Effect of Soil Type on Adsorption–Desorption, Mobility, and Activity of the Herbicide Norflurazon

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Adsorption–desorption studies of norflurazon on 17 soils of very different characteristics have been performed using a batch equilibration method and correlated to its mobility, activity, and persistence in soils. The influence of different soil properties and components on norflurazon adsorption was determined. The significant variables were organic matter (OM) content and iron and aluminum oxides, which accounted for 85 and 11% of the variability, respectively. Norflurazon desorption from soils was hysteretic in all cases, being more irreversible at the lowest herbicide concentrations adsorbed. The percentage of norflurazon eluted from columns of selected soils reached almost 100% in soils with sand content >80% and OM <1%, but in the soil which gave the highest sorption, herbicide residues were not detected at depths >16 cm. The herbicidal activity of norflurazon was followed by measuring its bleaching effect on soybean plants, and the herbicide concentration required to give 50% chlorophyll inhibition (CI_{50}) was calculated. CI_{50} was achieved on a sandy soil with 0.08 mg kg^{-1}, whereas 1.98 mg kg^{-1} was necessary for the soil that presented maximum norflurazon adsorption.

KEYWORDS: Norflurazon; soil; adsorption–desorption; mobility; activity

INTRODUCTION

Norflurazon is a fluorinated pyridazinone herbicide registered for soil-applied use in cotton, soybean, tree fruit and nut crops, citrus, and cranberries (*1*). Norflurazon is a potent inhibitor of carotenoid biosynthesis and chlorophyll accumulation and also interferes with membrane lipid formation. Its retention in soil is related to organic matter content but, according to Willian et al. (*2*) and Suba and Essington (*3*), it is not related to other soil parameters. However, other authors reported significant correlation to soil pH and cation exchange capacity (*4*), or to clay content (*5*), although Lo and Merkle (*6*) found a higher correlation with some clay minerals, such as montmorillonite and vermiculite, instead of the total clay content.

There is also controversy in relation to norflurazon mobility in soils. According to Ahrens (*1*), norflurazon does not leach appreciably. Singh et al. (*7*) and Mueller et al. (*8*) observed that it remained in the top layers of sandy and loamy sand soils, respectively. Willian et al. (*2*) observed in a leaching study that norflurazon concentration was greater in the 0–8 cm zone and was not detected below 15 cm in silt loam and loamy sand soils. On the contrary, norflurazon has been detected in surface- and ground-water monitoring studies (*9*, *10*), although such contamination is assumed to come partly from herbicide losses in runoff (*11*, *12*). Herbicide leaching not only causes ground-

water contamination but also reduces activity on weeds by decreasing available herbicide in the topsoil, where weed roots grow. Reddy et al. (*4*) and Morillo et al. (*13*) observed a large degree of norflurazon desorption in porous soils with low organic matter (OM) content, which suggests an increase in subsequent leaching through the soil profile. Appreciable leaching was observed by Singh et al. (*14*) in soil columns of a fine sandy soil, where norflurazon leached to a depth of 38 cm. To retard norflurazon leaching in soil, Boydston (*15*), Undabeytia et al. (*16*), and El-Nahhal et al. (*17*) prepared controlled-release formulations of norflurazon, to prevent this herbicide from reaching deep soil layers and injuring perennial crops grown on sandy soils under sprinkler and deep irrigation.

Norflurazon weed control activity depending on soil type has received very little attention, despite its being a very important factor when the herbicide has to be applied to soil (*18*). Schroeder and Banks (*19*) studied five soils (three of them classified as clay loam, one sandy loam, and one loamy sand) and observed that OM content was the primary factor influencing the activity response, but the clay component may have also contributed. Lo and Merkle (*6*) studied only three soils and deduced that soils containing vermiculite and montmorillonite clay minerals required higher norflurazon concentrations to induce the same level of plant injury.

The majority of studies related to norflurazon behavior in soils have been obtained using very few soils. Therefore, the objective of this paper is to find the factors affecting norflurazon

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Table 1. Land Use and Classifications of the Soils Used

soil	textural classification	USDA classification[a]	land use
1	sand	Typic Endoaquept	agricultural
2	sandy clay loam	Vertic Xerochrept	agricultural
3	silt loam	Aquic Dystric Eutrochrepts	agricultural
4	loam	Aquic Haploxeralf	agricultural
5	silt loam	Typic Eutrochrept	pasture
6	loam	Ultic Haploxeralf	agricultural
7	sandy loam	Typic Haphorthod	pasture
8	loam	Typic Dystrochrept	pasture
9	loamy sand	Typic Haplorthod	forest
10	loamy sand	Typic Xeropsament	agricultural
11	sandy clay loam	Typic Xerofluvent	agricultural
12	sandy loam	Typic Xerochrept	agricultural
13	loam	Typic Xerofluvent	agricultural
14	clay	Salorthidic Fluvaquent	agricultural
15	clay	Entic Pelloxerert	agricultural
16	sandy clay loam	Typic Xerorthent	agricultural
17	clay	Entic Pelloxerert	agricultural

[a] *Soil Taxonomy 1987.*

adsorption using 17 soils of very different characteristics and to correlate these factors with norflurazon mobility and activity in soils.

