

Controlled Release of Pesticides into Soils from Clay–Polymer Formulations

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Alachlor was released from a controlled-release formulation (CRF) when applied to a sandy loam soil under conditions of constant temperature and moisture and achieved concentrations of 0.1–0.2 mg/kg after 1 week. Soil concentrations of 0.2–0.8 mg/kg were maintained for at least an additional 8 weeks. A large portion (35–70%) of the active ingredient was still present in the CRFs at the conclusion of the experiment. Application of alachlor as the commercial formulation resulted in 50% dissipation after only 3–4 days. Alachlor released from CRFs with a smaller diameter resulted in higher soil concentrations (1.2 mg/kg) after 18 days. In column leaching studies the leaching of alachlor, atrazine, and trifluralin from CRFs was considerably reduced with respect to leaching of the same compounds from commercial formulations. The release of alachlor from an Al-pillared clay CRF and its subsequent transport in soil columns showed that pillared clays can be used for controlled release of herbicides, but more work is necessary before the effects of the many factors involved in the release of the active ingredients from pillared clays are completely understood.

Keywords: *Controlled release; alachlor; atrazine; trifluralin; herbicides; clay; alginate; pectin; diffusion; degradation; pillared clays*

INTRODUCTION

The danger posed to the environment by current pesticide usage can be reduced by improved pest control practices including reduction in the amount of active ingredient (ai) needed to obtain adequate pest control. To ensure adequate pest control for a sufficient period, pesticides are applied in concentrations greatly exceeding that required for control of the target organism. Much, if not most, of the amount of soil-applied pesticides are wasted due to losses resulting from physical, chemical, and biological processes (Gerstl, 1991; Triegel and Guo, 1994). The excessive quantities added increase the likelihood of runoff or leaching and thus the pollution of surface or ground water (Guyot, 1994). Ground water pollution by pesticides, in particular, the herbicides atrazine and alachlor, is quite common (Isensee and Sadeghi, 1995; Gish et al., 1994; Cohen, 1996; Williams et al., 1995).

The use of controlled-release formulations (CRFs) can, in many cases, supply the ai at the required rate, thus reducing the amount of chemical needed for pest control, on the one hand, and decreasing the risk to the environment, on the other. Controlled release of pesticides and other organic agrochemicals can, in many cases, permit safer, more efficient, and, at the same time, more economical crop protection.

The role CRFs have to play in the scheme of crop protection will be limited to those cases for which other, less expensive alternatives do not work, for example, with compounds that are degraded too rapidly in soils (e.g., alachlor) or with compounds that, while effective, are too readily leached to water sources (e.g., atrazine) or lost by volatilization (e.g., EPTC).

Clay minerals are widely used in pesticide formulations. Clays, especially smectites, are typified by a large surface area, considerable ion exchange capacity, and colloidal properties in suspension that make them very useful in many industrial applications. By a fairly simple procedure, smectites can be modified into pillared clays (PILC). PILCs are smectites in which the exchangeable cations (usually Ca^{2+} or Na^+) between the clay layers are replaced with large polyoxocations of a multivalent metal such as Al, Si, Cr, Zr, or Ti (Lahav et al., 1978; Sterte, 1986; Fetter et al., 1994; Tsou and Pinnavaia, 1988). The product is a zeolite-like structure in which the clay platelets are separated from each other by hydroxy-oxide pillars, exposing the large interlayer surface area. The spacing between the clay platelets is quite large (3 nm), and the pores formed are well-defined and larger than those of most zeolites (0.7–2 nm).

PILCs have a large surface area, large network of micropores ($0.15 \text{ cm}^3/\text{g}$; Stacey, 1988), both Lewis and Brønsted acidity (Poncellet and Schutz, 1986), and thermal stability (Ocelli and Laster, 1985). As a result, these clays have found use as molecular sieves and catalysts (Lussier et al., 1980; Ming-Yuan et al., 1988; Montarges et al., 1995). Montarges et al. (1995) added a large organic molecule to PILCs and was able to use them for removing chlorinated phenols from solution. Tsvetkov and Mingelgrin (1990) used PILCs as a solid phase in HPLC separations of a wide variety of compounds. Nakai et al. (1986) investigated the interaction of drugs and PILCs, but to the best of our knowledge no one has yet taken advantage of the unique properties of PILCs for controlled release of chemicals.

