

Montmorillonite–Phenyltrimethylammonium Yields Environmentally Improved Formulations of Hydrophobic Herbicides

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This study aimed to design formulations of hydrophobic herbicides, alachlor and metolachlor, by adsorbing them on the clay mineral montmorillonite preadsorbed by the small organic cation phenyltrimethylammonium (PTMA). An adsorption model that considers electrostatics and specific binding and the possibility of cation adsorption above the cation exchange capacity (CEC) could explain and yield predictions for PTMA adsorption in the presence of NaCl concentrations from 0 to 500 mM. Adsorption of alachlor and metolachlor from aqueous solution on a clay mineral preadsorbed by PTMA was determined by GC and modeled by Langmuir equation. Herbicide interactions with the organoclay were studied by Fourier transform infrared spectroscopy. Leaching of herbicides was determined by a bioassay using a column technique and *Setaria viridis* as a test plant. The adsorbed amounts of alachlor and metolachlor on montmorillonite preadsorbed by PTMA at a loading of 0.5 mol/kg (Mont–PTMA0.5) were higher than at a loading up to the CEC, that is, 0.8 mol/kg, and were higher than those obtained by using several other organic cations. Herbicide formulations based on Mont–PTMA0.5 yielded the largest shifts of the infrared peaks of the herbicides. These formulations based on Mont–PTMA0.5 gave slower release and showed improved weed control in comparison with formulations based on other organoclays. These formulations maintained herbicidal activity in the topsoil and yielded the most significant reduction in herbicide leaching.

Keywords: *Alachlor; metolachlor; montmorillonite; organoclays; phenyltrimethylammonium; release; leaching; herbicidal activity*

INTRODUCTION

The increasing use of alachlor and metolachlor 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, damage to other crops (Carter, 2000), and possible contamination of groundwater (Cohen et al., 1986; Koterba et al., 1993; Ritter et al., 1996; Thurman et al., 1996; Riparbelli, 1996; Pasquarell and Boyer, 1996). 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.

Ecologically acceptable organoclay-based herbicide formulations have recently been developed and have demonstrated improved herbicidal activity, inhibition of leaching and migration (El-Nahhal et al., 1997, 1998, 1999b), and reduced photochemical degradation and volatilization (El-Nahhal et al., 1999a). The improved

formulations were prepared by adsorbing the herbicides on montmorillonite preadsorbed with aromatic cations, such as benzyltrimethylammonium (BTMA). The strategy was to preadsorb on the hydrophilic clay mineral surface an organic cation that includes a phenyl ring to achieve stronger interactions between the organoclay surface and hydrophobic herbicides that include such a ring.

The adsorption of organic molecules on montmorillonite has been extensively studied (Theng, 1974; Chu and Johnson, 1979; Narine and Guy, 1981; Mortland et al., 1986; Boyd et al., 1988; Jaynes and Boyd, 1990, 1991; Boyd and Jaynes, 1992; Lagaly, 1995; Xu et al., 1997) and modeled (Cenens and Shoonheydt, 1988; Margulies et al., 1988a; Dobrogowska et al., 1991; Nir et al., 1994a; Rytwo et al., 1995, 1996a). The adsorption of certain organic cations denoted dyes on montmorillonite was not affected by the ionic strength at a loading below the cation exchange capacity (CEC), whereas their adsorbed amounts increased with the ionic strength for adsorption beyond the CEC. A different pattern of adsorption on montmorillonite was found for BTMA and benzyltriethylammonium (BTEA). At low levels of ionic strength the adsorbed amounts of these cations approached the CEC, whereas an increase in the ionic strength resulted in a reduction in their adsorbed amounts (Polubesova et al., 1997).

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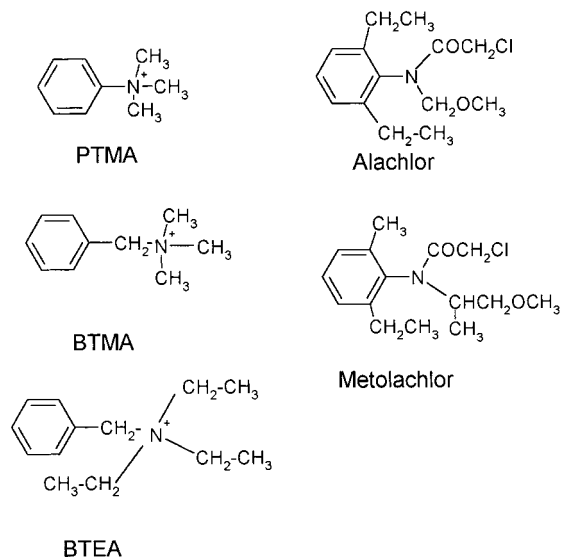


Figure 1. Chemical structures of the organic compounds used.

The overall objectives of this work have been (1) to investigate the effect of using a smaller aromatic cation such as phenyltrimethylammonium (PTMA) as a clay surface modifying agent for the development of improved organoclay formulations in terms of slower release and reduced leaching, while retaining herbicidal activity, and (2) to elucidate the mechanism of adsorption of PTMA on montmorillonite under different levels of ionic strength.

MATERIALS AND METHODS

Materials. The clay used was sodium montmorillonite SWy-2 (Mont) obtained from the Source Clays Repository, Clay Minerals Society, Columbia, MO. Analytical grade alachlor and metolachlor, purity 99% (Chem Service West Chester, PA), were used for making the organoclay formulations of both herbicides. The commercial formulation (EC) of alachlor [Alanex, 480 g of active ingredient (ai)/kg, Agan Chemical Manufacturers Ltd., Ashdod, Israel] and metolachlor (Dual, 960 g of ai/kg, Novartis) were used as standard formulations.

HPLC grade ethyl acetate and isooctane were purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO; Aldrich Chemical Co., Milwaukee, WI). Analytical grade NaCl was obtained from Frutarom Laboratory Chemicals (Haifa, Israel). PTMA was obtained as chloride salt from Aldrich Chemical Co. The chemical structures of these materials are shown in Figure 1. Soils were collected from 0–30 cm depth at the Faculty of Agriculture Experimental Station in Rehovot and Agricultural Experimental Station of EPRI in Gaza. Soil properties were as in El-Nahhal et al. (1998). *Setaria viridis* was used as a test plant.

Adsorption Studies. The adsorption of PTMA on montmorillonite was measured at added amounts of 0.3–6 mmol/g of clay. To measure the adsorption of the cation, aliquots of an aqueous 1×10^{-2} M solution of the cation were added to 5 mL of a 1% clay mineral suspension. The final volume was brought to 50 mL with distilled water. Adsorption was also measured in the presence of 50, 100, and 500 mM NaCl. The suspensions were equilibrated by continuous horizontal agitation for 48 h. The supernatants were separated by centrifugation at 1500g. The concentration of the organic cation at each filtrate was determined by measuring the optical density at 254 nm using a UV-vis spectrophotometer.

In certain cases the measurements also employed a CHNSO analyzer (Carlo-Erba 1108, Fisons Co., Milan, Italy). In this procedure standard amounts of the organic cation were used in advance to calibrate the equipment. To determine the elemental contents, 2 mg samples of the dried organoclay

complex were analyzed for carbon, hydrogen, oxygen, and nitrogen. All of the organoclay complexes were subjected to this analysis in duplicate.

Preparation of Organoclay Complexes. The organoclay complexes were prepared by dropwise addition of aliquots of a 10 mM aqueous solution of PTMA to a 1% (w/v) aqueous suspension of the clay under continuous stirring (Margulies et al., 1992). After 30 min of centrifugation (1500g), the precipitate was washed three times with distilled water, freeze-dried, ground to $<50 \mu\text{m}$, and kept in plastic bottles at room temperature.

