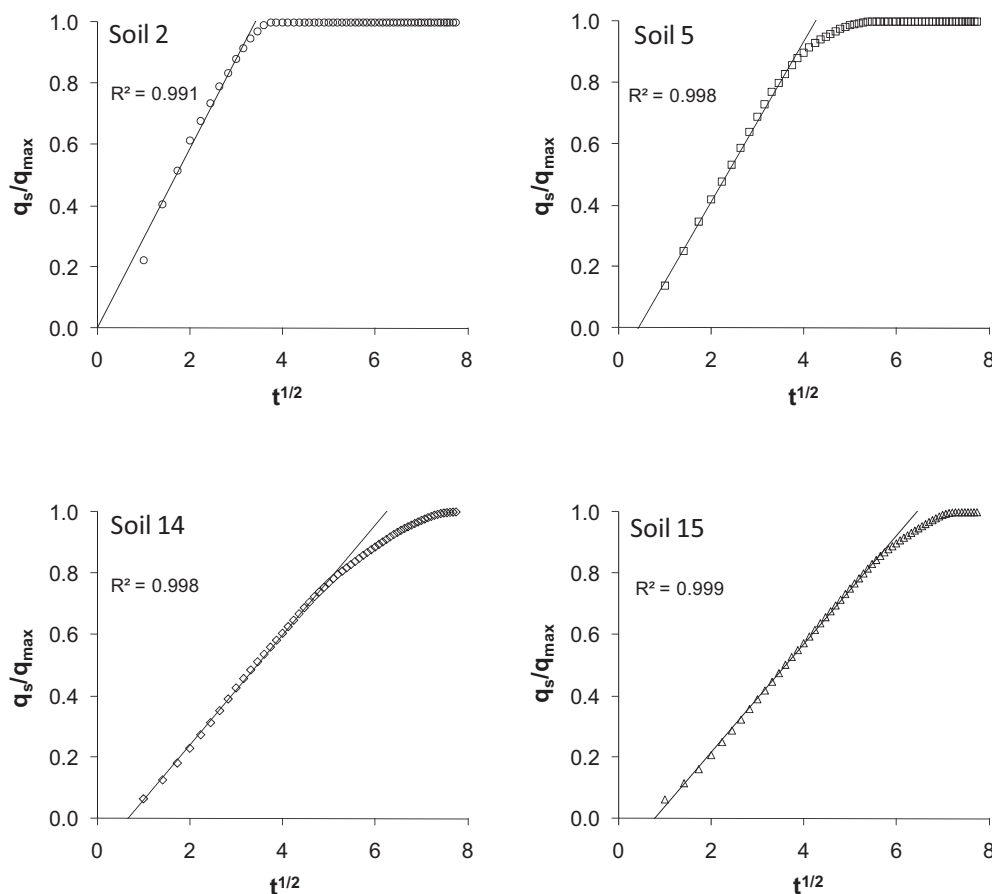
Fig. 4. Fractional cumulative adsorption (q_s/q_{max}) as a function of $t^{1/2}$ in the four soil samples used in the stirred flow chamber tests.

used and q_s (μmol kg^{-1}) the amount of carbofuran retained by the soil.

Table 5 shows the results of the fitting to this first-order kinetic equation. As can be seen, the maximum adsorption capac-

Fig. 5. Fractional cumulative adsorption (q_s/q_{max}) as a function $t^{1/2}$ in four of the soil samples used in the batch tests.

ity (q_{max}) ranged from 7.3 to 32.8 μmol kg^{-1}; also, it peaked in the soil with the highest organic carbon and clay contents (sample 14, with 17.1% and 44%, respectively) and was lowest in the soil with lowest contents in these two components (sample 5, with 1.4% and 13%, respectively). These results were consistent with those of the batch tests, where Freundlich's K_F was significantly correlated with soil organic matter and clay (Table 4). Other authors previously found the contents in clay and organic matter to play a key role in carbofuran retention by soils [10,30,37,38]. However, K_F was more markedly influenced by organic matter than by clay (Table 4). In general, the studied soils had very low clay contents; therefore, the correlation between clay and K_F in the batch tests may have resulted from a close relationship between the clay content and organic carbon in the soils ($r = 0.802$, $P < 0.05$).

