

# Controlled Release of Diuron from an Alginate–Bentonite Formulation: Water Release Kinetics and Soil Mobility Study

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The herbicide diuron was incorporated in alginate-based granules to obtain controlled release (CR) properties. The standard formulation (alginate–herbicide–water) was modified by the addition of different sorbents. The effect on diuron release rate caused by incorporation of natural and acid-treated bentonites in alginate formulation was studied by immersion of the granules in water under static conditions. The release of diuron was diffusion-controlled. The time taken for 50% release of active ingredient to be released into water,  $T_{50}$ , was calculated for the comparison of formulations. The addition of bentonite to the alginate-based formulation produced the higher  $T_{50}$  values, indicating slower release of the diuron. The mobility of technical and formulated diuron was compared by using soil columns. The use of alginate-based CR formulations containing bentonite produced a less vertical distribution of the active ingredient as compared to the technical product and commercial formulation. Sorption capacities of the various soil constituents for diuron were also determined using batch experiments.

**Keywords:** *Diuron; controlled release; bentonite; soil; sorption–desorption; leaching*

## INTRODUCTION

The reduction of the use and impact of pesticides is considered part of the drive toward sustainable agriculture (Francis et al., 1990). Controlled release (CR) pesticide formulations have several advantages over standard formulation, including an increased safety to the user and nontarget organisms, a reduction in the amount of pesticide applied, and reduced leaching potentials (Bahadir and Pfister, 1990; Riggle and Penner, 1990). Therefore, as a step toward sustainable pest control systems, controlled release technology has a role to play (Wilkins, 1995).

Many important efforts have contributed to the development of formulations for the controlled release of chemicals in agriculture (Connick, 1982; Schreiber et al., 1993; Darvari and Hasirci, 1996; Cotterill and Wilkins, 1996). Microencapsulation has shown the greatest commercial adoption due to its use in formulation concentrates for spraying (Beestman and Deming, 1990; Carr et al., 1991). Moreover, natural and biodegradable polymers used in larger particle sized formulations or devices such as gels, cross-linked polymers, and composites represent an important trend in the preparation of controlled release systems of pesticides (Wilkins, 1995). Alginates have been used as matrixes for controlled release of pesticides by several workers. Connick et al. (1984) have described a series of alginate–kaolin-based 2,6-dichlorobenzonitrile CR formulations. In aquatic release experiment, the authors reported that the sustained release of an active ingredient becomes longer as kaolin concentration was increased. Pepperman and Kuan (1993) investigated the controlled release of metribuzin CR formulations. In a water-release study, significant control of metribuzin release rates was

obtained with the addition of linseed oil. Johnson and Pepperman (1995) investigated the leaching potential of atrazine–alginate–linseed oil CR formulations. Atrazine CR formulations with and without linseed oil leached significantly less than a liquid atrazine formulation based on the technical material.

Bentonite is a natural silicate with a lamellar structure containing montmorillonite as a major constituent. The Almería region, in Andalucía (southeastern Spain) has important bentonite mining resources. This material has been previously studied and characterized by the present authors (González-Pradas et al., 1991). There is great technical interest in this material's behavior as an adsorbent either in natural conditions or under acid treatment.

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is a widely soil-applied herbicide for general weed control (Tomlin, 1994). CR formulations of diuron would potentially extend its effective lifetime, reduce risks of leaching or runoff on application, and be safer to the user and nontarget organisms. Cotterill et al. (1996) investigated the controlled release of diuron from granules based on a lignin matrix system. They reported that lignin from different sources could be used for matrix formulations, resulting in varying release rates. In soils, the adoption of lignin formulations of diuron would reduce water contamination.

Considerable evidence has accumulated to suggest that many water resources of Andalucía (Spain) are polluted with organic pesticides (Bosch et al., 1991; Parrilla et al., 1994; Chiron et al., 1995). The region of Almería has an intensive horticulture based on a raised layered bed system under plastic greenhouses irrigated from underground aquifers. The use of columns composed of uniform layers of the various soil constituents of the layered bed system (i.e., native soil, amended soil, peat, and sand) to assess leaching processes in the greenhouses is considered valid as each of the layers in the greenhouses are disturbed and mixed as much as

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**Table 1. Characteristics of the Sorbents**

sample	pH	surface area (m <sup>2</sup> g <sup>-1</sup> )	CEC (mequiv/100 g)	exchange acidity (mequiv/100 g)
B	8.31	72.7	65.6	22.3
B-0.5	2.78	183.0	76.9	67.4
B-2.5	3.31	484.8	54.4	50.4

**Table 2. Percentage (by Weight) of Component and pH of Controlled Release Formulations Containing Diuron**

	diuron (%)	sodium alginate (%)	B (%)	B-0.5 (%)	B-2.5 (%)	water (%)	pH <sup>a</sup>
DA	0.60	1.40				98.00	7.65 (0.13)
DAB	1.20	1.40	5.00			92.40	7.99 (0.04)
DAB-0.5	1.20	1.40		5.00		92.40	4.03 (0.03)
DAB-2.5	1.20	1.40			5.00	92.40	4.14 (0.05)

<sup>a</sup> Values in parentheses represent the standard deviation.

those in a laboratory layered soil column. Preliminary use of such columns combined with an appropriate leaching model supported this view (Blanco et al., 1994).