Adsorption Isotherms of Alachlor and Metolachlor. The adsorption isotherms were measured in the range of 0–700 μmol of alachlor or metolachlor/g of clay–PTMA complex at a loading of 0.5 or 0.8 mmol of PTMA/g of clay. To measure adsorption isotherms, appropriate aliquots of an aqueous stock solution of alachlor or metolachlor (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) clay–PTMA suspension in a 40 mL centrifuge tube. The final concentration of the organoclay complex was 0.83 g/L. The samples were kept under continuous horizontal agitation at $25 \pm 1^\circ\text{C}$ during 48 h. The supernatant was separated by centrifugation at 20000g for 1 h. The herbicides were extracted from the supernatant and determined by GC as described in El-Nahhal et al. (1998, 1999b).

Preparation of Herbicide Formulations. Appropriate amounts of alachlor or metolachlor were dissolved in 1 L of distilled water to form a stock solution of 700 $\mu\text{mol/L}$. Appropriate amounts of alachlor or metolachlor equivalent to 100–400 $\mu\text{mol/g}$ of clay complex were added to a 1 L volumetric flask. The final volume was brought to 1 L, and 1 g of clay–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 horizontal agitation. The pellets were separated by centrifugation at 15000g, and the adsorbed amounts of herbicides were measured as described above.

Model Calculations. *A. Adsorption of Organic Cations.* The program used considers cation binding to the negatively charged surface sites of the clay mineral and the electrostatic Gouy–Chapman equations and solves iteratively for the solution concentrations of all cations in a closed system. Cation adsorption is obtained by considering specific binding and residence in the double-layer region. If cation adsorption occurs at amounts below the CEC, then there is an excess of cations in the double-layer region, whereas if charge reversal occurs, as in the case of certain organic cations, then there is some exclusion of cations (Margulies et al., 1988a). The binding of organic monovalent cations is described in eqs 1–4 below.

Let X_i^+ denote a monovalent cation that binds to a singly charged negative site, P^- , on the surface of the silicate:

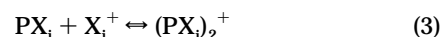


with a binding coefficient, K_i , given by

$$K_i = [PX_i]/([P^-][X_i(0)^+]) \quad (2)$$

in which $[X_i(0)^+]$ is the concentration of the cation at the surface.

Another type of complexation is considered in the case of organic cations:



with a binding coefficient of

$$\bar{K}_i = [(PX_i)_2^+]/([PX_i][X_i(0)^+]) \quad (4)$$

In eqs 2 and 4 the concentrations are given in units of mol L^{-1} , or M, and the unit of K_i or \bar{K}_i is M^{-1} .

The binding coefficients K and \bar{K} for PTMA were determined as in Margulies et al. (1988a), Nir et al. (1994a,b), and Rytwo et al. (1995). The values of the other binding coefficients were

Table 1. PTMA Adsorption on Montmorillonite: Experimental and Calculated Quantities

added PTMA (mol/kg)	adsorbed PTMA (mol/kg)		fraction of charged complex (%)	
	exptl	calcd $K = 1500 \text{ M}^{-1}$, $\bar{K} = 300 \text{ M}^{-1}$	$K = 1500 \text{ M}^{-1}$, $\bar{K} = 300 \text{ M}^{-1}$	$K = 3000 \text{ M}^{-1}$, $\bar{K} = 150 \text{ M}^{-1}$
0.3	0.3 ± 0.0	0.3	24	9.3
0.5	0.47 ± 0.03	0.48	32.7	15.2
0.5 (+ 50 mM NaCl)	0.38 ± 0.04	0.41	19.3	11.9
0.5 (+ 100 mM NaCl)	0.38 ± 0.04	0.38	18.3	11.2
0.5 (+ 500 mM NaCl)	0.32 ± 0.04	0.27	15.5	9.9
0.8	0.65 ± 0.09	0.7	41.4	23.9
1	0.68 ± 0.09	0.76	44.2	27.2
1.25	0.77 ± 0.09	0.79	45.5	28.8
1.25 (+ 50 mM NaCl)	0.59 ± 0.07	0.69	41.4	24.4
1.25 (+ 100 M NaCl)	0.70 ± 0.06	0.66	40.2	23.3
1.25 (+ 500 mM NaCl)	0.45 ± 0.06	0.53	37.7	21.3
1.6	0.72 ± 0.09	0.8	46.3	29.8
2.4	0.75 ± 0.09	0.81	47.3	31
4	0.87 ± 0.09	0.83	48.7	32.8
5	1 ± 0.1	0.84	49.5	33.7
5 (+ 100 mM NaCl)	1.02 ± 0.17	0.92	54.7	39.9
5 (+ 500 mM NaCl)	1.1 ± 0.18	0.96	59.4	44.7
6	1.09 ± 0.12	0.86	50.1	34.7
6 (+ 100 mM NaCl)	1 ± 0.16	0.95	56.4	42
6 (+ 500 mM NaCl)	1.13 ± 0.15	1.01	61.9	47.7

^a The fit of calculated to experimental values gave $R^2 = 0.89$ and root-mean-square error (RMSE) = 0.09.

as in Nir et al. (1986) and Rytwo et al. (1996b). As will be discussed, a quantity of interest is the fraction of charged complexes, which is given by $2[\text{P}(\text{X}_i)_2^+]/[\text{PX}_i]$.

Sorption of Herbicides by Organomontmorillonite. The Langmuir equation (or Scatchard equation), which is based on the assumption of the lack of interactions, that is, the lack of cooperativity between adsorbed molecules, was used to describe the sorption of the herbicides by the clay or organoclays. We presented results based on the use of a single parameter, k , the binding coefficient (M^{-1}).

Fourier Transform Infrared (FTIR). FTIR spectroscopy was used to examine the interaction of PTMA molecules with clay surfaces and between alachlor or metolachlor and the organoclay as previously described (Margulies et al., 1988b; El-Nahhal et al., 1998). Briefly, infrared spectra were obtained using KBr pellets with a Fourier transform infrared 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 in addition to difference spectra, which were obtained by subtracting the spectra of corresponding organoclay or homoionic clay from the spectra of clay–organic–herbicide complexes or clay–herbicide complexes.

Release Experiments. Release of the active ingredient from the complex to water was conducted by suspending equivalent amounts of the complex (clay–PTMA0.5–alachlor) in dialysis bags to form 1, 0.5, and 0.1% clay complex suspension within the dialysis bag, or 0.038, 0.12, and 0.24 and 0.5 g/L for the whole volume of the system. In this procedure equivalent amounts of the herbicide complex were added in a dialysis bag along with the equivalent amount of water to form the needed suspension and tied at both sides by a fine plastic string. Each bag was immersed in a volumetric flask containing 1 L of distilled water and a magnetic stirrer to ensure homogenized distribution of the released active ingredient. Samples were taken after 1, 2, 4, 8, 24, and 48 h from each volumetric flask, extracted, and analyzed by GC as described in the previous section on adsorption.

Another procedure was employed by adding 150 mg of clay–PTMA0.5 and clay–BTMA0.5 complex of the herbicide directly to a plastic tube containing 30 mL of distilled water to form a 0.5% clay suspension. Samples were kept under continuous horizontal agitation for 1–4 h and 1, 2, 4, and 7 days. Samples were then centrifuged at 15000g, and the supernatant was extracted and analyzed by GC as described above.

