

Effect of Soil Moisture on the Release of Alachlor from Alginate-Based Controlled-Release Formulations

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The release of alachlor from controlled-release formulations (CRFs) based on alginate–montmorillonite matrices into aqueous polyethylene glycol (PEG) solutions of different concentrations and into a soil at different moisture contents was studied. In distilled water and in PEG-containing solutions displaying -0.1 MPa potential and up, the beads imbibe water and swell. The ensuing increase in weight is about 5%, and the increase in the bead's diameter is about 10%. At water potentials of -0.5 MPa and lower, loss of weight and shrinkage of the beads were observed. The changes in weight and diameter of the alginate–clay beads incubated in a Hamra loamy sand soil at 26.5% moisture content (w/w; -0.18 MPa) were similar to those observed in PEG solutions of >-0.5 MPa moisture potential. The weight and diameter losses observed in the drier soils (12.0 and 7.1% water content; -0.49 and -1.11 MPa) were similar to those in the more concentrated PEG solutions. A decrease in the rate of release of the active ingredient from the beads into soil was observed as the water potential decreased (drier soils). The release of the active ingredient from the investigated CRFs displayed a linear relationship to the square root of time, suggesting a diffusion-controlled-release rate. Data extracted from this relationship enabled the formulation of a mathematical model that correlates rate of release to water content.

KEYWORDS: Alachlor; alginate; controlled release; polyethylene glycol; water potential

INTRODUCTION

Alginate is a water-soluble polysaccharide composed of two types of monomers, D-mannuronic acid and L-guluronic acid, at varying proportions and forms gels in aqueous media in the presence of polyvalent cations (1). The gel structure and porosity depend on many features such as chain length, polymer composition, and gelation conditions, including cation type and concentration. Alginate has been widely employed in formulations for the controlled release of pharmaceuticals (e.g., refs 2–4) and pesticides (e.g., refs 5–9). The extensive interest in this polysaccharide is attributed to its biodegradability, low toxicity, and capacity to integrate and release a wide range of chemicals.

The release rate of compounds from the alginate matrix is a function of properties of both the active ingredient and the composition of the matrix (10). The rate of release of an organic active ingredient is correlated with its aqueous solubility: the greater the solubility, the more rapid the release rate. The addition of montmorillonite (a clay mineral) to alginate gels decreases the rate of release of the active ingredient due to an increase in the adsorption capacity for the incorporated compound by the matrix and the enlarged tortuosity within the

gel (11, 12). The release of active ingredients from spherical, alginate-based controlled-release devices has been shown to be diffusion controlled (11, 12). For the nonvolatile active ingredient to diffuse out of the spherical polymer bead, it is necessary for a liquid phase to be present within the bead to allow the active ingredient to dissolve and to provide a continuous diffusion pathway with the liquid phase in the external soil system. Considering that the moisture content of soils is not constant, but rather fluctuates as the soil dries out or rewets, it is likely that the rate of diffusion of the active ingredient from a controlled-release formulation (CRF) will fluctuate as well.

The objective of this paper is to explore the effect of the soil's water content on the rate of release of alachlor from alginate-based controlled-release formulations. Polyethylene glycol (PEG) solutions of different concentrations were used to simulate different water potentials (e.g. ref 13). Release studies in soil were conducted to confirm the results obtained by using PEG solutions.

MATERIALS AND METHODS

Alginate as alginic acid sodium salt was purchased from Fluka, Buch, Switzerland, and the clay (Wyoming bentonite) was purchased from Fischer Scientific. Alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] (technical grade) was provided by Agan Chemicals, Ashdod, Israel. Pectin (Unipectine rouge 3 G), derived from fruit,

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Table 1. Polyethylene Glycol (PEG) Solutions Used for the Controlled-Release Studies and Their Equivalent Water Potentials (14)

PEG (g/L)	water potential (MPa)	equivalent soil-water potential (atm)
0	0	0
74.1	-0.1	0.99
203.5	-0.5	4.95
295.2	-1.0	9.9
366.8	-1.5	14.85

was obtained from Sanofi Bio-Industries, France. Polyethylene glycol 6000 (MW = 7000–9000 g/mol) and other reagents of analytical grade were purchased from Merck (Darmstadt, Germany). Solvents were all of HPLC grade purchased from BioLab Ltd., Israel. The soil used in all experiments was the surface horizon (0–20 cm) of a Hamra soil from Bet Dagan. This soil is classified as loamy sand, Typic Rhodoxeralf, containing 10% clay and 0.3% organic carbon.

