Norflurazon Mobility, Dissipation, Activity, and Persistence in a Sandy Soil As Influenced by Formulation

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Five ethylcellulose (EC) microencapsulated formulations (MEFs) of norflurazon were prepared and applied in soil to study their mobility, dissipation, activity, and persistence. The results show that the release into water of norflurazon from EC microspheres was retarded when compared with that of commercial herbicide. The mobility of norflurazon from MEFs into soil columns has been greatly diminished in comparison with that of its current commercial formulation (CF). Norflurazon distribution at different depths in the soil was higher in the upper ring (up to 50% of the initial application). In contrast, the residues from commercial norflurazon along the complete soil column were only about 2%. Degradation and bioassay experiments showed that the MEFs had greater persistence ($t_{1/2}$ values were 7.72 and 30.83 weeks for CF and MEFs, respectively) and herbicidal activity than the commercial formulation. The use of these formulations can be advantageous, because they can minimize the risk of groundwater contamination and permit herbicide use at reduced rates, maintaining the desired concentrations of herbicide in the topsoil layer for longer periods of weed control.

INTRODUCTION

Controlled release formulations (CRFs) have been developed to reduce herbicide losses from degradation, leaching, and volatilization. They imply a reduction of herbicide levels in the environment because less active ingredient needs to be applied to maintain biological efficacy (*1*−*4*). Moreover, the reduction of phytotoxicity due to improved pesticide selectivity allows the development of certain active ingredients, which would have been dropped from commercial consideration (*5*).

There are few studies evaluating the efficacy of cellulose-encapsulated formulations in weed control. However, the efficacy of several herbicides encapsulated in different cellulose polymers has been assayed by Daley et al. (*8*) as well as Daley and Dowler (*6*). The results obtained varied widely depending on the herbicide employed. The polymers demonstrating the most efficacy were cellulose acetate butyrate (CAB) and ethylcellulose (EC) for microcapsules of atrazine, alachlor, and metolachlor. In contrast, metribuzin microcapsules showed activities comparable to or slightly lower than that of the commercial formulation (*8*). Most surprisingly, CAB formulations of cyanazine were consistently less active than the commercial formulation (*6*).

EC is a hydrophobic polymer that has been used to prepare formulations of different herbicides by microencapsulation techniques (*1*, *6*). However, little information has been reported

about herbicides' mobility in soil from these different cellulose-encapsulated formulations (*3*, *7*).

Norflurazon [4-chloro-5-methylamino-2(α,α,α-trifluoro-*m*-tolyl)pyridazin-3(2*H*)-one] is a fluorinated pyridazinone herbicide that inhibits photosynthesis and is registered for soil-applied use in cotton, soybean, tree fruit and nut crops, citrus, and cranberries (*14*). Norflurazon, with a molecular weight of 303.67, has a water solubility of 28 mg/L and a vapor pressure of 2.0×10^{-8} mmHg at 20 °C (*14*). Unfortunately, this herbicide suffers losses when it is applied to soil. Photodegradation contributes significantly to field dissipation when norflurazon remains on the soil surface, with a half-life of 41 days. Leaching also plays an important role in norflurazon losses in agricultural applications. Norflurazon retention in soil is related to the organic matter content; however, this herbicide has been detected in groundwater monitoring studies (*15*). Reddy et al. (*16*) and Morillo et al. (*17*) observed a large degree of norflurazon desorption in porous soils with low organic matter content, which suggests an increase in subsequent losses by leaching through the soil profile. Likewise, Singh et al. (*18*) observed appreciable leaching in sandy soil columns. To retard norflurazon leaching in soil, Boydston (*19*) and Undabeytia et al. (*20*) prepared CRFs of norflurazon based on starch-encapsulated and organoclays, respectively, with positive results. In addition, its photodegradation was also reduced by using CRFs (*21*).

Whereas microencapsulation has been observed to increase the persistence of several herbicides (*9*−*11*), there is currently no information on the influence of microencapsulation on the

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Table 1. Different Conditions Used during Microsphere Formulation and Their Herbicide Loading[a]

formulation	EC40/N ratio	PVA (%)	PEG (%)	stirring speed (rpm)	HL (%)
N2	5	0.075		600	15.9 ± 0.59
N3	5	0.075		900	15.9 ± 0.05
N1	10	0.075		600	8.37 ± 0.57
N6	10	0.150		600	7.69 ± 0.16
N16	10	0.075	40	600	6.55 ± 0.45

[a] Values of HL are means ± SD; EC40, ethylcellulose 40; N, norflurazon; PVA, polyvinyl alcohol; HL, herbicide loading; PEG, polyethylene glycol.

persistence of norflurazon. In general, the influence of preparation conditions on the controlled release of this herbicide into water from ethylcellulose microspheres has been previously studied (*12*, *13*), but the behavior of norflurazon in soil from these cellulose CRFs has not been reported yet.

The present work evaluates several norflurazon EC formulations with respect to their mobility, stability, activity, and persistence in sandy soils in order to select the best composition to avoid groundwater contamination and maintain a high efficacy in the topsoil layer.