The objectives of the present work were (i) to evaluate the effect of desiccated and acid-treated bentonite incorporation into alginate formulations on the rate of diuron release and (ii) to evaluate the potential of alginate-bentonite-encapsulated CR formulations to reduce leaching of diuron.

## MATERIALS AND METHODS

**Chemicals.** The materials used as sorbents for this series of experiments were a natural bentonite (98% montmorillonite, containing sodium as exchange ion) from Almería (Spain) (crushed to a particle size less than 0.15 mm) previously described (González-Pradas et al., 1983) and two acid-activated bentonite samples.

Acid activation of bentonite was carried out in boiling solution of H<sub>2</sub>SO<sub>4</sub> (concentrations: 0.5 and 2.5 mol L<sup>-1</sup>) for 1 h. In all cases, the resulting samples were heated at 105 °C to constant weight. Chemical composition and textural properties of the samples were also previously studied by the present authors (González-Pradas et al., 1991). The two products so obtained and the natural bentonite are labeled in the text as B-0.5, B-2.5, and B, respectively.

Bentonite samples were analyzed by standard methods. Sample pH was determined in a 1:2.5 clay/water suspension using a glass electrode (Jackson, 1982). Surface area was determined from N<sub>2</sub> adsorption isotherms using a surface analyzer from Micromeritics, model II-2370; cation exchange capacity (CEC) and exchange acidity were calculated by using the barium acetate method (Primo-Yúfera and Carrasco-Dorrién, 1981). Properties of the bentonite samples are shown in Table 1.

Technical grade (TG) diuron (99.0%) and commercial formulation (CF) (Herbilane: 25% active ingredient) were kindly supplied by Industrias Afrasa S.A. Molecular formula and selected properties of diuron are as follows (Tomlin, 1994): molecular formula, C<sub>8</sub>H<sub>14</sub>ClN<sub>5</sub>; molecular weight, 215.7; melting point, 158 °C; vapor pressure (25 °C), 1.1 μPa; water solubility (25 °C), 42 mg L<sup>-1</sup>.

The sodium alginate (medium viscosity: 3500 cps for 2% solution) was obtained from Sigma Chemical Co. (St. Louis, MO).

**Preparation and Evaluation of Controlled Release Formulations.** The CR formulations prepared were based on the gelling properties of the alginate in the presence of divalent cations. Formulations containing different percents of sodium alginate (A), natural bentonite (B), acid-treated bentonite samples (B-0.5 and B-2.5), and technical diuron (D) were made up in water as shown in Table 2 and vigorously stirred for 1 h.

The alginate mixtures were dropwise added to a 300-mL gellant bath of 0.25 M CaCl<sub>2</sub> using the apparatus described by Connick (1982). The resulting beads were allowed to gel in the 0.25 M CaCl<sub>2</sub> solution for a total of 5 min, and then they were filtered and allowed to dry first at room temperature and then in an oven (40 °C) to constant weight. The products so obtained will be labeled in the text as DA, DAB, DAB-0.5, and DAB-2.5.

The actual concentration of diuron in the dry products was determined by dissolving the granules in a 0.03 M triphosphosphate solution and extraction into a water:methanol (80:20) mix. The resulting extract was filtered, and the herbicide concentration was determined by high-performance liquid chromatography (HPLC) using a diode-array detector and data station. Using an acetonitrile-water mix (60:40) and a LC-18 bonded-phase column, diuron was analyzed at 250 nm, its wavelength of maximum absorption. External standard calibration was used, and three replicates were carried out for each formulation.

**Experiment Carried out in Water. Static Immersion Tests.** Granules containing 20.0 mg of diuron in each sample and 5.3 mg of technical product (three replicates) were added to 50 and 500 mL of distilled water, respectively, and placed into stoppered conical flasks. Flasks were shaken in a thermostated bath at 25 ± 0.1 °C. At different time intervals, aliquots of 1 mL were removed for determination of diuron by HPLC as described above. Then, for granules all water was replaced with fresh to minimize saturation effects, whereas for the technical product unused sample portions were returned to the flasks.

