Organo-Clay Formulation of Acetochlor for Reduced Movement in Soil

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This study aimed to design ecologically acceptable formulations of acetochlor by adsorbing it on montmorillonite exchanged by a small organic cation, phenyltrimethylammonium (PTMA). Adsorption of acetochlor on the clay mineral exchanged with different organic cations and its release from these complexes were determined by GC and modeled by Langmuir equation. Interactions between acetochlor molecules and the exchanged organic cation on the clay surface were studied by Fourier transform infrared spectroscopy. Leaching of acetochlor in soil was determined by a bioassay using a column technique and *Setaria viridis* as a test plant. The adsorbed amounts of acetochlor on montmorillonite exchanged by PTMA at a loading of 0.5 mmol/g of clay were higher than at a loading up to the cation-exchange capacity, i.e., 0.8 mmol/g, and were higher than obtained by using a clay mineral exchanged by other organic cations. Preloading montmorillonite by PTMA at 0.5 mmol/g yielded maximal shifts of the infrared peaks of the herbicide. The above formulation of acetochlor yielded slow release in water and showed improved weed control in field and greenhouse experiments in comparison with the commercial formulation. The PTMA-clay formulation of acetochlor maintained herbicidal activity in the topsoil and yielded the most significant reduction in herbicide leaching and persistence under field conditions. The application of this formulation can minimize the risk to groundwater and can reduce the applied rates.

INTRODUCTION

Acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide] is one of the most commonly used herbicides of the chloroacetanilides chemical family. Acetochlor is a selective pre-emergence herbicide used to control broadleaf weeds and annual grasses in corn. It was registered for use in the United States in March 1994 to replace the widely used corn herbicides alachlor, atrazine, butylate, EPTC, 2,4-D, and metolachlor (*1*). The U.S. Environmental Protection Agency (EPA) registration document indicates that acetochlor is moderately persistent in the environment and is moderately to very mobile in soil. As a result, acetochlor residues are very likely to reach the groundwater and surface water (*1*). Acetochlor has been classified by the U.S. EPA as a B-2 carcinogen, and its registration can be canceled if its concentrations consistently exceed 0.10 μg/L in groundwater or 2.0 μg/L as an annual average of surface water (*1*).

Koplin et al. (*2*) have reported that acetochlor was detected in 29% of the rain samples from four sites from Iowa, 17% from the stream samples from 51 sites across

9 states, and 0% of the groundwater samples from 38 wells across 8 states. Acetochlor is classified as a leacher in soil, and its potential for contamination of groundwater is comparable with those of alachlor and metolachlor (*3*). The mobility of pesticides in soil is one of the principal parameters controlling the extent to which they may represent a risk for groundwater contamination (*4*). Adsorption on soil is one of the important factors for controlling pesticide movement toward groundwater (*5*).

Due to the extensive use of chloroacetanilide herbicides and their characteristics, they may pose serious environmental problems, which must be controlled to minimize their harmful effects. Leaching and migration of such herbicides may result in low efficacy and possible contamination of groundwater (*6–13*). Thus, only a small fraction of the applied herbicide contributes to the desired activity. This may result in repeated applications, increasing cost, and ecological damage.

One strategy to reduce the leaching of hydrophobic herbicides was to adsorb them on a clay-mineral whose surface was modified from hydrophilic to hydrophobic by pre-adsorbing it with an organic cation. The adsorption of organic molecules on montmorillonite has been extensively studied (*14–23*) and modeled (*24–30*). El-Nahhal et al. (*31, 32*) found that an organic cation which includes a phenyl ring was the best choice and could yield formulations of alachlor with significantly reduced leaching and, consequently, improved herbicidal activity. The rationale was to use organic cations that have

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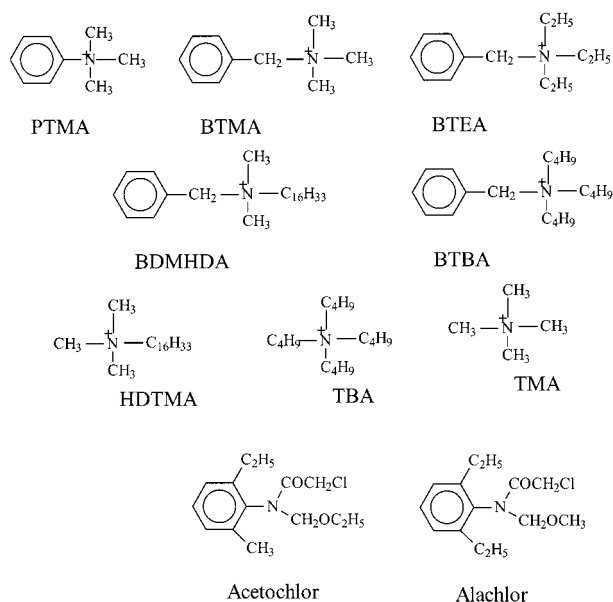[‡] Environmental Protection and Research Institute.