MATERIALS AND METHODS

Chemicals. Technical grade norflurazon (97.8% purity) and the commercial formulation of norflurazon (Zorial 80, content of norflurazon 80%) were kindly supplied by Syngenta Agro S.A. (Barcelona, Spain). Ethylcellulose (30−50 mPa, 48−49.5% w/w as ethoxyl) was purchased from Fluka (Buchs, Switzerland). Polyvinyl alcohol (PVA) with M_w 30000−70000 was obtained from Sigma (St. Louis, MO). Acofarma (Barcelona, Spain) supplied polyethylene glycol (PEG) with M_w 4000. HPLC-grade acetonitrile, methanol, and chloroform were purchased from Merck (Darmstadt, Germany). All reagents were of analytical grade.

Soil. Soil surface samples (0−20 cm depth) were collected, air-dried, sieved through a 2 mm sieve, and stored in plastic containers until used in experiments. The soil used was a loamy sand (classified as Typic Xeropsament) with 84 g/kg clay, 40 g/kg silt, 876 g/kg sand, 9.2 g/kg organic matter, pH 8.0, 69 g/kg calcium carbonate, and a cationic exchange capacity of 4.8 cmol$_c$/kg.

Microsphere Preparation and Characterization. Using the procedure previously described (*13*), five norflurazon−ethylcellulose formulations were prepared by the oil-in-water emulsion solvent evaporation technique, using EC as polymer and PVA as emulsifier. Briefly, EC (1 g) was dissolved in 15 mL of chloroform. Different amounts of norflurazon (0.1 and 0.2 g) were dissolved in this polymer solution at room temperature. The herbicide−polymer solution was then emulsified into an aqueous phase by dropwise addition into 150 mL of aqueous solution containing 112.5 mg (0.075%) or 225 mg (0.15%) of PVA with stirring at either 600 or 900 rpm. The ratio of organic to aqueous phase was the same in all of the experiments (1/10). In one of the formulations, 400 mg (40%) of PEG (used as a channel former) was added to the organic polymer solution prior to the formation of the emulsion with the aqueous phase. After 24 h of stirring to allow the total evaporation of the inner organic phase, the microspheres obtained were filtered and washed with 250 mL of distilled water to remove any undesired residuals. The product was dried in a vacuum desiccator until a constant weight was obtained. All experiments were performed in triplicate. The herbicide loading (HL) of microspheres (amount of herbicide encapsulated by the microspheres) was obtained by dissolving the microspheres (25 mg) in methanol (100 mL) and analyzing norflurazon by HPLC, using the following conditions: mobile phase, acetonitrile/water (50:50); flow, 0.6 mL/min; chromatographic column, Kromasil C18 (15 × 0.40 i.d.) (Teknokroma, Spain); diode array detector (Shimadzu SPD-M10AVP), at a wavelength of 215 nm. The conditions used to prepare the different norflurazon formulations are shown in **Table 1**.

Release Studies. Dissolution tests of commercial norflurazon and the five formulations selected were performed in triplicate with a rotating paddle apparatus (Sotax). Microspheres containing 5 mg of norflurazon were added to 1000 mL of deionized water as dissolution medium, at 25 °C with 50 rpm stirring. At appropriate time intervals (0.5, 1, 2, 3, 5, 22, 24, 27, 30, 45, 48, 54, 72, 75, 78, 94, 96, and 100 h), samples were taken and analyzed by HPLC.

Leaching Experiments in Soil Columns. Homogeneous soil columns were prepared by gently and uniformly packing the soil in 28 cm long methacrylate tubes with 3.0 cm internal diameter. The lower end of the columns was covered with nylon tissue padded with a thin layer of glass wool (0.5 g) to hold the soil firmly in the column. Into each column, 246 g of the soil was filled to obtain 24 cm columns of soil. The soil columns could be readily separated into six 4 cm segments after the leaching events. After herbicide application, a 1 cm layer of sand was added on the top of each column and covered with glass wool to prevent disturbance of the soil by the input liquid.

In a preliminary experiment, two soil columns 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 formulations containing 0.28 mg of norflurazon (3.96 kg of ai/ha) were added to the soil columns. Breakthrough curves (BTCs) were obtained by a daily application of 25 mL of distilled water during 40 days. There were three replicate soil columns per norflurazon formulation.

After the leaching experiments had been completed, the columns were sliced in six segments, and the soil (5 g) was blended with anhydrous sodium sulfate (7 g) and pulverized in an agate mortar to eliminate aggregates and remove residual water. The herbicide residues that remained adsorbed on the soil were extracted with methanol (20 mL), with shaking for 24 h at 20 ± 1 °C. The extraction was carried out in triplicate, and the pesticide was analyzed as indicated above.