In the final stage of the study, granules were removed from each flask to determine the amount of diuron that had remained incorporated in the granules. Release data were normalized at 100% by taking into account the amount of diuron released and the amount remaining incorporated in the granules when the experiment finished.

**Experiments Carried out in Soil.** Mobility of diuron from alginate-based CR formulations was investigated by using soil columns, simulating the typical arrangement of the different layers in a greenhouse, which is composed of sand, peat, amended soil, and native soil. Two alginate-based CR formulations containing bentonite samples were compared to a commercial formulation (CF) and technical grade (TG) diuron. Sorption-desorption experiments were also carried out for determining the sorption capacity of the different soil constituents for diuron.

**Static Experiments. Soil Characterization and Sorption-Desorption Studies.** The soils used were a calcareous soil (Camborthids) and an amended soil (Xerosol-Luvic), from the Almería region. A commercial peat was used as the organic matter layer (Hydro del Báltico, Navasa S.A.). The sand was obtained from an unused commercial greenhouse. The individual layers of the soil from the greenhouse were characterized in terms of their physical properties. Air-dried samples, less than 2 mm of particle size, were analyzed by standard methods. The pH was determined in a 1:2.5 soil/water suspension using a glass electrode (Jackson, 1982); organic matter content was determined by the Walkley-Black method (Walkley and Black, 1934); clay content was determined by the hydrometer method (Black et al., 1982); cation exchange capacity was determined by the barium acetate method (Primo-Yúfera and Carrasco-Dorrién, 1981); and water saturation and field capacity were determined following the guidelines by Hall et al. (1977). All these characteristics are shown in Table 3.

The sorption experiments were carried out as follows: 0.02 M CaCl<sub>2</sub> aqueous solution containing initial diuron concentrations (C<sub>0</sub>) between 2.1 and 24.4 mg L<sup>-1</sup> were used. Aqueous suspensions of the samples were prepared by adding 25 mL of each diuron solution to 3.0 g of native soil and amended soil, 3.0 g of sand, and 0.5 g of peat. Then they were placed in several stoppered conical flasks and shaken for 24 h (the time required for equilibrium to be reached between diuron sorbed and diuron in solution) in a thermostated shaker bath at 25 ± 0.1 °C. After being shaken, the solutions were centrifuged

**Table 3. Characteristics of the Four Layers of the Greenhouse Soil**

layer	pH	organic matter (%)	clay content (%)	field capacity (% v/v)	water saturation (% v/v)	CEC (mequiv/100 g)
sand	9.39	0.02		5.80	40	10.00
peat	3.28	81.32		77.0	128	116.25
amended soil	8.44	0.08	53.00	38.0	52	10.63
native soil	8.87	0.51	8.00	48.0	51	12.50

at 9250g for 10 min, and the concentration of diuron in the supernatant liquid was determined by HPLC using the method described above. The diuron sorbed was calculated from the difference between the initial and the final solution concentrations. Blanks containing no diuron and three replicates of each sorption point were used for each series of experiments.

Desorption experiments were carried out by adding 25 mL of a 0.02 M CaCl<sub>2</sub> solution to the stoppered conical flasks containing the higher initial pesticide concentration ( $C_0 = 24.4$  mg L<sup>-1</sup>), after removal of the sorption supernatant. This system was again shaken for a 24-h period to establish the new equilibrium. This treatment was also followed by centrifugation and determination of the new equilibrium concentration in the supernatant. The amount of diuron desorbed in the first equilibration was calculated. This process was repeated four times. Blanks containing no diuron were used for each case, and all desorption experiments were carried out in triplicate.

**Mobility Experiments.** *Column Preparation.* Soil columns were prepared by splitting a poly(vinyl chloride) (PVC) pipe (7 cm i.d., 60 length) longitudinally and applying 2-mm-thick silicone ridges around the inside of the column at 5-cm increments to minimize boundary flow (Weber and Pepper, 1977). The two parts of each column were then put together and sealed with waterproof adhesive paste. Nylon mesh with an effective pore diameter of 60 μm and lined with a layer of fiberglass wool was sealed to the bottom of each column to prevent displacement of the soil from the columns and minimizing the dead-end volume (Fleming et al., 1992). Each column contained, from the bottom to the top, native soil (20 cm), clay soil (20 cm), peat (2 cm), and sand (10 cm). The different layers of the soil, screened through a 2-mm sieve, were added to the column in small increments to minimize particle size obtaining the following final bulk densities: 1.17 (native soil), 1.43 (clay soil), 0.26 (peat), and 1.56 g cm<sup>-3</sup> (sand). Prior to application of the herbicide treatments, the columns were saturated with distilled water via capillarity and then left to drain for 1 day.