Experimental Procedures. Preparation of CRFs. Spherical alginate–clay beads of ~3 mm diameter containing 14.5% alachlor (w/w) were prepared according to the method described in Gerstl et al. (11). In the preparation of the alginate-based CRFs, advantage was taken of the propensity of alginate to undergo gelation in the presence of multivalent cations. A homogeneous mixture of alginate, clay, and alachlor (3, 4, and 2 g, respectively) was prepared in 100 mL of distilled water, and the suspension was then slowly added to a 0.5 M CaCl₂ solution by dripping it from the tip of a Pasteur pipet attached to a peristaltic pump. In this way the spherical shape of the drop was retained by the gelled suspension. The beads were left in the CaCl₂ solution for 4 min to ensure complete gelling and then separated from the solution in a Buchner funnel, rinsed twice with distilled water, and air-dried in a fume hood overnight. These beads will be referred to hereafter as the standard alginate beads.

To determine the load of alachlor in the CRFs, three beads were shaken overnight with 3 mL of 0.1 M sodium citrate until complete dispersion was accomplished. Following this step the suspension was extracted with 7 mL of a 1:1 mixture of hexane and ethyl acetate. The organic solvent mixture was separated and evaporated, and the residue was taken up in methanol for HPLC analysis.

Other CRF beads were prepared as well according to the method described above. Alginate/pectin (1:1)–clay beads (~3 mm diameter) of 14.2% loading were prepared as above but using a 1:1 mixture of alginate and pectin. Small alginate–clay beads (diameter < 1 mm) of 6.4% alachlor loading were prepared by using tips with a smaller diameter to give smaller drops.

Chromatographic Analysis. Alachlor analysis was carried out on a Shimadzu LC10AT HPLC, equipped with a photodiode array detector. The column was a 250 × 4 mm C18 LiChrospher, 5 μm particle size. The mobile phase was 20% double-distilled water and 80% methanol at a flow rate of 1 mL/min, and the detector was set at 230 nm.

Preparation of PEG Solutions. Solutions of PEG 6000 in distilled water were prepared (14) to give various water potentials in the range observed in soils (Table 1).

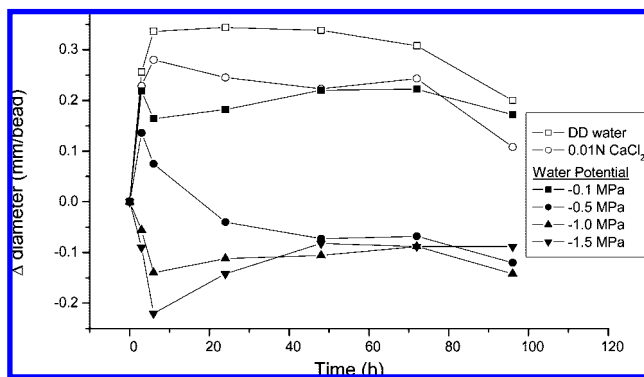
Changes in Bead Diameter and Weight. Air-dried CRFs were weighed and their diameters accurately determined with a micrometer. Five beads each were then placed in a set of covered beakers containing either distilled water, 0.01 N CaCl₂, or the various PEG solutions (Table 1) and allowed to equilibrate for 95 h. A 0.01 N CaCl₂ solution has an osmotic potential of 0.049 MPa and was studied as it is characteristic of a typical nonsaline and nonalkaline soil solution. Periodically the beads were removed from a selected beaker and their weight and diameter determined after gentle removal of external water with paper towels.

Release of Alachlor to Water. The rate of release of alachlor from the initially air-dried CRFs was determined in a closed system. Five beads were suspended on a stainless steel net in a glass beaker containing 70 mL of either distilled water, 0.01 N CaCl₂, or a PEG solution (Table 1), which was stirred with a magnetic stirrer. The alachlor in solution was determined by periodic sampling of the solution and determination of the herbicide content by HPLC. Three replicates of each treatment were run.

Table 2. Moisture Contents and Soil–Water Potential of the Soil Used for the CRF Studies

soil moisture content (%)	θ^a	equivalent saturation	soil–water potential ^b (MPa)
7.12	0.10	0.27FC ^c	-1.11
12.0	0.17	0.45FC	-0.49
26.5	0.37	FC	-0.18

^a θ is the volumetric water content (mL/mL) assuming a bulk density (ρ) of 1.4 g/cm³. ^b Based on Figure 1 of Russo and Bressler (19). ^c FC is the gravimetric moisture content at field capacity.

**Figure 1.** Changes in the diameter of the standard alginate–clay CRF beads in the various PEG solutions as a function of time.