Dissipation Experiments in Soil. Norflurazon dissipation from the commercial formulation (CF) and EC microencapsulated formulations (MEFs) used was studied using the loamy sand soil previously mentioned. For this purpose, 250 g of air-dried soil was mixed in triplicate with 0.44 mg of norflurazon applied as MEFs and CF (2.2 mg/kg of soil), shaking thoroughly for 24 h. After mixing, the samples were transferred to plastic pots, which were covered with aluminum foil and incubated in the dark for 12 weeks at 25 °C. The soil moisture content was maintained at field capacity by periodic addition of water. Quadruplicate soil samples (5 g) were taken at 0, 14, 28, 42, 56, 70, and 84 days after treatment and stored at −20 °C until analyzed. Before the samples were taken, the soil was thoroughly mixed to achieve homogeneity, and norflurazon residues were extracted with methanol from soil samples and analyzed by HPLC, as previously described. Linear regression equations describing the relationship between norflurazon concentration in soil [$y = \ln(\%$ of initial concentration)] and time ($x =$ weeks after application) were used to calculate dissipation half-lives of the formulation tested as

$$\text{Ln } C = \text{Ln } C_0 - Kt \tag{1}$$

where C is the norflurazon concentration in soil after time t, C_0 is the initial herbicide concentration in soil, and k is the dissipation rate constant. The time required to reach an alachlor dissipation of 50% in the soil is the half-life ($t_{1/2}$), which for a first-order kinetic can be defined as

$$t_{1/2} = 0.6932/k \tag{2}$$

Activity and Persistence Studies. To compare the herbicidal activity of norflurazon applied as two selected microencapsulated formulations (N1 and N2) with that of the CF, bioassay experiments, based on norflurazon bleaching effect on soybean plants, were carried out. For this purpose, 250 g of air-dried soil was mixed with different amounts of norflurazon applied as MEFs or CF to obtain concentrations of 0.2, 0.5, and 0.8 mg/kg of air-dried soil. A dose−response curve of pure

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norflurazon was established using appropriate quantities of the herbicide to achieve concentrations of 0.1, 0.2, 0.5, 0.9, and 1.17 mg/kg in order to measure plant bleaching as a result of herbicide concentration. To achieve homogeneity in the soil, the herbicide was previously dissolved in 25 mL of deionized water. After mixing, the soil samples were left for 24 h to equilibrate and were then mixed again thoroughly before being used for the bioassay. The treated soils were transferred to plastic pots, which had five holes at the bottom covered by tissue paper. Fifteen soybean seeds were placed on the treated soil surface of each pot and subsequently covered with a 1.5 cm layer of this soil. The soil samples were placed for 10 or 60 days in a growth chamber at 25 ± 1 °C with a photoperiod of 16 h of light having an intensity of 11 μEinstein/m²s. Samples were also moistened with distilled water every day.

The bleaching intensity was obtained by measuring the chlorophyll content in the plant shoot and determining the inhibition percentage as compared with the herbicide-untreated control. The chlorophyll content was determined by cutting the fresh shoot of soybeans plants and extracting with 15 mL of *N,N*-dimethylformamide. The extracts 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 fresh shoot. Each experiment was carried out in quadruplicate. The data obtained were used for regression analysis to estimate the CL_{50} (herbicide required to give 50% chlorophyll inhibition). Different equations were tested to describe the relationship between inhibition (percent) and herbicide concentration (milligrams per kilogram). The equation with the highest R^2 value was chosen to be the most appropriate.

The soybean bioassay data were subjected to two-way ANOVA and significant differences ($P < 0.05$) determined by LSD comparisons to identify if the efficacies of MEFs formulations were significantly different from the CF formulation for each concentration employed at the times considered.

To study the persistence of norflurazon in soil, fresh seeds were again sown in each of the pots, 60 and 120 days after treatment, to ensure that the herbicide was still active and the bleaching effect was not due to the fading of the plant with time.

RESULTS AND DISCUSSION

Microsphere Characterization and Herbicide Release in Water. The HL of the formulations obtained ranged from 6.55 to 15.9 (**Table 1**). For EC/herbicide ratios of 10 or 5, the theoretical values of HL (in the case that all applied herbicide is encapsulated) are 9.1 and 16.7, respectively. The HL values experimentally obtained were very close to the theoretical values, except for the formulations prepared with PVA 0.15% (N6) and PEG 40% (N16). In the first case, the use of an emulsifying agent such as PVA increases the solubility of norflurazon in the continuous phase, influencing the HL of the microspheres, because the amount of the herbicide encapsulated depends on its solubility in the processing medium (*22*). In the case of PEG, it has been previously demonstrated (*13*) that this compound is not completely leached from the microspheres to form the channels when it comes into contact with the aqueous medium, remaining partially trapped inside the microspheres. As a result, the total weight of the microspheres obtained was greater than that of the herbicide encapsulated.

The N3, N6, and N16 formulations provided greater norflurazon release rates in water than did the N2 and N1 ones (**Figure 1**). According to Sopeña et al. (*13*), decreasing the particle size of the microspheres (N3), adding PEG (N16), or increasing the percentages of PVA (N6) yields higher release rates of the herbicide, which is facilitated by a greater effective surface area, rougher surfaces, or higher microsphere porosity.