*Chemical Preparation and Application.* The herbicide treatments were applied at a rate of 6.5 kg a.i. ha<sup>-1</sup>. This rate is commonly used to prevent weed infestations and is enough to achieve adequate surface coverage.

All herbicide treatments (TG, CF, and alginate-based CR formulations) were applied to duplicate soil columns. TG and CF were applied following the next method: A methanol solution containing 10 mg of diuron was added to 50 g (0.5 cm) of washed sand. The washed sand/herbicide mixture was left to dry overnight at room temperature before being added to the top of each column. After application of the herbicide, an additional 0.5 cm of washed sand was added to the top of the column. The alginate-based CR formulations (DAB and DAB-0.5) were evenly distributed on the sand layer, after that an additional 1 cm of washed sand was added to the top of the column.

*Leaching and Leachate Collection.* The leaching solution used in all experiments was 0.02 M CaCl<sub>2</sub>. This was done to simulate the soil solution and to prevent dispersion of the soil during the leaching procedure (Johnson and Pepperman, 1995). To evaluate the effect of water volume applied on herbicide movement, two watering regimes were used in this study. One involving a water solution amount of 1.5 L (the amount of solution equivalent to that applied in greenhouses for one growth season and equivalent to approximately 2.72

column pore volume) and the other involving a water solution amount of 6.0 L (the amount of solution equivalent to that applied in greenhouses in four growth seasons and equivalent to approximately 9.09 column pore volume). Leaching solution was applied at a flow rate of 5 mL h<sup>-1</sup> using a Gilson Minipuls 3 peristaltic pump. The time and volume of each leachate were recorded. Aliquots were taken from the leachate, passed through 0.5 μm PTFE filters, and injected directly in the HPLC system. At the end of the leaching procedure, the columns were allowed to drain for 48 h.

*Column Analysis.* The columns were split vertically, and the soil was removed following the established division for the different layers of the column, obtaining four fractions corresponding to native soil, amended soil, peat, and sand. In addition, for the native soil and amended soil, a partition was made in two 10-cm portions labeled as (1) and (2) representing the upper and lower fractions, respectively. Each fraction was dried at room temperature and homogenized. Subsamples of soil, sand, and peat were extracted in conical flasks placed in a shaker bath for 24 h with 25 mL of HPLC grade methanol, filtered through Whatman No. 42 paper, and analyzed by HPLC as described above.

## RESULTS AND DISCUSSION

**CR Formulations.** Characteristics of alginate-based CR granules containing diuron are presented in Table 4. The granules were generally spherical in shape, and the technical grade diuron was readily incorporated in the alginate matrix, obtaining granules of size between 1 and 2.00 mm. The addition of bentonite to the alginate formulations led to larger and heavier granules that were more spherical and dried with less aggregation. It is also interesting to note from the data in Table 4 that inexpensive bentonite effectively increased granules yields and reduced the amount of alginate in the final product, permitting us in this way to obtain a cheaper formulation. In all cases, the encapsulation efficiency was higher than 98.3%.

**Release Kinetics in Water.** The cumulative release of diuron from alginate-based CR granules and the solubility profile for TG is shown in Figure 1. As can be seen, 91.63% of unformulated diuron is dissolved in less than 20 days while at least 137 days is necessary to release 90% of the active ingredient from the alginate-based CR formulation DAB-0.5.

The release data was analyzed by applying the empirical equation proposed by Ritger and Peppas (1987):

$$M_t/M_0 = Kt^n \quad (1)$$

where  $M_t/M_0$  is the percentage of active ingredient released at time  $t$ ,  $K$  is a constant that incorporates characteristics of the macromolecular network system and the active ingredient, and  $n$  is a diffusional parameter that is indicative of the transport mechanism.

The values of  $K$  and  $n$  obtained from the initial 60% release are presented in Table 5. There is a good correlation of the release profiles of diuron granules with the empirical equation. The correlation coefficient ( $r$ ) being higher than 0.99. The  $n$  values range from 0.43 for DAB-2.5 granule to 0.62 for DAB granule. Values close to 0.5 indicate that the release is diffusion-controlled (Ritger and Peppas, 1987). The complexity of the heterogeneous system involved together with the capacity of bentonite samples to interact with the diffusion agent can explain some deviation from the  $n$  value indicated above.

