

Environmentally Friendly Formulations of Alachlor and Atrazine: Preparation, Characterization, and Reduced Leaching

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Atrazine and alachlor formulations were designed by encapsulating the herbicide molecules into phosphatidylcholine (PC) vesicles, which subsequently were adsorbed on montmorillonite. PC and montmorillonite are classified as substances of minimal toxicological risk by the U.S. EPA. PC enhanced alachlor and atrazine solubilities by 15- and 18-fold, respectively. A 6 mM PC:5 g/L clay ratio was found as optimal for PC adsorption on the clay. Active ingredient contents of the PC–clay formulations ranged up to 8.6% for atrazine and 39.5% for alachlor. Infrared spectroscopy showed hydrophobic interactions of herbicide molecules with the alkyl chains of PC, in addition to hydrophilic interactions with the PC headgroup. Release experiments in a sandy soil showed a slower rate from the PC–clay formulations than the commercial ones. Soil column experiments under moderate irrigation and bioactivity experiments indicate that a reduction in the recommended dose of alachlor and atrazine can be accomplished by using PC–clay formulations.

KEYWORDS: Herbicides; liposomes; slow release formulations; bioactivity; leaching

INTRODUCTION

The use of pesticides is essential for needed food production all over the world. On reaching the soil, pesticides may go through dissipation pathways, such as microbial or chemical degradation, photodecomposition, volatilization, and colloidal soil sorption. Furthermore, losses can occur by surface runoff and leaching through the soil profile. This implies a reduction in the efficiency of conventional formulations that have been applied at larger rates to compensate for these losses, with subsequent environmental and economic costs (1, 2).

Because lower amounts or less frequent applications are required for biological effects (3–5), the design of controlled release formulations of pesticides is aimed at maintaining for longer periods the threshold concentration of the active compound (denoted active ingredient or a.i.) for pest control in soil by its release at the required rate and reducing its level in the environment. The use of dissolved or suspended polymers or surfactants or polymer–pesticide complexes can reduce volatilization, leaching, and wind drift (6, 7).

Clay minerals have been used in attempts to improve controlled release formulations. The release of pesticide from alginate beads is dependent on the solubility of the entrapped

pesticide; besides, the release profile is modified by the addition of clay minerals as fillers in the gelling process (8). Alginate formulations containing natural and acid-treated bentonite have been frequently reported (9–11). Numerous studies have been focused on the use of modified montmorillonite by preadsorbing organic cations as a support system for slow release.

Organoclay complexes of metolachlor and metribuzin prepared using hexadecyltrimethylammonium reduced their downward mobility in soil (12). Benzyltrimethylammonium (BTMA)-based formulations of alachlor and metolachlor reduced leaching in soil columns and showed herbicidal activity in the top 10 cm, whereas the commercial formulations were mostly bioactive at depths of 20–30 cm (13, 14). These formulations can be optimized by the choice of a suitable organic cation (15). Phenyltrimethylammonium (PTMA)–montmorillonites gave better reduction in the leached fraction of alachlor and metolachlor than BTMA–clays (16). Thioflavin-T was a better choice for norflurazon formulations (17).

A recent approach based on clay minerals has been developed by encapsulation of the pesticide molecules in micelles or vesicles formed by cationic surfactants in solution and their further adsorption on the clay mineral (18, 19). This method allows one to shorten the preparation time to less than 2 h (20) and may apply for slow release formulations of hydrophobic pesticides by avoiding the use of organic solvents or other chemicals that have been frequently added to enhance the solubility of the pesticide when using organoclays (21).

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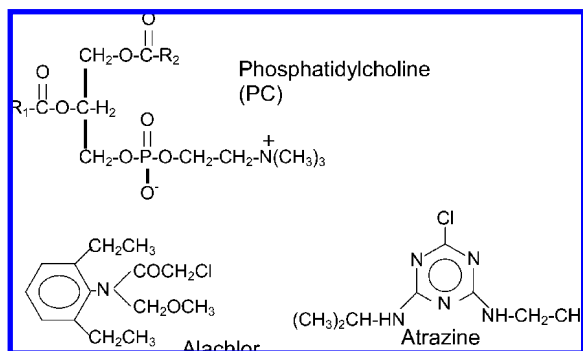


Figure 1. Structural formulas of the herbicides and PC.