Release of Alachlor into the Soil. The release of the active ingredient into soil from the initially air-dried alginate–clay CRF was determined as follows: Soil samples (200 g) were brought to a predetermined moisture content (Table 2); half of the soil was added to a beaker, after which four beads whose weight and diameters were accurately measured were placed onto the soil in a distinct pattern so that they could be identified later. The remainder of the soil was then added and the beaker tapped a number of times to pack the soil. The beakers were weighed and stored in an incubator at 25 °C after being covered with parafilm in which four small holes were made to ensure adequate air exchange. The incubated beakers were weighed twice a week, and water was added as necessary to replace water lost by evaporation. Three replicates were run for each type of CRF at each soil moisture content.

After various incubation periods, the soil from selected beakers was carefully removed to expose the beads that were then separated from the surrounding soil. Any soil clinging to the beads was carefully removed. The soil from the beakers was then thoroughly mixed and extracted with water and a 1:1 mixture of hexane and ethyl acetate. The organic solvent was separated and evaporated and the residue taken up in methanol for analysis by HPLC. The ratio of soil/water/organic mixture was 2:1:1, respectively. The extraction of alachlor from the beads was as described under Preparation of CRFs. Prior to extraction, the individual beads were weighed and their diameters measured.

RESULTS AND DISCUSSION

Time-Dependent Changes in Bead Properties. Changes in the alginate–clay CRF beads' diameter and weight as a function of incubation time in the different solutions are presented in Figures 1 and 2. The changes are not immediate, and the system takes about 5 h to equilibrate. As shown below, this has a strong influence on the kinetics of release of the active ingredient.

The effect of water potential on the behavior of the beads is clear. In distilled water and down to, and including, -0.1 MPa potential, the air-dried beads imbibe water and swell. The increase in weight is about 0.5 mg/bead or about 5%. Swelling of the beads varies with the water potential, and the growth in diameter is on the average 0.25 mm or a bit less than 10%. The increase in bead volume cannot be accounted for entirely by the changes in bead weight. If the increase in volume were

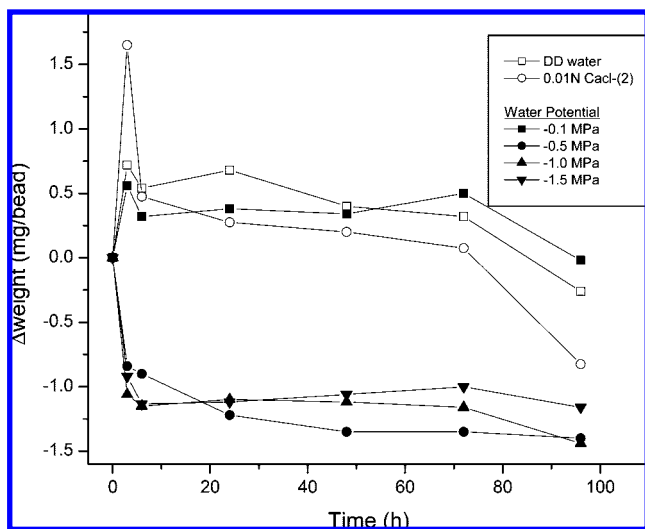


Figure 2. Changes in the weight of the standard alginate–clay CRF beads in the various PEG solutions as a function of time.

entirely due to the imbibed water, we should have had an increase of about 5 mg in weight, 10 times that observed. Thus, it would seem that the small amount of water taken up by the polymer was sufficient to cause a significant change in the gelled polymer's internal structure.

At water potentials of -0.5 and lower, a loss of weight and shrinkage of the beads were observed. It seems that the potential of the water retained in the air-dried beads is greater than -0.5 MPa, resulting in a negative gradient from the bead out.

Release of Alachlor into PEG Solutions. The release of alachlor into solutions of differing water potentials from the standard alginate–clay CRF is presented in **Figure 3a**. The strong effect of the water potential on active ingredient release is readily apparent. As expected, a decrease in the rate of release of the active ingredient was observed as the water potential decreased. Whereas at the higher water potentials, 0 and -0.1 MPa, practically no lag period was detected in alachlor release, at the lower water potentials a distinct lag period was observed (~ 5 h), during which time practically no active ingredient was released. This is despite the fact that most of the beads' weight loss (which is due to water held in the CRF moving into the PEG solutions) occurred during the initial 5 h of contact (**Figure 2**). Thus, the outflowing water transported hardly any alachlor with it, indicating that the active ingredient was found almost exclusively in the solid phase, rather than in the liquid phase. The aqueous phase in the air-dried beads that were immersed in the PEG solutions, even if saturated with the slightly soluble (~ 240 mg/L at 25°C) alachlor, carries only a negligible fraction of the beads' alachlor content (14.5% w/w). We postulate that the significant lag in release of alachlor observed at the lower water potentials is due to the initial outward diffusion of the water in the beads, which delays the formation of a continuum of the PEG solution within and outside the bead, a continuum that is necessary for a detectable rate of diffusion of alachlor from the bead into the solution to occur. In addition to the strong effect of PEG on the water potential, it may also enhance alachlor dissolution and desorption (e.g., ref 15), and hence a delay in PEG penetration into the bead will prolong the lag period in alachlor release. The enhancement of the dissolution of alachlor in the presence of PEG (although much less significant than the effect of PEG on the water potential as far as the rate of release of alachlor is concerned) improves the suitability of PEG solutions to serve as models for release of the active ingredient into soils. This is so because the enhance-

