Effect of the Simultaneous Addition of β-Cyclodextrin and the Herbicide Norflurazon on Its Adsorption and Movement in Soils

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The effects of β-cyclodextrin (BCD) on the sorption–desorption and transport processes of the herbicide norflurazon (NFL) in soils of different characteristics when both are applied simultaneously have been investigated. Adsorption–desorption studies of NFL on six soils of very different characteristics in the presence of BCD have been performed using a batch equilibration method and correlated to its mobility in homogeneous hand-packed soil columns. NFL determinations were undertaken by HPLC equipped with a diode array detector at a wavelength of 220 nm. BCD was also analyzed by HPLC with fluorimetric detection using a postcolumn reaction. The interaction of NFL with BCD yielded the formation of an inclusion complex in solution. When this complex is applied to soils, a large decrease in NFL adsorption capacity and an increase in its desorption were observed, due to the higher tendency of NFL–BCD complexes to remain in solution. The results obtained in adsorption and soil column experiments indicated that the influence of BCD on NFL mobility and availability depends on the different affinities of BCD to be sorbed on soils of different characteristics and on the concentration of BCD used. The lower the concentration of BCD added, the more tenaciously it adheres to the soil, and most of the BCD molecules would be adsorbed, providing a coating to soil particles that acts as a bridge between NFL and the soil surface, acting as an adsorbent and retarding the mobility of the herbicide. At higher concentrations of BCD, or in soils where its adsorption is very low, most of the BCD molecules are in the aqueous phase and NFL molecules tend to be complexed with BCD in solution, acting then as a solubilizing agent.

KEYWORDS: Norflurazon; β-cyclodextrin; adsorption–desorption; mobility; soils; soil columns

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides produced by the microbially induced breakdown of starch by bacteria and present a hydrophobic interior cavity and hydrophilic faces. CDs have the tendency to form inclusion complexes by reversibly incorporating a nonpolar compound into their hydrophobic central cavities. Due to the low-cost production of some of these CDs, in recent years, they have received considerable attention in various applied fields (biotechnology, organic chemistry, drugs, foods, pesticides), in which they are generally used to increase the water solubility of nonpolar compounds.

The complexation of pesticides with CDs may result in considerable improvement of their properties, such as enhancement of solubility and bioavailability (*1*–*4*). Some publications confirm the prediction that, in the coming years, a rapid development can be expected in the application of CDs to pesticide formulations (*5*–*8*).

In general, CDs have a range of desirable physicochemical properties that make them attractive for removing sorbed organic contaminants from contaminated subsurface systems. CDs are considered to be nontoxic and biodegradable, and, because of their rigid structure and nonionogenic functional groups, CDs are expected to exhibit relatively stable physicochemical properties over a range of solution chemical conditions. Due to these favorable properties CDs have recently been used as alternative agents for enhancing biodegradation in contaminated soils (*9*–*12*), and they have even been used to decontaminate wastewater due to their solubilization effects (*13*). Likewise, it has been demonstrated that natural α- and γ-CDs can enhance the solubilization of pesticides previously adsorbed on soils (*14*) and detoxify soils of pesticides employing synthetic CDs (*15*).

It has been previously reported (*16*) that the interaction of the hydrophobic herbicide norflurazon (NFL) with β-cyclodextrin (BCD) produced the formation of a new inclusion compound in solution with an apparent stability constant of 360 M^{-1}, a 1:1 stoichiometric ratio for the complex, and up to a 5-fold increase in NFL solubility. Villaverde et al. (*17*) have demonstrated also the high extracting power of BCD toward the herbicide NFL previously adsorbed on soils of different characteristics and its potential use for in situ remediation of pesticide contaminated soils.

NFL presents high adsorption in soils with medium-high organic matter and iron oxide content (*18*), and therefore it is of concern that NFL may persist in a nonbioavailable form in soil, leading to its inactivation as herbicide (with the consequent

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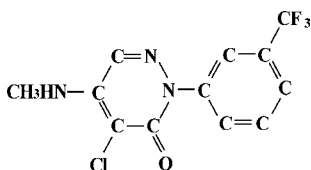
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Figure 1. Molecular structure of the herbicide norflurazon.

