

# Time-dependent sorption of norflurazon in four different soils: Use of $\beta$ -cyclodextrin solutions for remediation of pesticide-contaminated soils

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## Abstract

High pesticide concentrations in soil from spills or discharges can result in point-source contamination of ground and surface waters. Cost-effective technologies are needed for on-site treatment that meet clean-up goals and restore soil function. Remediation is particularly challenging when a mixture of pesticides is present.

$\beta$ -Cyclodextrins (BCD) solutions are employed to enhance the aqueous solubility of a hydrophobic organic compound. The interaction of norflurazon (NFL) with BCD yielded the formation of inclusion complexes at a 1:1 stoichiometric ratio in solution.

The change of the sorption parameter  $K_d$  as affected by the time, and desorption studies of NFL previously adsorbed on four different soils with different characteristics have been performed in the presence of 0.01 M BCD or 0.01 M  $\text{Ca}(\text{NO}_3)_2$  acting as extractant solutions. NFL sorption increased with the residence time in soil, making it more resistant to be desorbed. Likewise, leaching experiments were performed in packed soil columns eluting initially with distilled water, with the aim to simulate the herbicide drainflow losses because of rainfall, approaching to a more realistic environment, and later with 0.01 M BCD solutions to extract the residual NFL bound. The results showed that removal efficiencies of the different flushing systems were significantly influenced by their affinity and selectivity for the contaminants in the soil matrix as well as BCD adsorption on soils, since this could act like a bridge between pesticide molecule and soil particles increasing the stay of NFL in soil. These results are further information to be in condition to predict the potential effect of the BCD solutions on soil chemical decontamination in the field situation assessing the likelihood for bioremediation of a pesticide contaminated-soil, since the increasing in hydrosolubility of the contaminants means the first step before microorganism uptaken.

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## 1. Introduction

Soil contamination at agricultural land are not receiving timely attention because of high clean up costs and the negative impacts of public attention to the problem. Alternative low-cost and easy to implement are needed to accelerate the degradation and natural attenuation of pesticides [1]. Sorptive interactions between organic contaminants and the soil matrix are in function of the physico-chemical characteristics of soil/chemical combination. Further, there is an increasing evidence to support that sorptive effects are also a function

of the time [2,3]. Cox and Walker [4] showed that both the sorption and desorption partitioning coefficients increased with increasing incubation time. On the other hand, Koskinen et al. [5] concluded that sorption–desorption interactions of insecticide imidacloprid with soil determined its availability in soil for microbial degradation. Although the most researchers would agree that increasing the contact-time increases the sorption binding, thereby requiring a longer time to desorb, very little work has been performed to quantify this phenomenon [6,7]. On this basis, one of the objectives of this work will gain insight on this issue.

CDs have a low-polarity cavity within which organic compounds of appropriate shape and size can form inclusion complexes [8]. This property provides CD a capacity to increase the apparent solubility of several hydrophobic pollutants such as

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Table 1  
Some characteristics of the soils used

Soil	Textural classification	pH	CaCO <sub>3</sub> (%)	OM (%)	Sand (%)	Silt (%)	Clay (%)
1	Sandy clay loam	5.7	0.0	1.38	56.7	23.8	19.5
2	Silt loam	6.0	0.0	1.41	16.7	58.6	24.7
3	Loam	5.5	0.0	1.40	49.8	34.5	15.7
4	Clay	8.0	24.1	1.76	2.7	31.5	65.9

PAH, chlorinated solvents, pesticides, and nitroaromatic compounds and thus their bioavailability for biodegradation [9–13]. In the field of environmental research, because of non-toxicity and biodegradability, CDs have been applied to promote degradation of hazardous pollutants discharged in the aqueous environments. Furthermore CDs present several advantages over solvents and nonionic surfactants such as their lower toxicity and their higher biodegradability [14]. Although is a fact that surfactants have been shown to be capable of desorbing numerous organic contaminants [15–17] and subsequently enhance the mineralisation of them, however, there are potential drawbacks to the use of surfactants for *in situ* and *ex situ* remediation. This problem include sorption of the surfactant by soil, precipitation of the surfactant, phase separation, and foaming [18]. In addition, if surfactants are able to enhance the bioavailability of organic contaminants, then they must be compatible with the accompanying biological process. For example, nonionic surfactants have been shown to inhibit mineralisation of phenanthrene in soil water systems [19]. As discussed by McCray and Brusseau [20], CDs experience little or no sorption by soil and are not subject to precipitation, and hence they are easily removed from soil. On the other hand, based on published data, it would appear that CDs are becoming comparable in cost with surfactants [11]. Further, the cost of CDs has continuously decreased in recent years and investigations regarding their technical merit for soil remediation are justified.