ment of diffusion out of the CRF bead into the soil due to sinks such as sorption and degradation is mimicked by the increased solubility of alachlor due to the presence of PEG in the aqueous phase.

The above results suggest that wetting and drying of the soil's volume adjacent to the CRF beads in the range of water potentials common in soils should strongly affect the rate of release of active ingredients from clay–polymer-based formulations.

Mathematical Model. Alginate-based CRFs can be classified as monolithic devices in which the active ingredient, well in excess of its solubility, is evenly distributed within a polymer matrix. The release of the active ingredient from the investigated system is diffusion controlled (16, 17) and can thus be described by a linear relationship between the released active ingredient and the square root of time (**Figure 4**). This relationship fit the data for all three CRFs at all water potentials (except the observed lag period). We propose that the relationship of the slopes and intercepts of these plots to the water potential (MPa) can be approximated by a linear equation. Thus

$$\% \text{ released} = a\sqrt{t} + b \quad (1)$$

where a , the slope, can be formulated as a linear relationship

$$a = c \times \text{water potential (MPa)} + d \quad (2)$$

and b , the intercept as

$$b = e \times \text{water potential} + f \quad (3)$$

where c , d , e , and f are constants.

The nonzero intercepts of these plots correspond to the observed lag periods. The slopes and intercepts of the plots are presented in **Table 3** and are plotted as a function of the water potential in **Figure 5**. The resultant equations (eqs 2 and 3) were introduced into eq 1 to obtain the following relationship, which can be used to calculate the rate of release of alachlor at any given soil–water potential: standard alginate–clay CRF

$$\% \text{ released} = (3.76 \times \text{WP} + 5.39) \times (\text{time})^{1/2} - (1.45 \times \text{WP} + 2.41) \quad (4)$$

alginate/pectin–clay CRF

$$\% \text{ released} = (4.64 \times \text{WP} + 6.96) \times (\text{time})^{1/2} - (1.43 \times \text{WP} + 3.05) \quad (5)$$

small alginate–clay CRF

$$\% \text{ released} = (6.24 \times \text{WP} + 16.2) \times (\text{time})^{1/2} + (5.13 \times \text{WP} - 3.75) \quad (6)$$

WP is the water potential (MPa). These equations were used to fit curves to the experimental data for the different CRFs, and the results are presented in **Figure 3**, from which it can be seen that the predicted release curves fit the experimental data quite well (again, except for the observed lag periods). The equations for the alginate–clay and alginate/pectin–clay CRFs are rather similar as indicated by their slopes and intercepts. This similarity indicates that the size (i.e., diameter) of the investigated CRFs affected the rate of release of the active ingredient much more strongly than the matrix composition. This is borne out by the much greater slope for the small-diameter alginate–clay CRF.

Release of Alachlor into Soils at Different Water Potentials. The changes in weight and diameter of the alginate–clay