Table 1. Different Properties of the Soils Studied[a]

			soil			
	1	2	3	4	5	6
pH	7.6	6.5	5.7	8.0	4.8	8.0
$CaCO_3$ (%)	0.0	0.0	0.0	24.1	0.0	6.9
CEC (cmol$_c$ kg^{-1})	17.2	3.5	5.8	39.0	20.1	4.8
organic matter (%)	1.9	0.51	1.38	1.7	5.3	0.8
sand (%)	16.4	92.8	56.7	2.7	61.1	87.6
silt (%)	61.0	4.4	23.8	31.5	29.1	4.0
clay (%)	22.6	2.5	19.5	65.9	9.8	8.4
amorphous Al_2O_3 (g kg^{-1})	9.4	0.3	0.3	3.5	12.3	0.2
amorphous Fe_2O_3 (g kg^{-1})	10.8	0.3	1.4	0.8	23.3	0.4

[a] Data from Villaverde et al. (*17*).

result that higher amounts of herbicide have to be applied to obtain the desired results) and/or to soil contamination. The present study has been conducted to test the effect of the simultaneous application of NFL and BCD on the herbicide mobility and availability using soil columns and equilibrium batch assays in soils of different characteristics, in order to show preliminary results for future preparations of new formulations and to evaluate their possible environmental consequences.

MATERIALS AND METHODS

Technical grade NFL (97.8% purity), the structure of which is shown in **Figure 1**, was kindly supplied by Novartis, and BCD (99%) by Roquette (Lestrem, France). Six different soils (1−6) were employed to carry out the adsorption−desorption experiments. They were taken from the superficial horizon (0−20 cm), and their main physicochemical properties are shown in **Table 1**. All soils were from southwestern Spain except soil 5, which was from Scotland. Soil samples were crushed to pass a 2 mm sieve. They were analyzed for pH in a saturated paste, total carbonate content, particle size distribution, cationic exchange capacity, and organic matter content (OM). Organic carbon content (OC) was determined as follows: OC (%) = 0.58 × OM (%). The amorphous and organically bound iron and aluminum oxides were determined using ammonium oxalate−oxalic acid (*19*).

Herbicide Adsorption−Desorption Experiments in Soils. NFL adsorption−desorption experiments in soils were carried out in quadruplicate in 50 mL centrifuge tubes by mixing 10 g of each soil with 20 mL of 0.01 M Ca(NO₃)₂ solution (experiment 1) or 0.01 M BCD solution (experiment 2) containing various concentrations (4, 8, 12, 16, and 20 mg L^{-1}) of NFL. The samples were shaken for 24 h at 20 ± 1 °C. This time of reaction was chosen from preliminary kinetic studies (not shown), which showed that adsorption had reached pseudo-equilibrium. After that, the supernatant was removed after centrifugation and filtered through a 0.22 μm Millipore glass fiber membrane filter, and NFL concentration was determined in the filtrate by HPLC equipped with diode array detector (Shimadzu SPD-M10A) at a wavelength of 220 nm. The conditions were as follows: mobile phase, acetonitrile/water (60:40); flow rate, 0.6 mL/min; temperature, 30 °C; chromatographic column, kromasil C18 reverse phase. Five to nine calibration standard solutions containing NFL were prepared in water to produce concentrations ranging from 0.05 to 20 mg L^{-1}. The low detection limit of this analytical method was 0.05 mg L^{-1}. The standard solutions were routinely analyzed with each set of samples to measure accuracy and precision. The spiked replicates represent data collected from 60 NFL standard solutions throughout a 6 month period, with a mean recovery of 97% and a relative standard deviation of <8%. NFL

adsorbed was calculated from the differences between its concentration before and after equilibrium. Adsorption isotherms were obtained by plotting the amount of NFL adsorbed by the soil (micromoles per kilogram) versus the respective concentrations in equilibrium solution (micromoles per liter).

In both experiments, desorption studies were carried out after adsorption equilibrium was reached, for the points corresponding to NFL initial concentrations of 4, 12, and 20 mg L^{-1}, by removing the supernatant after centrifugation, replacing it by 20 mL of a 0.01 M Ca(NO₃)₂ solution, allowing equilibration for an additional 24 h period, and finally operating as in the adsorption experiments. Three consecutive desorptions were carried out.

Sorption isotherms were fitted to the logarithmic form of the Freundlich equation

$$\log C_s = \log K_f + n \log C_e$$

where C_s (μmol kg^{-1}) is the amount of herbicide sorbed at the equilibrium concentration C_e (μmol L^{-1}) and K_f and n are constants, which characterize the relative sorption capacity and the sorption intensity, respectively, for the herbicide. K_f and n values were determined from the straight line obtained by plotting log C_s versus log C_e (intersection with *y*-axis and slope, respectively). The constant K_f is the amount of pesticide sorbed for an equilibrium concentration of 1 μmol L^{-1} and hence represents adsorption at low adsorbate concentration. K_f values can be used to compare the adsorption capacity of the different soil samples toward NFL.

The fitted equation was used to calculate sorption distribution coefficients (K_d) at a selected C_e (10 μmol L^{-1}) in order to calculate the organic carbon normalized distribution coefficient (K_{oc}). K_{oc} is often used in the discussion of sorption of nonpolar hydrophobic compounds, the concept being compatible with the idea of organic carbon (OC) having the same affinity for a nonpolar compound independent of the source of OC.