Leaching Experiments in Soil Columns. The results obtained from soil column experiments have been represented as BTCs, with the pore volumes as abscissa and the herbicide concentration relative to that initially added (C/C_0) as ordinate.
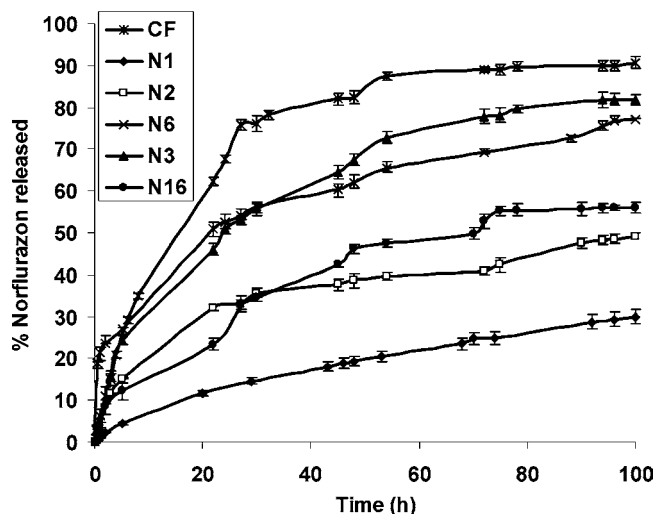

Figure 1. Amount of norflurazon released into water from the commercial formulation (CF) and the different MEFs used.

The pore volume of the soil used was 57.5 mL. When the commercial formulation was applied, the percentage of herbicide eluted reached almost 100% (**Figure 2**), but when norflurazon microspheres were applied, only a part of the herbicide was eluted, the rest remaining distributed among the different depths in the soil column.

Norflurazon BTCs show different profiles depending on the formulations applied (**Figure 2a**). The maximum of the BTC obtained from commercial norflurazon occurs earlier (about 2.5 pore volumes) than for the rest of the formulations, indicating the MEFs result in higher soil retention and slower release. Furthermore, each formulation eluted different percentages (**Figure 2b**), and this result could be attributed to different release percentages of norflurazon in water (**Figure 1**). The close relationship between the amount of herbicide dissolved in the water release experiments and the amount that eluted from the soil columns indicated that the release in water curves could provide a reasonable prediction about the leaching behavior of the different microencapsulated formulations in soils.

Only 2.1% of the commercial herbicide initially applied was found in the soil columns after leaching (0.6, 0.2, 0.2, 0.3, 0.3, and 0.5% in the upper, second, third, fourth, fifth, and sixth rings, respectively; data not shown). On the contrary, greater quantities of the ME-formulated norflurazon remained in the upper ring (0−4 cm, >50% for N16) and gradually much lower amounts in the deeper ones, indicating a high persistence of the herbicide in the surface horizon of the soil (**Figure 3**).

Similar results were reported by Boydston (*19*) and Undabeytia et al. (*20*), who found that norflurazon leaching from starch and organoclay formulations was retarded in soil columns when compared to commercial formulations. In particular, they obtained a reduction in norflurazon leaching by about 21%, whereas EC microsphere formulations yielded a higher reduction of norflurazon leaching, in the range from 37 to 73%. Also, Boydston (*19*) observed that norflurazon remained in the surface layer of soil (0−2.5 cm) when applied as a starch-encapsulated formulation, although 1 or 2 weeks was needed for the release of norflurazon to begin. An initial burst of the pesticide release has been observed when EC microspheres were used. This greater herbicide persistence in the surface horizon could provide greater weed control.