Norflurazon (NFL) was first registered as a pesticide in the U.S. in 1974. NFL is a selective preemergent herbicide widely used to control germinating annual grasses and broadleaf weeds in fruits, vegetables, nuts, cotton, peanuts, and soybeans [21]. NFL presents problems with its retention in soils with high organic matter and iron oxides contents [22], and therefore it is a concern that NFL may persist in soils implying a great risk as long-term contaminant, since this compound could gradually be desorbed and available if the soil conditions change.

It has been recently demonstrated the formation of an inclusion complex between BCD and the herbicide NFL in solid and solution state [12], and in this way this work will mean an extension of the previous paper from a point of view to obtain an efficient *in situ* soil decontamination tool.

The main objective of this work is to test the potential effect of BCD to remediation of contaminated-pesticide soil, through determination of the influence of the type of soil and the contact-time between the herbicide and soil. Likewise, studies about BCD adsorption on soil were carried out to clarify the decontamination mechanism.

## 2. Materials and methods

### 2.1. Materials

Technical NFL (purity 97.8%) was kindly supplied by Novartis, and  $\beta$ -CD (99%) by Roquette (Lestrem, France). Four different soils were employed to carry out the herbicide behaviour experiments in soil. They were taken from superficial horizon (0–20 cm) and their main physico-chemical properties are shown in Table 1. All reagents were of analytical grade. Soils are from southwestern Spain. Soils were sterilised (in autoclave) and analysed for pH in saturated paste, total carbonate content, particle size distribution, and organic matter content (OM).

### 2.2. NFL adsorption–desorption experiments

Triplicate adsorption experiments were performed by mixing 5 g of the soil samples with 10 ml of 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> solution, containing 20 mg l<sup>-1</sup> NFL solution in 50 ml polypropylene centrifuge tubes. The samples were shaken at 20 ± 1 °C. After shaking, the suspensions were centrifuged and the concentration of NFL in the supernatant was determined by using a Shimadzu HPLC equipped with diode array detector (Shimadzu SPD-M10A) at a wavelength of 220 nm. BCD was not detected using this analytical method, and therefore, it did not interfere with the assay. The conditions were as follows: mobile phase, acetonitrile:water (60:40); flow, 0.6 ml/min; temperature, 30 °C; chromatographic column kromasil C18 reverse phase. The difference in pesticide concentration between the initial and final pseudoequilibrium solutions was assumed to be due to sorption, and the amount of NFL retained and therefore the adsorbed was calculated.

Desorption experiments were performed after adsorption pseudoequilibrium was reached, by removing the supernatant after centrifugation and replacing it by 10 ml of 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> or BCD extractant solutions, allowing equilibration for an additional 24-h shaken-period, and after that operating as in the adsorption experiment. This process was repeated twice more. Adsorption–desorption experiments were repeated with new centrifuge tubes taken at different selected time. These selected time intervals were 1, 15 and 30 days.

### 2.3. Leaching experiments in soil columns

Leaching experiments were done in triplicate for feasible selected soils. Homogeneous soil columns were prepared by packing gently and uniformly the soils in 18-cm long metacrylate tubes of 3.0 cm of 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, in order to prevent disturbance of the soil by the input liquid. Different amounts of each soil were put in the columns in order to obtain 12 cm of the column occupied by soil (125, 100, 120 g in the case of soils 1, 2 and 3, respectively).

In a preliminary experiment, two soil columns of each soil were saturated by capillarity with distilled water to obtain 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.