Leaching Studies (Greenhouse Condition). Tin macrocolumns, 10 × 10 cm surface area, 25 cm height, and microcolumns made of polyethylene tubes, surface area of 5

cm^2 , 25 cm height, were used to evaluate herbicide leaching in a sandy soil as previously described (El-Nahhal et al., 1998, 1999b). The macrocolumn surface was sprayed with various formulations of alachlor or metolachlor at 2.0 kg of ai/ha using an atomizer, whereas in microcolumns the herbicide formulation was applied with a pipet. The columns were carefully irrigated with 500 m^3/ha (50 mm), applied in portions during 3–5 h with 20 min intervals. The macrocolumns were left for 24–48 h for equilibration, and then the tin columns were sliced along their lengths, hence forming two pots 10 × 5 × 25 cm each. Green foxtail was sown in each column half in two rows. Percent of shoot growth inhibition at a particular soil depth was calculated according to the following formula:

$$\% \text{ growth inhibition} = 100 \times (P_c - P_t)/P_c \quad (5)$$

where P_c and P_t are the shoot height of the control and the treated samples at any soil depth.

Data Analysis. Adsorption data were subjected to analysis of variance, and main effects and interactions were tested for significance using repeated measures ANOVA. Means of adsorption data were compared by linear regression analysis. Univariate comparisons of mean growth inhibition at different depths were performed by Tukey's test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Adsorption of PTMA on Montmorillonite. The results in Table 1 demonstrate that when the added amount of PTMA is up to about half of the CEC of montmorillonite, most of the added amount is adsorbed, whereas when the added amount is twice the CEC, the fraction adsorbed is less than half. When the added amount of PTMA is 5-fold of the CEC or above, the adsorbed amount exceeds the CEC. From the fact that at lower added amounts the adsorption of PTMA is almost complete, it can be deduced that its binding coefficient for adsorption on montmorillonite is at least several fold larger than those of the exchangeable cations, similar to the results with other organic cations (Margulies et al., 1988a; Nir et al., 1994a; Rytwo et al., 1995). Unlike the larger cations, BTMA or BTEA, which have structural similarity to PTMA (Figure 1), the adsorbed amounts of PTMA exceed the CEC, which implies that the binding coefficient, \bar{K} (eq 4) is larger in the case of PTMA. On the other hand, for adsorption

below CEC, the fraction of PTMA adsorbed is less than that of BTMA or BTEA (Polubesova et al., 1997) and is reduced more extensively in the presence of increasing NaCl concentrations. Accordingly, it may be anticipated that K values for the formation of the neutral complexes with the negatively charged sites of the clay mineral would be smaller than those of BTMA/BTEA, whereas the value of \bar{K} , the binding coefficient for the formation of charged dimers (eqs 2 and 4) would be larger. The corresponding values of the parameters employed are $K = 1500 \text{ M}^{-1}$ and $\bar{K} = 300 \text{ M}^{-1}$, with $\sim 50\%$ uncertainty. The corresponding values for BTMA/BTEA are $K = 5000 \text{ M}^{-1}$ and $\bar{K} = 20 \text{ M}^{-1}$ and 5 M^{-1} , respectively. Table 1 indicates that the calculations yielded fair simulations and predictions for the adsorbed amounts of PTMA for NaCl concentrations varying from 0 to 500 mM. The model explains well the trend of reduction and increase in the adsorbed amounts of PTMA with an increase in the ionic strength for the adsorption below and above the CEC, respectively. As stated before (Margulies et al., 1988a; Nir et al., 1994a; Rytwo et al., 1995), the model predicts that the amount of certain adsorbed monovalent organic cations, for example, PTMA, will increase with the ionic strength whenever charge reversal occurs, that is, for PTMA adsorption beyond the CEC.

Table 1 also shows the fraction of PTMA forming charged dimers, when the calculations employ the parameters that give the best fit, $K = 1500 \text{ M}^{-1}$ and $\bar{K} = 300 \text{ M}^{-1}$. We also provide these fractions for a fit that is only slightly worse, with a smaller \bar{K} value, e.g., $K = 3000 \text{ M}^{-1}$ and $\bar{K} = 150 \text{ M}^{-1}$.

The effect of the charged dimers will be elaborated under Discussion. At this stage it may be noted that the above fractions increase when \bar{K} is larger and K is smaller as can be expected by an inspection of eqs 1–4. For adsorbed amounts of PTMA below the CEC, the fraction of the charged dimers decreases in the presence of high NaCl concentrations, whereas the opposite trend is observed above the CEC. This trend was previously explained and predicted (Margulies et al., 1988a; Nir et al., 1994a). An increase in the clay concentration results in a small increase in the above fraction (results not shown).

Adsorption of Alachlor and Metolachlor. The adsorption isotherms of alachlor and metolachlor on a clay mineral preadsorbed with PTMA at a loading of 0.5 or 0.8 mmol/g of clay are shown in Figure 2. As previously reported, alachlor (Yen et al., 1994; El-Nahhal et al., 1998) and metolachlor (El-Nahhal et al., 1999b) poorly adsorbed on montmorillonite alone, whereas their adsorption on a clay mineral preadsorbed with PTMA resulted in a dramatic increase in the adsorbed amounts of both herbicides (Figure 2). The low adsorption of both herbicides on the unmodified clay surfaces is due to the hydrated mineral surface of the clay and the hydrophobicity of the herbicide molecules. Partial saturation of the clay with PTMA at a load of 0.5 mmol/g of clay resulted in better adsorption of alachlor or metolachlor than that at a loading corresponding to the CEC (0.8 mmol/g of clay). A similar trend was obtained by using BTMA as a clay-modifying agent (El-Nahhal et al., 1998). These data indicate that achieving maximal transformation of the clay surface from hydrophilic to hydrophobic does not necessarily imply optimal interactions between the herbicide molecules and the organoclay complex. The adsorption of

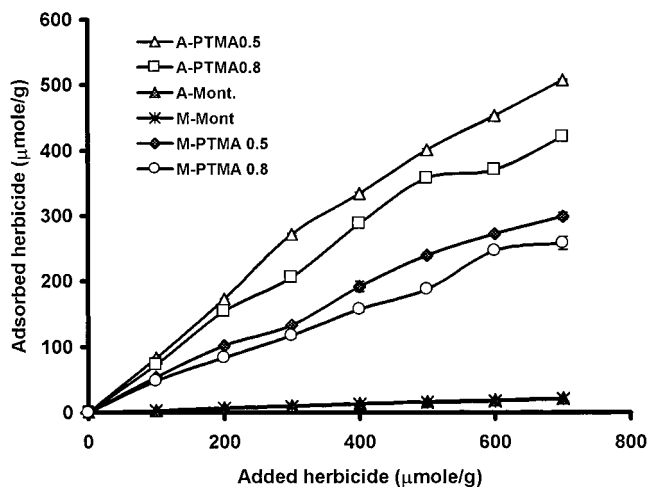


Figure 2. Adsorption isotherms of alachlor and metolachlor on a clay mineral preadsorbed with PTMA at a loading of 0.5 or 0.8 mmol/g of clay. "A" and "M" represent alachlor and metolachlor, respectively. Bars indicate standard errors.

Table 2. Binding Coefficients Describing Sorption of Alachlor and Metolachlor on Montmorillonite and Mont-PTMA Prepared at Several Loads

system	organic cation	loading (mol/kg)	$K (\text{M}^{-1})$	R^2
alachlor	none		50	0.99
	PTMA	0.5	11000	0.999
	PTMA	0.8	5000	0.99
metolachlor	none		45	0.99
	PTMA	0.5	2880	0.99
	PTMA	0.8	1900	0.98

both herbicides increases almost linearly as their concentration in the equilibrium solution is increased.