The kinetic constant k_s ranged from 0.047 to 0.195 min^{-1} (Table 5) and peaked in the soil with the lowest content in organic carbon. By contrast, the lowest k_s value was that for a soil with a medium content of this component (sample 2, with 4.3%). This result shows that the decrease in carbofuran adsorption rate as a function of the amount of pesticide retained is not so clearly dependent on the soil organic carbon content. No relationship between k_s and any other soil characteristic was found. On the other hand, k_s was significantly correlated with n ($r = 0.965$, $P < 0.05$) in the Freundlich equation. High values of n are indicative of very weak forces [39]; therefore, the weaker was the retention of carbofuran by soil components, the larger was its kinetic constant.
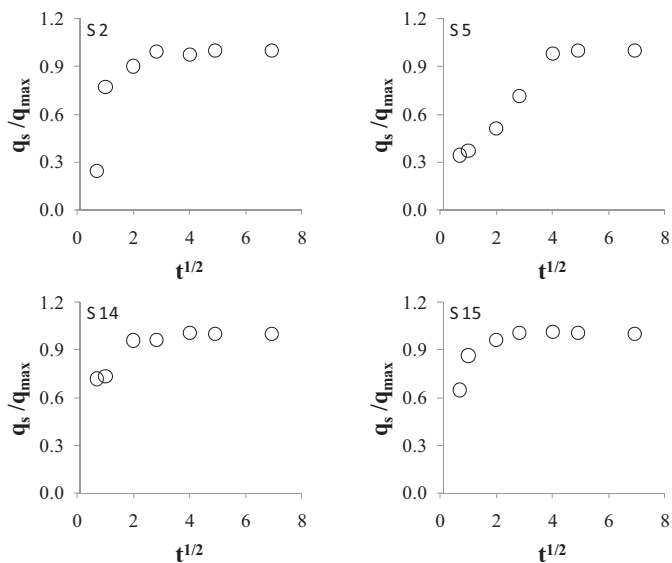
Table 5
Fitting of the results of the SFC tests to first-order rate equations.

Sample	Carbofuran adsorption			Carbofuran desorption		
	q_{max} (μmol kg^{-1})	k_s (min^{-1})	R^2	q_0 (μmol kg^{-1})	k_d (min^{-1})	R^2
2	23.0	0.047	0.977	8.0	0.137	0.987
5	7.3	0.195	0.950	7.8	0.139	0.952
14	32.8	0.055	0.980	7.1	0.086	0.967
15	17.2	0.117	0.977	7.5	0.195	0.983

Table 6
Carbofuran desorption (μmol kg^{-1}) as function of the amount previously added and proportion desorbed (in brackets).

Sample	Carbofuran added (μmol kg^{-1})						
	23	34	45	67	88	134	178
1	nd	nd	nd	nd	nd	nd	nd
2	nd	nd	nd	nd	nd	nd	nd
3	nd	nd	0.4 (10)	1.2 (17)	1.2 (15)	1.8 (18)	1.8 (15)
4	nd	nd	0.8 (20)	2.2 (52)	1.5 (35)	2.2 (41)	3.4 (42)
5	nd	nd	2.1 (30)	2.6 (31)	4.3 (49)	4.5 (47)	5.0 (49)
6	nd	nd	0.9 (48)	1.3 (39)	2.1 (38)	3.0 (49)	3.4 (53)
7	nd	nd	1.6 (30)	2.0 (32)	4.3 (58)	5.4 (71)	6.4 (69)
8	nd	nd	0.7 (16)	0.8 (17)	0.8 (13)	0.9 (12)	1.2 (12)
9	nd	nd	1.2 (41)	1.6 (35)	2.2 (39)	2.8 (27)	3.1 (26)
10	nd	nd	0.7 (24)	0.8 (28)	0.9 (26)	2.0 (32)	2.4 (31)
11	nd	nd	0.6 (14)	0.9 (14)	1.0 (18)	1.7 (16)	1.7 (14)
12	nd	nd	0.9 (18)	1.2 (21)	1.5 (18)	2.1 (23)	2.6 (23)
13	nd	0.1 (0)	0.3 (3)	1.3 (8)	1.9 (11)	3.1 (13)	3.0 (8)
14	1.1 (13)	1.2 (9)	1.3 (7)	1.6 (7)	1.8 (5)	1.9 (5)	2.9 (6)
15	nd	nd	nd	nd	nd	nd	nd
16	nd	nd	0.5 (13)	0.8 (11)	1.0 (13)	1.4 (16)	1.5 (14)

nd: not detected. Limit of quantitation = 0.04 μmol kg^{-1}.