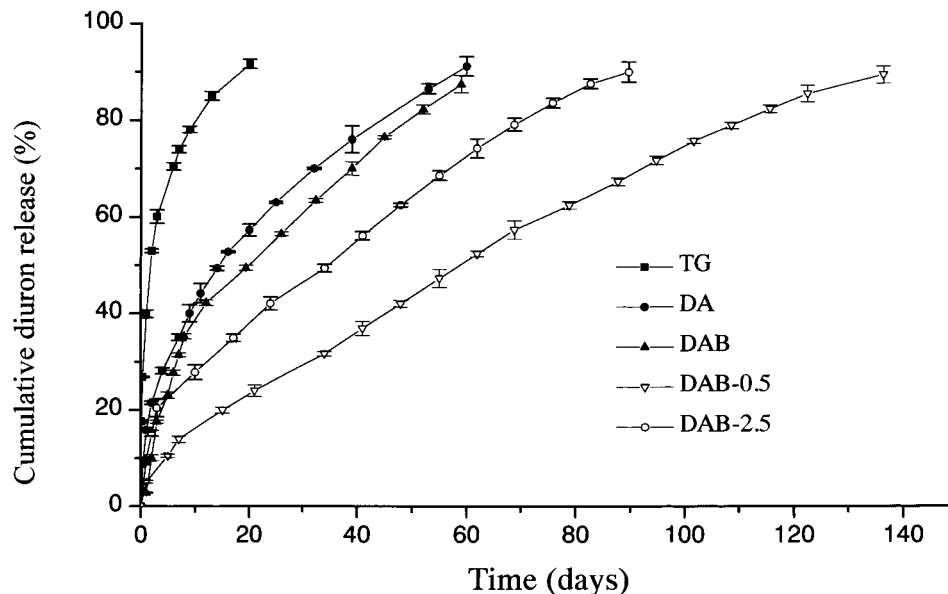
From the constants in Table 5, the  $T_{50}$  value (the time taken for 50% of the diuron to be released) was



**Table 4. Characteristics of Controlled Release Granules Containing Diuron**

	diuron (%)	Ca <sup>2+</sup> (%)	yield <sup>a</sup> (%)	average weight (mg/granule)	encap effic <sup>b</sup> (%)
DA	21.53 (0.28) <sup>c</sup>		2.73	0.90 (0.07)	98.85
DAB	12.75 (0.23)	8.30 (0.42)	11.54	2.66 (0.04)	98.56
DAB-0.5	13.09 (0.12)	9.25 (0.29)	11.22	2.77 (0.15)	98.33
DAB-2.5	13.57 (0.31)	13.36 (0.67)	11.44	2.77 (0.02)	98.56

<sup>a</sup> Yield = weight of dry product × 100/weight of formulation processed. <sup>b</sup> Encapsulation efficiency = amount of diuron in formulation processed × 100/amount of diuron in dry product. <sup>c</sup> Values in parentheses represent the standard deviation.



**Figure 1.** Cumulative release of diuron from granules into static water (error bars represent the standard deviation of three replicates).

**Table 5. Constants from Fitting the Empirical Equation  $M_t/M_0 = Kt^n$  to Release Data of Diuron in Water**

product	$K$ (days) <sup>-n</sup>	$n$	$r$	$T_{50}$ (days)
DA	0.13 ± 0.004 <sup>a</sup>	0.51 ± 0.011	0.994 <sup>b</sup>	14.03
DAB	0.08 ± 0.014	0.62 ± 0.054	0.992 <sup>b</sup>	19.22
DAB-0.5	0.05 ± 0.005	0.55 ± 0.036	0.993 <sup>b</sup>	65.79
DAB-2.5	0.11 ± 0.008	0.43 ± 0.021	0.996 <sup>b</sup>	33.83

<sup>a</sup> These values represent the standard error. <sup>b</sup> Significant at the 0.001 probability level.

calculated for the alginate-based CR granules. These values are also shown in Table 5. The  $T_{50}$  values range from 14.03 days for DA granule to 65.79 days for DAB-0.5 granule. The CR granules can be ranked in order of increasing  $T_{50}$  values:

$$DA < DAB < DAB-2.5 < DAB-0.5$$

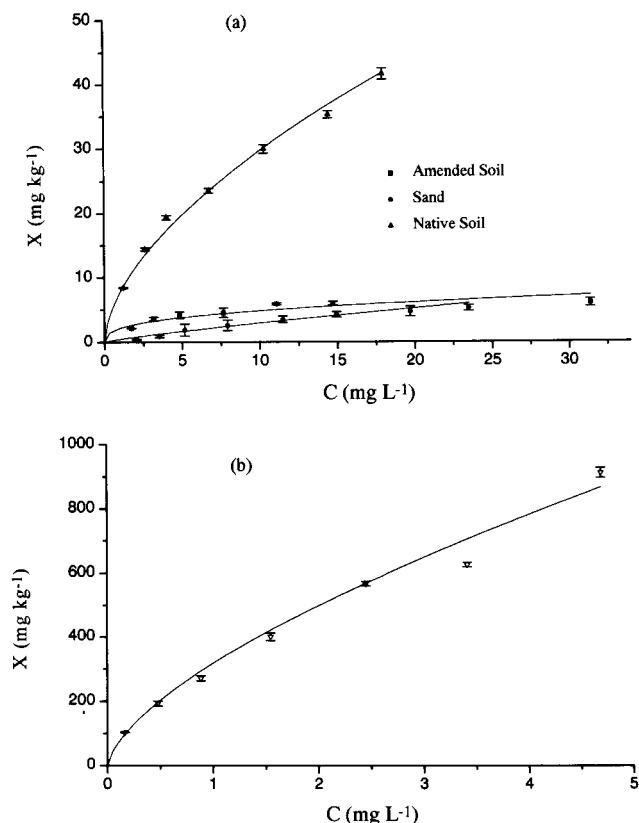
The lower value of  $T_{50}$  corresponds to the DA granule, which means that this CR preparation produces the fastest diuron release in water. The addition of bentonite to alginate-based formulations reduces the rate of release, the acid-treated bentonite samples producing the slower release rate as compared to the natural bentonite. This behavior seems to be in agreement with the results obtained in batch sorption experiments with bentonite samples and diuron (Gonzalez-Pradas et al., 1993). In that study, the authors reported that the sorption capacities of acid-treated bentonites (B-0.5 and B-2.5) for diuron were much higher than that obtained with natural bentonite (B). The variety shown for  $T_{50}$  values in Table 5 for the granules used in this study might be useful for selecting the most appropriate formulation depending on the type of soil.

**Experiments Carried out in Soil. Static Studies: Sorption–Desorption Studies.** Figure 2 shows the sorption isotherms of diuron on the different sorbents: sand, amended soil and native soil (Figure 2a), and peat (Figure 2b). According to the initial portion of the curves, these isotherms may be classified in general as the L type of the Giles classification (Giles et al., 1960), which suggests that the samples have an average affinity for the herbicide diuron and that there is no strong competition from the solvent for sorption sites. To evaluate the sorption capacities of the different layers of the soil columns, the experimental data points were fitted to the Freundlich equation (Adamson, 1982). The linear form of this equation is

$$\log X = \log K_f + n_f \log C \quad (2)$$

where  $X$  is the amount of herbicide sorbed (mg/kg of sorbent),  $C$  is the equilibrium solution concentration (mg L<sup>-1</sup>), and  $K_f$  and  $n_f$  are constants that characterize the sorption capacity for the herbicide. The constant  $K_f$  is the amount of pesticide sorbed for an equilibrium concentration of 1 mg L<sup>-1</sup>, and  $n$  is a measurement of the intensity of adsorption and reflects the degree to which adsorption is a function of the concentration (Calvet, 1980). The  $K_f$  and  $n_f$  values were calculated from the least-squares method applied to the linear form of the Freundlich equation, and their values are summarized in Table 6. As can be seen from this table, the  $K_f$  values increase from 0.50 mg kg<sup>-1</sup> for the sand to 302.7 mg kg<sup>-1</sup> for the peat sample, the variation order being

$$\text{sand} < \text{amended soil} < \text{native soil} \ll \text{peat}$$



**Figure 2.** Sorption isotherms of diuron on the different layers of a greenhouse soil (error bars represent the standard deviation of three replicates): (a) sand, amended soil, and native soil; (b) peat.

**Table 6. Parameters of the Freundlich Equation and Correlation Coefficients**

sample	$K_f$	$n_f$	$r$
sand	$0.50 \pm 0.24$	$0.76 \pm 0.07$	$0.988^b$
peat	$302.66 \pm 16.36$	$0.70 \pm 0.04$	$0.999^b$
amended soil	$2.45 \pm 0.79^a$	$0.32 \pm 0.13$	$0.976^b$
native soil	$8.41 \pm 1.06$	$0.54 \pm 0.05$	$0.998^b$

<sup>a</sup> These values represent the standard errors. <sup>b</sup> Significant at the 0.001 probability level.

The accumulated percentage of desorbed diuron from the different sorbents, after four desorption cycles, is presented in Figure 3. These values range between 52.48% for the peat sample to 100% for the amended soil and sand. For these experiments, the variation order is in general inversely related to that obtained for the  $K_f$  values.

**Mobility Studies.** The amount of diuron recovered per kilogram in each portion of the columns is presented in Table 7. In addition, the total percentages of diuron recovered in the soil, leachate, and granules referred to the total amount of herbicide applied in the experiments are also indicated in Table 7.

When a water volume equivalent to that applied in one growth season was added to the columns, diuron was not detected in the leachate. In this experimental condition, differences were not observed in the distribution patterns of diuron between TG and CF preparation, but differences are clearly visible between the TG and CF and both DAB and DAB-0.5 granules.