MATERIALS AND METHODS

Technical grade norflurazon (97.8% purity) was kindly supplied by Syngenta (Basel, Switzerland). Its structural formula is shown below.
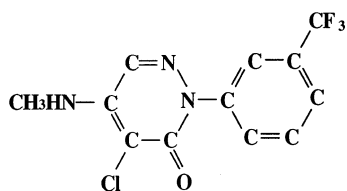
The top 20 cm of 17 soils were collected. They were dried and crushed to pass a 2 mm sieve and were not sterilized before using. Land use and textural and USDA classification of the soils are shown in **Table 1**. All soils are from southwestern Spain except soils 7, 8, and 9, which are from Scotland, Wales, and Germany, respectively. They were analyzed for pH in saturated paste, total carbonate content, particle size distribution, cationic exchange capacity, and organic matter content. The above-indicated properties of the soils used are given in **Table 2**. Organic carbon content (OC) was determined as follows: OC (%) = 0.58 × OM (%). The amorphous and organically bound iron, manganese, and aluminum oxides were determined using ammonium oxalate−oxalic acid (*20*) and are shown in **Table 3**.

Adsorption−Desorption Studies in Batch Experiments. Quadruplicate adsorption experiments were performed by mixing 10 g of the soil with 20 mL of 0.01 M Ca(NO$_3$)$_2$ solution, containing various concentrations (4, 8, 12, 16, and 20 mg L^{-1}) of norflurazon, in 50 mL polypropylene centrifuge tubes. 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 shaking (on an orbital shaker), the suspensions were centrifuged, and the concentration of norflurazon in the supernatant was determined by using a Shimadzu HPLC equipped with a fluorescence detector, according to the method described by Willian and Mueller (*21*). The difference in pesticide concentration between the initial and final equilibrium solutions was assumed to be due to sorption, and the amount of norflurazon retained by the adsorbent was calculated.

Desorption experiments were performed after adsorption equilibrium had been reached for the points corresponding to norflurazon initial concentrations of 4, 12, and 20 mg L^{-1} by removing half of the

Table 2. Some Characteristics of the Soils Used

soil	pH	CaCO$_3$ (%)	OM (%)	CEC (cmol$_c$ kg^{-1})	sand (%)	silt (%)	clay (%)
1	6.5	0.0	0.51	3.5	92.8	4.4	2.5
2	5.7	0.0	1.38	5.8	56.7	23.8	19.5
3	6.0	0.0	1.41	12.4	16.7	58.6	24.7
4	5.5	0.0	1.40	7.8	49.8	34.5	15.7
5	7.6	0.0	1.90	17.2	16.4	61.2	22.6
6	5.8	0.0	2.48	9.5	34.2	48.2	17.6
7	4.8	0.0	5.34	20.1	61.1	29.0	9.8
8	5.8	0.0	6.44	18.3	46.4	36.8	17.0
9	4.6	0.0	15.92	32.7	81.6	12.7	6.0
10	8.0	6.9	0.79	4.8	87.6	4.0	8.4
11	8.4	13.4	1.45	12.3	54.5	24.0	21.6
12	8.7	15.8	0.78	7.6	75.3	11.7	13.0
13	8.4	19.7	1.50	12.8	44.8	32.6	22.6
14	7.9	22.0	1.59	20.9	3.0	34.9	62.2
15	8.0	24.1	1.76	39.0	2.7	31.5	65.9
16	7.9	27.0	0.53	9.4	57.6	21.1	21.3
17	8.0	38.8	1.67	29.2	6.9	28.4	64.7

Table 3. Amorphous Iron, Manganese, and Aluminum Oxides in the Soils

soil	Fe$_2$O$_3$ (g kg^{-1})	MnO (g kg^{-1})	Al$_2$O$_3$ (g kg^{-1})	total (g kg^{-1})
1	0.3	<0.1	0.3	0.6
2	1.4	<0.1	0.3	1.7
3	8.4	9.2	8.5	26.1
4	1.9	0.1	1.0	3.0
5	10.8	9.8	9.4	30.0
6	2.7	0.1	1.1	3.9
7	23.3	<0.1	12.3	35.6
8	4.8	0.4	2.9	8.1
9	0.5	<0.1	2.0	2.5
10	0.4	<0.1	0.2	0.6
11	0.8	<0.1	1.0	1.8
12	0.5	0.1	0.7	1.3
13	1.1	<0.1	1.2	2.3
14	2.5	0.2	2.0	4.7
15	0.8	0.2	3.5	4.5
16	0.3	0.1	0.9	1.3
17	0.7	0.1	1.1	1.9

supernatant after centrifugation, replacing it by 10 mL of 0.01 M Ca-(NO$_3$)$_2$ solution, allowing equilibration for an additional 24h period, and after that operating as in the adsorption experiment. This process was repeated twice.