Soil columns were treated with 5 pore volumes of a 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution to equilibrate them with the background electrolyte, and subsequently 14 ml of 20 mg l<sup>-1</sup> (3.96 kg ai ha<sup>-1</sup>) NFL solution was applied. Breakthrough curves (BTCs) were obtained by a daily (soil 1) application of 10 ml of distilled water, when it was practicable, until no herbicide was detected in the

leachate. Following an only dose of 10 ml of 0.01 M BCD solution was applied to extract the NFL residues bound obtaining new BTCs. Only in the cases of soils 1 and 3 a daily application of 10 ml of water was possible due on one hand to low porosity showed by soil 2 and on the other hand no leaching experiments could be performed with soil 4 which has a very high clay content (65.9%) and therefore no leachate could be collected.

#### 2.4. BCD adsorption experiments in soil

BCD adsorption experiments in soils 1, 2 and 3 were carried out in triplicate using the same conditions mentioned previously, but mixing the soils with solutions containing various BCD concentrations ( $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$ ,  $5 \times 10^{-4}$ ,  $7.5 \times 10^{-4}$ ,  $1 \times 10^{-3}$  M) during 24 h. BCD remaining in the supernatant was analysed by HPLC with fluorimetric detection using a postcolumn reaction based on the enhancement of fluorescence post intensity of 2-(*p*-toluidino) naphthalene-6-