After 12.5 days of leaching at the rate of 5 mL h<sup>-1</sup>, 90.93% and 93.66% of the total amount of diuron applied were extracted from the soil layers when diuron was

applied as TG and CF, respectively, showing in both cases similar distribution and reaching the first portion of the native soil.

In comparison to the percentage of diuron found in soil columns after application of the TG and CF products, the amount of diuron recovered from the soil was less in columns treated with alginate-based CR formulations (DAB and DAB-0.5 granules). For these columns, diuron leached only to the peat layer. The amount of diuron recovered per kilogram is higher in all cases for the peat layer than for the rest of the soil layers according to the values of the  $K_f$  parameter obtained in sorption experiments. The characteristics of release under these soil conditions are related to those obtained by release into static water; that is, the release of diuron from the alginate-based CR formulation DAB-0.5 is slower than that observed for the alginate-based CR formulation DAB.

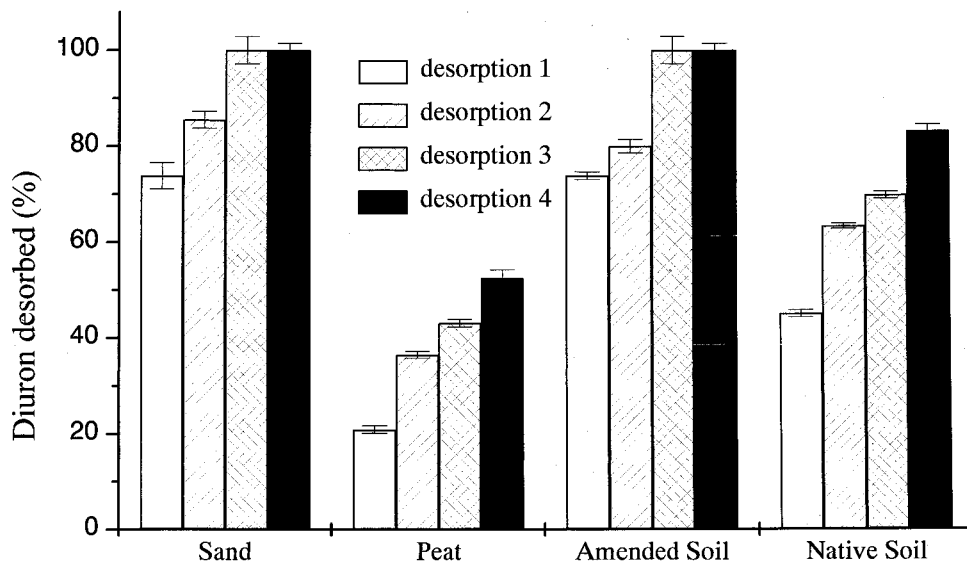
The distribution of diuron from TG and alginate-based CR DAB-0.5 formulation, when a water volume equivalent to that applied in four growth seasons was applied to the columns, is also presented in Table 7. After 50 days of leaching at a rate of 5 mL h<sup>-1</sup>, no diuron was found on the top layer of the column (sand) when applied as TG. In the soil, 36.51% was recovered and 24.56% appeared in the leachate. When diuron was applied as alginate-based CR formulation (DAB-0.5), 22.89% of total applied was recovered in the soil, 9.81% appeared in the leachate, and 39.74% was extracted from the granules. It can be seen that lesser vertical movement takes place when diuron is applied as alginate-based CR formulation (DAB-0.5).

Total recovery of diuron at 50 days from the columns treated with alginate-based DAB-0.5 granules was 72.44% of the total applied, higher than in those treated with TG (61.07%). The granules recovered from the soil did not show any signs of disintegration or major degradation at the end of the experiment. The integrity of the CR granule is an important feature of non-erodible controlled formulations, as unpredictable fracture formation and breakage would increase the release surface of the matrix and thus the amount of active ingredient release.

The cumulative diuron leached from TG and alginate-based CR formulation (DAB-0.5) is shown in Figure 4. Significant differences were noted in the leaching patterns between TG and DAB-0.5 treatments. For the TG, diuron was first detected in the leachate at approximately 2.1 L. The amount leached increased steadily over time to approximately 24.56% at the termination of the experiment. For the alginate-based CR formulation (DAB-0.5), diuron was detected in the leachate later (2.56 L). The amount leached increased to 9.81% of that applied by the termination of the leaching procedure. It can be seen that the use of the alginate-based CR formulation (DAB-0.5) reduces leaching of diuron as compared to the technical grade product in soil columns. Several researchers have demonstrated reduced leaching of pesticides with CR formulations. Gish et al. (1991) found that starch encapsulation reduced leaching of atrazine as compared to technical atrazine in soil columns. Johnson and Pepperman (1996) found that CR-oil formulation resulted in a decreased leaching potential for alachlor in soil as compared to technical alachlor.