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Figure 1. Chemical structures of the organic compounds used.

structural similarity to that of the herbicide. Out of a series of such organic cations, the most suitable was benzyltrimethylammonium (BTMA). The same trend was also observed in a study on metolachlor (*33*). It turned out that further improvement could be achieved by using a smaller organic cation with a phenyl ring, phenyltrimethylammonium (PTMA) (*34*). Nir et al. (*35*) presented further evidence for the interactions between the phenyl rings of the herbicide molecules and organic cations and presented a theoretical explanation for the fact that the largest binding coefficients of the herbicides alachlor, metolachlor, and norflurazon on montmorillonite-BTMA were for a loading of the organic cation at five-eighths of the cation-exchange capacity (CEC) of the clay mineral.

The overall objective of this work has been to develop ecologically acceptable organo-clay formulations of acetochlor and at the same time to develop a systematic procedure that consists of the following stages: (i) optimization of herbicide adsorption; (ii) determination of herbicide release from the organo-clay formulation to water; (iii) choice of optimal herbicide formulations for test of leaching and bioactivity in soil columns under greenhouse conditions; and (iv) choice of optimal organo-clay formulations for tests of herbicidal activity and leaching under field conditions.

MATERIALS AND METHODS

Materials. The clay used was sodium montmorillonite SWy-2 (Mont) obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). HPLC-grade ethyl acetate, isooctane, PTMA, BTMA, benzyltriethylammonium (BTEA), benzyltributylammonium (BTBA), hexadecyltrimethylammonium (HDTMA), benzyldimethylhexadecylammonium (BDMHDA), tetrabutylammonium (TBA), and tetramethylammonium (TMA) were purchased as chloride salts from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO; Aldrich Chemical Co., Milwaukee, WI). The chemical structures of the organic compounds are shown in Figure 1. Analytical-grade NaCl was obtained from Frutarom Laboratory Chemicals (Haifa, Israel). Soils were collected from 0 to 30 cm depth at the Faculty's Experimental Farm in Rehovot and at the Agricultural Experimental Station of EPRI in the Gaza Strip. Soil properties are shown in ref *32*. Green foxtail (*Setaria viridis* (L.)

Beauvois) and/or wheat (*Triticum* ae*stivum* L., cv. Ariel) were used as test plants.

Analytical-grade acetochlor, purity 98% (supplied by Agan Makhteshim, Israel) was used for making the organo-clay formulation. The commercial formulation (EC) of acetochlor (Harness) (Monsanto Chemicals 900 g ai/kg) was used as a standard formulation.

Preparation of Organo-Clay Complexes. The organo-clay complexes were prepared by dropwise addition of aliquots of a 10 mM aqueous solution of PTMA to a 1% (w/v) aqueous suspension of montmorillonite under continuous stirring (*36*). After 30-min centrifugation (20000*g*), the precipitate was washed three times with distilled water, freeze-dried, ground to <50 μm, and kept in plastic bottles at room temperature.

Adsorption of Acetochlor on Montmorillonite Exchanged with Organic Cations. Adsorption of acetochlor on clay exchanged with different organic cations was measured at room temperature. Adsorption was measured at 740 μmol of acetochlor/g of clay exchanged with different organic cations at a loading of 0.5 or 0.8 mmol/g of clay. In addition, for several cases, adsorption isotherms were determined and simulated by Langmuir equation. To measure the adsorbed amounts, appropriate aliquots of an aqueous stock solution of acetochlor (8×10^{-4} M) were diluted by distilled water in 25 mL and were added under continuous stirring to 5 mL of 0.5% (w/w) exchanged clay suspension in a 40-mL centrifuge tube. The final concentration of the organo-clay complex was 0.83 g/L. The samples were kept under continuous horizontal agitation at 25 ± 1 °C during 48 h. The supernatant was separated by centrifugation at 20000*g* for 1 h. Since acetochlor is a structural analogue of the chloroacetanilide herbicides alachlor and metolachlor, it was extracted from the supernatant and determined by GC as described in refs *32–34*.

Adsorption experiments also included montmorillonite-PTMA either alone at a load of 0.5 mmol/g of clay or at a load of 0.3 or 0.4 mmol/g combined with BTMA at a load of 0.2 or 0.1 mmol/g, to have a total loading of the clay with both organic cations of 0.5 mmol/g. For a comparison, a clay exchanged with PTMA at 0.5 mmol/g of clay was used in the study. These complexes were used to determine adsorption isotherms of acetochlor on different organo-clays. In this procedure, the adsorption isotherms were measured in the range of 0–700 μmol of acetochlor/g of exchanged clay.

Preparation of Acetochlor Formulations. Appropriate amounts of acetochlor were dissolved in 1 L of distilled water to form a stock solution of 700 μmol/L. Appropriate amounts of acetochlor equivalent to 100–500 μmol/g of clay complex were added to a 1-L volumetric flask. The final volume was brought to 1 L, and 1 g of a clay exchanged with PTMA (0.5 or 0.8 mmol/g) was added to each volumetric flask to form 0.1% clay suspension. The samples were kept for 48 h under continuous magnetic stirring. The pellets were separated by centrifugation at 20000*g*, air-dried, and kept in plastic bottles at room temperature for use. The adsorbed amounts of herbicides were measured as described by ref *34*.