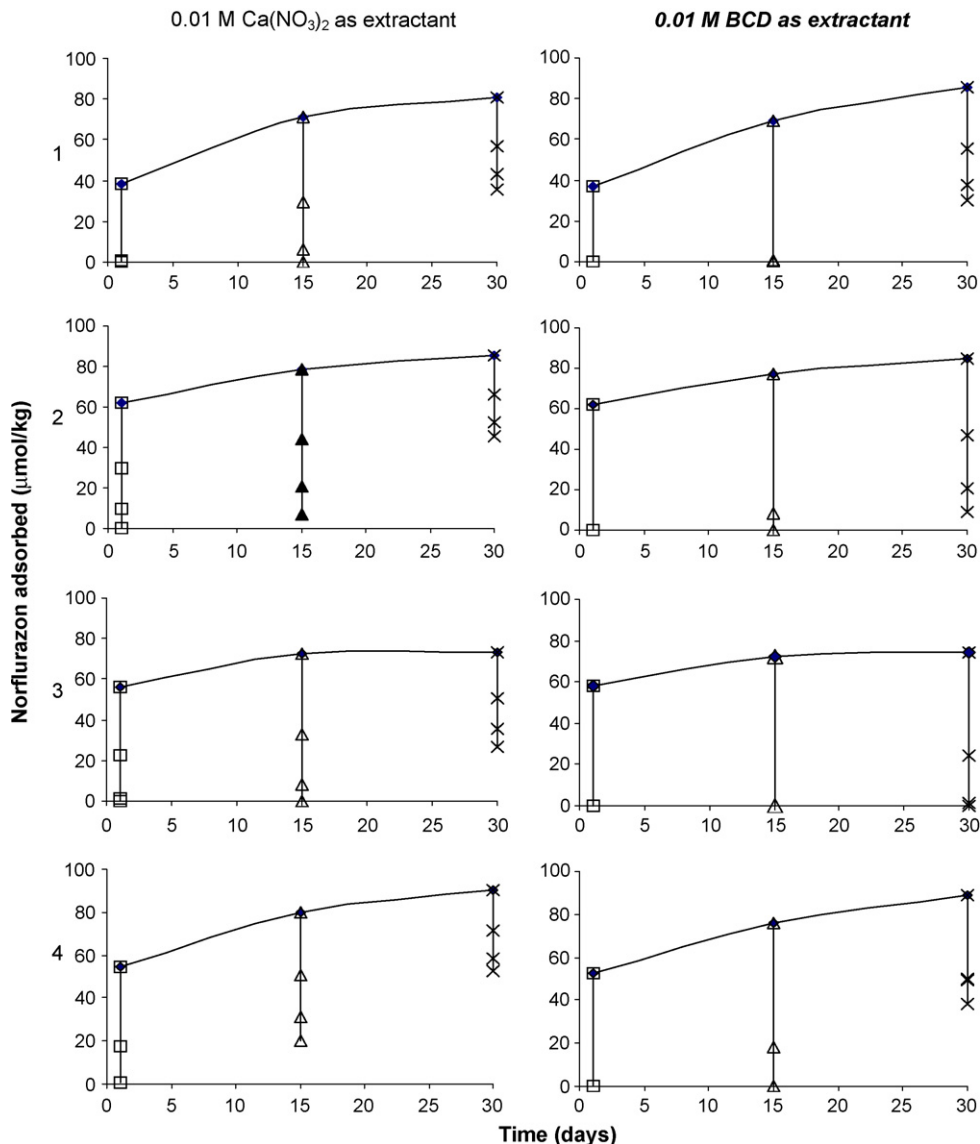


Fig. 1. Norflurazon adsorption–desorption with time for soils under study, using 0.01 M  $\text{Ca}(\text{NO}_3)_2$  and BCD as extractant solutions.

sulfonic acid (TNS Sigma) following the method proposed by Takeuchi and Miwa [23]. 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 nm and 465 nm, respectively.

### 3. Results and discussion

In a previous work [12], the formulation of inclusion complex in solution of the herbicide NFL as guest and BCD as host was studied, and the interaction produced the formation of an inclusion complex in solution state with an apparent stability constant of  $360 \text{ M}^{-1}$ , a 1:1 stoichiometric ratio for the complex, and up to five-fold in NFL hydrosolubility.

#### 3.1. Adsorption–desorption experiments

Adsorption–desorption kinetic experiments were carried out to elucidate which is the influence of the contact-time in the adsorption–desorption capacity of the soils under study as well as the influence of their properties. The observation of sorption fluctuation and hysteresis has a significant implication from the viewpoint of remediation, since the treatment efficiency may be varied with time and it may be difficult to remove the sorbed chemicals because of the resistant fraction.

In Fig. 1 are shown the plots (NFL adsorbed versus time) corresponding to soils 1, 2, 3, and 4. Measurements of NFL in the supernatant from the soil at selected intervals, during the laboratory experiment, demonstrated an apparent increase in the strength of adsorption with time in all soils, especially in the case of soil 1 where adsorption was increased by an average factor of 2.20 after 30-day shaken-period. The increase in the adsorption on the others soils was by the range 1.30–1.70.

In Table 2, sorption coefficients ( $K_d$ ) are shown. In general,  $K_d$  values increased with time for all soils under study, obtaining values by the range of 0.91–1.79 (after 1 day) and 3.15–4.77  $\text{mg l}^{-1}$  (after 30 days) what would show up that not only the physico-chemicals properties of soil would influence on increment of NFL adsorption, since the  $K_d$  values obtained varied not only between the different soils but also with time. These increases in  $K_d$  with time had been previously observed for a variety of pesticides such as atrazine and metolachlor [24], isoproturon [25],

atrazine [26]. Imidacloprid sorption, as indicated by  $K_d$  values, increased by a factor of 2.8 in three soils during a 16-week period [27,7], this fact was held to herbicide diffusion to less accessible or stronger binding sites with time. Likewise, Tsai et al. [28] performed adsorption kinetics onto bleaching earth of herbicide paraquat relating, in this case, the intra-particle diffusion mechanism with the increasing of the adsorption. Lesan and Bhandari [29] obtained an important conclusion from their experiments with the herbicide atrazine, indicating that physico-chemical processes which occurring at intra-mineral and intra-organic matter sites continue to influence the fate of organic pesticides long after their application in soils. On the other hand, Van Beinum et al. [30] carried out experiments based on pesticide sorption in soils is controlled by time-dependent processes such as diffusion into soil aggregates and microscopic sorbent particles. Other authors [24,31,32] came also to reach this conclusion and stating that diffusion process in soil are a cause of time-dependent sorption, since this step would influence in the intra-particle soil sorption.