BCD Adsorption Experiments in Soils. BCD adsorption experiments in some selected soils were carried out using the same conditions mentioned previously, but mixing the soils with solutions containing various concentrations (5 × 10^{-5}, 1 × 10^{-4}, 2.5 × 10^{-4}, and 3.5 × 10^{-4} M) of BCD. BCD remaining in the supernatant was analyzed by HPLC with fluorometric detection using a postcolumn reaction based on the enhancement of fluorescence intensity of 2-(*p*-toluidino)-naphthalene-6-sulfonic acid (TNS, Sigma) following the method proposed by Takeuchi and Miwa (*20*). TNS fluorescence increases rapidly when CD is added to the aqueous solution. The eluent from the column was mixed with 0.01% (w/v) TNS solution at a flow rate of 0.5 mL/min. The conditions used were as follows: mobile phase, methanol/water (20:80); flow rate, 0.5 mL/min; temperature, 30 °C; chromatographic column, kromasil C18 reverse phase; fluorescence detector (Shimadzu RF-535), with excitation and emission wavelengths of 280 and 465 nm, respectively.

Herbicide Leaching Experiments in Soil Columns. Leaching experiments were done in triplicate for some selected soils (1, 2, and 6). Homogeneous soil columns were prepared by packing gently and uniformly the soils in 30 cm long methacrylate tubes of 3.0 cm internal diameter. The lower end was covered with nylon tissue padded with a thin layer of glass wool (0.5 g) to hold the soil firmly into the column. The top end of the soil column was also covered with glass wool, to prevent disturbance of the soil by the input liquid. Different amounts of each soil were put in the columns (197, 300, and 246 g for soils 1, 2, and 6, respectively) to obtain 24 cm of the column occupied by soil. The soil column could be readily separated into 4 cm segments after the leaching event.

In a preliminary experiment, two soil columns of each soil were saturated by capillarity with distilled water to obtain a moisture content of the soil column of 100% of the field capacity. The difference between the weight of the saturated soil column and its dry weight was used to calculate the value for 1 pore volume. Their pore volumes were 41.0, 88.0, and 57.45 mL for soils 1, 2, and 6, respectively.

Soil columns were treated with 5 pore volumes of a 0.01 M Ca-(NO₃)₂ solution to equilibrate the soils, and subsequently 0.28 mg of NFL (3.96 kg of active ingredient ha^{-1}) was applied, as either 0.01 M
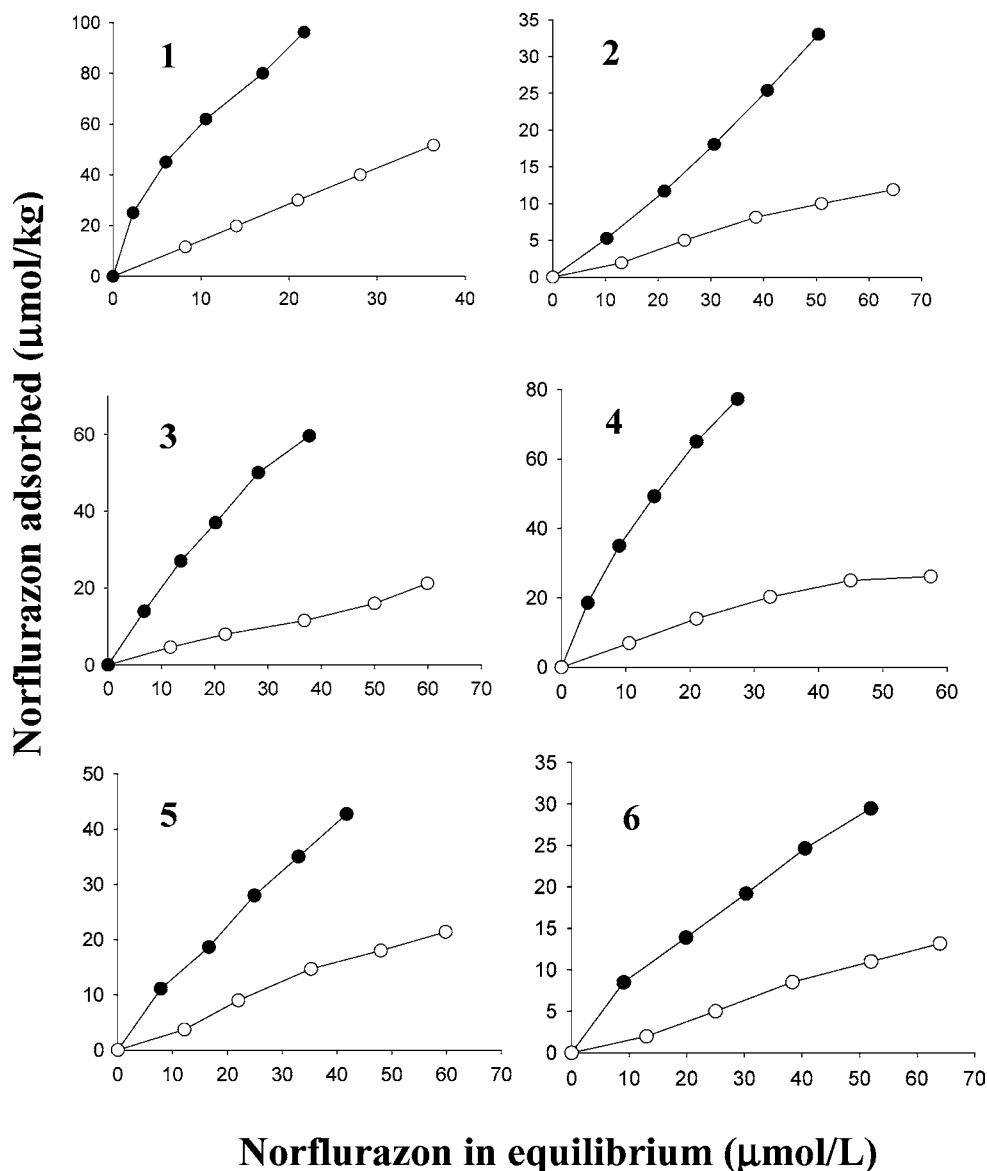
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Figure 2. Adsorption isotherms of norflurazon on the soils under study in the presence of 0.01 M Ca(NO$_3$)$_2$ (●) or 0.01 M BCD (○) solutions.