Model Calculations. The Langmuir equation (or Scatchard equation), which is based on the assumption of the lack of interactions, i.e., lack of cooperativity between adsorbed molecules, was used to describe the sorption of the herbicides by the clay or organo-clays. As in ref *35*, we presented results based on the use of a single parameter, *k*, the binding coefficient (M^{-1}). The calculations were also used to estimate the amounts of acetochlor released from the formulation in aqueous suspensions after long incubations.

Fourier Transform Infrared (FTIR). FTIR spectroscopy was used to examine the interaction of PTMA molecules with clay surfaces and between acetochlor and the organo-clay as previously described (*32, 37*). Briefly, infrared spectra were obtained using KBr pellets with a FTIR spectrometer (Nicolet Magna-IR-550, Madison WI). The FTIR spectra were recorded at room temperature in the range of 4000–600 cm^{-1}. Full spectra were directly used to evaluate interactions.

Release Experiments. Release of acetochlor molecules from the complex to water was conducted by suspending equivalent amounts of the air-dried pellets (clay-PTMA0.5-

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acetochlor) in water to form 0.008, 0.083, 0.1, 0.5, 0.8, and 1% (w/v) suspensions. In this procedure, equivalent amounts of the herbicide complex were added in a 100-mL plastic tube along with the equivalent amount of water to form the needed suspension. Samples were kept under continuous horizontal agitation for 8 h and 1, 2, and 7 d for some cases. Samples were then centrifuged at 20000*g*. Acetochlor was extracted from the supernatant and analyzed by GC as described (*34*). The pellets were air-dried and tested for leaching studies.

Leaching Studies. *Greenhouse Condition.* Tin macrocolumns (10 × 10 cm surface area, 25 cm height) and microcolumns made of polyethylene tubes (surface area of 5 cm², 25 cm height) were used to evaluate herbicide leaching in a sandy soil as previously described (*32, 34*). The macrocolumns were filled with sandy soil from Gaza or Rehovot, and their surfaces were sprayed with the field rate (2.0 ai kg/ha) either as EC formulation or acetochlor adsorbed on clay exchanged with PTMA using an atomizer. The microcolumns were filled with sandy soil from Gaza. The herbicide formulations were applied with a pipet at the same field rate (2 kg ai/ha). The columns were carefully irrigated with 500 m³/ha (50 mm), applied in portions during 3–5 h with 20-min intervals and left for 24–48 h for equilibration. Then the tin columns were sliced along their lengths, forming two pots 10 × 5 × 25 cm each, whereas the microcolumns were sealed from the top and sliced along their length forming one pot. Green foxtail seeds were sown in each column half of the macrocolumn in two rows and in one row in the microcolumns. Percent of shoot growth inhibition at a given soil depth was calculated according to the following formula:

$$\% \text{ growth inhibition} = 100 \times (P_c - P_t)/P_c \qquad (1)$$

where P_c and P_t are the shoot height of the control and the treated samples at any soil depth. Shoot heights were determined 2 weeks after treatments.

Effects of Release on Reducing Acetochlor Leaching. The collected acetochlor pellets from the first release experiments were air-dried and added in plastic bottles having the same amount of water as described in the section on release experiments. After 24 h of being shaken, the pellets were separated as described above, air-dried, and used for a leaching experiment as described above.

Field Experiment. Wheat seeds were sown on November 20, 2000, in sandy soil at the Faculty's Experimental Farm using an experimental planter (140 kg of seeds/ha) on prepared beds. Five rows were sown in each plot (1.2 × 8 m, 25 cm high bed). On the following day, acetochlor (1.5 kg ai/ha) was applied either as the commercial formulation (EC; Harness, 90% ai) or the organo-clay formulation in a randomized block design with five replications. The commercial formulation was applied in 270 L/ha of water, whereas the organo-clay formulation was applied in a volume of 2.2 m³/ha using a motorized knapsack sprayer. A few hours later, the whole field was sprinkler irrigated (500 m³/ha) at a rate of 5 mm/h. Wheat seedlings emerged 7 days later. Following the first irrigation of 500 m³/ha, the experimental plots were irrigated 1 week later with an additional 100 m³/ha. The rainfall was measured automatically by a meteorology station. The total rainfall during the 2-month period was 127 mm.

Dissipation of the Active Ingredient from the Upper 5 cm. On each of the 5 following weeks after planting, 1.5 kg of the upper 5 cm soil was sampled from each plot using a big spatula. The soil was transferred to two pots (6.5 × 6.5 cm surface area), and 10 seeds of green foxtail were planted. Three weeks after each sampling date, the heights of the plants in the pots were measured, and the inhibition rate was calculated for the average plant height in each pot according to eq 1. The pots were arranged in a complete randomized design with five replications.