The results suggest that alachlor or metolachlor sorption on the organoclay complex is not primarily due to partitioning. The absence of a methylene bridge in the structure of the organic cation such as in PTMA resulted in a dramatic increase in the adsorbed amounts for both herbicides compared with those obtained by using organic cations having a methylene bridge between the phenyl ring and the ammonium nitrogen, such as BTMA or BTEA (El-Nahhal et al., 1998, 1999b). These results suggest that alachlor and metolachlor sorption on organoclays is dependent on the size and shape of the organic cations preadsorbed on the clay, as previously reported for alachlor (El-Nahhal et al., 1998) and other cases (Lee et al., 1989). The results suggest that the absence of a methylene bridge optimizes the interactions between the phenyl ring of the aromatic cation (PTMA) and the phenyl ring of herbicide molecules. 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 suggested by Stevens and Anderson (1996).

Table 2 illustrates that alachlor and/or metolachlor have larger sorption affinity on clay-PTMA than on clay-BTMA/BTEA (El-Nahhal et al., 1998, 1999b). A similar trend for enhanced interactions between alachlor or metolachlor and Mont-PTMA as compared with Mont-BTMA or Mont-BTEA was observed in leaching experiments. These data may indicate that the use of clay-PTMA-based formulations of alachlor or metolachlor would be better than the use of clay-BTMA/

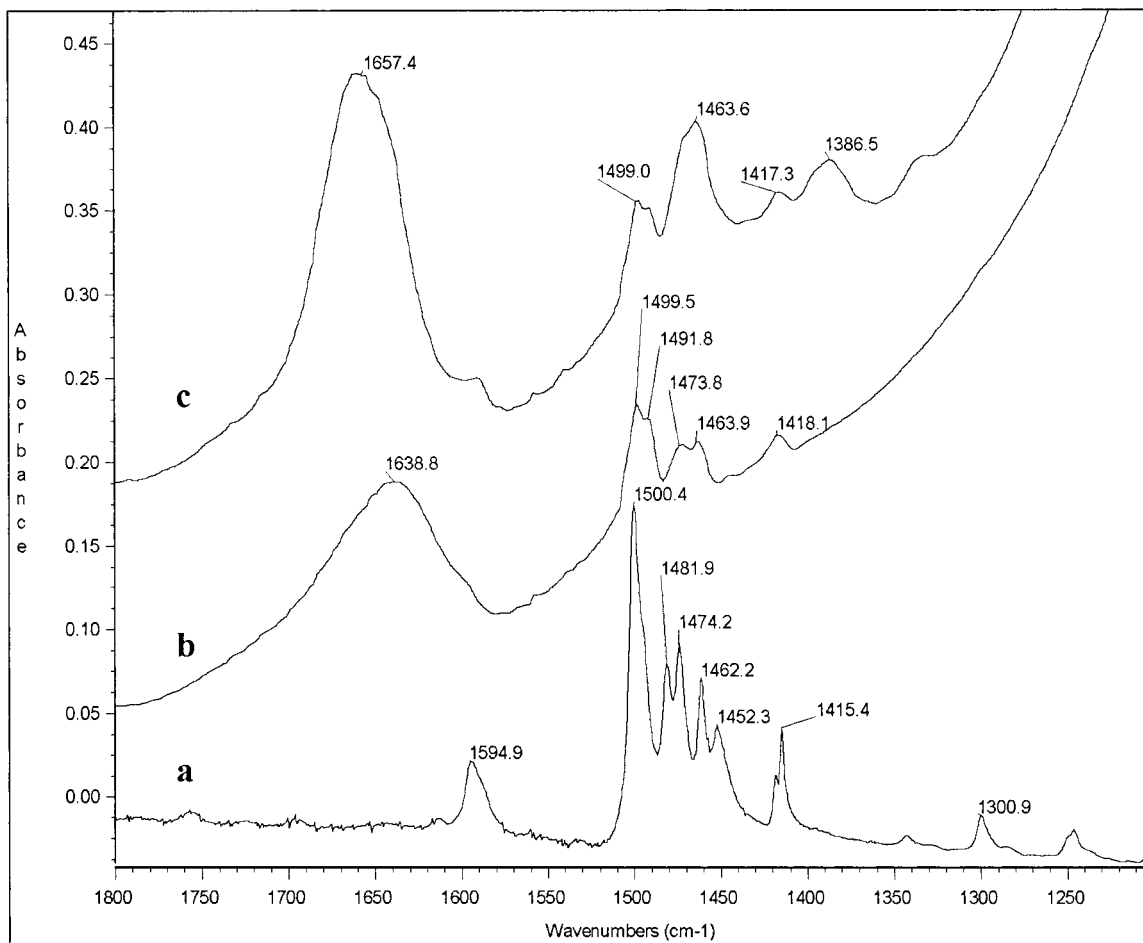


Figure 3. FTIR absorption spectra of free PTMA (a), PTMA adsorbed on montmorillonite (b), at a loading of 0.8 mol/kg of clay, and Mont-PTMA0.8-alachlor 5% (c).

BTEA, which in turn was shown (El-Nahhal et al., 1998) to be much better than the use of clay-HDTMA (hexadecyltrimethylammonium).

Adsorption isotherms for alachlor and metolachlor were not significantly different at low concentrations, but at higher concentrations adsorption of alachlor exceeded significantly that of metolachlor. Higher adsorption of alachlor than metolachlor by these organoclays suggests that alachlor would be less mobile in the soil profile or more slowly released from the complex to an aqueous or soil environment. The lower affinity of metolachlor for binding by the organoclay complex is correlated with its higher solubility in water; metolachlor has a lower $\log P$ (2.9) than that of alachlor (3.09). It has been reported that compounds with lower water solubility are adsorbed to a larger extent on soil organic matter than compounds of higher solubility (Carringer et al., 1975).

FTIR. Detailed information on the interactions between alachlor or metolachlor molecules and the Mont-PTMA complex was obtained by using infrared spectroscopy. Figure 3 shows the spectra of PTMA in its free form (a) and adsorbed on Mont at a loading of 0.8 mol/kg (b) and of Mont-PTMA0.8-alachlor 5% (c). The peaks in the spectrum of free PTMA (a) were assigned to the stretching vibrations of the phenyl group at 1500.4, 1474.2, and 1462.2 cm^{-1} and the ammonium group (1300.9 cm^{-1}).

The main differences among the spectra are disappearance of the peak at 1300.9 cm^{-1} of the free PTMA

(a) due to strong interaction between the ammonium nitrogen (positive charge) and the adsorption sites on the clay surfaces (negative charge). This interaction resulted in a fixation of the ammonium group on the clay surfaces. Addition of alachlor to the complex (Mont-PTMA0.8) at a loading of 5% (c) resulted in a disappearance of the peak at 1473.8 cm^{-1} in spectrum c and the increased intensities of the peaks 1499 at 1463.6 cm^{-1} (phenyl group). These results suggest that adsorption of PTMA on montmorillonite provides suitable adsorption sites for the aromatic hydrophobic herbicides due to interactions between phenyl rings.