Ca(NO$_3$)$_2$ or 0.01 M BCD solution (14 mL). These solutions remained in contact with the soils for 24 h. Breakthrough curves (BTCs) were obtained by a daily application of 25 mL of distilled water until no herbicide was detected in the leachate. After the leaching experiments, the columns were sliced into six 4 cm segments and the soil was air-dried. The herbicide residues that remained adsorbed on the soil from each segment were extracted with methanol. The extraction was carried out in triplicate.

RESULTS AND DISCUSSION

Herbicide Adsorption−Desorption in Soils. To evaluate the effect of the simultaneous addition of BCD and norflurazon on the adsorption and desorption processes of this herbicide in soils, experiment 2 has been carried out (adsorption of NFL in the presence of 0.01 M BCD), and the results are compared with those obtained in experiment 1 [adsorption of NFL in the presence of 0.01 M Ca(NO$_3$)$_2$ as background electrolyte]. The results of experiment 1 have been discussed in a previous paper (*17*), and only a summary will be shown here.

Experiment 1: In the Presence of 0.01 M Ca(NO$_3$)$_2$. NFL adsorption isotherms on the six soils under study in the presence of 0.01 M Ca(NO$_3$)$_2$ as background electrolyte are presented in **Figure 2**. They were well described by the linearized Freundlich

equation (**Table 2**). For the soils under study K_f was between 15.54 and 0.35 μmol kg^{-1}, indicating the strong influence of soil characteristics on NFL adsorption. K_f values of our isotherms indicated that the affinity of the soils for NFL was related to their OM content; however, this relationship was not true in case of soil 5, with the highest OM content but lower adsorption capacity due to the fact that amorphous iron and aluminum oxides were covering the organic surfaces on this soil, decreasing sorption by blocking its organic surfaces (*18*).

The role of hydrophobic bonds on NFL adsorption on organic matter of these soils can be compared by normalizing the distribution coefficient, K_d, to the percentage of organic carbon of the different samples (K_{oc}) (**Table 2**). K_{oc} values obtained were between 575 and 42 μmol kg^{-1}, indicating the strong influence of other soil characteristics on NFL adsorption and/or the influence of the type of OM of each soil.