Data Analysis. Acetochlor release data were subjected to analysis of variance, and the main effects and interactions were tested for significance using repeated measures ANOVA. Means of adsorption data were compared by linear regression
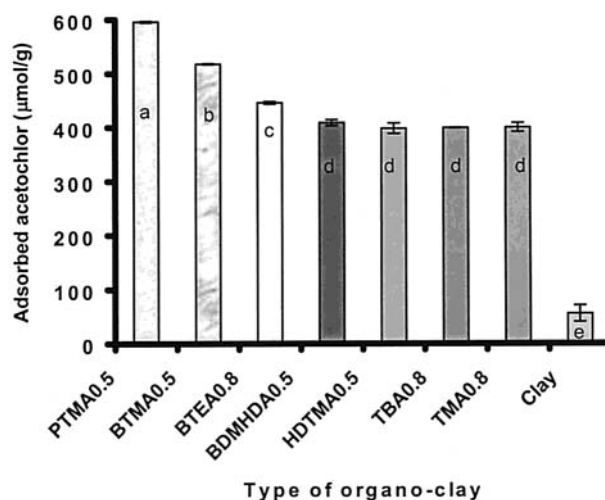

Figure 2. Adsorption of acetochlor on montmorillonite exchanged with different organic cations and loadings. Bars indicate standard error. Acetochlor was added at 740 μmol/g of clay complex. Columns that have the same letter are not significantly different at $p = 0.05$ level of significance.

analysis. Multiple mean comparisons of growth inhibition at different depths were performed by Tukey's test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Adsorption of Acetochlor. Adsorption of acetochlor on a clay mineral alone or exchanged with different types of organic cations is shown in Figure 2. It can be seen that a little amount of acetochlor was adsorbed on the clay mineral alone, whereas exchanging the clay with an organic cation resulted in a dramatic increase in the adsorbed amounts of acetochlor. As previously reported, chloroacetanilide herbicides, e.g., alachlor (*32, 38*) and metolachlor (*33*), are poorly adsorbed on montmorillonite alone, whereas their adsorption on an exchanged clay mineral with PTMA resulted in a dramatic increase in the adsorbed amounts of both herbicides (*34*). The same trend was observed for acetochlor adsorption in accord with the fact that acetochlor is a structural analogue of alachlor (Figure 1). The low adsorption of acetochlor on the hydrophilic clay surfaces is due to the hydrated mineral surface of the clay and the hydrophobic nature of acetochlor molecules. In contrast, the organo-clay surfaces sorbed higher amounts of acetochlor (Figure 2) due to a preferred interaction between acetochlor molecules and the organic molecules on the clay surfaces in comparison with their interaction with the solvent. This result is in accord with a report (*39*) that showed good correlation between the organic matter content of soil and the adsorption of chloroacetanilide herbicides in soil. It can also be seen that exchanging the clay with an aromatic cation (e.g., BTMA) increased the adsorbed amounts of acetochlor more than obtained by using a clay mineral exchanged with an aliphatic cation (e.g., HDTMA). The highest adsorbed amount of acetochlor was observed when the clay was exchanged with the smaller aromatic cation (PTMA). Our explanation for these results is that the smaller aromatic cation (PTMA) has a bond length between the ammonium nitrogen and the phenyl ring similar to that of the bond between the phenyl ring and the amide nitrogen of acetochlor. The larger aromatic cations (e.g., BTMA, BTEA) have a methylene bridge between the ammonium nitrogen and the phenyl ring, which increases the bond length and apparently reduces
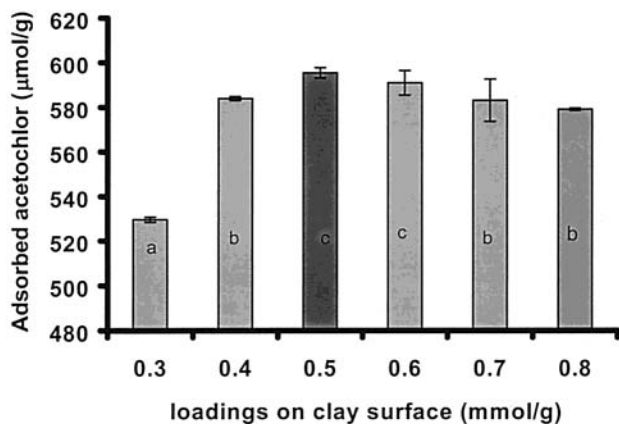
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Figure 3. Adsorption isotherms of acetochlor on montmorillonite exchanged with PTMA at loadings of 0.3−0.8 mmol/g of clay. Acetochlor was added at 740 μmol/g. Bars indicate standard errors. Columns that have the same letter are not significantly different at $p = 0.05$ level of significance.

the strength of the interaction between acetochlor and the adsorbed organic cation. These interactions, which are possibly $\pi-\pi$ interactions, are optimized due to the better geometrical matching of the bond lengths on both molecules and hydrogen bonding via the carbonyl and the anilidic groups, as recently demonstrated by refs *40* and *34*.