Dissipation Experiments in Soil. Norflurazon degradation in soil of the ME formulations was in most cases lower than that of the CF (**Figure 4**). In general, MEFs protected against
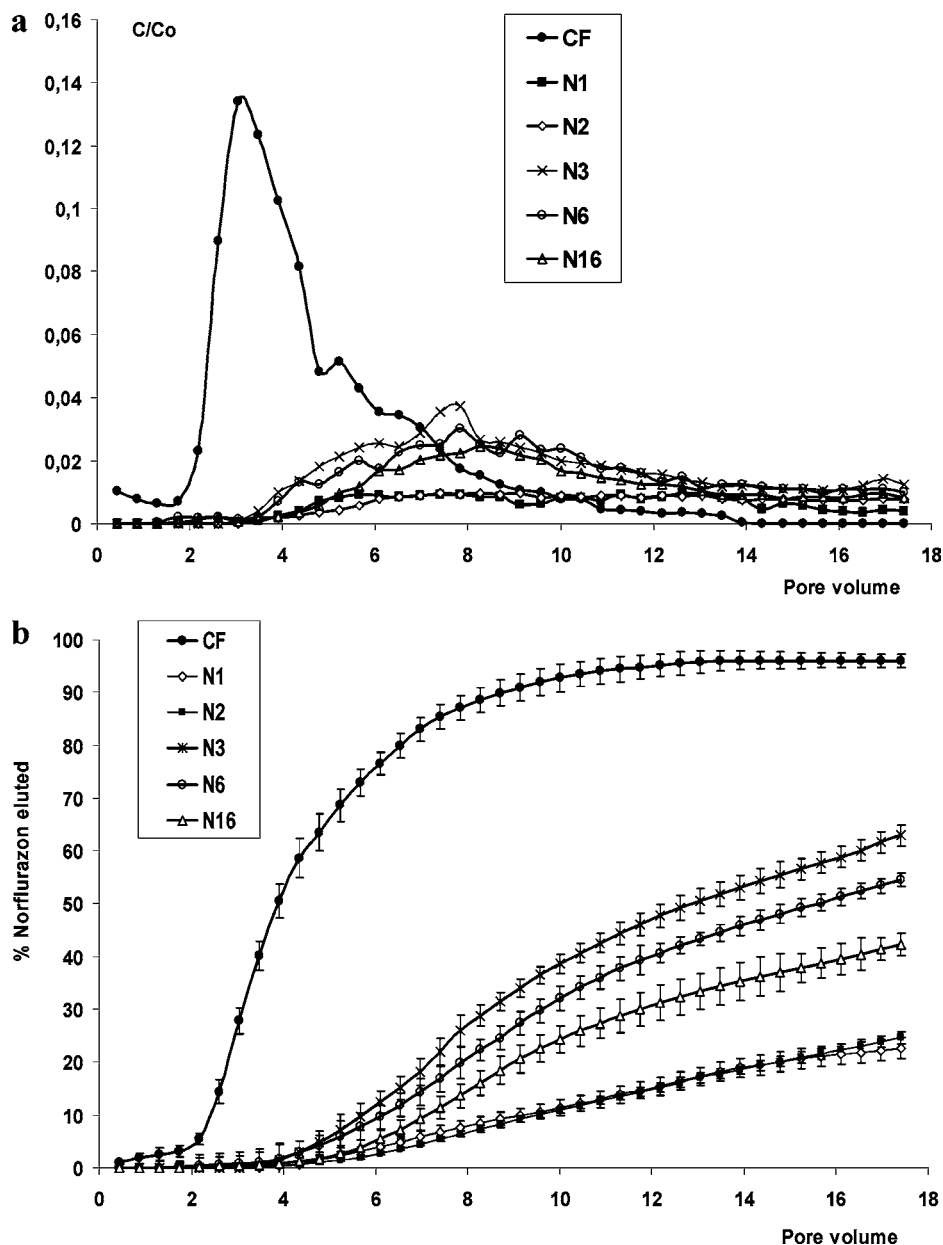
Figure 2. Breakthrough curves (**a**) and cumulative percentage of norflurazon eluted (**b**) from soil columns using the commercial herbicide (CF) and the five MEFs tested.

herbicide dissipation in sandy soil better than CF, especially on time scales below 8 weeks. Soil degradation of norflurazon followed first-order kinetics, with regression coefficients of 0.99, with the exception of N16 (0.97), indicating that the assumption of a first-order kinetic mechanism was acceptable (**Table 2**). Half-life values ($t_{1/2}$) in soil samples for each formulation are also reported in **Table 2**. $t_{1/2}$ in soil for CF was >7 weeks, which is similar to values obtained by other authors (*14, 23*). However, after 12 weeks, the order of norflurazon concentration in soil was N3 = N16 > CF > N6 > N2 > N1 (**Figure 4**). As can be observed in **Figure 4** and according to the $t_{1/2}$ values in **Table 2**, formulation N3 did not present any advantage in comparison to CF with respect to its dissipation in soil. In fact, it was the formulation that presented the closest release into water compared to CF (**Figure 1**), and therefore both of them are rapidly exposed to dissipation in soil environment. In contrast, the slower release rate into water observed for N1 and N2 could be the reason for the major persistence in soil compared to CF and other MEFs. This explanation is in agreement with that given by Gan et al. (*5*), who obtained major persistence of

thiobencarb in soil treated with alginate−kaolin-based controlled release formulation and also attributed their results to the gradual release of active ingredient, keeping a part confined in the formulation and thus protected from environmental losses.

Formulations N6 and N16 show a singular behavior. As can be observed in **Figure 4**, norflurazon from N16 and N6 suffered less dissipation than the others for the first 2 weeks, but their dissipation in the soil is significantly increased at later times, especially in the case of N16.