Our objective was to study the release of agrochemicals from clay and clay-polymer-based CRFs. To determine the ability of these CRFs to release active ingredients at desired rates, while reducing potential

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Table 1. Selected Properties of the Pesticides Studied

compound	log K_{ow}^a	solubility ^b (mg/L)	vapor pressure ^b (mPa)
alachlor	2.77	240	1.9
atrazine	2.47	33	0.04
trifluralin	4.55	0.3	14.7

^a Gerstl (1990). ^b Hornsby et al. (1996).

environmental pollution, we set as specific objectives the determination of the rate of release of ai into soil and the comparison of the movement of the ai in soils when released from CRFs and from conventional formulations.

MATERIALS

The two polymers studied were alginate and pectin. The alginate used was purchased from Fluka (Buchs, Switzerland; sodium alginate for immobilization of microorganisms, No. 71238). The pectin (Unipectine rouge, 3 g), derived from fruit, was obtained from Sanofi Bio-Industries, France, and had a degree of esterification of 18–30%.

The clay used was a sodium montmorillonite (Fisher Scientific, Fair Lawn, NJ) as previous studies showed that other clays had little or no effect on release (Gerstl et al., 1998).

The following pesticides were studied: alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide]; atrazine [6-chloro-*N*-ethyl-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine]; and trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine]. Technical grade and formulated products (alachlor, Alanex 48EC, 480 g/L; atrazine, Atranex 50WP, 500 g/kg; trifluralin, Triflurex 48EC, 480 g/L) were provided by Agan Chemicals, Ashdod, Israel. Selected physicochemical properties of the pesticides are presented in Table 1. All reagents were of analytical grade and purchased from Merck (Darmstadt, Germany).

The soil used for all column and batch studies was the surface horizon (0–20 cm) of a Hamra soil from Bet Dagan. The soil is classified as a loamy sand, Typic Rhodoxeralf, and contains 10% clay and 0.3% organic carbon. The soil was air-dried and ground to pass an 0.8 mm sieve. Field capacity of the soil was determined by placing 10 g of soil on a metal framework lined with filter paper and which was supported several centimeters above the bottom of a flat dish. Water was slowly applied dropwise until the first drop was seen to form under the filter paper. A soil sample was then taken for moisture content determination by drying at 110 °C. The soil was also checked for residues of herbicides by extraction with water and ethyl acetate (1:1) and GC analysis. No residues were found in the soil.

EXPERIMENTAL PROCEDURES

Preparation of Polymer-Based Beads. Preparation of the polymer-based CRFs took advantage of their propensity to undergo gelation in the presence of multivalent cations. A mixture of polymer, clay, and ai was prepared in the ratio of 3:4:2 by weight. Water was added to bring the final polymer concentration to 3%. The suspension was mixed until uniform and stable. The suspension was slowly added to a 0.5 M CaCl₂ solution by dripping through 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, then separated from the solution in a Büchner funnel, rinsed twice with distilled water, and air-dried in a fume hood overnight.

The loading of the ai was determined by destroying the bead structure by shaking several beads overnight with 0.1 M sodium citrate. The resulting suspension was then extracted with a 1:1 mixture of hexane and ethyl acetate, and the pesticide concentration was determined by GC–NPD.

Preparation of PILC. The preparation of PILCs was carried out according to the following procedure:

(a) *Preparation of Sodium Montmorillonite.* The clay was dispersed in distilled water and allowed to settle. The time for particles with an equivalent radius of $>2 \mu\text{m}$ to settle below a given depth was calculated from Stoke's law, and the suspension above this level was collected, washed five times with 1 N NaCl, and then washed with distilled water until free of chlorides as determined by testing with AgNO₃.

(b) *Preparation of the Pillaring Agent Al(OH)_x.* A stirred solution of 0.2 M AlCl₃ was titrated with 0.2 M NaOH until a molar [OH/Al] ratio of 1.85 was obtained. This solution was kept at room temperature for a minimum of 6 days to allow the polymeric Al(OH)_x to stabilize.