In our case, it is emphasizeable how the lowest increase in the sorption parameter ( $K_d$ ) was obtained for the soil 3 (1.79–3.01). This fact can be linked to the lowest clay content of this soil (Table 1) regarding to the other soils under study where similar increases were obtained. Hwang and Cutright [33] found similar results for the pyrene sorption in soil after a contact-time period of 10 days, attributing it to a clay interlayer expansion upon wetting, resulting in a large internal surface area, where the chemical could be easily adsorbed.

The contact-time may be associated with the continuous diffusion of contaminant into small pores where NFL can be retained by adsorption, and it also means that toxic organic chemicals that have been in contact with the soil matrix for a long time are unlikely to be available to humans, animals or plants [34]. However, it is not known long this fraction remains in this state or whether the contaminant will be remobilized and so become extractable and bioavailable [35]. In order to test the influence of contact-time on possibility that NFL could return to the soil solution thus herbicide was bioavailable for biodegradation, desorption experiments were also performed.

Replicated soil samples were periodically desorbed using two different extractants solutions: 0.01 M BCD and 0.01 M  $\text{Ca}(\text{NO}_3)_2$ . These different solutions were aimed at showing up the potential soil decontamination effect of BCD solutions regarding to occasional rainwater application. In Fig. 1 it can be clearly observed how as time goes is more difficult the NFL desorption for both extractant solutions. Likewise, in Table 3 percentage of NFL desorbed (%D) from soil are shown. When 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution was employed it was not be able to extract 100%D in any soil after 30-day shaken-period, being outstanding the cases of soils 2, and 4 where %D were only 46.65% and 41.93%, respectively, even after 30-day shaken-period. The difficulty for the NFL desorption as time goes is in that NFL molecules are able to reach the sorptive points in the soil. Lu and Pignatello [36] showed that irreversible sorption can occur when a sorbate causes structural changes in the sorbent that enhance the sorption strength.

Table 2  
Sorption coefficients ( $K_d$ ) at different periods of time for the soils under study

Soils	$K_d$ ( $\text{mg l}^{-1}$ )		
	1 day	15 days	30 days
1	0.91 ± 0.03	2.76 ± 0.15	4.44 ± 0.61
2	1.61 ± 0.08	3.61 ± 0.17	4.77 ± 0.07
3	1.79 ± 0.06	3.01 ± 0.01	3.15 ± 0.07
4	1.29 ± 0.06	2.63 ± 0.37	4.52 ± 0.15

Table 3  
Percentage of NFL desorption (%D) at different periods of time for the soils under study, using 0.01 M calcium nitrate (CN) and BCD as extractant solutions

Soils	%D using CN			%D using BCD		
	1 day	15 days	30 days	1 day	15 days	30 days
1	100.00 ± 0.00	99.88 ± 0.20	55.74 ± 3.70	100.00 ± 0.00	100.00 ± 0.00	64.87 ± 7.73
2	100.00 ± 0.00	91.25 ± 8.78	46.65 ± 1.91	100.00 ± 0.00	100.00 ± 0.00	89.39 ± 2.39
3	100.00 ± 0.00	99.98 ± 0.02	63.73 ± 4.20	100.00 ± 0.00	100.00 ± 0.00	100.00 ± 0.00
4	100.00 ± 0.00	74.57 ± 11.69	41.93 ± 2.39	100.00 ± 0.00	100.00 ± 0.00	57.02 ± 1.46

On the other hand, when 0.01 M BCD extractant solution was employed only from the 30-day shaken-period it was not able to extract 100%D except in the case of soil 3. This latter result would be related with its low clay content (15.7%) what show up its low NFL sorption capacity, but in any case when this extractant solution was employed %D was always higher compared to 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution, even in the case of soil 2 reaching a %D close to 90%. NFL desorption after three consecutive steps (3 days) has been already reported [13] and 100%D was obtained employing only and stoichiometric BCD concentration regarding the NFL previously adsorbed on six soils with different textures. From these results the effectiveness of BCD solution as *in situ* remediation tool, is again proved for a realistic environment, since its application will be after a definite period of time. Recently, Doick and Dew [37] emphasized that to assess the potential of a contaminated site for bioremediation, it would be desirable to know how much of the contaminant is available for microbial degradation to know the likelihood of successful bioremediation and on this basis it was concluded the great potential of the CD extraction in the assessment of soil prior bioremediation.