## CONCLUSIONS

The use of untreated bentonite and acid-treated bentonite samples as filler agents of an alginate–diuron

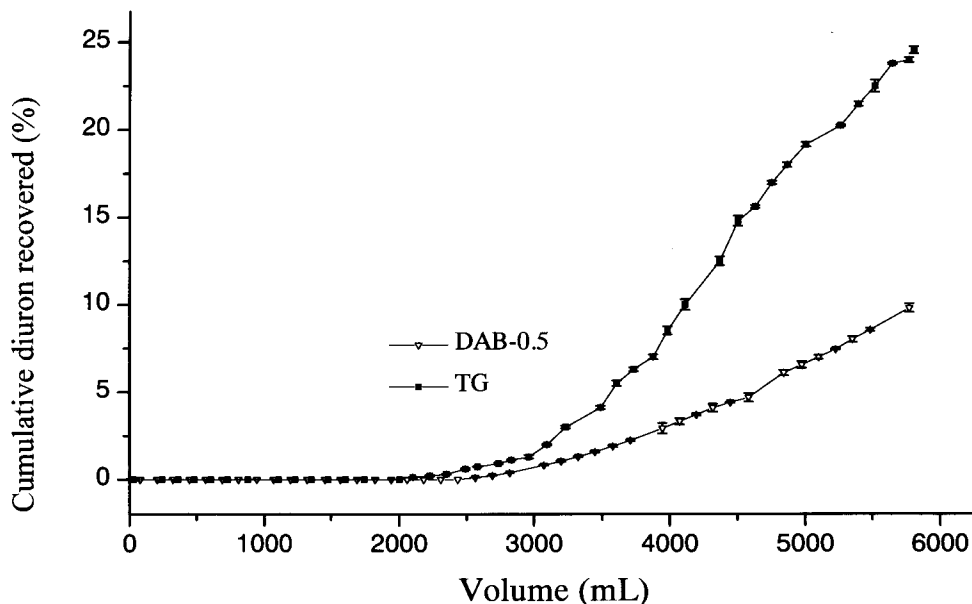


**Figure 3.** Cumulative diuron desorbed from the different layers of a greenhouse soil (error bars represent the standard deviation of three replicates).

**Table 7.** Mean of Values of Extracted Diuron from the Soil Layers and Total Percentages of Diuron Recovered from the Granules, Soil, and Leachates

layer	water volume equivalent to one growth season				water volume equivalent to four growth seasons	
	TG (mg kg <sup>-1</sup> )	CF (mg kg <sup>-1</sup> )	DAB (mg kg <sup>-1</sup> )	DAB-0.5 (mg kg <sup>-1</sup> )	TG (mg kg <sup>-1</sup> )	DAB-0.5 (mg kg <sup>-1</sup> )
sand	11.28 (0.43) <sup>a</sup>	10.71 (0.20)	0.46 (0.08)	1.47 (0.06)		0.17 (0.01)
peat	86.50 (1.65)	125.8 (3.01)	103.0 (2.16)	62.61 (1.31)	50.32 (1.14)	28.19 (2.07)
amended soil (1) <sup>b</sup>	0.44 (0.05)	0.32 (0.01)			0.09 (0.01)	0.25 (0.04)
amended soil (2)	0.40 (0.03)	0.15 (0.02)			0.09 (0.02)	0.24 (0.05)
native soil (1)	0.29 (0.07)	0.46 (0.04)			2.46 (0.37)	1.75 (0.19)
native soil (2)					3.43 (0.15)	1.37 (0.09)
% diuron recovered in soil	90.93	93.66	22.99	19.50	36.51	22.89
% diuron recovered in leachate					24.56	9.81
% diuron recovered in granules			76.10	80.25		39.74

<sup>a</sup> (1) and (2) represent the upper and lower fractions in amended soil and native soil. <sup>b</sup> Values in parentheses represent the standard deviation.



**Figure 4.** Cumulative diuron leached from TG and DAB-0.5 formulation in a greenhouse soil (error bars represent the standard deviation of two replicates).

formulation reduces the release rate of the herbicide in comparison with the technical product and with alginate formulation. The release of diuron from the various

alginate-based CR formulations into water has been shown to be diffusion controlled. The release of the active ingredient from alginate-based CR granules in

water is affected not only by the addition of natural bentonite to the alginate–diuron-based formulations but also, and to a greater extent, by the addition of the acid-treated bentonite sample (B-0.5). Soil studies indicate that the use of CR granules reduces the vertical mobility of diuron into the soil layer columns; the peat layer showing the highest sorption capacity both in static and dynamic conditions. From these results, it could be inferred that the use of formulations such as those described in this paper would reduce the possibility of diuron to reach and contaminate the groundwater.

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