3.3. Carbofuran desorption

3.3.1. Batch tests

The results of the desorption batch tests are shown in Table 6. Expressing the results in μmol kg^{-1} revealed a marked increase in carbofuran desorption with increase in the amount of carbofuran previously added to the soil (paired t-test, Table 7). This suggests that carbofuran is sorbed to less specific sites and with weaker bonds when its proportion is close to that of saturation. However, expressing the results as a percentage of previously adsorbed carbofuran exposed no significant differences as a function of the amount of pesticide previously added (paired t-test, Table 7). Interestingly, no carbofuran desorption was detected (quantification limit <0.04 μmol kg^{-1}) at low carbofuran doses or in some samples at high carbofuran concentrations (no. 1, 2 and 15; see Table 6). These results are quite surprising as they relate to none of the soil variables studied. If these three samples are excluded and the desorption data for the highest carbofuran dose used, then the amount of desorbed carbofuran is a potential function of that previously adsorbed (Fig. 6). This suggests that carbofuran desorption decreases with increasing sorption capacity of the soil. Above a certain adsorption threshold (about 10 μmol kg^{-1}), desorption depends on other variables as well. Thus, the percent desorption

at the highest carbofuran dose used (an addition of 178 μmol kg^{-1}) was negatively correlated with eCEC ($r = -0.732$, $P = 0.004$, $n = 13$) and the clay content ($r = -0.569$, $P = 0.042$, $n = 13$). On the other hand, there was no linear relationship between Freundlich's K_F and the amount of carbofuran desorbed at the different concentrations used in the tests; consequently, carbofuran is adsorbed and desorbed in soil via two different mechanisms.

3.3.2. Stirred flow chamber tests

Carbofuran desorption in the SFC tests immediately following carbofuran adsorption (Fig. 7), ranged from 5.1 to 7.0 μmol kg^{-1} (16–92% of retained carbofuran). The percent carbofuran desorption was negatively correlated with the soil organic carbon content (Fig. 8); therefore, this variable is a key to the irreversibility of carbofuran adsorption in soil. As can be seen from Fig. 8, carbofuran desorption increased rapidly at an organic carbon content below 4%. One plausible explanation for this result is that clay plays a more

Table 7
Paired t-test for desorption batch test expressing the results in μmol kg^{-1} and as a percentage of previously adsorbed carbofuran.
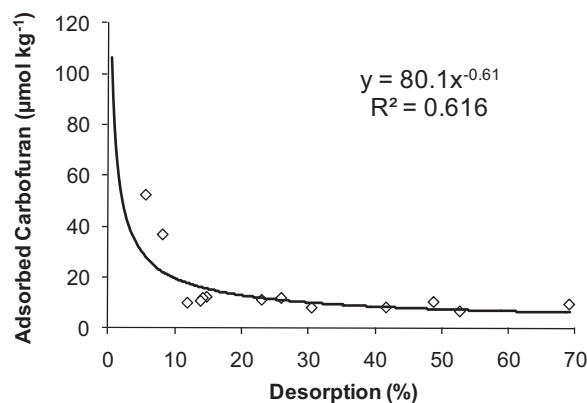
ACC	Carbofuran desorption			
	(μmol kg^{-1})		(%)	
	t	Sig	t	Sig
45 vs. 67	−4.702	0.001	−1.200	.253
67 vs. 88	−2.210	0.047	−0.582	.571
88 vs. 134	−6.207	0.000	−1.399	.187
134 vs. 178	−3.760	0.003	0.953	.359

ACC: added carbofuran concentrations (μmol L^{-1}).