However, the employed organic cations as well as those mostly used in the synthesis of organo-montmorillonite formulations are not considered to be of minimal toxicological risk. Despite the environmental and economical advantage of slow release formulations, the rate of their acceptance by farmers has been slow, due mainly to the slow process of their registration. Recent research has focused on the replacement of certain organic cations by other ones more environmentally friendly, preferably EPA approved (22, 23). In the current work, we demonstrate the potential use of the neutral nontoxic lipid phosphatidylcholine (PC) for the development of environmentally friendly formulations of the herbicides alachlor and atrazine, which have been frequently detected in surface waters and groundwater (24). The molecules of these hydrophobic herbicides are incorporated within PC liposomes formed in solution, which subsequently were adsorbed on montmorillonite.

In a first report on this system (25), we studied the optimization of PC adsorption on montmorillonite for its application to slow release formulations of herbicides. In that study, we combined the adsorption of PC by the clay with X-ray diffraction and fluorescence studies, which elucidated the kinetics of structural changes of PC liposomes interacting with the clay.

In the current study, we have prepared herbicide formulations of alachlor and atrazine by optimizing the a.i. content, followed by Fourier transform infrared (FTIR) studies for characterizing the system clay-(PC) liposome-herbicide. We will show tests of these formulations for slow release first in funnel experiments and then in soil columns. Our main focus in the current study is on the combination of leaching and bioactivity in soil column experiments.

MATERIALS AND METHODS

Materials. The clay used was Wyoming Na-montmorillonite (SWy-2) obtained from the Source Clays Repository of The Clay Minerals Society (Columbia, MO) (cation exchange capacity of 0.8 mmol/g). PC (SPC-3) (74% distearoyl-PC and 26% 1-palmitoyl-2-stearoyl-PC) was kindly supplied by Lipoid GmbH (Ludwigshafen, Germany). High-performance liquid chromatography (HPLC) methanol was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO); HPLC acetonitrile from Teknokroma S.A. (Barcelona, Spain). The analytical herbicides alachlor and atrazine were purchased from Sigma-Aldrich Co. Commercial formulations of alachlor (Alanex, 480 g/L a.i.) and atrazine (Herbimur Atrazina, 475 g/L a.i.) were kindly provided by Makhteshim Agan Industries Ltd. (Tel-Aviv, Israel) and Agroservicios López Pastor S.A. (Seville, Spain), respectively. The structural formulas of the herbicides and the lipid are shown in **Figure 1**.

The upper 20 cm of a sandy soil from Coria (Seville, Spain) was sieved at 2 mm before use. This soil contains 86 g kg⁻¹ of CaCO₃ and 7 g kg⁻¹ of organic matter, and its pH is 7.8. The particle size distribution is 26 g kg⁻¹ clay, 20 g kg⁻¹ silt, and 954 g kg⁻¹ sand.

Preparation of PC Vesicles. The PC used was a mixture of 74% distearoyl-PC and 26% 1-palmitoyl-2-stearoyl-PC. PC (6 mM) was

Table 1. Clay-Vesicle Formulations^a

clay added (g/L)	herbicide added (mM)	notation of formulation	a.i. (w/w %)
		alachlor	
5	1.5	A5/1.5	3.4
5	8	A5/8	15.0
5	14	A5/14	24.0
1.6	14	A1.6/14	39.5
		atrazine	
5	1.8	AT5/1.8	3.0
5	2.4	AT5/2.4	4.6
1.6	2.4	AT1.6/2.4	8.6

^a The PC initial concentration was always 6 mM.

dissolved in methanol. The solvent was removed under a gentle stream of nitrogen gas, and the lipid film was first dried under high vacuum for 1 h and then hydrated under agitation for another hour. The hydration of the lipid film produced multilamellar liposomes that were converted into unilamellar and sized down by 13 times of sequential extrusion through polycarbonate filters with a 0.1 μm pore size (Avanti Mini-extruder; Avanti Polar Lipids, Inc., Alabaster, United States). The lipid hydration and sizing procedures were performed at 65 °C, which is above the gel-to-liquid crystalline phase transition temperature (*T_m*) of the lipid with the higher *T_m* in the mixture (59.5 °C).

Adsorption of PC Vesicles on Montmorillonite. The adsorption of liposomes on the clay was carried out in duplicate in polypropylene tubes by mixing 10 mL of a 6 mM lipid solution with montmorillonite under continuous stirring. The final clay concentrations in the tubes were 1.6 and 5 g/L. After they were shaken for 1 and 3 days at 20 °C, the tubes were centrifuged at 12100g for 20 min, and the PC concentration in the supernatants was determined by HPLC using a postcolumn fluorescence system as in Postle (26). No statistical difference was noticed in the amounts adsorbed after 1 or 3 days of incubation.