Adsorption of acetochlor on a clay exchanged with PTMA at varied loadings (0.3−0.8 mmol/g of clay) is shown in Figure 3. It is evident that partial saturation of the clay with PTMA at a loading of 0.3 mmol/g of clay resulted in a significantly larger adsorbed fraction of acetochlor than that obtained using a clay alone. Increasing the loading up to 0.5 mmol of PTMA/g of clay significantly increased the adsorbed amounts of acetochlor as compared to that obtained at a loading of 0.3 mmol/g of clay and yielded larger adsorbed amounts than at other loadings (0.4−0.8). Loading the clay surface up to the CEC reduced the adsorbed amount of acetochlor below that obtained at a loading of 0.5 mmol/g of clay. These data indicate that a loading of 0.5 mmol of PTMA/g of clay optimizes the adsorption of acetochlor, probably due to a better geometrical fit and/ or a reduction of the fraction of charged complexes as discussed before (*34, 35*) for other cases. The observed reduction of the adsorbed amounts of acetochlor when the clay surface is saturated with PTMA up to the CEC indicates that achieving maximal transformation of the clay surface from hydrophilic to hydrophobic does not necessarily imply optimal interactions between the herbicide molecules and the organo-clay complex. An important element is to exchange the clay mineral with a suitable organic cation that can yield optimal interactions with the herbicide molecules on the clay surface.

Figure 4 presents the data of adsorption isotherms of acetochlor on a clay-mineral exchanged with HDTMA, PTMA alone at a loading of 0.5 mmol/g of clay, or PTMA combined with BTMA at loading of 0.2 or 0.1 mmol/g. Our idea behind co-exchanging the clay with BTMA at 0.2 mmol/g of clay along with PTMA at 0.3 mmol/g was based on the possibility of a reduction of charged complexes. At a lower concentration, no significant difference was observed between the adsorbed amount of acetochlor on a clay exchanged with PTMA alone or combined with BTMA. At a higher concentration, the data confirm the effect of similarity in the chemical structure, which optimizes the interaction between the
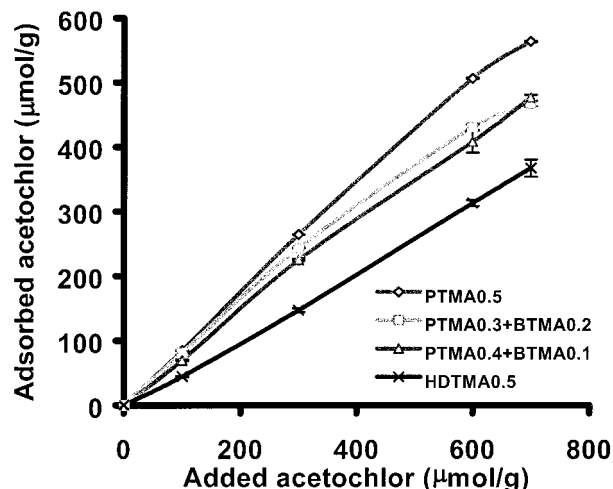

Figure 4. Adsorption isotherms of acetochlor on montmorillonite exchanged with PTMA alone at loadings of 0.5 or combined with BTMA at 0.2 or 0.1 mmol/g of clay and with HDTMA 0.5. Bars indicate standard errors.

Table 1. Binding Coefficients Describing Sorption of Acetochlor on Montmorillonite and mont-PTMA Prepared at Several Loads

organic cation and loading (mol/kg)	k (M^{-1})	R^2
none	85	0.99
PTMA0.5	16 000	0.99
PTMA0.4 + BTMA0.1	7 400	0.995
PTMA0.3 + BTMA0.2	7 000	0.996
HDTMA0.5	2 600	0.940

herbicide molecules and the organic cation molecules on the clay surface.

The Langmuir equation yielded a good fit to the adsorbed amounts (see Table 1). The results suggest that acetochlor sorption on a clay mineral exchanged with organic cations is not primarily due to partitioning. It is dependent on the size and shape of the organic cations exchanged on the clay, as previously reported for alachlor and metolachlor (*32, 34, 35*) and for benzene and other aromatic molecules (*41*).

The binding coefficients of the three hydrophobic herbicides (acetochlor, alachlor, and metolachlor) for adsorption on PTMA0.5-montmorillonite (i.e., 16 000 (Table 1), 11 000, and 2880 M^{-1}; *35*), respectively, are inversely correlated with their solubility in water (223, 240, and 530 mg/L). In fact, the same sequence of binding coefficients is also exhibited for adsorption of these herbicides on montmorillonite (85, 50, and 45 M^{-1}) where the values are 2 orders of magnitude lower.

FTIR. To better understand the adsorption mechanisms that define the observed sorption, we obtained FTIR spectra of acetochlor in its free form and adsorbed on montmorillonite exchanged with PTMA at a loading of 0.5 mmol/g. Detailed information on the interactions between PTMA molecules and the clay mineral surface has recently been provided by ref *34*.