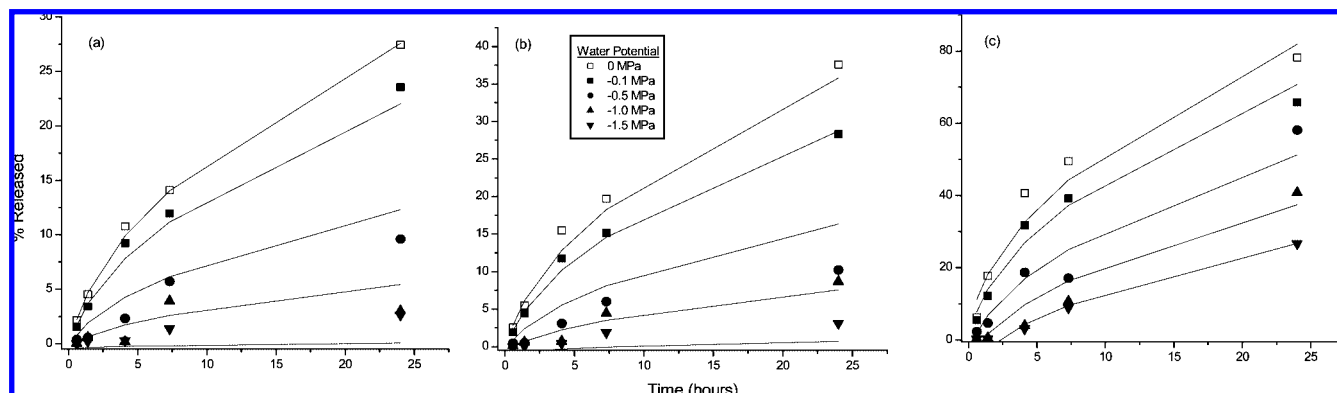


Figure 3. Release of alachlor from the different CRFs into the various PEG solutions: (a) standard alginate–clay; (b) alginate/pectin–clay; (c) small alginate–clay (symbols, experimental data; solid lines, calculated using eqs 4–6).

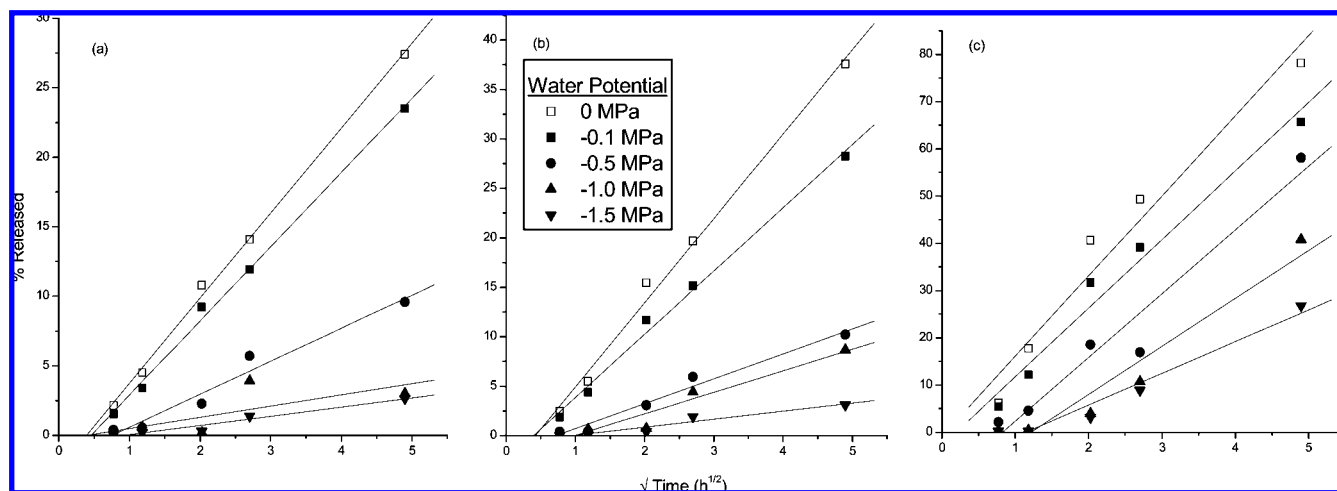


Figure 4. Release of alachlor from the different CRFs into the various PEG solutions as a function of \sqrt{t} . (a) standard alginate–clay; (b) alginate/pectin–clay; (c) small alginate–clay (symbols, experimental data; solid lines, calculated using eqs 4–6).

Table 3. Slopes and Intercepts of the Diffusion-Controlled-Release Equations (from Figure 4)

water potential (MPa)	standard alginate–clay			pectin/alginate–clay			small alginate–clay		
	slope	intercept	r^2	slope	intercept	r^2	slope	intercept	r^2
0	6.12	–2.28	0.99	8.52	–3.58	0.99	16.95	–0.82	0.96
–0.1	5.34	–2.46	0.99	6.39	–2.52	0.99	14.51	–2.75	0.97
–0.5	2.38	–1.81	0.97	2.52	–1.79	0.98	13.49	–11.1	0.95
–1.0	0.809	–0.33	0.54	2.18	–2.14	0.94	10.17	–12.3	0.94
–1.5	0.66	–0.616	0.95	0.806	–0.75	0.93	6.71	–7.66	0.96

CRFs incubated in the Hamra soil at different soil moisture contents are shown in Figure 6 and 7. The change in weight (and in diameter) of the beads in the soil at 26.5% moisture content (–0.18 MPa) was similar to that in PEG solutions of –0.1 to 0 MPa water potential. In both cases the increase in weight is about 0.5 mg/bead. In the soil, however, the bead begins losing weight after about 35 days, whereas in the stirred PEG solutions weight loss was significant already after 70 h. It appears that the weight loss is related to the release of active ingredient from the beads. After 70 h, 30–50% of the alachlor is released into the PEG solutions and thus the release of mass is significant. In soils where the release of the active ingredient is slower, the weight loss due to that release becomes discernible only after ~35 days. The weight loss observed in the two drier soil samples occurs immediately, similar to the results observed for the PEG solutions at –0.5 MPa and lower. The weight loss is about 1–2 mg/bead as compared to 1–1.5 mg/bead in the more concentrated PEG solutions. The effect

of water potential on the bead diameter was also similar in the PEG solutions and in the soil. These observations indicate that the fate of the CRF beads in soils can be estimated from their behavior in PEG solutions, at least as far as the effect of the water potential on that fate is concerned.