NFL desorption isotherms carried out in experiment 1 showed in all cases positive hysteresis, indicating that desorption of NFL from these soils was not completely reversible, especially for soil 1. Total percentages of NFL desorbed (%D) for each concentration under study in experiment 1 are shown in **Table 3**. In general, NFL adsorption on soils was more irreversible

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Table 2. Freundlich Adsorption Isotherm Parameters (K_f and n Values) and Distribution (K_d) and Organic Carbon Normalized Distribution Coefficients (K_{oc}) of Norflurazon Sorption on the Soils Used in Experiments 1[a] and 2

		soil					
	expt	1	2	3	4	5	6
K_f	1	15.54 ± 0.54	0.35 ± 0.02	2.80 ± 0.26	6.56 ± 0.25	2.00 ± 0.21	1.70 ± 0.15
	2	1.40 ± 0.2	0.11 ± 0.01	0.50 ± 0.02	1.12 ± 0.02	0.27 ± 0.01	0.10 ± 0.01
n	1	0.61 ± 0.01	1.15 ± 0.02	0.85 ± 0.03	0.75 ± 0.01	0.81 ± 0.03	0.72 ± 0.03
	2	1.00 ± 0.05	1.14 ± 0.02	0.89 ± 0.03	0.80 ± 0.02	1.08 ± 0.01	1.02 ± 0.06
K_d	1	6.33 ± 0.15	0.49 ± 0.02	1.98 ± 0.19	3.69 ± 0.09	1.29 ± 0.02	0.89 ± 0.05
	2	1.42 ± 0.13	0.19 ± 0.02	0.35 ± 0.01	0.70 ± 0.11	0.39 ± 0.01	0.19 ± 0.02
K_{oc}	1	575 ± 7.6	166 ± 5.4	247 ± 3.6	361 ± 6.7	42.0 ± 2.3	193 ± 5.2
	2	398 ± 5.9	60.0 ± 4.2	66.0 ± 4.6	273 ± 2.6	19.0 ± 0.9	70.0 ± 3.4

[a] Experiment 1 data from Villaverde et al. (*17*).

Table 3. Percentage of Norflurazon Desorbed (%D) from the Soils after Its Adsorption from Ca(NO$_3$)$_2$ (Experiment 1[a]) or BCD Solutions (Experiment 2)

		%D	
soil	NFL initial concn (mg L^{-1})	0.01 M Ca(NO$_3$)$_2$ solution	0.01 M BCD solution
1	4	2.0 ± 0.9	13.7 ± 3.0
	12	11.7 ± 0.3	18.3 ± 2.6
	20	13.7 ± 0.2	5.84 ± 1.4
2	4	31.5 ± 7.4	100.0 ± 2.2
	12	97.6 ± 6.2	71.4 ± 2.3
	20	83.6 ± 6.5	77.0 ± 1.8
3	4	34.1 ± 2.0	48.8 ± 3.4
	12	36.6 ± 2.0	34.8 ± 4.5
	20	58.1 ± 1.6	69.6 ± 2.5
4	4	8.2 ± 1.7	62.4 ± 9.0
	12	13.8 ± 0.3	33.8 ± 1.3
	20	15.3 ± 1.4	37.5 ± 2.7
5	4	41.8 ± 0.5	100.0 ± 4.6
	12	44.4 ± 0.4	80.0 ± 1.6
	20	53.0 ± 1.0	79.0 ± 3.8
6	4	31.9 ± 5.7	100.0 ± 8.6
	12	54.3 ± 3.5	87.9 ± 2.6
	20	72.3 ± 8.0	87.5 ± 0.4

[a] Experiment 1 data from Villaverde et al. (*17*).

(lower %D) at low concentrations adsorbed (desorption from an initial concentration of 4 mg L^{-1}); that is, NFL molecules are more strongly sorbed at low surface coverage.

The percentages of desorption obtained show that the higher the K_f value, the lower the desorption percentage. Accordingly also with K_f values, soil 5 presented a considerable %D, despite its high OM content, indicating that OM is not the only factor that controls NFL desorption from this soil.

Experiment 2: In the Presence of 0.01 M BCD. The objective of this experiment was to observe the effect of the direct application of NFL–BCD solutions on the adsorption–desorption of the herbicide on the different selected soils. The corresponding adsorption isotherms can be also observed in **Figure 2**. These isotherms were also well described by the linearized Freundlich equation (R^2 >0.986). In all of the soils studied a large decrease in NFL adsorption capacity was observed, in comparison with the adsorption obtained when NFL–Ca(NO$_3$)$_2$ solutions were used. This behavior is also reflected in K_f values obtained in experiment 2 (**Table 2**), which are quite lower (ranging between 1.40 and 0.10) than those corresponding to experiment 1 (ranging between 15.54 and 0.35). Consequently, K_d and K_{oc} values are also lower than in

experiment 1. The reason for this decrease in NFL adsorption in soils is the presence of BCD and the formation of an inclusion complex with NFL with a higher water solubility than that of the pure herbicide and, therefore, with a higher tendency to remain in solution as NFL–BCD complex than to be adsorbed on the soil.