(c) *Preparation of the Al–PILC.* A 200 mg/L suspension of sodium montmorillonite was prepared. To each 500 mL of suspension was added 2.8 mL of the Al(OH)_x solution while undergoing strong mixing. The mixture was left for 2 h to allow floc formation and settling, after which time the supernatant solution was removed. The flocs were then freeze-dried and stored until use.

Preparation of alachlor containing Al–PILC was accomplished as described above with alachlor, at a rate of 200 mg/L, being added to the suspension of sodium montmorillonite prior to addition of the pillaring agent. The alachlor loading of the Al–PILC/alachlor complex was determined by extraction with a 1:1 ratio of water and ethyl acetate and analysis of the organic phase by GC.

Release and Degradation of the ai in the Soil. The release of the ai into the soil from the CRFs, and its subsequent degradation, was determined and compared to that of a commercial formulation. Two hundred gram samples of soil were brought to field capacity and placed into 250 mL beakers. After addition of half the amount of soil to each beaker, three to four preweighed beads were placed onto the soil. The remainder of the soil was then added and the beaker tapped a number of times to pack the soil around the beads. The beakers were then covered with Parafilm in which four small holes were made to ensure adequate air exchange, weighed, and stored at 25 °C in an incubator. Subsequently, the beakers were weighed twice a week and water added as necessary to replace water lost by evaporation. The commercial formulation was mixed with the entire 200 g soil sample and served as a control.

The soil from the various beakers was sampled periodically. The control beakers were sampled and reweighed, whereas the sampling for the CRF-containing beakers was destructive. The soil from these beakers was carefully removed to expose the beads, which were separated from the surrounding soil. The soil was then thoroughly mixed and analyzed. The soil was extracted with water/ethyl acetate at a 1:1 ratio. The extraction of the ai from the beads was as described above. Extraction efficiency of the pesticides from the soil exceeded 95%.

Transport of the ai in Soil Columns. The soil was packed into Plexiglas columns (54 mm i.d. and 50 cm length) to a bulk density of 1.3 g/cm³. The soil was packed by inserting a funnel to which a wide bore tube reaching the bottom of the column was attached. Soil was placed into the funnel until both the tube and funnel were full. The tube was then slowly extracted from the column while the column was tapped to ensure uniform and compact packing. The column was filled to a height of 35 cm, upon which a second 5 cm layer of treated soil was placed. The treated soil contained either the conventional formulation or the polymer–clay-based CRFs uniformly mixed into the soil. In the case of the PILC CRF the column was filled to a height of 39 cm and the PILC CRF was added and mixed uniformly in 1 cm of soil. The columns were then irrigated with tap water to field capacity. Once a week for 5 weeks, the columns were weighed and water was added according to loss due to evaporation. Upon completion of the experiment, the soil was extruded from the columns by applying air pressure from the top of the column and the extruded soil was divided into 2 cm sections for extraction and analysis of the active ingredient. The CRF beads were removed from the top soil layer prior to extraction. The soil moisture content was also determined.

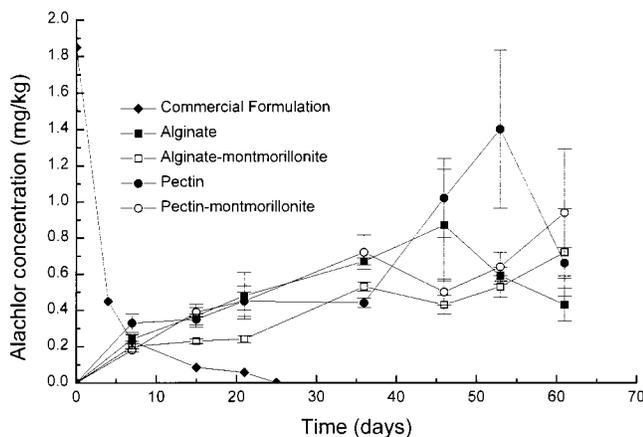


Figure 1. Release of alachlor from polymer-based CRFs into a Hamra soil.