The concentration of alachlor in the soil after release from the standard alginate–clay CRF is shown in Figure 8a. The concentration of alachlor in the soil at 26.5% moisture content (–0.18 MPa) peaks after about 10 days and stabilizes at about 2–3 mg/kg. The concentration of active ingredient in the drier soils leveled off at about 1 mg/kg. These concentrations are slightly greater than those observed in a similar soil near field capacity by Gerstl et al. (12) and may be due to the fact that the degradation of alachlor in that latter soil was unusually rapid ($t_{1/2}$ of ~3–4 days, as compared to an expected $t_{1/2}$ in soils of ~8 days; e.g., ref 18). Although we did not measure the rate of degradation of alachlor in the soil sample used in the present study, a slower degradation rate could explain the higher buildup of alachlor in the soil because it was taken from a different field. A look at the cumulative amount of alachlor released from the CRF as measured from the active ingredient remaining in the beads (Figure 8b) shows that after 90 days, close to 80% of the active material was released in the moist soil and only about 40% in the drier soils. It is evident that the effect of soil moisture content on the rate of release of the active ingredient is strong and has to be accounted for in any model on release and transport of pesticides from CRFs.

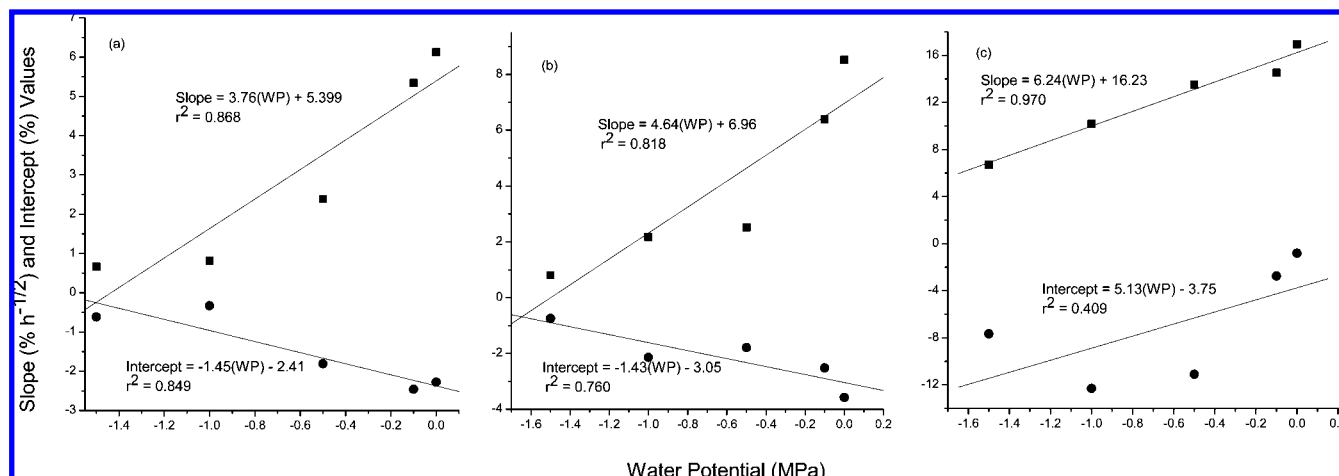


Figure 5. Slopes and intercepts of the diffusion-controlled-release plots (Figure 4) versus water potential: (a) standard alginate-clay; (b) alginate/pectin-clay; (c) small alginate-clay.

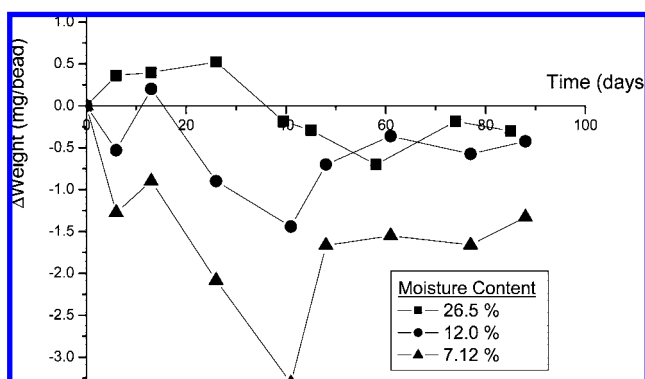


Figure 6. Change with time in the weight of standard alginate-clay beads incubated in a Hamra soil at three moisture contents.