The lower degradation of norflurazon applied as the N6 and N16 formulations could be attributed to the microsphere composition (N16 was the only one prepared with PEG, and N6 was prepared with highest percentage of PVA), which influences not only the release rate (*13*) but also the norflurazon dissipation in soil, according to Meghir (*9*) and Negré et al. (*10*), who observed that the differences of polymer character-istics in the microencapsulated formulations were responsible for the increased persistence of parathion-methyl (*9*) and alachlor (*10*). In this sense, part of the PEG polymer, which is not leached during the N16 microsphere formation process, is trapped inside
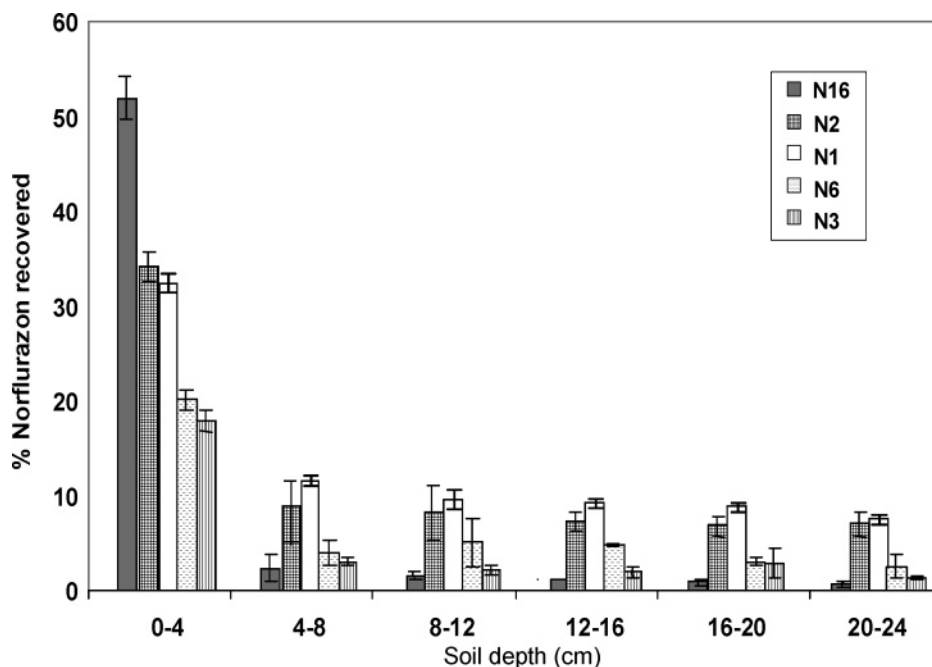
Figure 3. Distribution (percent) of norflurazon at different depths in the soil columns after leaching of the five formulations tested (error bars represent the standard deviation of the three replicates).
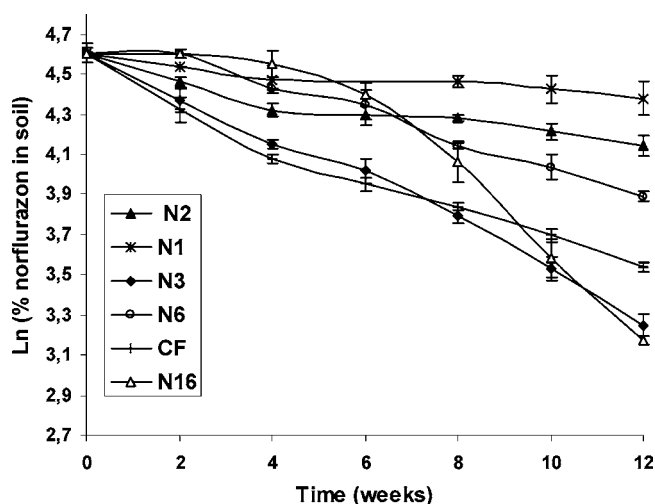

Figure 4. Norflurazon dissipation in soil from ethylcellulose-microencapsulated (N1, N2, N3, N6, and N16) and commercial formulations (CF).

Table 2. Predicted Half-Life Values ($t_{1/2}$ in Weeks)[a]

formulation	$t_{1/2}$	k	r^2
CF	7.72 ± 0.03	0.090	0.9972
N3	6.35 ± 0.05	0.109	0.9920
N16	9.11 ± 0.12	0.076	0.9702
N6	12.09 ± 0.10	0.057	0.9939
N2	17.90 ± 0.09	0.039	0.9986
N1	30.83 ± 0.06	0.022	0.9990

[a] Degradation constants (k in weeks^{-1}) and determination coefficients (r^2) corresponding to norflurazon dissipation in soil treated with commercial formulation (CF) and the five MEFs tested. Values are means ± SD.

the microspheres (*13*) and may offer certain resistance to degradation, protecting the herbicide or delaying its loss in soil for 7 weeks. After that, the microsphere matrix could be very susceptible to environmental degradation. It has been reported that PEG can be degraded by soil microorganisms (*24*) and was used to modify the degradation of some pollutants in soil (*25*). In our work, the norflurazon degradation from PEG-containing