Figure 5 shows the spectra of acetochlor in its free form (panel a) and adsorbed on the organo-clay (panel b). The three peaks at 1682.6, 1464.4, and 1375.5 cm^{-1} in the spectrum of free acetochlor (panel a) were assigned to the stretching vibrations of the −C=O group (1682.6), the phenyl ring (1464.4), and the anilidic group (1375.5). These peaks are similar to those of alachlor. The peak at 1682.6 cm^{-1} (carbonyl group) of the free acetochlor (Figure 5a) was shifted to a lower wavenumber at 1661.8 cm^{-1} (Figure 5b). The peak at 1464.4 cm^{-1}

Table 2. Acetochlor Release from Organo-Clay Formulations[a]

herbicide formulation	total herbicide concn (μM)	clay concn % (w/w)	% release after				equilibrium (calcd)
			8 h	1 d	2 d	7 d	
clay-PTMA0.5 − acetochlor	8	0.008	23.1 ± 2	22.5 ± 2	39.1 ± 3	nd[b]	51
clay-PTMA0.5 − acetochlor	71	0.1	nd	nd	15.0 ± 2.0	nd	9
clay-PTMA0.5 − acetochlor	356	0.5	nd	nd	4.4 ± 0.5	nd	2
clay-PTMA0.5 − acetochlor	711	1.0	2.6 ± 0.3	2.4 ± 0.3	2.4 ± 0.3	nd	1
clay-PTMA0.5 − acetochlor	569	0.8	nd	nd	3.2 ± 0.4	nd	1
clay-PTMA0.3 + BTMA 0.2	797	1.0	nd	10.3 ± 1.5	9.9 ± 1.5	7.9 ± 1.2	2
clay-PTMA0.5 − acetochlor[c]	3333	1.0	nd	nd	27.2 ± 3.0	nd	76

[a] Comparison of measured release in water with calculated release at equilibrium. [b] nd, not determined. [c] Acetochlor was added to the organo-clay from acetone.
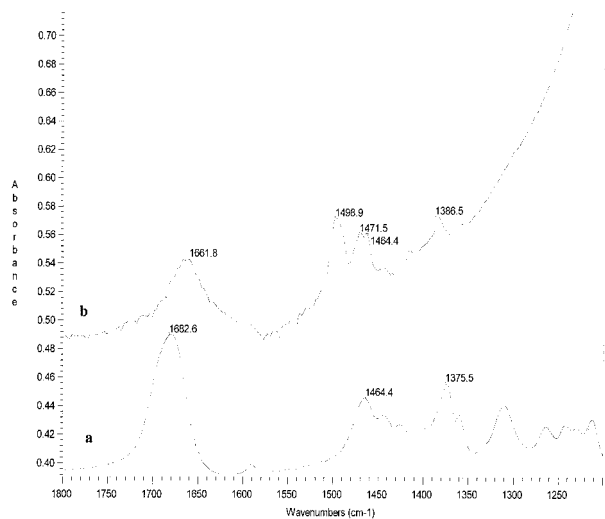

Figure 5. FTIR spectra of acetochlor in its free form (a) and adsorbed to montmorillonite exchanged with PTMA at a loading of 0.5 mmol/g of clay (b).

(phenyl group) of free acetochlor (Figure 5a) was shifted to a higher wavenumber at 1471.5 with a shoulder at 1464.4 cm^{-1} (Figure 5b). The peak at 1375.5 cm^{-1} (Figure 5a) (anilidic group) was shifted to a higher wavenumber at 1386.5 cm^{-1} (Figure 5b). The peak at 1498.9 cm^{-1} (Figure 5b) appears to be due to the interactions between the phenyl rings of PTMA and the acetochlor molecules. These shifts indicate that acetochlor molecules interact strongly with montmorillonite exchanged with PTMA through the phenyl rings, the anilidic group, and the carbonyl group. By comparing FTIR of acetochlor before and after adsorption, it appears that the carbonyl group of acetochlor interacts with the clay surface. This is reflected by a shift of the C=O stretching vibrations band from 1682.6 cm^{-1} of free acetochlor to 1661.8 cm^{-1} of adsorbed acetochlor (Figure 5). Formation of coordination bonds was proposed to occur between alachlor and the hydrated clay surface (42) or the partially saturated surface with organic cations (32, 34). Two types of bond formation might have occurred on the clay exchanged with PTMA:

(i) Interaction between carbonyl oxygen (C=O) and amide nitrogen (C−N) of acetochlor and PTMA exchanged on the clay surfaces.

(ii) Formation of π−π charge−transfer bonds between the phenyl rings of acetochlor and the exchanged PTMA. This was evident due to the emergence of a peak at 1498.9 cm^{-1}. A similar observation was shown for alachlor and metolachlor (34). Our explanation for these results is that in the case of PTMA, the bond length between the phenyl ring and the ammonium nitrogen is probably the same as in acetochlor, which might

enhance the interaction between phenyl rings at the clay surface. These results are in accord with the higher adsorbed amounts of acetochlor in comparison with alachlor and metolachlor on montmorillonite exchanged with PTMA. Upward shifts of ring vibrations due to π−π interactions were noted before (43). Another explanation for the upward shifts of the vibrations of the phenyl ring and the anilidic group is that these groups interact more strongly in free molecules in the liquid than in the adsorbed state.

Release Experiments. The release of acetochlor from clay exchanged with PTMA is shown in Table 2. Clearly, the rates and extents of release depend on the clay concentration in the suspension. For instance, the clay-PTMA-acetochlor suspensions at 0.008%, 0.1%, and 1% (w/w) released 39%, 15%, and 2.4% of their content of acetochlor, respectively, after 2 d.