Desorption isotherms (not shown) also presented the same positive hysteresis observed previously, although the percentages of NFL desorbed from each soil (%D) were in general higher than in the case of NFL application to soil without BCD (**Table 3**). The contrary tendency of %D values in each soil, in comparison to the previous experiment 1, is also remarkable because in this case, in general, the lower the amount of NFL adsorbed, the higher the %D. Taking into account that during the desorption steps all of the supernatant is separated from the soils, this implies that no BCD was present in the desorption solutions, only a small amount of BCD which could be desorbed from that previously adsorbed during adsorption step. It can be concluded that the presence of BCD in soil surfaces after adsorption experiments may have modified the soil properties, altering the desorption behavior of the soil. Jozefaciuk et al. (*21, 22*) demonstrated that soil physical properties were greatly modified by randomly methylated β-cyclodextrin (RAMEB) treatment. RAMEB increased water adsorption and surface areas in sandy soils and decreased them in clayey soils, and the desorption of nonpolar pollutants was enhanced in RAMEB-treated soils.

Herbicide Mobility in Soils. Although adsorption–desorption processes allow the evaluation of adsorption mechanisms, these results cannot be directly extrapolated to the dynamic flow regime that occurs through the soil, due, among other reasons, to the nonequilibrium conditions and to the highly different soil/solution rates in soil columns. For these reasons experiments using soil columns have been carried out to emulate more closely the real conditions in soil.

Three soils (1, 2, and 6) were selected to study the mobility of NFL in hand-packed soil columns. The results obtained from soil column experiments have been represented in the form of breakthrough curves (BTCs), with the number of pore volumes as abscissa and the herbicide concentration relative to that initially added (C/C_0) as ordinate. **Figure 3** shows the BTCs for NFL leaching through these soils [NFL applied as Ca(NO$_3$)$_2$ or BCD solutions], and **Table 4** shows the cumulative amount of NFL eluted in the leachates from the soil columns, as well as the amount of NFL remaining at different depths in the soil columns.

When NFL is applied as Ca(NO$_3$)$_2$ solution, the low amount of herbicide eluted in the case of soil 1 is remarkable; the percentage of the herbicide eluted was only 3.21%. **Table 4**
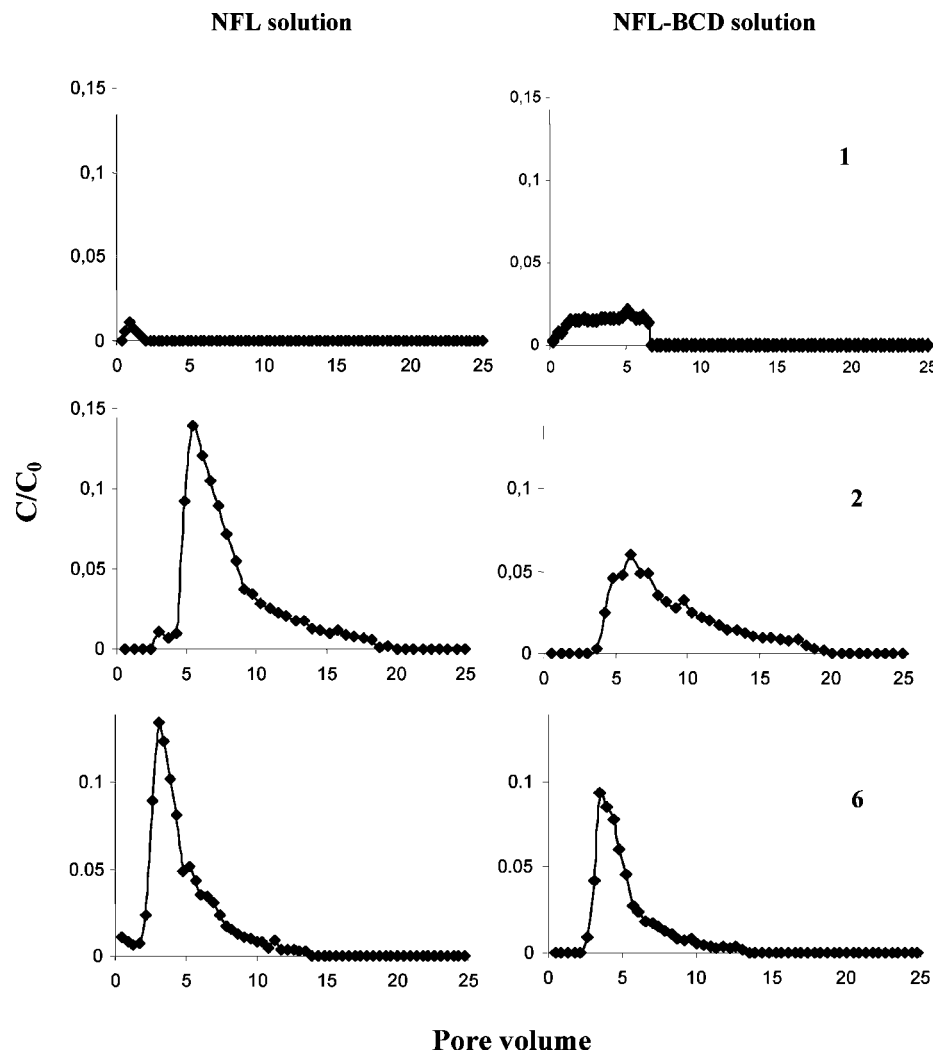
Figure 3. NFL breakthrough curves in selected soils using NFL–Ca(NO$_3$)$_2$ or NFL–BCD solutions.