Sorption−desorption 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 that characterize the relative sorption capacity and the sorption intensity, respectively, for the herbicide. 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.

Multiple linear regression analysis was used to identify predictive equations for norflurazon adsorption affinity (expressed as its distribution coefficient, K_d) as a function of the properties of the soils used. Using the stepwise procedure in the statistical analysis program JMP version 3.1 (*22*), the soil properties given in **Tables 2** and **3** were evaluated as predictors of its adsorption affinity. The stepwise procedure performs a multiple-regression analysis in which parameters are added to or subtracted from the regression, depending on the contribution of each parameter on R^2. Parameters were added to the model in order of
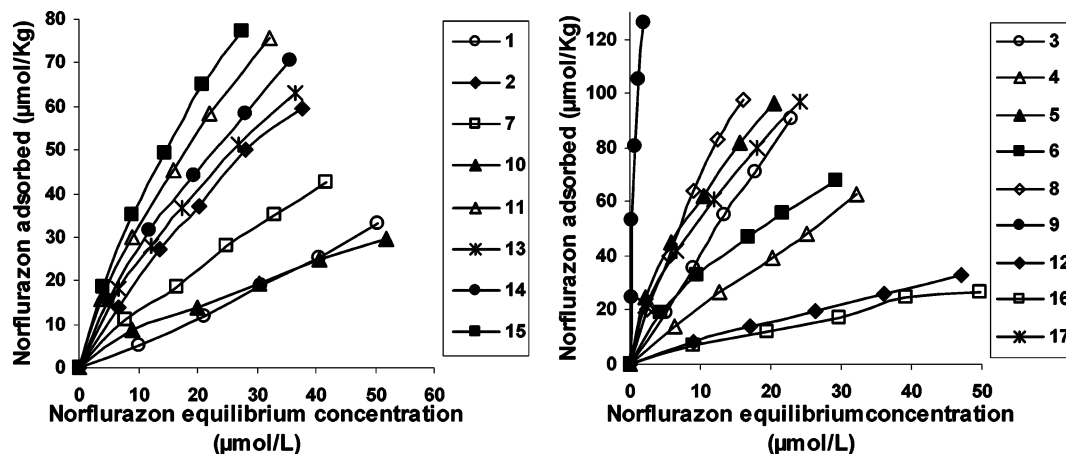
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Figure 1. Norflurazon adsorption isotherms on soils.

significance, if the significance level (*p* value) of the slope coefficient was ≤0.10. In a final step, nonsignificant (*p* > 0.05) variables were eliminated, leaving only significant variables at *p* ≤ 0.05 in the final model.

Hysteresis coefficients, *H*, for the sorption−desorption isotherms were calculated according to

$$H = n_a/n_d$$

where n_a and n_d are the Freundlich *n* constants obtained from the sorption and desorption isotherms, respectively. This ratio n_a/n_d has been also used by other authors to describe the hysteretic behavior of desorption from soils (*23, 24*).

Leaching Experiments in Soil Columns. Leaching experiments were done in triplicate for selected soils. 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 to obtain 24 cm of the column occupied by soil. The soil column could be readily separated into 4 cm segments after a 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.

The soil columns were treated with 5 pore volumes of a 0.01 M Ca(NO$_3$)$_2$ solution to equilibrate them with the background electrolyte, and subsequently 14 mL of 20 mg L^{-1} (3.96 kg of ai ha^{-1}) norflurazon solution was applied. Breakthrough curves (BTCs) were obtained by a daily application of 25 mL of distilled water until no herbicide was detected in the leachate. In soils with low porosity the application of 25 mL of water was not possible every day, due to the low leaching velocity. 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.

Activity Measurements Using Bioassays. One method of following herbicide movement in soil is by bioassay utilizing a plant indicator. The bioassay method has also been used to develop standard curves for converting indicator plant dry weight or bleaching to herbicide concentration. The herbicidal activity of norflurazon in soil was followed by measuring its bleaching effect on soybean plants after 10 days, in comparison to a control that did not receive any application of the herbicide. A dose−response curve was established, shaking thoroughly for 24 h 20 g of each selected soil with appropriate quantities of the herbicide to achieve concentrations between 0 and 2 mg kg^{-1}. Five soybean seeds were placed on 10 g of soil in 3 cm diameter plastic disposable containers and were covered with another 10 g of the soil.