Figure 4 shows the difference spectra of alachlor in its free form (a) and adsorbed on Mont-PTMA at a loading of 0.5 mmol/g (b). The four peaks at 1690.3, 1458.7, 1406.2, and 1373.5 cm^{-1} in the spectrum of free alachlor (a) were assigned to the stretching vibrations of the -C=O group (1690.3 cm^{-1}), the phenyl ring (1458.7 and 1406.2 cm^{-1}), and the anilidic group (1373.5 cm^{-1}) (Charles, 1981; Bosetto et al., 1993). The main differences among the spectra include the following: (1) The peak at 1690.3 cm^{-1} (carbonyl group) of the free alachlor (a) shifts to a lower wavenumber at 1665.4 cm^{-1} (b). (2) The peaks at 1458.7 and 1406.2 cm^{-1} (phenyl group) of free alachlor (a) were shifted to higher wavenumbers at 1462.2 with a shoulder at 1468.6 and 1421.4 cm^{-1} , respectively. (3) The peak at 1373.5 cm^{-1} (a) (anilidic group) was shifted into two peaks at 1380.3 and 1390.3 cm^{-1} (b). These shifts indicate that alachlor molecules interact strongly with the Mont-PTMA com-

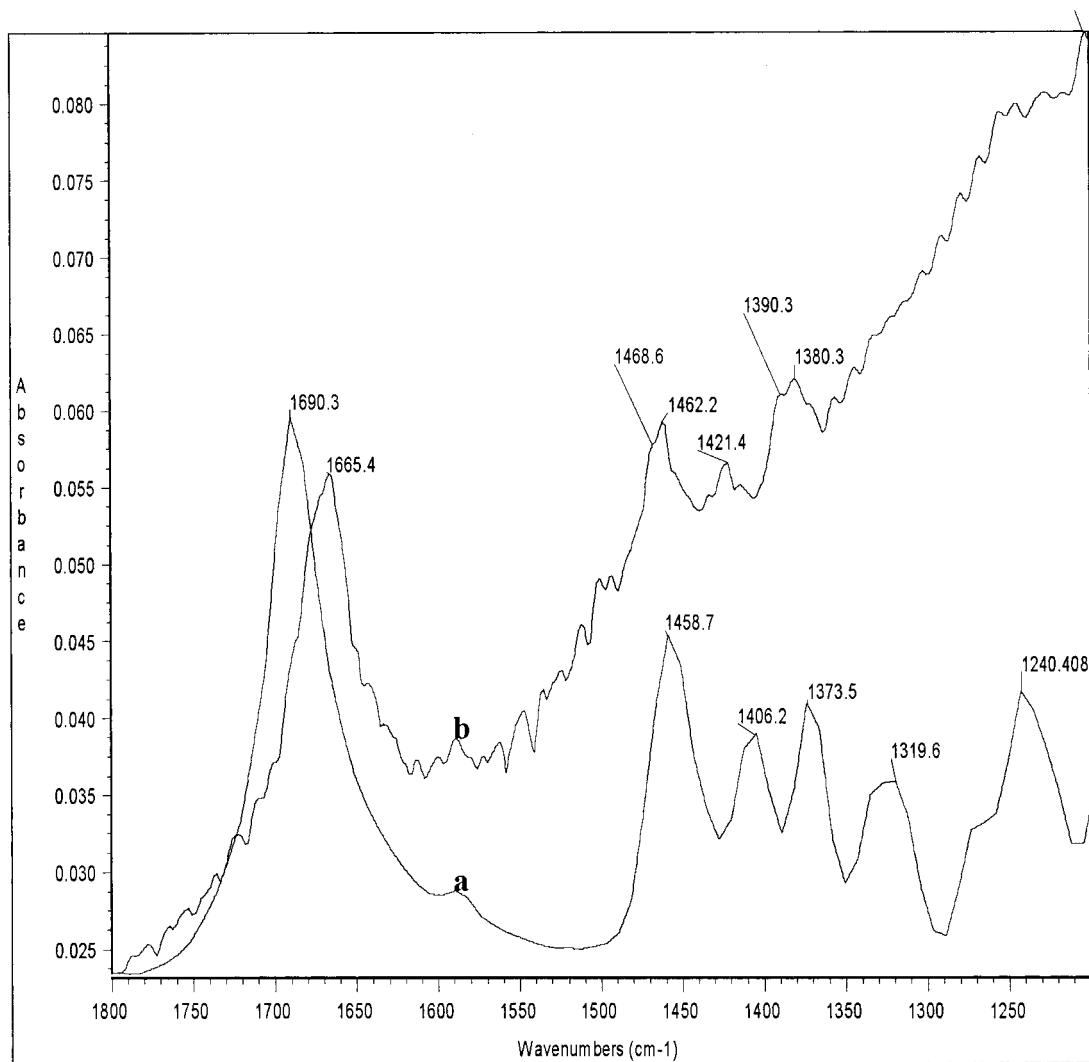


Figure 4. FTIR absorption spectra of free alachlor (a) and alachlor adsorbed on montmorillonite preadsorbed by PTMA at a loading of 0.5 mol/kg of clay (b). Difference spectra were obtained by subtracting Mont-PTMA0.5 from Mont-PTMA0.5-alachlor.

plex through the phenyl rings, the anilidic group, and the carbonyl group. A comparison of the spectra in Figure 4 with those of alachlor adsorbed on BTMA-Mont or BTEA-Mont (El-Nahhal et al., 1998) indicates that the interactions of the carbonyl and the anilidic groups are stronger with PTMA than with the larger organic cations, BTMA or BTEA. In the latter cases the stretching vibration of the carbonyl group was shifted to lower wavenumbers 1683.9 and 1684.8 cm^{-1} , respectively; the anilidic group was shifted to 1375.5 with a shoulder at 1387.6 and 1381 cm^{-1} respectively, and the stretching vibration of the phenyl ring at the peak at 1406.2 cm^{-1} was not significantly changed (El-Nahhal et al., 1998). In the case of PTMA, the bond length between the phenyl ring and the ammonium nitrogen is probably the same as in alachlor, which might enhance the interaction between phenyl rings at the clay surface. In addition, this may provide a suitable interaction site with the carbonyl group as shown by the higher shifts of the corresponding bands. These interactions were less effective in the case of BTMA (El-Nahhal et al., 1998), probably due to the presence of the methylene group between the ammonium nitrogen and phenyl ring in the organic cation (Figure 1). The presence of this group may increase the bond length, which decreases the interaction. These results are in

accord with the higher adsorbed amounts of alachlor on Mont-PTMA, in comparison with the other organoclays.

Figure 5 shows the difference spectra of metolachlor in its free form (a) and adsorbed on Mont-PTMA at a loading of 0.5 (b) and at a loading of 0.8 mol/kg (c). The three peaks at 1674.9, 1458.7, and 1366.3 cm^{-1} in the spectrum of free metolachlor (a) were assigned to the stretching vibrations of the $-\text{C}=\text{O}$ group (1674.9 cm^{-1}), the phenyl ring (1458.7 cm^{-1}), and the anilidic group (1366.3 cm^{-1}) (Charles, 1981; Bosetto et al., 1994). The main differences among the spectra are shifts of (1) the peak at 1674.9 cm^{-1} of free metolachlor (a) to lower wavenumbers at 1662.9 cm^{-1} (b) and 1671.7 cm^{-1} (c), (2) the peak at 1458.7 cm^{-1} of free metolachlor (a) to a higher wavenumber at 1466.5 cm^{-1} with an inverted peak at 1500.5 cm^{-1} (b) and 1458.9 cm^{-1} with an inverted peak at 1500.5 cm^{-1} (c), and (3) the peak at 1366.3 cm^{-1} (a) to a higher wavenumber at 1387.6 cm^{-1} (b) and 1385.4 cm^{-1} (c). These results indicate larger shifts of the peaks at PTMA loading of 0.5 mol/kg than at a loading up to the CEC.