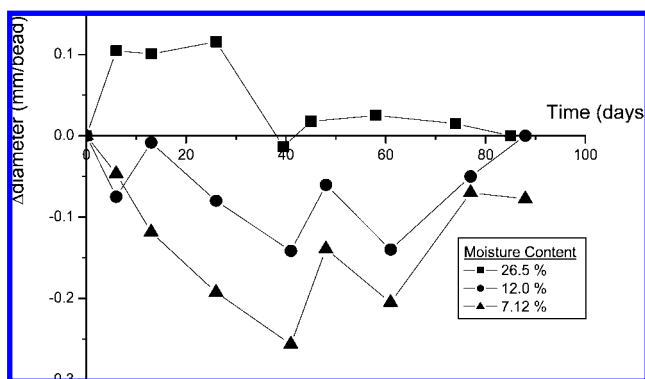


Figure 7. Change with time in the diameter of standard alginate-clay beads incubated in a Hamra soil at three moisture contents.

Conclusions. The observed changes with time in bead diameter and weight as a function of the water potential were similar in PEG solutions and in soils. Thus, moisture-related effects on CRF beads embedded in soils can be deduced from the beads' behavior in PEG solutions. The effect of water potential on the behavior of the beads is considerable. At high water potentials, beads imbibe water and swell, whereas at low potentials beads shrink and lose weight. There is a decrease in the rate of release of the active ingredient as the water potential decreases (drier soils), and at low enough water potentials, a significant lag phase in the release of the active ingredient is observed. The strong effect of the water potential (or soil moisture content) has to be considered in the development of

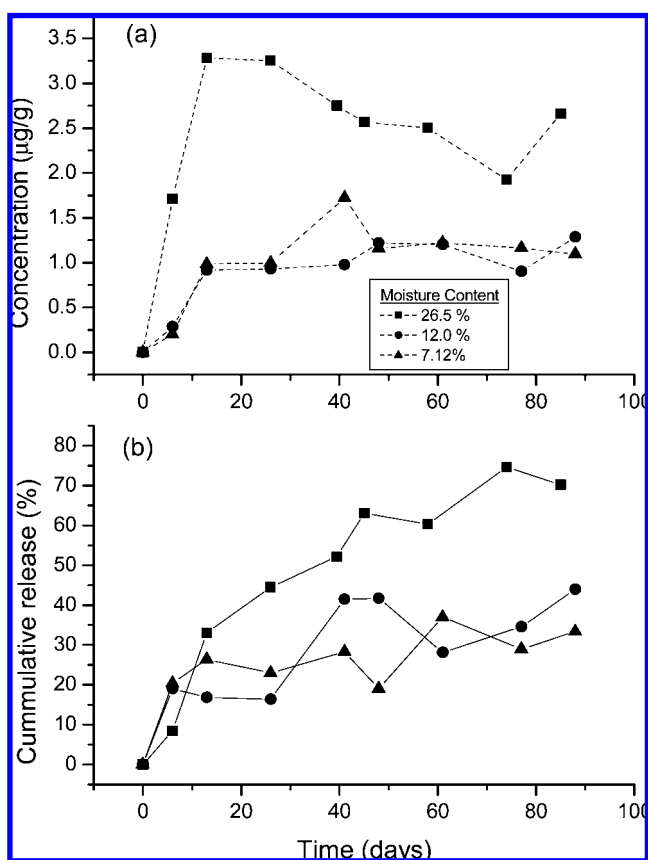


Figure 8. Release of alachlor from standard alginate-clay CRFs incubated in a Hamra soil at three moisture contents: (a) concentration in the soil (mg/kg); (b) cumulative alachlor released (%).

any reliable model on release and transport of pesticides from CRFs into the soil.

The calculations of release of the active ingredient from alginate-based CRFs as a function of water potential that were performed with the aid of the diffusive-release model fit well the experimental data. More studies are needed to better correlate the release of the active ingredient in solutions to that in soil. However, the present study shows that model calculations such as those reported here can be used to approximate the rates of release of active ingredients in systems similar to those studied as well as be incorporated into future transport models for systems that include CRFs or other restricted release sources.