A comparison of the data of formulations at a 1% suspension shows that exchanging the clay with PTMA alone at a loading of 0.5 mmol/g of clay was better in reducing the release of acetochlor than combining it with BTMA. In Table 2, we also present one case where the herbicide was added to the organo-clay from acetone rather than from an aqueous solution. In accord with previous results for metolachlr (33), using acetone as the solvent resulted in higher release of acetochlor and, correspondingly, the herbicide leached to larger depths in soil columns (results not shown).

By using the binding coefficients in Table 1, we calculated the fraction of herbicide expected to be released at equilibrium. Thus, for the most dilute case the release after 2 d (39.1%) was below the expected value at equilibrium (51%), which implies that the equilibration time is certainly longer than 2 d.

Table 2 demonstrates that most of the release occurred during the first day (or perhaps even 8 h) and that, in the cases measured, there was no significant difference between the fractions of herbicide released after 1, 2, or 7 d. In fact, it might even appear that after a while a small fraction of the released herbicide readsorbs. The calculated fraction of herbicide released in more concentrated suspensions turns out to be smaller than the fraction released after 2 d. Of course, 1% release (calculated) in comparison to 2.4% amounts to a negligibly small difference (within the experimental error) between the calculated adsorbed fraction (99%) and the experimental one (97.6%). However, it may be of interest to test the speculation that there is a first burst of herbicide release due to a certain loosely bound fraction. This issue may be of importance since the existence of a very small fraction of herbicide, which is loosely bound, can have an effect on the leaching. Indeed, a brief washing of the organo-clay formulation of acetochlor reduced the leaching depth (results not
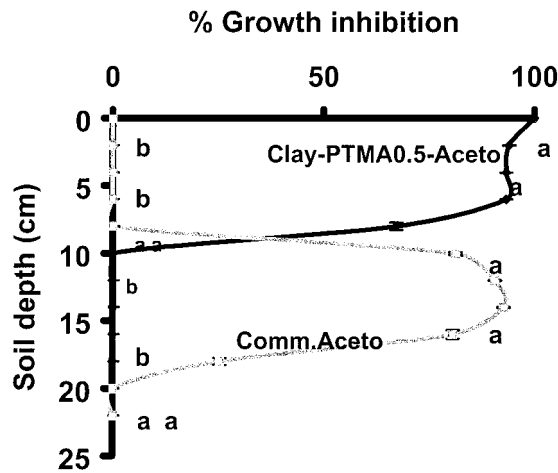
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Figure 6. Leaching of acetochlor (2.0kg/ha) in macrocolumns filled with sandy soil from Gaza following irrigation with 500 m³/ha. Green foxtail growth was used to estimate the presence of acetochlor at certain depths. Acetochlor formulations were commercial EC formulation (Comm.Aceto) and acetochlor adsorbed on montmorillonite exchanged with PTMA (0.5 mmol/g) at 1.92% (w/w). Means followed by different letters at a representative depth are significantly different at $p = 0.05$ level.

Figure 7. Leaching of acetochlor (1.5 kg/ha) under field conditions in Rehovot soil following irrigation with 600 m³/ha. Green foxtail growth was used to estimate the presence of acetochlor at a certain soil depth. Acetochlor formulations were commercial EC formulation (Comm.) and acetochlor adsorbed on clay exchanged with PTMA at a loading of 0.5 mmol/g. The organo-clay-based formulation contained 4% acetochlor. Means followed by different letters at a representative depth are significantly different at $p = 0.05$ level.

shown), but the significance of this result has to be tested more extensively.

Leaching Studies in Greenhouse. Results of the laboratory experiments using macrocolumns (Gaza and Rehovot) filled with sandy soil were similar. For brevity, only the results from Gaza are shown in Figure 6. As is clearly shown, acetochlor applied as the commercial EC formulation at the recommended rate (2.0 kg/ha) followed by irrigation of 500 m³/ha disappeared from the top 8 cm of the soil and accumulated at a deeper depth between 10 and 18 cm, where it caused ca. 85% growth inhibition of the test plant. In microcolumns (data not shown), the EC acetochlor formulation was active from the topsoil up to soil depth of 20 cm, indicating more leaching. The enhanced activity in the topsoil in the microcolumns vs the macrocolumns was probably due to possible interaction between acetochlor molecules and the microcolumn walls (polyethylene tubes).

These results clearly demonstrate the effectiveness of organo-clay formulations of acetochlor in reducing the leaching and improving the herbicidal activity. The explanation of these results is that montmorillonite exchanged with PTMA interacts strongly with acetochlor (see Figures 2 and 5 and Table 1) and yields slow release, as also shown in Table 2.