The interaction of metolachlor with Mont-PTMA is more pronounced than its interaction with montmorillonite preadsorbed by larger organic cations such as BTMA or BTEA. For instance, the band describing the stretching vibration of the phenyl ring of the free

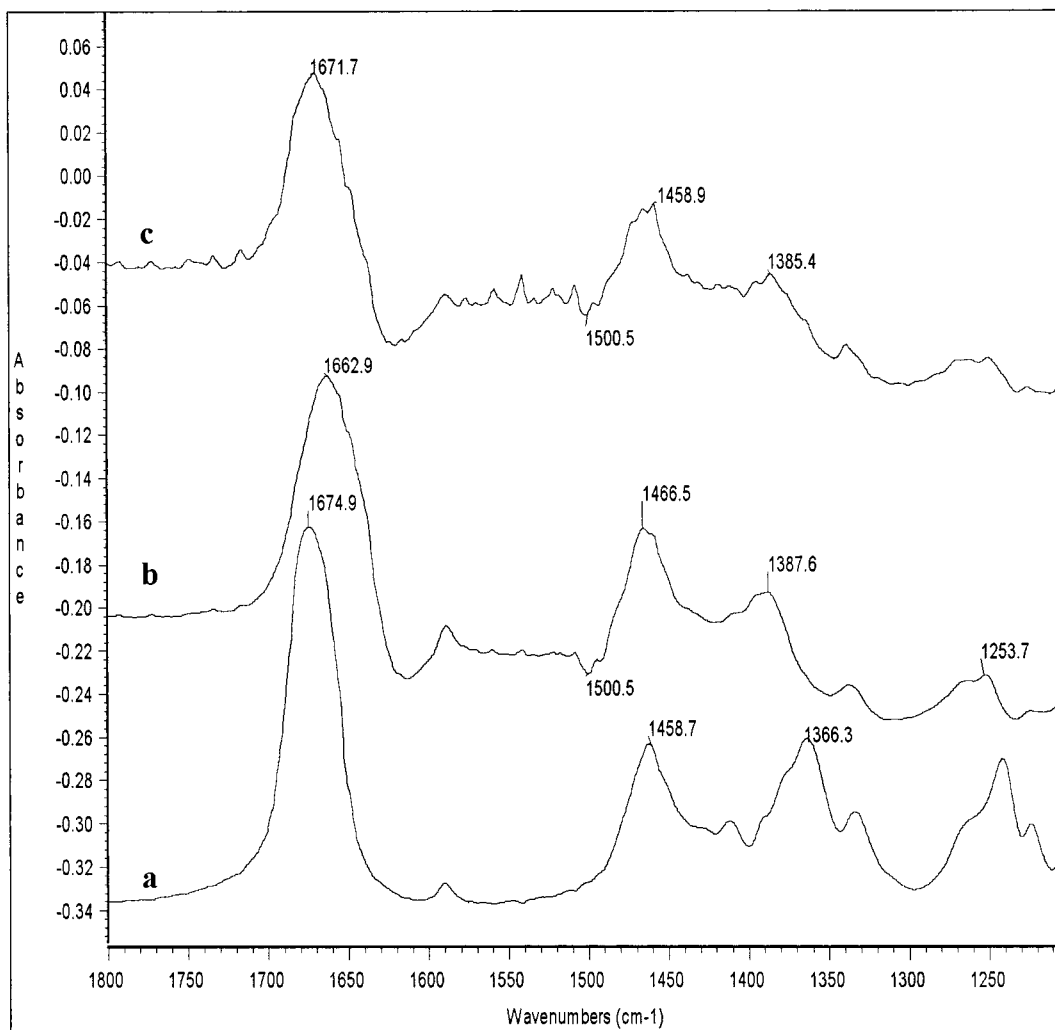


Figure 5. FTIR absorption spectra of free metolachlor (a) and metolachlor adsorbed on montmorillonite preadsorbed by PTMA at loadings of 0.5 and 0.8 mol/kg of clay (b and c, respectively). Difference spectra were obtained by subtracting Mont-PTMA0.5 from Mont-PTMA0.5-metolachlor and Mont-PTMA0.8 from Mont-PTMA0.8-metolachlor.

metolachlor molecules was shifted to 1466.3 cm^{-1} with an inverted peak at 1489.7 cm^{-1} in Mont-BTMA and to 1466.7 cm^{-1} with Mont-BTEA (El-Nahhal et al., 1999b).

The higher shift of stretching vibration of the anilidic group in metolachlor adsorbed on Mont-PTMA in comparison with other complexes suggests the importance of the bond length and the chemical structure of the preadsorbed organic cation. Our explanation of these data is similar to that given for alachlor (Figure 3). These data are in accord with adsorption, release, and leaching results.

Release Experiments. The release of alachlor and metolachlor from several organoclay formulations is shown in Figures 6 and 7. Clearly, the rates and extents of release depend on the clay concentration in suspension. For instance, the Mont-PTMA0.5-alachlor suspensions at 0.0038, 0.012, 0.024, and 0.5 (w/w)% released after 48 h 43, 14.4, 10.0 and 1.1% of their contents of ai, respectively.

In Table 3 we provide estimates based on the binding coefficient, k (Table 2), for the percent of herbicide release expected under equilibrium conditions. We also provide the effective rate of herbicide release in water, which initially followed first-order kinetics

$$I = I_0 e^{-Dt}$$

where I_0 and I are the initial bound and unreleased herbicide concentrations at time t , respectively, and D is the rate constant of release (days^{-1}). The release rate constant (D) was calculated by linear regression from the first-order rate equation, $\ln I = \ln I_0 - Dt$.

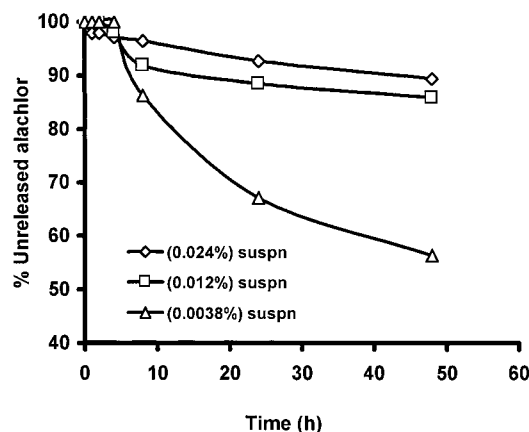
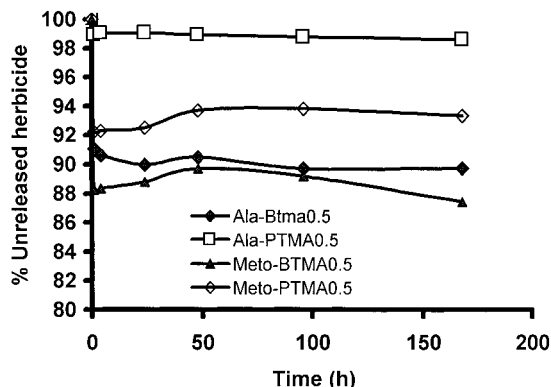
The approximate validity of the above equation follows from the fact that during the first hours the percent of herbicide released is still significantly less than the percent released expected under equilibrium conditions (Nir et al., 1994b).

The herbicide formulations based on Mont-PTMA0.5 yielded slower rates of release than those deduced for Mont-BTMA0.5. It is remarkable that even after 7 days the fraction of alachlor released is still about half of the expected value at equilibrium; for metolachlor it amounts to ~ 0.8 . This demonstrates that the organoclay herbicide formulations are excellent candidates for reducing herbicide leaching and contamination of groundwater. The ability of the organoclay formulations to yield slow release probably stems from their structure in suspension, which results in hysteresis.