LITERATURE CITED

- (1) Vollner, L. Agrochemical formulations for improved efficacy and reduced environmental impacts: slow release formulations with natural polymers. In *Study and Prediction of Pesticides Behaviour in Soils, Plants and Aquatic Systems*; Mansour, M., Ed.; GSF: Neuherberg, Germany, 1990; pp 136–145.
- (2) Kim, M. S.; Park, G. D.; Jun, S. W.; Lee, S.; Park, J. S.; Hwang, S. J. Controlled release tamsulosin hydrochloride from alginate beads with waxy materials. *J. Pharm. Pharmacol.* **2005**, *57*, 1521–1528.
- (3) Chan, L. W.; Heng, P. W. S. Effects of aldehydes and methods of cross-linking on properties of calcium alginate microspheres prepared by emulsification. *Biomaterials* **2002**, *23*, 1319–1326.
- (4) Wong, T. W.; Chan, L. W.; Kho, S. B.; Heng, P. W. S. Design of controlled-release solid dosage forms of alginate and chitosan using microwave. *J. Controlled Release* **2002**, *84*, 99–114.
- (5) Fernandez-Perez, M.; Flores-Cespedes, F.; Gonzalez-Pradas, E.; Villafranca-Sanchez, M.; Perez-Garcia, S.; Garrido-Herrera, F. J. Use of activated bentonites in controlled-release formulations of atrazine. *J. Agric. Food Chem.* **2004**, *52*, 3888–3893.
- (6) Fernandez-Perez, M.; Villafranca-Sanchez, M.; Flores-Cespedes, F.; Garrido-Herrera, F. J.; Perez-Garcia, S. Use of bentonite and activated carbon in controlled release formulations of carbofuran. *J. Agric. Food Chem.* **2005**, *53*, 6697–6703.
- (7) Kumber, S. G.; Dave, A. M.; Aminabhavi, T. M. Release kinetics and diffusion coefficients of solid and liquid pesticides through interpenetrating polymer network beads of polyacrylamide-g-guar gum with sodium alginate. *J. Appl. Polym. Sci.* **2003**, *90*, 451–457.
- (8) Gonzalez-Pradas, E.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Martinez-Lopez, F.; Flores-Cespedes, F. Use of bentonite and humic acid as modifying agents in alginate-based controlled-release formulations of imidacloprid. *Pestic. Sci.* **1999**, *55*, 546–552.
- (9) Davis, R. F.; Wauchope, R. D.; Johnson, A. W.; Burgoa, B.; Pepperman, A. B. Release of fenamiphos, atrazine, and alachlor into flowing water from granules and spray deposits of conventional and controlled-release formulations. *J. Agric. Food Chem.* **1996**, *44*, 2900–2907.
- (10) Pepperman, A. B.; Kuan, J. C. W. Controlled release formulations of alachlor based on calcium alginate. *J. Controlled Release* **1994**, *34*, 17–23.
- (11) Gerstl, Z.; Nasser, A.; Mingelgrin, U. Controlled release of pesticides into water from clay–polymer formulations. *J. Agric. Food Chem.* **1998**, *46*, 3803–3809.
- (12) Gerstl, Z.; Nasser, A.; Mingelgrin, U. Controlled release of pesticides into soils from clay–polymer formulations. *J. Agric. Food Chem.* **1998**, *46*, 3797–3802.
- (13) Williams, C. F.; Nelson, S. D.; Gish, T. J. Release rate and leaching of starch-encapsulated atrazine in a calcareous soil. *Soil Sci. Soc. Am. J.* **1999**, *63*, 425–432.
- (14) Michel, B. E.; Kaufman, M. R. The osmotic potential of polyethylene glycol 6000. *Plant Physiol.* **1973**, *51*, 914–916.
- (15) Bai, T.-C.; Yan, G.-B.; Hu, J.; Zhang, H.-L.; Huang, C.-G. Solubility of silybin in aqueous poly(ethylene glycol) solution. *Int. J. Pharm.* **2006**, *308*, 100–106.
- (16) Hannoun, B. J. M.; Stephanopoulos, G. Diffusion coefficients of glucose and ethanol in cell-free and cell-occupied calcium alginate membranes. *Biotechnol. Bioeng.* **1986**, *28*, 829–835.
- (17) Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzalez-Pradas, E.; Martinez-Lopez, F.; Flores-Cespedes, F. Controlled release of carbofuran from an alginate-bentonite formulation: water release kinetics and soil mobility. *J. Agric. Food Chem.* **2000**, *48*, 938–943.
- (18) Kidd, H., James, D. R., Eds. *The Agrochemicals Handbook*, 3rd ed.; Royal Society of Chemistry Information Services: Cambridge, U.K., 1991; pp 10–12.
- (19) Russo, D.; Bresler, E. Field determinations of soil hydraulic properties for statistical analyses. *Soil Sci. Soc. Am. J.* **1980**, *44*, 697–702.

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