Preparation of Herbicide-PC-Clay Formulations. PC formulations of the herbicides were prepared by dissolving several amounts of the herbicide in a 6 mM PC solution by sonication and further addition to montmorillonite. The added concentrations of herbicides were 1.5, 8.0, and 14.0 mM for alachlor and 1.8 and 2.4 mM for atrazine. The clay concentrations were 1.6 and 5 g/L. After they were shaken for 24 h, the suspensions were centrifuged at 12100g for 20 min, the supernatants were analyzed for the remaining herbicide, and the pellets were dry-frozen. A nomenclature for PC-clay formulations was introduced (see **Table 1**) where the first letters indicate the herbicide (A, alachlor; AT, atrazine), the first number denotes the clay concentration, and the second one gives the initial herbicide concentration.

Herbicide Analysis. Herbicides were analyzed by HPLC (Shimadzu model 10A) equipped with a photodiode array detector. The reverse phase column was a 15 cm Kromasil 100 C18. The flow rate was 1.0 mL min⁻¹. The mobile phases were 60% acetonitrile and 40% water for alachlor and 50% methanol and 50% water for atrazine. The wavelengths were set at 220 nm for alachlor and 230 nm for atrazine. The retention times were 6.26 and 5.13 min for alachlor and atrazine, respectively.

FTIR Spectroscopy. FTIR spectra of the herbicides, PC-clay complex, and herbicide formulations were recorded in KBr pellets (2 wt % sample) using a Nicolet spectrometer (510P), in the range of 4000 to 400 cm⁻¹. The resolution was 2 cm⁻¹. Three hundred scans were accumulated for improving the signal-to-noise ratio in the spectra.

Release of Herbicides. The release of herbicides from PC formulations as well as those from the commercial products was conducted in triplicate by using Büchner funnels. In this procedure, 98.9 g of a sandy soil was added to each Büchner funnel (9.5 cm internal diameter) that had a paper filter on the bottom. The soil layer was homogenized to a 0.5 cm height. The soil surface was uniformly sprayed with the different herbicide formulations. The applied amount of a.i. was 1 kg ha⁻¹. The soil layer in each funnel was irrigated 43 times with 15 mL

of distilled water, each washing corresponding to 2.12 mm of rain at 20 min intervals or a total equivalent to 91 mm of rain. The volume eluted after each irrigation was collected and analyzed for the herbicide.

Soil Columns Experiments. Metacrylate tubes of 3.0 cm diameter were cut into 4 and 8 cm sections, and three units of 4 cm were glued together with a 8 cm unit at one end to construct a 20 cm column. The column was covered at the end opposite to the 8 cm unit with 1 mm nylon screen padded with a thin layer of glass wool (0.5 g) to hold the soil firmly in the column. Sand soil (0.164 kg) was packed from the top of the column (8 cm section), creating a 16 cm soil column that could be readily separated into 4 cm segments. The pore volume was determined to be 46 mL.

Three milliliters of suspensions of the commercial and PC–clay formulations of atrazine and alachlor were sprayed at the soil surface at a rate of 3 kg a.i. ha⁻¹. Soil column experiments were performed in triplicate. Distilled water equivalent to 70 mm of rain (50 mL) was added at the top of the column in two portions, and the soil was allowed to equilibrate for 24 h between additions and after the final addition. The leachates were collected and analyzed for the herbicide. A parallel experiment for alachlor formulations was also performed by adding water equivalent to 140 mm of rain.

Each soil column was separated into six 4 cm segments. Two grams of soil in duplicate was dried at 100 °C for 24 h to determine the humidity of each soil segment. The amount of herbicide remaining in each segment was extracted in triplicate by shaking 5 g of soil with 15 mL of methanol for 24 h. The suspensions were centrifuged, and the herbicide was analyzed by HPLC.

A bioassay was used to calculate the residual activity of the herbicides throughout the first two upper rings of the soil column. Six beakers containing 15 g of soil of each segment for each formulation were planted with seven seeds of *Setaria viridis* and were irrigated daily for 2 weeks. The bioactivity of the formulations was determined by measuring the reduction in fresh weight per shoot of *S. viridis* with respect to a control.

RESULTS AND DISCUSSION

Preparation of Herbicide Formulations. The preparation of herbicide formulations required the optimization of two processes: (i) PC adsorption on the clay and (ii) solubility enhancement of the herbicide molecules by the PC vesicles to achieve a high a.i. content in the formulations.

An optimal vesicle–clay formulation of herbicides in which a large fraction of the herbicide is adsorbed by the vesicle–clay complex can be obtained for particular vesicle–clay ratios, for which most of the vesicles are adsorbed without undergoing premature decomposition (20). As a first choice, a 6 mM PC/5 g/L clay ratio was tentatively tested for PC adsorption because this was the maximized ratio for the adsorption of cationic herbicides (18). PC adsorption was 95%; this ratio was considered sufficient for an optimal concentration of PC in the clay complex, giving rise also to a solubility enhancement of the herbicides.