Table 4. Percentage of Norflurazon Extracted from Soil Columns and Eluted in Leachates, Employing 0.01 M Ca(NO$_3$)$_2$ as Eluent Solution

	soil					
	1		2		6	
depth (cm)	NFL[a]	NFL–BCD[b]	NFL	NFL–BCD	NFL	NFL–BCD
0–4	30.73	10.94	0.30	5.02	0.60	5.36
4–8	27.69	10.36	0.11	5.31	0.22	6.10
8–12	25.94	10.70	0.09	5.61	0.19	6.11
12–16	5.01	11.20	0.14	5.79	0.28	6.36
16–20	0.00	10.37	0.15	6.28	0.30	6.76
20–24	0.00	9.92	0.26	8.87	0.50	9.50
total extracted	89.37	62.49	1.05	36.88	2.09	40.19
total eluted	3.21	38.42	98.59	59.55	96.88	59.13
total recovered	92.58	100.91	99.64	96.43	98.97	99.32

[a] NFL, norflurazon applied as 0.01 M Ca(NO$_3$)$_2$ solution. [b] NFL–BCD, morflurazon applied as 0.01 M BCD solution.

also shows that, on the contrary, the percentage of NFL eluted reached almost 100% for soils 2 and 6. NFL leached rapidly through these sandy soils because of their low OM content and high porosity. The behavior of soil 1 is quite different because a very low release of the pesticide was obtained. These results are in agreement with those obtained in the adsorption experiments, because the K_f value obtained for soil 1 was much higher (15.54) than those obtained for soils 2 and 6 (0.35 and 1.70, respectively).

Table 4 also shows the distribution of NFL residues in the soil columns, as a function of column depth, after completion of leaching. NFL residues extracted from soils 6 and 2 at each soil depth were practically negligible when NFL was applied as Ca(NO$_3$)$_2$ solutions, because almost 100% of the pesticide initially applied had been eluted from the soil columns. In soil 1 higher amounts of NFL residues were extracted from the upper three segments when NFL−Ca(NO$_3$)$_2$ solutions were applied, and it was not detected at depths below 16 cm, indicating a high retention of the herbicide in the surface horizons of this soil. The amount recovered after extraction from the six rings of the columns was 89.37% of that initially applied, very close to the total amount of herbicide retained by the soil column.

To observe the effect of the presence of BCD on NFL leaching through the soils, herbicide mobility experiments were carried out in soil columns by applying the herbicide as 0.01 M BCD solutions (**Figure 3**). The herbicide lixiviation in soil 1 was 38.42% when applied as BCD solution versus 3.21% of NFL elution obtained when the herbicide was applied in Ca-(NO$_3$)$_2$ solution. This increase in herbicide movement through the soil columns indicates that when NFL is applied to the soil column as a complex NFL−BCD in solution, its adsorption on the soil is lower than in the case of being applied in the absence of BCD, indicating the higher tendency of the NFL−BCD complex to remain in soil solution than to be adsorbed, in agreement with the results obtained in adsorption experiments previously discussed.

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On the contrary, the behavior observed in sandy soils 2 and 6 is completely different; a smaller amount of leached herbicide was obtained in comparison with leaching in the absence of BCD (from 98.59 to 59.55% and from 96.88 to 59.13% for soils 2 and 6, respectively, **Table 4**), and a diminution of the maximum of BTC could be also observed. In both soils, the amount of herbicide eluted from the columns was reduced by ≈40%, confirming the reduction of herbicide lixiviation observed in the absence of BCD.

This behavior has been observed in the adsorption of other pesticides in soil in the presence of other organic compounds such as surfactants, this effect being attributed to the surfactant adsorption in the soil (23). Sánchez-Camazano et al. (24) observed, in certain kinds of soils and surfactant concentrations, an increase in atrazine adsorption to soil through the "bridge effect" caused by the surfactant. Chapell et al. (25) also hypothesized that atrazine partitioning into surfactant micelles on external surfaces of smectite led to enhanced retention of atrazine by the solid phase. The enhanced adsorption of the insecticide methidation on soils was also observed due to the higher hydrophobic character of the soil surface when it is amended with surfactants (26). Enhanced sorption of other organic contaminants in soil through the modification of its surfaces by the adsorption of surfactants has been also reported (27, 28).