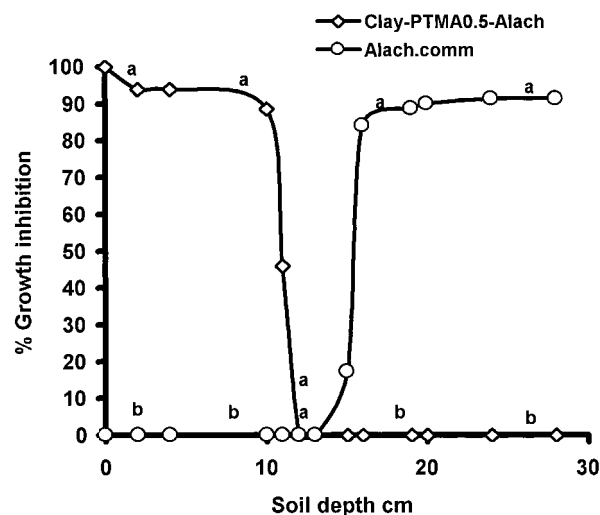
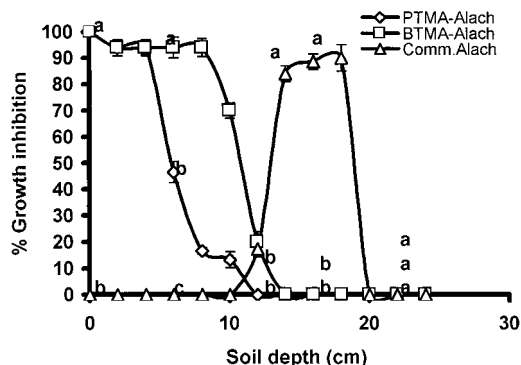
Leaching Studies under Laboratory Conditions. Results of the laboratory experiments using microcolumns (Gaza) and macrocolumns (Rehovot) filled with

Table 3. Herbicide Release: Comparison with Calculated Release at Equilibrium

herbicide formulation	total herbicide concn (μM)	clay concn (% w/w)	% release after 48 h	% release after 7 days	% release at equilibrium (calcd)	rate constant of release (days^{-1})
Mont-PTMA0.5-alachlor ^a	17.01	0.024	10.6 \pm 1.4		33.5	0.056
Mont-PTMA0.5-alachlor ^a	8.50	0.012	14.4 \pm 1.9		49.7	0.078
Mont-PTMA0.5-alachlor ^a	2.66	0.0038	43.0 \pm 6.0		75.0	0.28
Mont-PTMA0.5-alachlor	413.00	0.50	1.1 \pm 0.04	1.4 \pm 0.01	2.5	0.0055
Mont-BTMA0.5-alachlor	174.14	0.50	9.5 \pm 0.24	10.3 \pm 0.7	21.6	0.036
Mont-PTMA0.5-metolachlor	324.00	0.50	6.3 \pm 0.1	6.7 \pm 0.1	8.6	0.032
Mont-BTMA0.5-metolachlor	133.84	0.50	10.3 \pm 0.2	12.6 \pm 0.3	28.4	0.078

^a In dialysis bag.**Figure 6.** Release of alachlor from Mont-PTMA0.5 in a suspension of 0.024, 0.012, and 0.0038% (w/w) of the complex in an aqueous suspension. Standard deviation was below the size of the symbols.**Figure 7.** Release of alachlor and metolachlor from Mont-PTMA0.5 in a suspension of 0.5% (w/w) in water under continuous horizontal agitation. Standard deviation was $<1\%$.

sandy soil have shown that the commercial EC alachlor formulation applied pre-emergence at the recommended rate (2 kg/ha) followed by irrigation corresponding to 500 m³/ha leaches below the top 14 cm of the column (Figures 8 and 9). The leaching depths were somewhat larger with the microcolumns than with the macro ones. Strong herbicidal activity was detected at soil depths of 15–25 cm (Figure 8) and 14–20 cm (Figure 9), indicating that most of the herbicide applied leached into the soil depth. Little reduction in leaching was observed for alachlor formulated with montmorillonite without any surface modification (El-Nahhal et al., 1998). Alachlor formulated with either clay-PTMA0.5 or clay-BTMA0.5 complex resulted in an excellent herbicidal activity limited to the top 10 cm (Figure 8) and 5 cm (Figure 9). These data indicate that alachlor was released at a slower rate from the PTMA0.5-clay formulation than from the BTMA0.5-clay in accord

**Figure 8.** Leaching of alachlor (2.0 kg/ha) in columns filled with sandy soil from a Gaza farm following irrigation with 500 m³/ha. Green foxtail growth was used to estimate the presence of alachlor. Alachlor formulations were commercial EC formulation (Comm.Alach) and alachlor adsorbed on montmorillonite preadsorbed by PTMA (0.5 mmol/g), clay-PTMA-Alach. The organoclay-based formulation contained 13% alachlor. Means followed by a different letter at a representative depth are significantly different at the $p = 0.05$ level.**Figure 9.** Leaching of alachlor (2.0 kg/ha) in columns filled with sandy soil from a Rehovot farm following irrigation with 500 m³/ha. Green foxtail growth was used to estimate the presence of alachlor. Alachlor formulations were commercial EC formulation (Comm.Alach) and alachlor adsorbed on montmorillonite preadsorbed by PTMA or BTMA (0.5 mmol/g), PTMA-Alach or BTMA-Alach. The organoclay-based formulation contained 5% alachlor. Means followed by a different letter at a representative depth are significantly different at the $p = 0.05$ level. Bars indicate standard error.

with the data in Table 2. Herbicidal activity of alachlor released from PTMA0.5/BTMA0.5-clay complexes was almost 100% in the topsoil layer (8–10 cm) and zero at a depth >11 cm. The organoclay complex with a load of 0.5 mmol of PTMA/g of clay was optimal in inhibiting the leaching, whereas more leaching was observed for

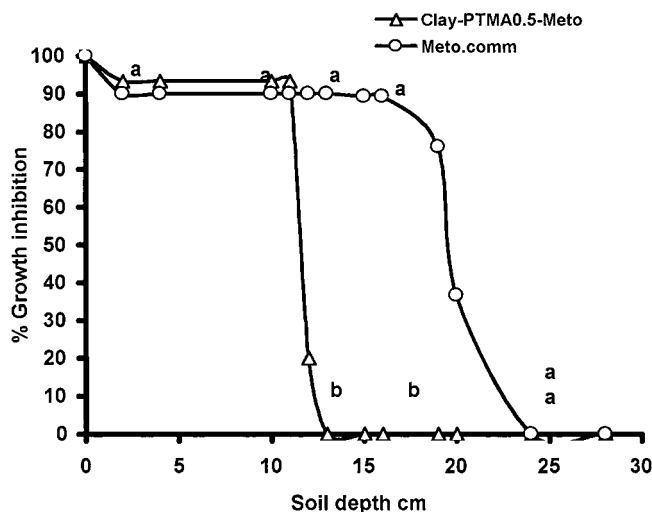


Figure 10. Leaching from formulations of metolachlor (2.0 kg/ha) in microcolumns filled with sandy soil from a Gaza farm following irrigation with 500 m³/ha using microcolumn techniques. Metolachlor formulations were commercial EC formulation (Meto.comm) and metolachlor adsorbed on montmorillonite preadsorbed by PTMA (0.5 mmol/g) Mont-PTMA0.5-Meto. The organoclay-based formulation contained 5% metolachlor. Means followed by a different letter at a representative depth are significantly different at the $p = 0.05$ level. Standard deviation was <0.8%.