Table 4. Freundlich Adsorption Isotherm Parameters (K_f and *n* Values), Coefficients of Determination (R^2) and Distribution (K_d), and Organic Carbon Normalized Distribution Coefficients (K_{oc}) of Norflurazon Sorption on the Soils Used

soil	OM	K_f	*n*	R^2	K_d	K_{oc}
1	0.51	0.35 ± 0.02	1.15 ± 0.02	0.999	0.49	166
16	0.53	1.15 ± 0.25	0.81 ± 0.06	0.983	0.74	241
12	0.78	1.42 ± 0.10	0.81 ± 0.02	0.997	0.92	203
10	0.79	1.70 ± 0.15	0.72 ± 0.03	0.995	0.89	193
2	1.38	2.80 ± 0.26	0.85 ± 0.03	0.999	1.98	247
4	1.40	2.58 ± 0.14	0.91 ± 0.02	0.998	2.10	258
3	1.41	3.35 ± 0.46	1.05 ± 0.05	0.993	3.76	460
11	1.45	5.91 ± 0.07	0.73 ± 0.00	0.999	3.17	372
13	1.50	4.33 ± 0.07	0.74 ± 0.01	0.999	2.38	273
14	1.59	4.83 ± 0.17	0.75 ± 0.01	0.999	3.22	348
17	1.67	13.28 ± 0.23	0.62 ± 0.01	0.999	5.54	572
15	1.76	6.56 ± 0.25	0.75 ± 0.01	0.998	3.69	361
5	1.90	15.54 ± 0.54	0.61 ± 0.01	0.998	6.33	575
6	2.48	7.34 ± 0.18	0.65 ± 0.01	0.999	3.28	228
7	5.34	2.00 ± 0.21	0.81 ± 0.03	0.995	1.29	42
8	6.44	16.21 ± 0.53	0.86 ± 0.02	0.997	6.67	178
9	15.92	93.04 ± 5.38	0.61 ± 0.05	0.981	27.89	301

The soil samples were placed in a growth chamber at 25 ± 3 °C and moistened with distilled water every day. The bleaching intensity was obtained by measuring the chlorophyll content and determining the inhibition percentage in relation to the chlorophyll content for the control soil (no herbicide added). The chlorophyll content was determined by cutting the fresh shoot of soybean plants and extraction with 4 mL of *N,N*-dimethylformamide. The solutions were incubated for 48 h, and the chlorophyll content was measured by visible spectroscopy at 664 and 647 nm and related to the weight of the fresh shoot. The experiment was carried out in quadruplicate. The data obtained were used for regression analysis to estimate the CI$_{50}$ (herbicide required to give 50% chlorophyll inhibition). Different equations were tested for their suitability to describe the relationship between inhibition and herbicide concentration. The equation with the highest R^2 value was judged to be the most appropriate.

RESULTS AND DISCUSSION

Adsorption Experiments. Figure 1 shows the sorption isotherms of norflurazon on the soils studied. On the whole, the isotherms were "L" type (concave initial curvature) according to the classification of Giles et al. (*25*), and in all cases norflurazon adsorption isotherms were well described by the linearized Freundlich equation. The sorption isotherms were compared using the K_f parameter of the Freundlich equation (**Table 4**). 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

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can be used to compare the adsorption capacity of the different soil samples toward norflurazon. K_f varied between 0.35 and 93.04 μmol kg^{-1}, indicating the strong influence of soil characteristics on norflurazon adsorption.

Norflurazon adsorption has been previously related to the OM content of soils (*2*), and, in most cases, K_f values of our isotherms indicated that the affinity of the soils for norflurazon was related to their OM content (**Table 4**). However, this relationship was not true in some cases, such as in soil 6, with higher OM content than others (soils 5 and 17) but lower adsorption capacity. It indicates that OM content may not be the only factor determining norflurazon adsorption in this soil (*4*).

The role of hydrophobic bonds on adsorption of nonpolar hydrophobic herbicides on organic matter of soils can be compared by normalizing the distribution coefficient, K_d, to the percentage of organic C of the different samples (K_{oc}). The more hydrophobic a molecule is, the higher the probability for partition from the aqueous phase to the organic phase. K_{oc} can be used as a measure of this property in soils, and it is independent of other soil properties. When hydrophobic bonds are responsible for the adsorption of a herbicide, K_{oc} values should be relatively constant among different soils.