After optimizing the PC/clay ratio, a study was performed to determine the maximal solubility enhancement of alachlor and atrazine for a 6 mM PC solution. Water solubilities of alachlor and atrazine at 25 °C were 242 (0.90 mM) and 33 (0.15 mM) mg/L, respectively. Stable suspensions of PC enabled 15- and 18-fold solubility enhancement of alachlor and atrazine up to 14 and 2.4 mM, respectively.

Table 1 shows clay–PC-based formulations of alachlor and atrazine prepared by first dissolving several amounts of the herbicides into a 6 mM solution of PC vesicles followed by their adsorption on montmorillonite at 5 g/L. The a.i. content ranged from 3.4 to 24% for alachlor and from 3 to 4.6% for atrazine. A 1.6 g/L clay concentration was also used to increase

the a.i. contents, since the adsorption of the vesicles was still high, that is, 85% of the total PC added. At this clay concentration, the a.i. content was increased to 39.5% for alachlor, which is quite close to that of the commercial formulation (48%), and to 8.6% for atrazine.

FTIR Results. FTIR measurements can provide information about the molecular interactions occurring in the PC–clay–herbicide systems. The spectra of clay, PC, PC–clay complex, alachlor, atrazine, and the PC–clay-based formulations A5/14 and AT5/1.8 are shown in **Figure 2**.

For the clay–lipid complex, three distinct regions can be assigned in the infrared spectrum according to the potential modes of interaction of PC with the clay: (i) the hydrophobic chain region, which involves the C–H stretching modes and CH₂ scissoring; (ii) the interfacial region consisting of C=O stretching; and (iii) the polar headgroup region comprising of PO₂⁻ and ⁺N(CH₃)₃ asymmetric stretching bands, respectively (27). The asymmetric stretching vibration of PO₂⁻ is observed at 1245 cm⁻¹. The location of this peak reflects hydration, which lowers the wavenumber from 1260 cm⁻¹ in pure, dry PC (28). The PC spectrum also shows this absorption band at the same frequency, indicating that the PC molecules employed in the current study were also hydrated. Grdahnik and Hadži (29) reported this band at 1243 cm⁻¹ upon hydration of pure dipalmitoyl-PC with about six water molecules per one lipid. Water intercalation will weaken the interaction between the phosphate and the ammonium groups of the polar headgroup by increasing the distance between these two groups that are in close contact in the dry PCs, thus facilitating a close interaction between the positively charged choline group and the clay surface.

Previous studies showed PC adsorbing on layer silicates by developing extended bilayers with a water layer intercalated between the clay surface and the interacting moiety of the lipid headgroup (30, 31). As a result, the water solvating the choline group increases its polarity through H-bonding with the hydrophilic clay surface, and the OH stretching vibration of water is shifted to a higher frequency (3437 cm⁻¹) from the absorption at 3421 cm⁻¹ in pure PC. Direct visualization of the interaction of the choline group with the clay surface through water molecules could not be followed in this study by the shift of the ⁺N(CH₃)₃ asymmetric stretching absorption band at 968 cm⁻¹, which is very sensitive to dipolar interactions, because of its overlapping with that of the Si–O stretching mode of the clay at 1043 cm⁻¹.

The absorption band at 1737 cm⁻¹ is due to the stretching of nonhydrogen-bonded C=O groups of the glycerol moiety (28). The bands assigned to the hydrophobic chain are located at 2850 and 2920 cm⁻¹ for the symmetric and asymmetric methylene stretching, respectively, and at 1473 cm⁻¹ for the methylene scissoring. The position of the band at 2850 cm⁻¹, which is very sensitive to conformational changes, indicates that the fatty acyl chains are tightly packed in all-trans conformation since an increase in the number of gauche conformers would have shifted this band to higher frequencies (32).