This higher retention of NFL in columns of soils 2 and 6 seems to be in contradiction with the large decrease in NFL adsorption in these soils observed in the isotherms previously discussed when NFL−BCD solutions were used. However, it must be taken into account that in those experiments the amount of BCD used was much higher (22.7 mg of BCD g^{-1} of soil), whereas in soil column experiments the amounts used were between 28- and 43-fold lower: 0.806, 0.529, and 0.646 mg of BCD g^{-1} of soils 1, 2, and 6, respectively. If BCD tends to be adsorbed on soil surfaces, the lower the concentration of BCD in solution, the more tenaciously it adheres to the sorbent. At higher concentrations there would be more BCD molecules in soil solution and a higher possibility that NFL molecules are complexed with BCD in solution, whereas at low concentrations a great part of BCD molecules would be adsorbed, providing a coating to soil particles that retards the mobility of NFL.

BCD Adsorption in Soils. To test if the higher retention of NFL in the columns of soils 2 and 6 was related to the adsorption of BCD on these soils, BCD adsorption experiments were performed using BCD concentrations that gave BCD/soil ratios similar to those used in mobility experiments. The contact time used was 24 h, the same time that BCD applied in the soil columns remained in contact with the soil before the addition of the first 25 mL of distilled water for leaching. Although batch adsorption experiments are not totally comparable with the dynamic conditions of leaching experiments and the soil/solution ratio used is different, the results obtained in the batch adsorption experiments are crucial to explain if the different retention of the herbicide observed in soil columns is due to a different adsorption of BCD in each soil.

Table 5 shows the percentage of BCD adsorbed on soils 1, 2, and 6 for the BCD concentrations used. It is remarkable that the amount of BCD adsorbed in soil 1 is lower than that adsorbed in soils 2 and 6, in which 100% of BCD was adsorbed at the two lowest BCD concentrations used, originating H-type isotherms (not shown), whereas in the case of soil 1 a C-type isotherm (constant partition) was obtained. This indicates the high affinity of BCD to be adsorbed on soils 2 and 6 in comparison to soil 1, indicating that in the cases of soil columns

Table 5. Percentage of BCD Adsorbed on Soils 1, 2, and 6 for Various BCD Concentrations Used

| BCD | | % adsorbed | | |
concn used (M)	mg g^{-1} of soil	soil 1	soil 2	soil 6
5×10^{-5}	0.113	30.1	100	100
1×10^{-4}	0.227	20.8	100	100
2.5×10^{-4}	0.567	20.7	86.4	95.6
3.5×10^{-4}	0.794	20.7	60.0	48.3

2 and 6 a great part of BCD (applied as BCD−NFL complex) may be adsorbed on these soils, yielding a strong NFL retention effect, because BCD would act as a bridge between NFL molecules and the soil surfaces. BCD adsorption on soil had been previously proved (29, 30), observing also as result a higher 2,4-D adsorption and a delay effect in its lixiviation in soil. On the contrary, in soil 1 most of the BCD applied is not adsorbed in the soil column, remaining then in soil solution higher concentrations of NFL as an inclusion complex with BCD.

The results obtained with the different soils employed indicated that BCD could play a double role depending on the soil type. On the one hand, BCD is able to act as a solubilizing agent in soils such as soil 1 due to its lower BCD adsorption. The advantage of this behavior for this kind of soil, with a high adsorption capacity for the herbicide and a very low desorption, would be the increase of availability of hydrophobic herbicides for weeds, because BCD decreases their high retention in soils, avoiding the use of higher amounts of herbicide, with the consequent environmental and economic disadvantage. On the other hand, its role as an agent that decreases the leaching of hydrophobic herbicides in sandy soils such as 2 and 6 is clear, due to the higher adsorption of BCD on these soils, acting as a bridge toward herbicide molecules. The main advantage in these soils, which have a low adsorption capacity for hydrophobic herbicides, could be a decreased leaching and, therefore, lower loss of active ingredient and a lower risk of groundwater contamination, because a great part of the herbicide remains in the upper horizons of the soils, where it would carry out its biological action on the roots of weeds.

An important conclusion that can be deduced from the results obtained in the present work is the necessity of carrying out an in-depth study about the interaction of different CDs used in soil treatments with soils presenting a wide variety of characteristics and properties, to determine the potential behavior of each CD in each kind of soil, because with the data that are available in the present paper, it is difficult to say too much about the extent and mechanisms of adsorption of BCD to the different fractions of the soils (silica sand, iron oxide coating, 1:1 and 2:1 clay minerals, and organic matter). This study is in progress.

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