The estimated distribution coefficients, K_d, and the OC normalized distribution coefficient, K_{oc}, are also shown in **Table 4**. K_d values for herbicide adsorption on these soils ranged between 0.49 (soil 1) and 27.89 (soil 9). Such a wide range of K_d values suggests weak to moderate binding capacity of these soils for norflurazon. Some K_d and K_{oc} values found in this study were similar to those reported by other authors. Reddy et al. (*4*) found K_d values between 0.63 and 2.20. Similar results were obtained by Hubbs and Lavy (*5*), with K_d values ranging from 0.54 to 2.75. Alva and Singh (*26*) observed a K_d value of 16 in the case of norflurazon adsorption on a soil with an OM content of 3.4%; however, K_d presented values between 0.4 and 2.3 in soils with OM contents below 1.4%. Suba and Essington (*3*) obtained K_d values between 2.04 and 12.15.

Although the K_{oc} mean value given for norflurazon is 248 (*27*), the values obtained in this study ranged from 42 to 575. Values similar to those in our study were observed by Reddy et al. (*4*) (K_{oc} from 144 to 373), Hubbs and Lavy (*5*), with an average K_{oc} of 78, and Alva and Singh (*26*) (average K_{oc} of 122). Suba and Essington (*3*) reported higer K_{oc} values (ranging from 456 to 551), which did not vary greatly with soil OC content, illustrating the influence of this parameter on norflurazon adsorption. In our case, K_{oc} values demonstrated a wide range, indicating that the sorption mechanism is perhaps related to some other soil properties in addition to OC content.

There are some soils with very high K_{oc} values (soils 3, 5, 11, 14, 15, and 17), and soil 7 has a very low K_{oc} (**Table 4**). If these soils are not taken into consideration, the mean K_{oc} value obtained for the rest of the soils was 229, very similar to that given in the literature. In relation to the size particle distribution, all of the soils that presented high K_{oc} values (except soil 11) have the highest percentages of silt and clay fractions (fine fractions): 83.3, 83.8, 97.0, 97.4, and 93.1% for soils 3, 5, 14, 15, and 17, respectively. Moreover, soils 3 and 5 presented high amounts of iron, aluminum, and manganese amorphous oxides (**Table 3**), which have a large surface area, that could be good adsorptive surfaces for norflurazon.

Soil 7 also presented an extremely high content of amorphous and organically bound iron and aluminum oxides (3.56%), besides a high OM content (5.34%), but, despite this, norflurazon adsorption was not very high, and, for this reason, its K_{oc} was

Table 5. Regression Equations for the Distribution Coefficients of Norflurazon (K_d) as a Function of Significant Predictive Variables

R^2	linear regression eq
0.85	$K_d = -0.91 + 2.14$ OM (%)
0.91	$K_d = 0.17 + 2.23$ OM (%) $- 3.78$ Fe$_2$O$_3$ (%)
0.96	$K_d = -0.90 + 2.22$ OM (%) -10.98 Fe$_2$O$_3$ (%) $+ 12.60$ Al$_2$O$_3$ (%)

very low (*42*). Some authors have reported that the interassociation processes between different soil components may block sorptive functional groups on mineral and organic surfaces (*28*). Amorphous iron and aluminum oxides can be covering the organic surfaces on soil 7, decreasing sorption by blocking specific sorption sites for norflurazon. The use of calculated sorption parameters such as K_{oc} may result in deviation from the reality, because the sorption capacity of a natural particle is highly dependent on the nature and amount of surface ultimately exposed, which is determined by the degree of interassociation of the individual constituents.

To determine if iron and aluminum amorphous oxides are impeding the adsorption of the herbicide on the organic matter of this soil, adsorption experiments were carried out after these oxides had been eliminated using the method of McKeague et al. (*20*). The adsorption experiments were performed as it was explained previously under Materials and Methods. For the maximum norflurazon initial concentration used (20 mg kg^{-1}) the amount adsorbed by soil 7 before oxides elimination was 42.72 μmol kg^{-1}, and after their elimination, the adsorption increased to 72.10 μmol kg^{-1}, indicating that such oxides may have been impeding somewhat the adsorption of the herbicide on the organic mater of this soil. Alva and Singh (*29*) reported previously a decreased adsorption of four herbicides after equilibration of the soil with iron or aluminum salt solutions. They concluded that any practice that would increase the content of Fe and Al in soils is likely to increase the leaching of the herbicides due to their decreased sorption, because Fe and Al may act as coating materials on the sorption sites, thus making these sites unavailable for sorption of herbicides.