Alachlor interaction within the PC–clay complex gave new absorption bands at 1679 and 1377 cm⁻¹ assigned to the stretching vibration of the C=O group and the anilidic group vibration, respectively. These peaks are shifted from 1688 and 1372 cm⁻¹ in the spectrum of free alachlor, which indicates formation of H-bonds between the C=O and the hydration water of the PC headgroup. As a result of the new interaction, the double-bond nature of C=O is reduced, lowering the frequency for its resonance, and this results in an increased double bond

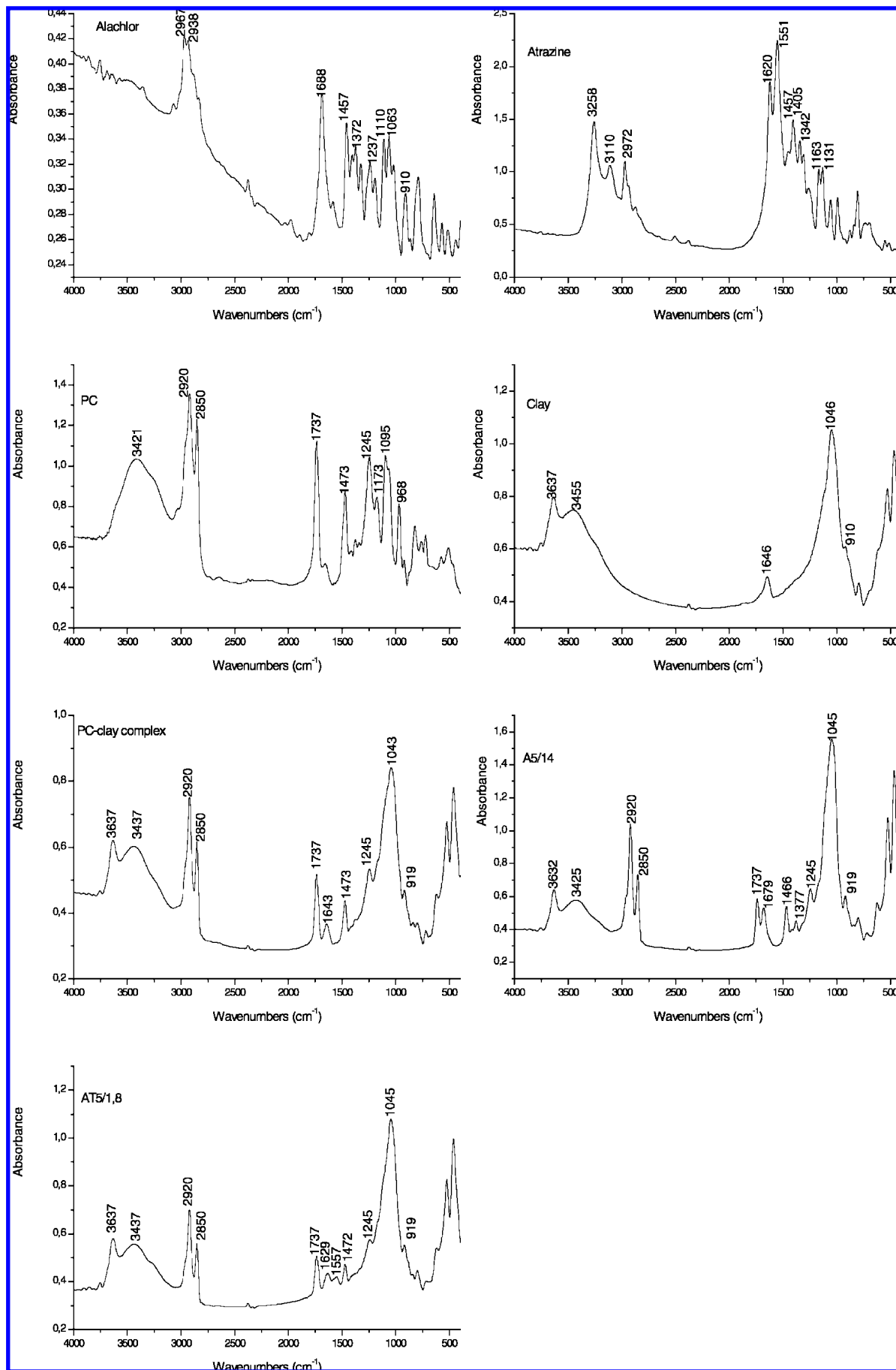


Figure 2. Infrared spectra of herbicides, clay, PC, PC–clay complex (6 mM PC:5 g/L), and herbicide formulations.