Chromatographic Analysis. Analysis of the various pesticides was carried out on a Varian 3300 GC equipped with an NP detector. A DB-5 megabore column (0.53 mm i.d. \times 30 m) was used with nitrogen as the carrier at a flow rate of 10 mL/min. The detection limit for the herbicides was generally better than 0.05 $\mu\text{g/mL}$, which is equivalent to 0.05 mg/kg.

RESULTS AND DISCUSSION

Alachlor Release in Soil. Alachlor concentrations in soil after application of polymer-based CRFs or the commercial formulation are presented in Figure 1.

Alachlor degradation is basically microbial (Novick and Alexander, 1985; Sun et al., 1990), and reported half-lives in soil, which vary with temperature and moisture content, range between 2 and 41 days (Walker and Brown, 1985; Beestman and Deming, 1974). Soil concentrations of alachlor of ~ 0.5 – 1.5 mg/kg for up to 60 days are required for adequate weed control depending on the soil and weed being controlled (B. Rubin, personal communication). With a half-life of ~ 4 days when applied as the commercial formulation (Figure 1), application rate and/or application frequency would have to be high to achieve adequate weed control. After 2 weeks, only $\sim 5\%$ of the initial quantity of herbicide applied remains in the soil.

With the CRFs we find that after an initial period of about a week, bioeffective concentrations of the herbicide are found in the soil and by 5 weeks the concentration appears to be stabilizing at ~ 0.6 mg/kg, which should be adequate for weed control (B. Rubin, personal communication). The alginate CRF containing montmorillonite exhibits slightly slower release rates than the other CRFs, which is in accord with findings of the previously reported release studies (Gerstl et al., 1998).

Soil concentrations of alachlor applied in pectin-based CRFs are similar to those from the alginate-based formulations following the same general pattern exhibited by the alginate-based beads, a short period of time in which soil concentrations increase after which the soil concentrations remain relatively stable with time. After 5 weeks, a sharp increase in concentration of alachlor in the soil occurs, followed by a sharp decrease. Toward the end of the experiment it was no longer possible to find the pectin-based beads in the soil. We postulate that during the several weeks of incubation in the soil, the pectin beads slowly disintegrated, most probably due to microbial attack. This disintegration increased the rate of release of alachlor in the soil. After 50 days, the alachlor was no longer protected within the

Table 2. Mass Balance of Alachlor for the Alginate–Clay and Pectin–Clay CRFs

treatment	incubn time (days)	initial alachlor content (μg)	alachlor remaining in CRF (%)	alachlor in soil (%)	alachlor degraded (%)
commerc formln	20	3640		3.1	96.9
	60	3640		0.0	100
alginate–clay	20	1544	94	3.1	2.9
	60	1561	57	9.2	33.8
pectin–clay	20	1667	77	5.4	17.6
	60	1680	49.3	11.2	39.5

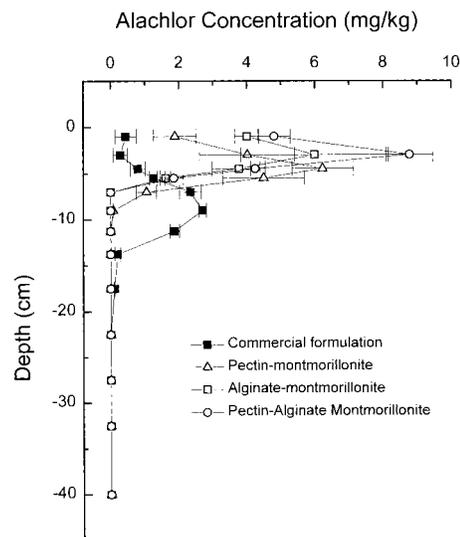


Figure 2. Distribution of alachlor in a Hamra soil 35 days after application as a commercial formulation or in polymer–clay-based CRFs (initial application depth of 0–5 cm).