The influence of the different soil characteristics (**Tables 2** and **3**) on norflurazon adsorption was determined using a statistical approach. Using the stepwise procedure, the significant variables for prediction of K_d values were organic matter and the iron and aluminum oxide content. Among these soil properties, the organic matter content is the most significant variable (**Table 5**), accounting for 85% of the variability (although this value increased to 94% when soil 7 was excluded). By including iron and aluminum oxide contents, the resulting multiple-regression equations gave an 11% increase in evaluation accuracy compared with evaluation on organic matter alone. As mentioned before, norflurazon adsorption has been related to the OM of the soils by several researchers, and in some cases it has been also related to soil pH and cation exchange capacity (*4*), clay content (*5*), or soil cation (*29*). However, we have not found any reference about the influence of amorphous oxides on norflurazon adsorption in soils. The contribution of the OM and amorphous oxide content is not additive in all cases, because in the case of soil 7, with a high proportion of amorphous iron and aluminum oxides, their presence in the soil decreased the adsorption of the herbicide due perhaps to the partial masking of the organic surface of the soil. Although both soil constituents favor norflurazon adsorption on soils, the contribution of the organic matter is higher (85%) than that of the amorphous oxides (11%), and that is the reason
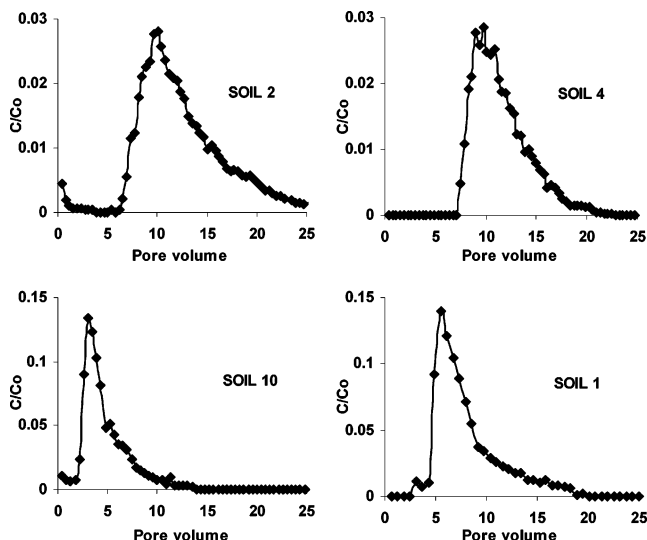
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Figure 2. Norflurazon breakthrough curves in soils 1, 2, 4, and 10.

Table 6. Percentage of Norflurazon Desorbed (%*D*) and Hysteresis Coefficients (*H*) for the Soils Studied

	%*D*			*H*		
soil	4 mg L^{-1}	12 mg L^{-1}	20 mg L^{-1}	4 mg L^{-1}	12 mg L^{-1}	20 mg L^{-1}
1	12.3	34.0	48.5	17.3	5.3	2.8
2	34.1	36.6	58.1	2.5	2.4	1.9
3	48.8	32.3	27.1	1.1	1.8	2.9
4	38.2	40.3	35.6	2.0	2.0	2.7
5	2.0	11.7	13.7	18.9	3.3	2.2
6	14.4	20.5	38.5	1.0	2.6	1.4
7	41.8	44.4	53.0	1.9	1.8	1.4
8	17.7	22.5	24.5	2.9	2.1	1.9
9	0.40	2.07	1.44	709.3	89.6	52.6
10	31.9	54.3	72.3	2.5	1.5	0.9
11	24.8	10.0	32.9	7.4	4.3	1.1
12	68.9	94.4	69.2	1.0	0.5	0.9
13	50.6	49.5	50.7	0.8	1.0	1.2
14	0.0	15.8	25.8	-	2.8	2.6
15	8.2	13.8	15.3	19.5	8.2	6.9
16	40.1	64.6	75.2	1.7	1.3	0.9
17	0.0	6.8	11.4	-	14.0	7.1

the masking of soil organic surface with such oxides may decrease herbicide adsorption.

Desorption Experiments. Norflurazon desorption from soils was hysteretic in all cases (figures not shown); that is, the desorption behavior deviated markedly from those corresponding to the adsorption isotherms, indicating that norflurazon adsorption on the soils was not completely reversible. Desorption isotherms were also described by the Freundlich equation, and hysteresis coefficients were calculated using the Freundlich *n* value. Hysteresis coefficients (*H*) and the percentage of norflurazon desorbed with respect to that previously adsorbed during adsorption process (%*D*) are shown in **Table 6**. In general, norflurazon adsorption on soils is more irreversible (lower %*D*) at low concentrations adsorbed (desorption from an initial concentration of 4 mgL^{-1}), showing higher hysteresis coefficients, *H* (**Table 6**). That is, norflurazon molecules are more strongly sorbed at low surface coverage, and consequently, it is more difficult to desorb them.