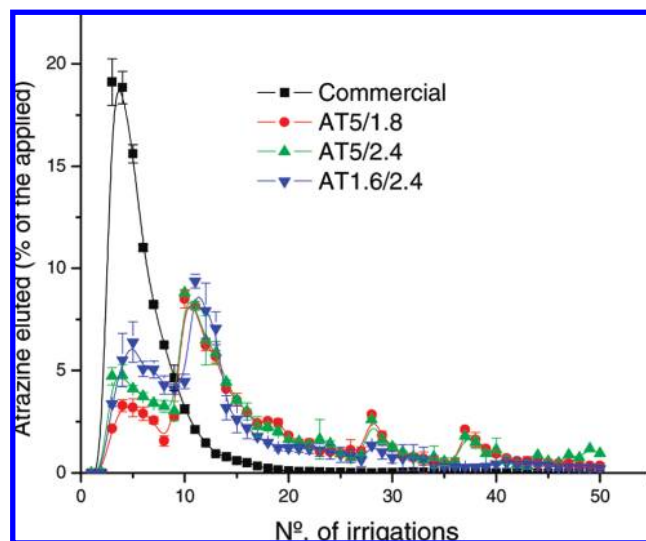


Figure 3. Herbicide release from PC–clay formulations of atrazine.

nature of the anilidic group, producing a shift to a higher frequency (33, 34). The formation of water bridges between alachlor and PC did not cause any significant shift in the frequency of the P=O group, indicating weak interactions with the most external hydration sphere of the headgroup.

In addition to the appearance of these new bands, there are some important changes in the bands of the adsorbed PC. The intensity of both absorption bands at 2920 and 2850 cm^{-1} decreases notably, whereas the absorption due to the scissoring methylene vibration is lowered to 7 from 1473 cm^{-1} . These features indicate a strong interaction of alachlor with the hydrophobic chain.

In the case of atrazine, the most characteristic absorption bands used as fingerprints for studying its interactions are the ring stretching modes in the 1400–1600 cm^{-1} region. The interaction of this herbicide with the PC–clay complex showed an increase in frequency at the absorptions at 1620 and 1551 cm^{-1} to 1629 and 1557 cm^{-1} , respectively, indicating formation of H-bonds through the lone pair electron of the nitrogen atom to OH groups of the headgroup-solvating water (the P=O moiety). A similar mechanism was observed in the interaction of atrazine with humic substances (35, 36). As previously observed with alachlor, there is also a decrease in the intensity of the bands due to methylene stretching modes, suggesting interactions of the alkyl chains of PC with atrazine molecules.

Funnel Experiments: Release of Herbicides in Soil. **Figure 3** shows the elution curves obtained for the commercial formulation of atrazine as well as those based on PC. For PC formulations of atrazine, two elution peaks are evident, which is ideal for slow release formulations, because a significant fraction of bound molecules of the herbicide is initially released in the early stages where a high bioefficacy is desired, whereas the remaining fraction is released more gradually than in the case of the commercial formulation, as noted in the lower ascendant part and longer extended tail.

Atrazine–PC formulations showed considerable reduction in release. After eight irrigations, the cumulative amount of herbicide released was $79.3 \pm 0.3\%$ for the commercial formulation, whereas values of 15.7 ± 0.1 , 24.2 ± 0.2 , and $26.3 \pm 4.3\%$ were obtained for AT5/1.8, AT5/2.4, and AT1.6/2.4, respectively, with percentage reductions of release ranging from 67 to 80%. The total released percentages were 101.8 ± 1.8 for the commercial formulation, 95.7 ± 5.5 for AT5/1.8,

103.4 ± 3.4 for AT5/2.4, and 100.4 ± 0.8 for AT1.6/2.4, indicating again that no irreversible binding of the herbicide occurs in the PC–clay formulations. Essentially, a similar pattern was obtained for alachlor formulations (25).

Soil Column Experiments. In the previous experiments, the funnels were excessively irrigated to test whether PC formulations gave a significant reduction in herbicide release as compared to the commercial formulations. The aim of soil column experiments was to follow the mobility and bioactivity of alachlor and atrazine formulations along the soil columns due to irrigation under conditions similar to those existing in the field in Mediterranean regions.

The formulations employed were selected on the basis of their slow release and high a.i. content. In the case of alachlor, two PC–clay formulations were chosen, one with the highest a.i. content (A1.6/14) and another one with an intermediate a.i. value (A5/8), whereas in the case of atrazine, the three PC–clay formulations were examined.

The amounts of atrazine and alachlor of the commercial and PC–clay formulations were extracted from each soil segment. **Figure 4** shows the distribution of alachlor and atrazine residues at different depths in the soil columns at the end of the experiments. The data show a considerable reduction in leaching in the upper rings from PC–clay formulations.

The amount of atrazine retained in the upper layer (0–4 cm) from the PC–clay formulations in **Figure 4a** was about 75% of the applied vs a value of 53% for the commercial, which amounts to a 29% reduction in leaching. In the following segment (4–8 cm), the amount of atrazine detected from the commercial formulation was about 2.5-fold larger than those from PC–clay formulations. No leached amount was detected at the lowest depth (12–16 cm) for the PC–clay formulations of atrazine, unlike the commercial one. These data were corroborated by measuring the herbicidal activity in the upper rings (**Figure 5a**). A very high inhibition percent (70–76%) was obtained for PC–clay formulations. This inhibition percent in the top layer is 2-fold larger than that of the commercial formulation. The opposite trend is observed in the following segment, a 2-fold larger bioactivity from the commercial than that of the PC–clay formulations, in good agreement with the extracted amounts.