Table 3. Norflurazon Concentration in Soil As Affected by Formulation and Initial Concentration (0.2, 0.5, and 0.8 mg/kg)[a]

formu-lation	concen-tration (mg/kg)	days after treatment		
		1	60	120
CF	0.2	0.171 ± 0.007	0.046 ± 0.003	0.045 ± 0.0003
	0.5	0.417 ± 0.009	0.167 ± 0.017	0.113 ± 0.006
	0.8	0.874 ± 0.008	0.182 ± 0.017	
N1	0.2	0.042 ± 0.0002	0.014 ± 0.0002	0.011 ± 0.003
	0.5	0.108 ± 0.012	0.047 ± 0.008	0.041 ± 0.008
	0.8	0.134 ± 0.013	0.056 ± 0.008	
N2	0.2	0.121 ± 0.003	0.087 ± 0.017	0.076 ± 0.006
	0.5	0.251 ± 0.009	0.234 ± 0.002	0.191 ± 0.013
	0.8	0.315 ± 0.028	0.249 ± 0.014	
LSD$_{0.05}$[b]		0.154	0.019	0.015

[a] Values are means ± SD. [b] LSD$_{0.05}$ values for norflurazon concentration in soil at 0.05 level.

microspheres (N16) can occur in two phases due to the presence of PEG: a slow initial phase followed by a second faster phase, when a decrease of the remaining norflurazon was observed after 7 weeks (**Figure 4**). This mechanism is according to that of Modeli et al. (*26*), who studied the extent and rate of degradation of cellulose fibers in flax, in both the native state and after chemical modification (either acetylation or PEG grafting). They found that PEG-modified fibers degraded more slowly than native fibers in soil, although their total biodegradability was significantly unaffected by chemical modifications.

The use of formulation N16 could be advantageous, for instance, when a high herbicidal activity is necessary in a short period or rapid dissipation is needed to prevent damage to subsequent crops. In contrast, the behavior of formulations N1 and N2 is advantageous when a long herbicidal activity is required to avoid successive applications of the herbicide with the consequential economic and environmental cost.

Activity and Persistence Studies. The microencapsulated formulations selected to carry out these experiments were N1
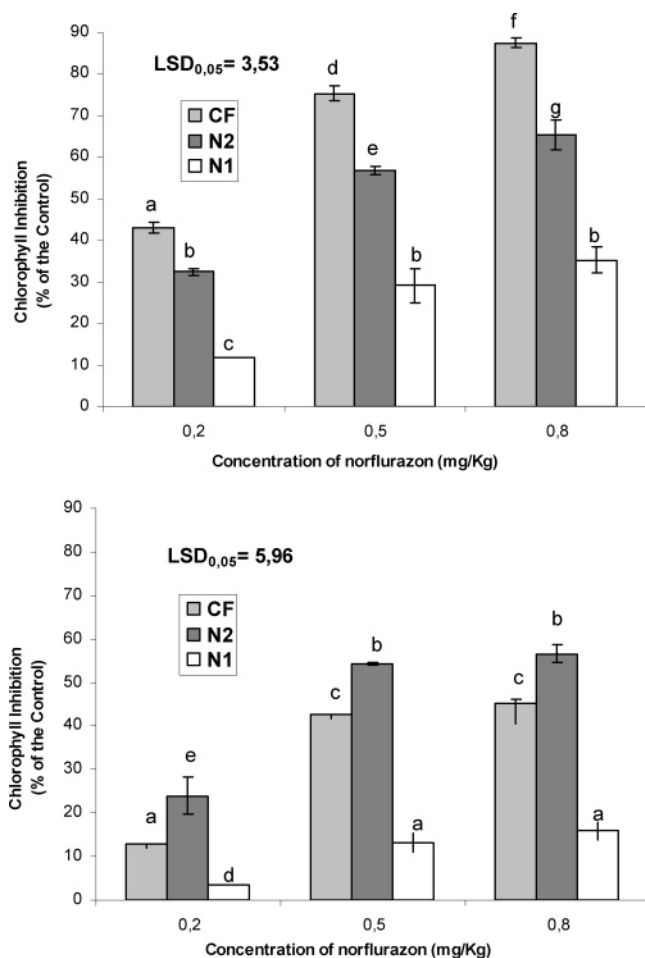
Figure 5. Effect of norflurazon formulations on soybean chlorophyll content at 10 (top) and 60 days (bottom) after treatment. Columns having the same letter are not significantly different at the *P* = 0.05 level.

and N2 on the basis of their appropriate herbicide loading, their reduced leaching, and their low dissipation in soil. Also, a dose–response curve for pure norflurazon was used to convert indicator plant bleaching into active herbicide concentration in soil. The activity of norflurazon in the loamy sandy soil employed was very high, which is similar to the results reported by Morillo et al. (*17*), in soil with low organic matter content. Regression analysis of chlorophyll inhibition versus herbicide concentration indicated that the polynomial equation $y = -44.358x^4 + 292.64x^3 - 434.66x^2 + 325.96x - 1.164$, where y = chlorophyll inhibition percent of control and x = mg of ai/kg of soil, provided the best fit. The norflurazon required to give 50% chlorophyll inhibition (CL_{50}) in the soil used was 0.208 mg of ai/kg (data not shown). For this reason, the concentrations of norflurazon selected to carry out these experiments were 0.2, 0.5, and 0.8 mg/kg of soil.