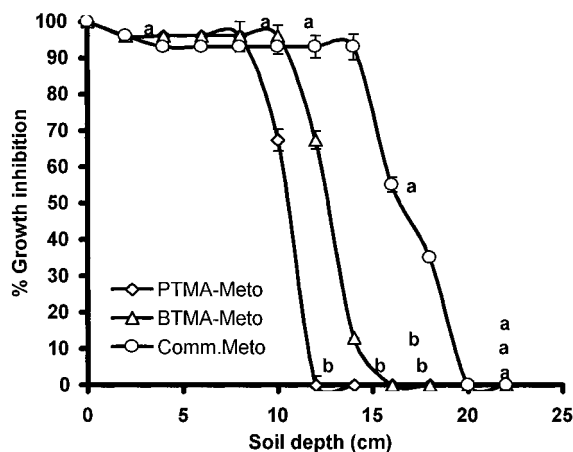


Figure 11. Leaching from formulations of metolachlor (2.0 kg/ha) in columns filled with sandy soil from a Rehovot farm following irrigation with 500 m³/ha using macrocolumn technique. Metolachlor formulations were commercial EC formulation (Meto.comm) and metolachlor adsorbed on montmorillonite preadsorbed by PTMA or BTMA (0.5 mmol/g), PTMA-Meto and BTMA-Meto. The organoclay-based formulation contained 5% metolachlor. Means followed by a different letter at a representative depth are significantly different at the $p = 0.05$ level. Bars indicate standard deviation.

the alachlor formulation based on 0.8 mmol of PTMA/g of clay (data not shown). The results demonstrate that optimal adsorption of alachlor paralleled optimal reduction in leaching and optimal herbicidal activity at the topsoil, in accord with the release experiments (Figures 6 and 7).

Statistical analysis showed significant difference between the results obtained by employing the organoclay formulation and the commercial one both in Gaza and in Rehovot soils.

The commercial formulation of metolachlor (EC) applied pre-emergence at the recommended rate (2.0 kg/ha) using microcolumns in Gaza and macrocolumns in Rehovot filled with sandy soil followed by irrigation

corresponding to 500 m³/ha leached to a depth of up to 20 cm (Figures 10 and 11). The herbicidal activity detected below that depth declined rapidly. Similar mobility of metolachlor in soil was previously reported (Gorski et al., 1989; El-Nahhal et al., 1999b). More leaching was observed in the Gaza soil (Figure 10). Formulating metolachlor with montmorillonite without any preadsorption with organic cation did not show any reduction in leaching compared to that of the commercial formulation (El-Nahhal et al., 1999b). Formulating metolachlor with montmorillonite preadsorbed with PTMA at a load of 0.5 mol/kg (5% w/w) resulted in a significant inhibition of leaching, with herbicidal activity limited to the top 11 and 9 cm (Figures 10 and 11). Adding metolachlor at a lower load of 5% (w/w) to montmorillonite preadsorbed with PTMA at a load of 0.5 mol kg⁻¹ of clay further reduced the leaching (data not shown). Metolachlor formulated with BTMA0.5 leached more than that formulated with PTMA0.5 (Figure 11). Clearly, the smaller organic cation PTMA enhances the interaction with herbicide molecules on the organoclay surface and reduces the rate of its release and leaching depth.

GENERAL DISCUSSION

This work presents an attempt to improve the recently developed organoclay formulations of hydrophobic herbicides, such as alachlor and metolachlor, in terms of reduced leaching and migration and enhanced efficacy. The order of effectiveness of the formulations in reducing herbicide leaching is PTMA0.5 > PTMA0.8 > BTMA0.5 > BTMA0.8 > BTEA0.8 >> HDTMA0.5 (hexadecyltrimethylammonium adsorbed to the clay at 0.5 mmol/g) > clay alone. This order is also observed in the adsorbed amounts of alachlor and metolachlor (Figure 3) and in the rate of herbicide release (Figure 7 and Table 3).

Table 2 gives k values for alachlor and metolachlor adsorption on Mont-PTMA0.5 and Mont-PTMA0.8, which are significantly larger than those obtained for the adsorption of these herbicides on other complexes between montmorillonite and an organic cation. Thus, the smaller preadsorbed organic cation, PTMA (Figure 1), yields stronger interactions with alachlor and metolachlor. Similar to the reasoning in Nir et al. (2000), we suggest that these stronger interactions of alachlor and metolachlor with PTMA are due to interactions between the anilidic group and phenyl ring of a herbicide molecule and that of the preadsorbed PTMA.

Our arguments are as follows:

The k values, which reflect the strength of the interactions of alachlor and metolachlor with the clay mineral itself, are small. The corresponding k values for organoclays, where the preadsorbed organic cation is smaller, become progressively larger according to the sequence PTMA > BTMA > BTEA >> HDTMA > clay, in which HDTMA which does not include a phenyl ring has a significantly larger hydrophobic part than PTMA. Consequently, the deduction is that the larger contribution of the preadsorbed organic cation to the interaction with the herbicide molecules is not due to the bulk of the organic ligand but rather due to the anilidic group and phenyl ring.

The FTIR results show directly shifts of the bands associated with the phenyl rings of the herbicides. The FTIR results also show a shift in the band associated with the phenyl ring of PTMA, when the herbicides are added.

The results in Table 1 are based on calculations employing $K = 300 \text{ M}^{-1}$ (150–300) for the binding coefficient of formation of adsorbed dimers of PTMA. This value is significantly larger than K values deduced for BTMA and BTEA, which are decreasing with the size of the cation, being 20 and 5 M^{-1} , respectively. Hence, with a decrease with the size of the organic cations, their fraction participating in surface dimers increases. This increase is presumably due to the increased interaction between their phenyl rings, because van der Waals interactions between their other hydrophobic parts are expected to be smaller than in the case of the larger organic cations. Thus, we expect the strength of interactions between the phenyl ring of alachlor or metolachlor and that of the organic cation to follow the sequence PTMA > BTMA > BTEA. As in Nir et al. (2000), we explain the fact that the adsorption of the hydrophobic herbicides alachlor and metolachlor is optimal on the complex Mont–PTMA0.5 rather than on Mont–PTMA0.8 on the basis that significantly more charged dimers of the organic cations are formed in Mont–PTMA0.8 than in Mont–PTMA0.5 (Table 1). We suggest that in the charged dimers the phenyl rings are less accessible for interacting with those of the herbicides and, in addition, the charged dimers form hydrophilic sites on the clay mineral. Consequently, the interaction between alachlor and metolachlor with the organoclay surface is optimized for a loading of $\sim 0.5 \text{ mmol/g}$. At this loading the shifts of the IR bands are larger than at a loading of PTMA corresponding to the CEC of montmorillonite.

This study demonstrates an approach combining two principles for improving clay-based formulations of hydrophobic herbicides:

1. It is needed to modify the clay surface from hydrophilic to hydrophobic by preadsorbing on it an aromatic cation having a structure that would enable optimal interactions between the molecules of the herbicides and the surface sites of the organoclay complexes.

2. The degree of coverage of the clay surface by the organic cation has to be optimized. Thus, achieving maximal transformation of the clay surface from hydrophilic to hydrophobic by loading the clay up to its CEC does not necessarily imply optimal interactions between the herbicide and the organoclay complex.

The formulations based on Mont–PTMA0.5 were optimal in reducing herbicide leaching and in maximizing herbicidal activity. Thus, the application of the new organoclay formulations of alachlor and metolachlor enables a reduction in the applied amounts relative to those of the commercial formulation. These characteristics make the new formulations promising from environmental and economical points of view.

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