In general, those soils with OM contents not greater than 1% showed the highest desorption percentages (%*D*) and the lowest *H* values. However, the soils with higher OM contents did not all behave similarly. Only soil 9 showed a noticeably low herbicide desorption, and very high *H* values, indicating the practical irreversibility of norflurazon adsorption, due to its high

Table 7. Percentage of Applied Norflurazon Extracted from Soil Columns and Eluted in Leachates

depth (cm)	soil 1	soil 2	soil 4	soil 5	soil 10
0–4	0.30	2.82	0.30	30.73	0.60
4–8	0.11	2.23	0.57	27.69	0.22
8–12	0.09	2.69	0.84	25.94	0.19
12–16	0.14	2.30	1.32	5.01	0.28
16–20	0.15	3.81	1.91	0	0.30
20–24	0.26	3.15	2.08	0	0.50
total extracted	1.05	17.00	7.02	89.37	2.09
total eluted	98.59	51.53	40.68	3.21	96.54
total recovered	99.64	68.53	47.70	92.58	98.63

OM content. Soils 6−8 presented considerable desorption percentages and low *H* values (**Table 6**), despite their moderately high OM contents. However, soils 17 and 15, with OM contents of ∼1.7, showed very low desorption percentages and high hysteresis (**Table 6**). This seems to indicate that OM is not the only factor that controls norflurazon desorption from some soils.

The behavior of soil 7 (5.34% OM) in the desorption processes is especially noteworthy because the amount of herbicide adsorbed was very low and the amount desorbed was very high. The reason for the high desorption observed could be due also to the presence of amorphous oxides on soil 7, which probably presents an ultimately exposed surface with less affinity for norflurazon adsorption than the organic surface of the soils.

Mobility Experiments. 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. Five soils of different characteristics (soils 1, 2, 4, 5, and 10) were selected to study the mobility of norflurazon in hand-packed soil columns. Their pore volumes were 41.0, 64.8, 66.9, 88.1, and 57.5 mL, respectively. **Figure 2** shows the BTC for norflurazon leaching through soils 1, 2, 4, and 10, and **Table 7** shows the cumulative amount of norflurazon eluted in the leachates from the soil columns. Note that the norflurazon elution curve through soil 5 is not shown in **Figure 2**, because the percentage of herbicide eluted was only 3.21% (**Table 7**). **Table 7** also shows that the percentage of norflurazon eluted reached almost 100% for soils 1 and 10 but only 40.68 and 51.53% for soils 4 and 2, respectively.

Norflurazon leached very rapidly through the sandy soils 1 and 10, because of their lower OM content and high porosity, and, consequently, the application of 25 mL of water was possible every day. Leaching was much slower in soils 2 and 4, for which it was possible to collect 25 mL of leachate only after 3 and 6 days, respectively. For this reason, norflurazon elution curves (**Figure 2**) show different profiles for soils 1 and 10: the maximum of the BTC occurs earlier in soils 1 and 10 (approximately 6 and 4 pore volumes, respectively) than in soils 2 and 4 (approximately 10 pore volume in both cases), indicating a higher retention and lower release of the herbicide. The behavior of soil 5 is quite different because a very low release of the pesticide was obtained, although the application of 25 mL of water was possible every day.

Table 7 also shows the distribution of norflurazon residues in the soil columns after completion of leaching as a function of column depth. The distribution in the columns was obtained by extracting the herbicide with methanol. Norflurazon residues extracted from soils 1 and 10 at each soil depth were practically negligible, because almost 100% of the pesticide initially applied had been eluted from the soil columns. In soil 5 high amounts
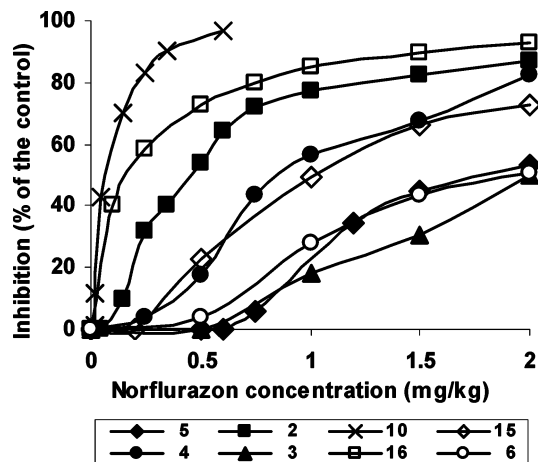
Adsorption–Desorption, Mobility, and Activity of Norflurazon

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Figure 3. Chlorophyll inhibition curves (percent of the control) in selected soils.