$$y = 80.1x^{-0.61}$$
$$R^2 = 0.616$$

Fig. 6. Relationship between the amount of carbofuran sorbed and the proportion desorbed from the most concentrated solution (178 μmol kg^{-1}).
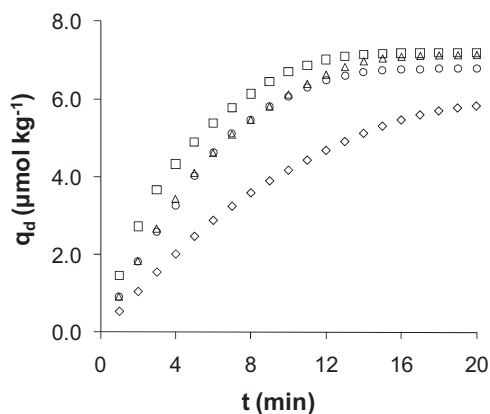
Fig. 7. Cumulative carbofuran desorption (q_d) as function of time in samples no. 2 (triangles), 5 (circles), 14 (diamonds) and 15 (squares).

prominent role in carbofuran adsorption in soils containing little organic carbon. Wahid and Sethunathan [40] found organic matter levels above 2% to favour the adsorption of pesticides onto organic components and lower levels to result in preferential adsorption by clays and inorganic colloids. Similarly, Weber et al. [41] found the mobility of pesticides in soils with low organic matter contents (<5%) to be largely governed by the inorganic fractions (particularly clay). Organic matter in our soils, which contained little clay, not only increased carbofuran adsorption, but also formed more irreversible bonds, especially at organic carbon levels above 4%. These results are consistent with those obtained in the batch tests. Since most of studied soils had organic carbon contents lower than 5%, we can reasonably assume that carbofuran desorption is mainly governed by eCEC and the clay content. The data obtained for the carbofuran desorption kinetics were fitted to the first-order kinetic model (Eq. (4)).

$$\frac{d_{q_d}}{d_t} = k_d(q_0 - q_d) \qquad (4)$$

where d_{q_d}/dt (μmol kg^{-1} min^{-1}) is the desorption rate of carbofuran, k_d its desorption kinetic constant (min^{-1}), q_0 (μmol kg^{-1}) the maximum amount of carbofuran that can be desorbed under the experimental conditions used, and q_d (μmol kg^{-1}) that desorbed from the soil.

Parameter q_0 ranged from 7.1 to 8.0 μmol kg^{-1} (Table 5) and accounted for 21 and 100%, respectively, of the soil retention capacity (q_{max}). The desorption kinetic constant, k_d, ranged from 0.086 to 0.195 min^{-1} and was in general higher than the adsorption kinetic constant (k_s). Therefore, carbofuran was more rapidly desorbed
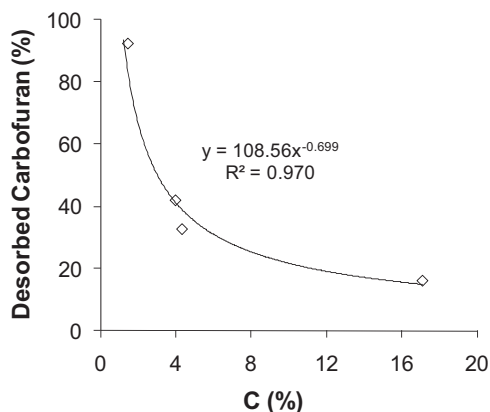
than it is adsorbed by the soil (twice on average, except in soil 5, where adsorption and desorption occurred at a similar rate). This is consistent with previous observations of Achik et al. [15].

4. Conclusion

The Freundlich K_F values obtained under equilibrium conditions in the batch tests afford the same conclusion as the q_{max} values provided by the stirred flow chamber tests: that carbofuran adsorption is influenced by soil organic carbon and clay. However, as shown in this work, the SFC-based method is clearly superior for studying the carbofuran sorption kinetics. In fact, SFC tests allow data to be acquired on a smaller time scale and a considerably greater number of samples. The SFC tests revealed that carbofuran was adsorbed largely (>80%) via fast reactions. The irreversibility of carbofuran retention depends strongly on the organic carbon content of the soil. Thus, the percent carbofuran desorption was relatively low in soils with a proportion of organic carbon higher than 4%. Below this threshold, carbofuran desorption increased rapidly up to 100% of previously adsorbed carbofuran. Also, constant n in the Freundlich equation was correlated with the adsorption kinetic constant (k_s) as determined from the results of the SFC tests.

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$y = 108.56x^{-0.699}$
$R^2 = 0.970$

Fig. 8. Relationship between the amount of soil organic carbon and the proportion of desorbed carbofuran in the stirred flow chamber tests.

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