In **Figure 4b**, the remaining alachlor in the top 0–4 cm layer was $12.3 \pm 0.9\%$ of the total applied for the commercial, whereas 2.3-fold larger amounts were determined for PC–clay formulations. No clear difference was detected at the lowest depth (12–16 cm) between the PC–clay formulations and the commercial that was largely accumulated at 8–12 cm, whereas PC–clay formulations were nearly evenly distributed in the first 12 cm. The herbicidal activity at the top layers of the soil columns between the commercial and the PC–clay formulations was the same despite the different extracted amounts (**Figure 5b**), which may be rationalized on the basis that methanol extracts not only the a.i. from PC–clay formulations, which is acting immediately, but also the bound fraction of the herbicide, which is released slowly yielding a longer herbicidal activity with leaching events. The fast released fraction present in the upper layers is sufficiently bioactive to achieve a good weed control, because of the high sensitivity of the tested plant to this herbicide as seen by the high inhibition percent obtained for the commercial formulation, although the amount of herbicide in the upper layer was quite low. To test this possibility, a parallel experiment was performed by increasing the added water to 140 mm of rain, so that the differences in the extracted amounts and the herbicidal activities in the upper

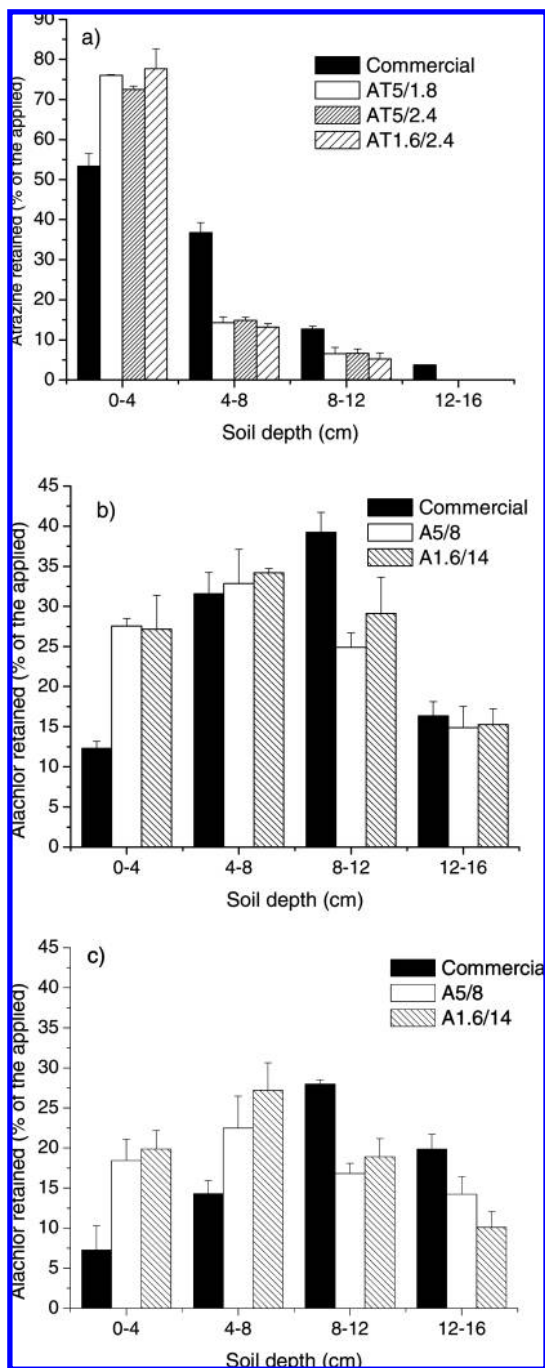


Figure 4. Percents retained of atrazine (a) after 70 mm of rain and alachlor after 70 (b) and 140 (c) mm of rain in soil columns along the depth in leaching experiments.

layers between the commercial and the PC-clay formulations were more pronounced. The added water was larger than the pore volume of the soil column so that a fraction of the total amount applied was leached out from the soil column, amounting to $30.3 \pm 0.7\%$ for the commercial formulation vs values of 18.7 ± 3.5 and $15.1 \pm 3.0\%$ for the A5/8 and A1.6/14 formulations, respectively. The PC-clay formulations not only reduced by 2-fold the eluted amount from the commercial formulation, but also changed the distribution pattern of the remaining amounts in the soil column with respect to that at a lower irrigation. In **Figure 4c**, the total remaining amounts of alachlor at 0–4 and 4–8 cm depths were significantly larger by 2.63- and 1.74-fold, respectively, than those of the commercial formulation. The opposite trend was observed at larger