### 3.2. Mobility experiments

The aim of this experiment was to test the BCD solutions effect in a dynamic equilibrium context on herbicide-contaminated soils 30 days after application. In the previous NFL adsorption–desorption experiments, the time-dependent NFL soil sorption and the NFL availability to be desorbed have been clearly demonstrated. In batch equilibrium tests, the contact times of the pesticide with the soil are considered to be very rapid, whereas a limitation in transport of the active ingredient to the sorption sites occurs in soil column and field experiments. In batch pseudoequilibrium experiments, therefore, this may not play a role owing to the complete dispersion of the soil particles. Based on this fact 0.01 M BCD solution has been used on hand-packed soil columns after 30 days carrying out successive distilled water applications, attempting to simulate the soil solution replacing provoked by irrigating or rainfall.

The results obtained from soil columns 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. Three soils (1, 2, and 3) were selected to study the mobility of NFL in hand-packed soil columns and their pore volumes were: 32.40, 53.33, and 32.80, respectively. Fig. 2 shows the BTCs for the soils under study, and Table 4 shows the percentage of NFL

eluted in the leachates from the soil columns. Soil 1 showed a BTC profile where two maximums can be clearly observed corresponding to distilled water application and later to 0.01 M BCD solution application. In the case of soil 2, no leaching could be detected during the distilled water application and in soil 3 only a slight flat peak was observed. On the other hand, in soil 3, both of peaks underwent a delay compared to others soils, since in this case the NFL leaching resulted in a slower rate.

It is emphasize how when distilled water was applied for the soil 2, NFL was not practically eluted (0.06%), whereas in the cases of soils 1 and 3 a 40.68% and 45.31% was eluted,

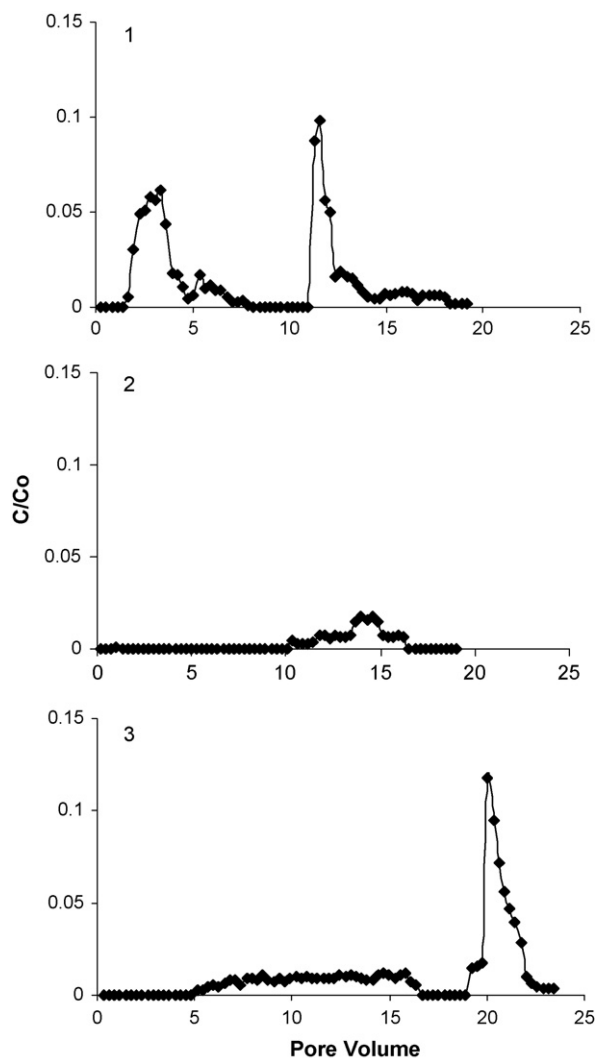


Fig. 2. Norflurazon breakthrough curves in soils.