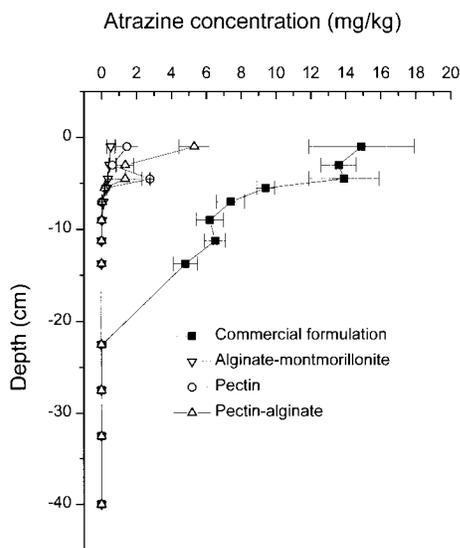
beads from microbial decomposition and was therefore rapidly decomposed, as in the case of the commercial formulation. The presence of montmorillonite in the CRF may stabilize the polymer or protect it from microbial attack by complexation. As long as the alachlor is retained in a stable polymeric structure, it will be protected from microbial attack. A similar, but less sharp, increase in release of alachlor from the alginate-based beads was observed after 45 days, which may indicate structural disintegration; however, these beads could still be found intact after 60 days.

A mass balance for two of the CRFs at two different sampling dates is presented in Table 2. The mass balance clearly shows the effectiveness of the polymer–clay CRFs in protecting the alachlor from microbial degradation.

Release of Herbicides from CRFs and Their Leaching. Alachlor distribution in the columns of sandy loam soil 35 days after application and intermittent irrigation is presented in Figure 2. Alachlor, when uniformly applied as the commercial formulation in the upper 5 cm of the soil column, displays considerable leaching. The maximum concentration, ~ 3 mg/kg, is at 9 cm depth, and significant amounts were found as deep as 15 cm. On the other hand, alachlor application in all of the CRFs resulted in considerably less leaching and at the same time provides relatively high concentrations in the application zone. The leaching of alachlor from the pectin–montmorillonite beads is slightly greater than from the other CRFs, probably due to the aforementioned degradation of the pectin in the CRF, but still much less than from the commercial formulation. A mass balance analysis of the alachlor in the columns

Table 3. Mass Balance of Alachlor in Columns after 35 Days

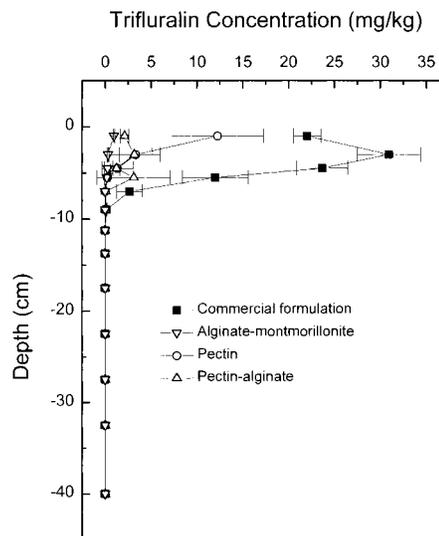
preparation	alachlor applied (mg)	alachlor in soil (%)	alachlor in bead (%)	alachlor degraded (%)
commercial formln	0.48	12.0		88.0
alginate-montmorillonite	0.47	17.5	30.5	52.0
pectin-montmorillonite	0.40	25.0	15.3	59.7
alginate-pectin montmorillonite	0.31	24.2	11.6	64.2

**Figure 3.** Distribution of atrazine in a Hamra soil 35 days after application as a commercial formulation or in polymer-clay-based CRFs (initial application depth of 0–5 cm).

(Table 3) shows that in the columns to which alachlor was added in CRFs, large reserves remain available in the bead. Similar results for the release of alachlor and atrazine from alginate-based CRFs with kaolinite or linseed oil have recently been reported by Johnson and Pepperman (1995, 1996).

The distribution of atrazine in the soil columns is presented in Figure 3. Application of the commercial formulation results in high concentrations of the herbicide in the application zone but also quite significant leaching to depths of >20 cm. The release of atrazine from the alginate-montmorillonite formulation is extremely low, resulting in only negligible amounts of the herbicide in the soil. The use of pectin-containing beads increases the release of the ai, giving higher and hence more effective concentrations of atrazine in the soil. With all CRFs leaching of atrazine below the application layer was successfully prevented.