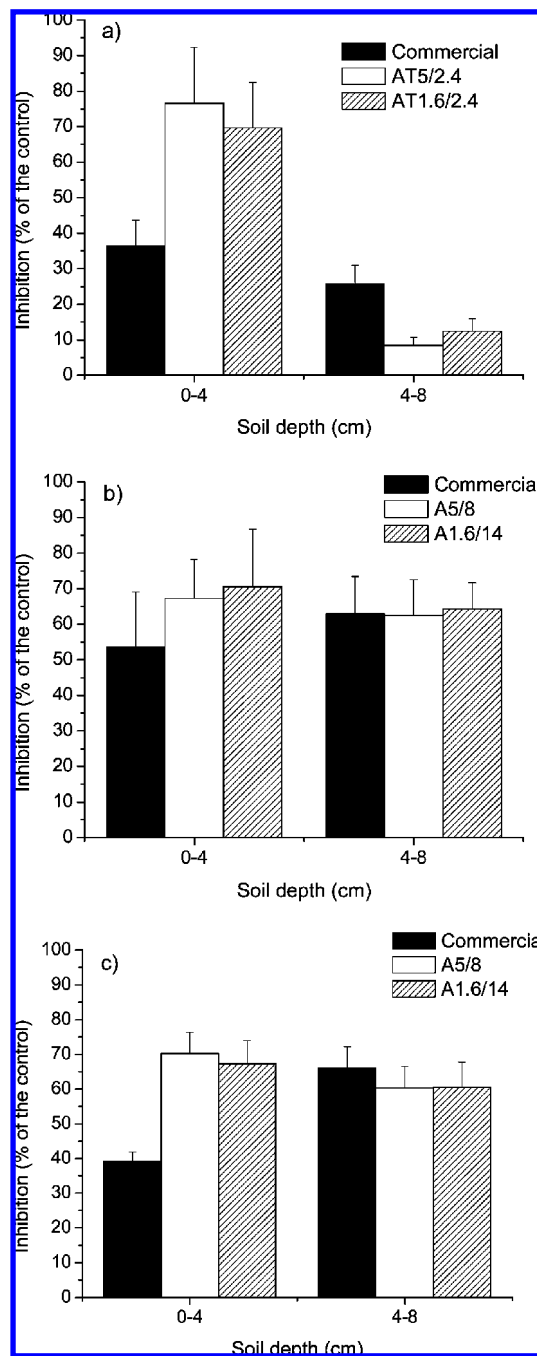


Figure 5. Herbicidal activity in the upper rings of the soil columns from formulations of atrazine (a) after 70 mm of rain and alachlor after 70 (b) and 140 (c) mm of rain.

depths, where the amounts of alachlor from the commercial were always significantly larger than those from the PC-clay formulations. These formulations were mainly accumulated at the 4–8 cm depth, whereas the commercial was concentrated in the 8–12 cm segment. The differences in the remaining amounts of alachlor in the upper layer were noticed by a larger herbicidal activity from the PC-clay formulations than that of the commercial formulation (**Figure 5c**).

The combined results of the extracted amounts, the plant growth inhibition percents, and the eluted amounts indicate that a large reduction in the recommended dose of alachlor and atrazine, respectively, can be accomplished by using PC-clay formulations. The success in designing a slow release formulation of atrazine with an appreciable percentage of a.i. is remarkable in view of our many previous unsuccessful attempts

of designing formulations based on organo-clay and micelle-clay complexes (unpublished results).

In the current study, PC-clay formulations were designed for triazine and acetanilide herbicides, such as atrazine and alachlor, respectively. However, this approach may be extended to many other herbicides, whose molecules can interact with the hydrophobic chains of PC molecules. Other modes of interaction, such as H-bonding, can operate between the polar functional groups of the herbicides and the PC headgroup.

Slow release formulations should be designed to obtain a compromise between the reduction in leaching and the herbicidal activity in the top soil layer. PC-clay formulations fulfill both of these requirements since the amount of herbicide leached was reduced several-fold and the biological activity was enhanced in the upper layer of the soil, which is of prime concern for long-term weed control. In addition, PC-clay formulations can be classified as environmentally friendly because their use poses the advantage that PC and the clay mineral montmorillonite are approved substances of minimal toxicological risk by the U.S. EPA.

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