Field Experiments. Under field conditions at the Rehovot farm (Figure 7), the exchanged clay formulation of acetochlor (clay-PTMA0.5-aceto) showed about 80% growth inhibition in the top 0−5 cm of the soil profile, whereas with the commercial EC formulation, little herbicidal activity was observed in the top 5 cm, and it was strongly active at a depth of 14−18 cm. These results are in agreement with the results of acetochlor leaching under laboratory conditions and indicate that the exchanged clay formulation of acetochlor is also stable and active under field conditions. It is evident from the results that the organo-clay formulation reduces leaching of acetochlor significantly in comparison with the commercial EC formulation. In most situations, retention of the active ingredient of the herbicide at the topsoil layer will likely result in an improvement of weed control efficacy.
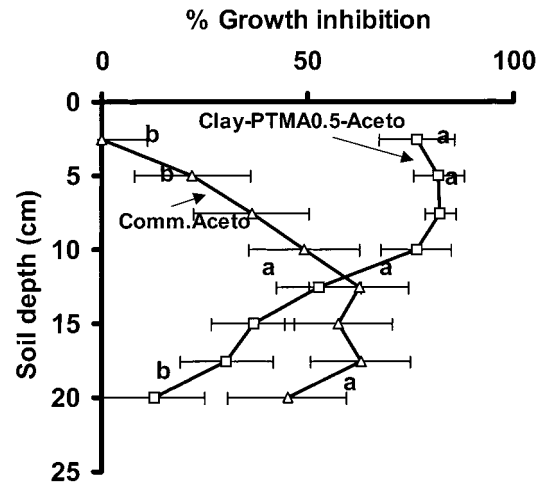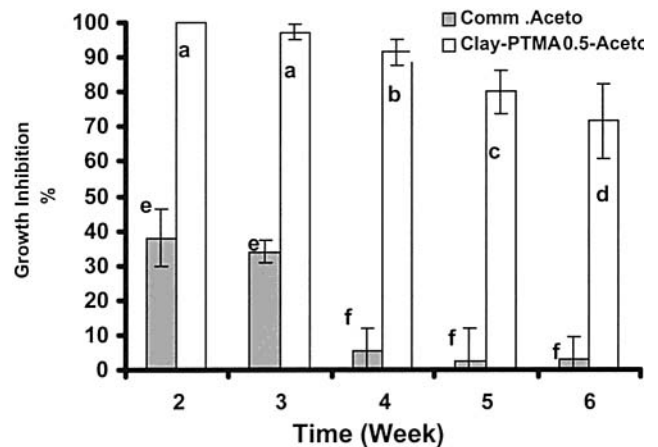

Figure 8. Effect of acetochlor formulations applied in field study on green foxtail growth as determined several weeks after application. As described in Materials and Methods, soil samples were collected from field plots at a depth of 0−5 cm. Total irrigation (including rain) was equivalent to 60, 70, 92, 142, and 146 mm on 2, 3, 4, 5, and 6 weeks after application, respectively. Acetochlor formulations were commercial EC formulation (Comm.Aceto) and acetochlor adsorbed on clay exchanged with PTMA at a loading of 0.5 mmol/g (Clay-PTMA0.5-Aceto). The organo-clay-based formulation contained 4% acetochlor. Columns labeled by the same letter are not significantly different at $p = 0.05$ level.

Retention of Acetochlor in the Upper 5 cm. Following irrigation of 600 m³/ha and 127 mm of rainfall, the formulation based on exchanging clay with PTMA at 0.5 mmol/g of clay was found very effective in weed control even 6 weeks after application, whereas the herbicidal activity of the commercial EC formulation was significantly lower. The data in Figure 8 present the results of field experiments in Rehovot. The formulation based on montmorillonite exchanged with PTMA contains 4% (w/w) pure acetochlor. The herbicidal activity of acetochlor adsorbed on clay exchanged with PTMA resulted in 97−80% growth inhibition as determined by shoot height for 2−6 weeks after application.

It is evident from the results that the organo-clay formulations, unlike the EC formulation, gave excellent weed control for extended periods, which we attribute to slow release of the active ingredient from the organo-clay complex into the topsoil layer. In addition, adsorption of acetochlor by clay-mineral exchanged with PTMA may reduce its possible loss by volatility (*44*). From the environmental point of view, the maintenance of the active ingredient of the herbicide in the topsoil layer reduces the hazard of contamination of groundwater.

CONCLUDING REMARKS

This study presents an attempt to reduce the leaching and migration of acetochlor in soil. Our approach for designing clay-based formulations combined two principles:

(i) Modification of the clay surface from hydrophilic to hydrophobic by pre-adsorbing it by an organic cation whose structure would enable optimal interactions between the herbicide molecules and the surface sites of the exchanged clay.

(ii) The degree of coverage of the clay surface by the organic cation should be optimized. Exchanging the clay up to its CEC with the organic cation does not necessarily imply optimal interactions between the herbicide molecules and those of the exchanged organic cations.

The formulations based on exchanging montmorillonite with a suitable organic cation at five-eighths of the CEC were optimal in reducing herbicide leaching and in maximizing herbicidal activity. Thus, the application of the new organo-clay formulations of acetochlor enables a reduction in the applied amounts relative to those of the commercial formulation as observed in the field experiment. These characteristics make the new formulations promising from the environmental and economical points of view.

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