Trifluralin solubility is considerably lower than that of atrazine, so leaching is generally not considered to be a problem. However, due to the high vapor pressure of trifluralin, losses via volatilization can be significant, especially in no-till systems where the material is not incorporated into the soil. The results of trifluralin release and leaching (Figure 4) show that with the commercial formulation the soil surface layer does show signs of trifluralin loss but considerable amounts of ai are still present in the soil. Such high amounts are necessary under field conditions to prevent volatilization losses, because environmental conditions in the field, for example, wind, result, in much greater losses from volatilization than expected in the laboratory. The relative release of trifluralin from the different CRFs is similar to that of atrazine: little to no release from

**Figure 4.** Distribution of trifluralin in a Hamra soil 35 days after application as a commercial formulation or in polymer-clay-based CRFs (initial application depth of 0–5 cm).

the alginate-montmorillonite CRF and greater release from pectin-based preparations. Burton et al. (1983) reported that the concentration of trifluralin in the soil required for control of 13 different weeds is between 0.3 and 6.4 $\mu\text{g/g}$. In a recent study (Z. Gerstl, unpublished results) it was found that concentrations as low as several nanograms per gram of trifluralin were enough to affect corn growing in a sand culture. Thus, it seems that the concentrations found in the soil loaded with trifluralin-containing CRFs should be adequate for weed control.

PILCs and Controlled Release from Pillared Clays. Release of Alachlor from PILC-CRFs in Soil Columns. The release and transport of alachlor applied in PILC were compared to those of the commercial and the alginate-montmorillonite formulations. The application layer for the PILC-CRF was only 1 cm, not 5 cm as described for the polymer-based beads. The leaching results (Figure 5) show that alachlor release from the PILC-CRF differs from the polymer-clay CRF in that leaching was slightly greater, although still considerably less than when applied as the commercial formulation. The concentration observed in the treated layer is extremely high because it was not possible to distinguish between the ai left in the PILC and that released into the soil. However, the break at ~15 mg/kg at a depth of 2 cm could indicate that the material in the surface layer was associated with the PILC, whereas that below this depth was material released into the soil.

In a study of the sorption of alachlor by sodium montmorillonite and by Al-PILC (Nasser et al., 1997), XRD results indicated that the sorbed molecules are located in the interlayer spaces of the sodium clay and of the Al-PILC. On the basis of the sorption studies and the column leaching results, we may conclude that despite the extremely small particle size of the PILC-CRF it exhibits controlled-release behavior. In previous work on the release of parathion from a series of clay minerals (Gerstl and Yaron, 1981) no slow or controlled-release properties could be attributed to the clays. More work is necessary, however, before the effect of the many factors involved in the release of active ingredients from PILCs is completely understood.

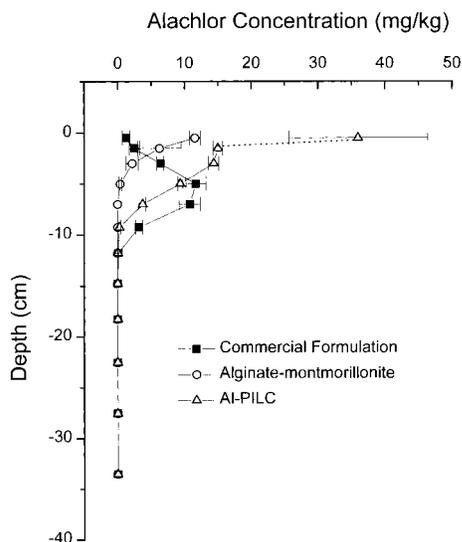


Figure 5. Distribution of alachlor in a Hamra soil 35 days after application as a commercial formulation, in a polymer-clay CRF, and as a PILC-CRF (initial application depths of 0–5 cm for the commercial and polymer-clay formulations and 0–1 cm for the PILC-CRF).

Summary. The use of clay and clay-polymer combinations for the preparation of controlled-release formulations was studied. In a series of laboratory experiments the release of the active ingredients into soil from the different preparations was determined.

The use of pillared clays for CRFs was also studied. The release of alachlor from Al-PILC in soil column studies showed that these clays can be used for controlled release of herbicides, but much more work is necessary before the effect of the many factors involved in the release of the ai from PILCs is completely understood.

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