Table 8. Predicted CI_{50} Values and Corresponding Equations for the Relationship between Chlorophyll Inhibition (Percent) and Herbicide Concentration in Each Selected Soil

soil	CI_{50} (mg kg^{-1})	eq	R^2
10	0.08	$y = 26.938 \ \text{Ln}(x) + 118.38$	0.991
16	0.22	$y = -54.135(x)^4 + 258.54(x)^3 - 431.75(x)^2 + 308.26(x) + 0.9992$	0.995
2	0.43	$y = 292.45(x)^4 - 627.87(x)^3 + 351.11(x)^2 + 63.74(x) - 2.0393$	0.992
4	0.87	$y = 50.714(x)^4 - 211.54(x)^3 + 263.49(x)^2 - 45.582(x) + 0.3079$	0.997
15	1.04	$y = 6.2708(x)^4 - 35.069(x)^3 + 49.584(x)^2 + 29.675(x) - 2.5987$	0.995
5	1.68	$y = 11.825(x)^4 - 75.801(x)^3 + 149.42(x)^2 - 63.571(x) + 0.275$	0.996
3	1.94	$y = -5.4208(x)^5 + 46.613(x)^4 - 144.88(x)^3 + 186.99(x)^2 - 55.257(x) + 2 \times 10^9$	0.999
6	1.98	$y = -3.8465(x)^3 + 22.03(x)^2 - 2.993(x) - 0.7613$	0.995

of norflurazon residues were extracted from the upper three segments, 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 was 89.37% of that initially applied, very close to the total amount of herbicide retained by the soil column. The behavior observed for soils 2 and 4 was very different; the total percentages recovered (extracted plus eluted) were 68.53 and 47.70%, respectively, indicating that some of the herbicide must have degraded. This was probably caused by the longer period of time in which norflurazon was in contact with the soils in the columns. The half-life of norflurazon in soils is 45−180 days, depending on the type of soil (*1*). For soils 2 and 4 column experiments were longer (75 and 150 days, respectively) than for soils 1, 5, and 10 (33, 35, and 30 days, respectively), and probably some degradation of the herbicide took place in the former due to the longer contact period with the soil. In fact, the lowest recovery of the herbicide was in soil 4, which had the longest time in contact with the soil. It could be possible that in these soils not all of the herbicide adsorbed could have been extracted, but previous experiments (not shown) demonstrated that norflurazon adsorbed was completely extracted with methanol from soils 2 and 4 when the extraction was done immediately after adsorption.

Herbicidal Activity. Because norflurazon is a soil-applied herbicide, soils of different characteristics have been selected for measuring its activity in relation to the type of soil. The soils selected were the following: 2−6, 10, 15, and 16. **Figure 3** shows the effect of the amount of herbicide in soil on the inhibition percentages of soybean plants measured by its bleaching effect on the shoots, in comparison to a control without herbicide. Inhibition was increased, but not proportionally, by increasing herbicide concentrations. Regression analysis of chlorophyll inhibition versus herbicide concentration in soil gave the corresponding equation that provided the best fit for each soil (**Table 8**). The comparison between the estimated CI_{50} values showed that the order of inhibition observed was as follows: 10 > 16 > 2 > 4 > 15 > 5 > 6 > 3. A simple correlation of CI_{50} with the percentage of OM gives an R^2 of 0.65, which is not bad considering that we are dealing with adsorption phenomena on soils and phytotoxicity phenomena in plants.

The herbicidal activity of norflurazon on sandy soil 10 was very high, because it was effective for very low amounts of herbicide applied to the soil, reaching almost 100% inhibition with amounts <0.6 mg kg^{-1}. On the contrary, for the same

amount of herbicide in soil 5, no inhibition was observed. Soils 3, 5, and 6 were those that presented the lowest inhibition percentages.

The lower activity of the herbicide can be mainly attributed to the presence of increasing amounts of organic matter in soil, although this relationship is not directly proportional. Similar results were reported by Peter and Weber (*30*) and Vasilakoglou et al. (*31*) in the case of alachlor herbicidal activity. For example, soils 3 and 5 contain lower OM contents (1.41 and 1.90, respectively) than soil 6 (2.48), but the CI_{50} values are more or less the same for soils 3 and 6 and very close to that for soil 5. It may be due to the presence of higher amounts of amorphous oxides in soils 3 and 5 (26.1 and 30.0 g kg^{-1}, respectively; **Table 3**) in comparison to soil 6 (3.9 g kg^{-1}), which contribute effectively to norflurazon adsorption in soils and, consequently, to its partial inactivation.

The results obtained in soils 3 and 5, in which no inhibition was observed below 0.5 mg kg^{-1} of norflurazon in soils, imply that in these soils a great part of the herbicide applied was not available due to its high adsorption in soil, and higher amounts of norflurazon are required to maintain an adequate herbicide activity.

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