Soybean chlorophyll inhibition was increased with increasing norflurazon concentration (**Figure 5**). At 10 days after application, CF reduced soybean chlorophyll content more than MEFs. This could be due to the slow release rate of the active ingredient from microspheres into the soil solution. Considering the CF, an immediate release of the herbicide soon after the application could occur, whereas a slow release from both MEFs was obtained and, therefore, less active ingredient is immediately available in the soil solution after its application. This is in agreement with release into water, leaching, and degradation experiments, as mentioned above. Similar results were reported by other authors, who carried out a phytotoxicity study to evaluate

the herbicidal activity from different microencapsulated formulations of acetochlor (*2*), alachlor (*27*), and pendimethalin (*28*). They found that only acetochlor formulation activity was similar to CF due to its fast release after the application, whereas the rest of the microencapsulated formulations showed lower activity than CF (*2, 27, 28*).

In the soybean plants sowed 60 days after treatment, the herbicidal activity of CF and N1 formulations decreased compared to the inhibition found 10 days after treatment, but this was not the case for the N2 (**Figure 5**). Likewise, for all concentrations, N2 showed a bleaching effect greater than CF. The percentage of inhibition from CF decreases at least 50% in comparison with that obtained in the first sowing. This reduction in the herbicidal activity can be explained by taking into account the half-life of norflurazon in soil, which is 45–180 days, depending on the soil type (*14*). In addition, for each formulation, there were no significant differences between 0.5 and 0.8 mg/kg (**Figure 5**). This may be due to that the fact that those concentrations could correspond to the part of the inhibition curve where a "steady state" is reached, as can seen in the dose–response curve for technical norflurazon (**Figure 4**).

Considering MEFs, the herbicidal activity of N2 was much greater than that of N1. In fact, 0.2 mg kg^{-1} of norflurazon from N2 produced the same chlorophyll inhibition as 0.5 mg kg^{-1} from N1 (**Figure 5**). Some authors indicate that the herbicidal activity differences among MEFs can result from different release behaviors as a consequence of their composition and the physicochemical properties of the microsystem obtained (*2, 27, 28*). As previously reported, the MEFs employed in this work have different compositions, which are responsible for the different release rates of norflurazon (*13*). Therefore, different release rates can explain the different herbicidal activities observed between N1 and N2 formulations in the present bioassays (**Figure 5**). In the first as well as the last sowing, N1 provided less inhibition than N2, regardless of the concentration employed, because norflurazon release is much slower from N1 than from N2. The herbicide is strongly trapped in the ethylcellulose matrix of the N1 microspheres, which increases protection for the herbicide against biodegradation or leaching, but also considerably reduces norflurazon bioavailability. These results are in accord with the results of mobility and degradation experiments, which indicate that norflurazon from the N2 formulation is protected from degradation agents and yields a slow release, but enough to maintain an adequate concentration in topsoil for weed control. In contrast, a rapid dissipation was observed from CF because norflurazon was readily available for mobility and degradation agents in sandy soil. This behavior agrees with explanations given by other authors, who have evaluated the mobility and biological effect of herbicides from controlled release formulations. In particular, Gish et al. (*29*) studied the field-scale mobility and persistence of starch-encapsulated atrazine. They found that the reduction in atrazine leaching and its high persistence were likely due to the slow release from the starch granules and subsequent diffusion into the soil matrix where it is less subject to preferential flow processes. In addition, the organoclay formulation of alachlor evaluated by El-Nahhal (*30*) showed persistence, reduced mobility, and prolonged efficacy because it yielded a slow release of active ingredient into the topsoil layer, maintaining the threshold concentration needed for weed control.

In conclusion, the results of this study show that a prolonged release of norflurazon to soil solution was successfully achieved by using ethylcellulose microspheres. The mobility of the

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herbicide in a soil−water system has been greatly diminished, reducing its losses from leaching while maintaining the threshold concentration of the herbicide in the topsoil and concomitantly reducing potential groundwater contamination. The ethylcellulose microencapsulated formulations of norflurazon protected against dissipation in soil and remained biologically active longer than the commercial formulation. Likewise, formulation parameters influenced not only on the norflurazon released in the soil−water system but also its dissipation in soil. In this sense, factors such as a higher EC40/N ratio and the use of higher stirring, PVA, or PEG positively influenced the amount of norflurazon released and, hence, exposed to environmental action. In addition, the presence PVA or PEG in the microsphere composition protected the herbicide or delayed its loss in soil for 7 weeks. In this instance, formulations containing PEG would be useful when a relatively short period of herbicidal activity is desired. Therefore, suitable pesticide release, reduced leaching, and adequate herbicidal activity could be achieved by modifying the formulation parameters and/or by combination of different types of microspheres.

The use of these formulations may be an advantage, because a constant release of herbicide may not necessarily be desired for weed control problems. Frequently, an initial burst of pesticide release may be more effective, after which a smaller amount in the surface horizon is necessary to maintain the effect. This controlled release would result in a longer period of weed control due to the slow release of the active ingredient to the soil environment.

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