Table 4

Percentage of NFL applied eluted from soil columns using distilled water and after 0.01 M BCD as extractant solutions

Soils	Distilled water	0.01 M BCD solution	Distilled water + 0.01 M BCD solution
1	40.68 ± 2.42	40.20 ± 2.00	80.88 ± 4.42
2	0.06 ± 0.01	18.67 ± 0.85	18.73 ± 0.86
3	45.31 ± 1.83	43.28 ± 3.05	88.59 ± 4.88

Table 5

BCD applied (mg) applied per gram of soils (1, 2 and 3) and % BCD adsorbed

BCD concentration applied (M)	mg BCD applied/g soil	% BCD adsorbed		
		Soil 1	Soil 2	Soil 3
Batch experiments				
$5 \times 10^{-5}$	0.1125	14.99 ± 0.51	53.06 ± 1.01	0.00 ± 0.00
$1 \times 10^{-4}$	0.2674	21.51 ± 0.78	36.47 ± 0.85	0.00 ± 0.00
$2.5 \times 10^{-4}$	0.6685	18.72 ± 0.62	27.19 ± 0.75	0.00 ± 0.00
$5 \times 10^{-4}$	1.337	17.15 ± 0.59	19.28 ± 0.60	0.00 ± 0.00
$7.5 \times 10^{-4}$	2.005	13.46 ± 0.94	16.59 ± 0.55	0.00 ± 0.00
$1 \times 10^{-3}$	2.674	10.01 ± 0.41	14.72 ± 0.45	0.00 ± 0.00
mg BCD applied/g soil				
Soil 1		Soil 2		Soil 3
Mobility experiments				
0.908		1.135		0.945

respectively. These results were mainly related with soil texture (Table 1), that is to say, those soils with a high sand content, 56.7% and 49.8% for the soils 1 and 3, respectively, showed the highest percentage of lixiviation and the soil 2 with only a 16.7% in sand content showed a very low elution capacity. Renaud et al. [38] carried out leaching experiments of three pesticides in four soils with different properties and ranging in the texture from sandy loam to clay, observing a rapid decline in leached loads of isoproturon and chlortoluron as time from application to irrigation increased.

When BCD solution was used in all cases it was obtained an increase of the total NFL eluted, even in the case of soil 2 where NFL eluted was increased up to 18.73%. This fact is due to that all NFL is not available to be leached through the packed-soil column by only adding distilled water, being necessary the addition of an extractant as 0.01 M BCD solution. It is emphasize that even employing only one dose of BCD solution in no case a 100% of NFL eluted was reached and a 88.59% was the maximum percentage obtained, corresponding to the soil 3. This fact is in according to results previously obtained in the desorption batch experiments where using BCD solution after 30 days shaken-period only in soil 3 a 100% of %D was obtained.

### 3.3. BCD adsorption experiments

In order to test if the higher retention of NFL in the column of soils 2 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. Table 5 shows the BCD applied on soils

1, 2 and 3, and their corresponding percentages of BCD sorbed. It is remarkable that in the case of soil 3 the BCD applied was not adsorbed at the concentrations under study. In Table 5 can be also observed mg BCD applied in the mobility experiments with a proportion ranged from 0.908 to 1.135 mg BCD/g soil which correspond to a BCD concentration used in batch experiments between  $2.5 \times 10^{-4}$  and  $5 \times 10^{-4}$ . In this range % BCD adsorption were as following order: soil 2 > soil 1 > soil 3. These results are crucial to explain the percentages of NFL eluted obtained after BCD solution was applied in soils 1, 2 and 3 (40.20, 18.67 and 43.28, respectively), that is to say, as higher BCD adsorption lower NFL availability for leaching. This fact is because of when BCD is adsorbed on soil it would act as a bridge between NFL molecules and the soil surfaces. BCD adsorption on soil had been previously reported by Pérez-Martínez et al. [9,39] observing as result a higher 2,4-D adsorption and delay effect in its lixiviation in soil.

What can be inferred from this result is that the effectiveness of application of BCD solutions as an *in situ* soil decontamination tool it is going to depend on their physico-chemical properties and texture, and therefore previous studies about the contaminated soil should be carried out.

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