

Organoclay Formulations of Acetochlor: Effect of High Salt Concentration

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This study aimed to evaluate new methodology for designing ecologically acceptable formulations of acetochlor. Modification of montmorillonite with phenyltrimethylammonium chloride (PTMA) or benzyltrimethylammonium chloride (BTMA) and organoclay formulations of acetochlor were prepared in the presence of high concentrations of sodium chloride (150 g/L). Acetochlor concentration in the equilibrium solutions was determined by HPLC. Release of acetochlor in a water system was performed by a funnel experiment. 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 or BTMA were increased as NaCl concentration increased in the equilibrium solution. Leaching of acetochlor from organoclay formulations was significantly inhibited to the top soil layer (0–5 cm) when the formulations were prepared at extreme NaCl concentration (100–150 g/L). These results are in accord with a funnel experiment that showed a reduction in acetochlor release from the montmorillonite-based formulations. The application of this method for herbicide formulation would produce ecologically acceptable herbicide formulations that can significantly minimize the risk to groundwater pollution.

KEYWORDS: Acetochlor; montmorillonite; sodium chloride; leaching; slow release

INTRODUCTION

The available commercial formulation (emulsifiable concentrate, EC) of acetochlor suffers rapid loss of biological activity due to leaching to deep layers in soil (1). Leaching of herbicides may result in contamination to the groundwater as previously reported (2, 3). The risk of contaminating the environment with herbicides or their degradation products has stimulated interest in developing less hazardous formulations. These include starch encapsulated (4, 5), microencapsulated (6, 7), tablet (8–10), controlled-release (11, 12), slow release (13), ecologically acceptable organoclay (1, 14–17), and clay micelle formulations (18, 19).

Recent development of organoclay formulations of acetochlor (1) showed a reduced leaching and migration of acetochlor under laboratory and field conditions.

Previous studies did not include NaCl concentration in the preparation of formulations. Relatively little information about the effect of high salinity on the adsorption of hydrophobic molecules to modified montmorillonite (20–22) is available.

However, the effects of high NaCl concentration on herbicide adsorption/desorption and formulations with organoclays are not yet available. In the case of acetochlor no data are available about the effect of extreme NaCl concentration in further improvement of organoclay formulations. This paper describes the effect of NaCl in further developing ecologically acceptable organoclay formulations of acetochlor for reduced leaching.

MATERIALS AND METHODS

Materials. Sodium montmorillonite SWy-2 (Mont) was obtained from the Source Clays Repository, Clay Minerals Society, Columbia, MO. HPLC grade ethyl acetate, isooctane, and organic cations [phenyltrimethylammonium (PTMA) and benzyltrimethylammonium (BTMA) as chloride salts] were purchased from Sigma-Aldrich (Sigma Chemical Co.). The chemical structures of the organic compounds were shown previously (1). Analytical grade NaCl was obtained from E. Merck (Darmstadt, Germany). Soils were collected from 0 to 30 cm depth at the Agricultural Experimental Station of EPRI in the Gaza Strip. Soil properties were shown in El-Nahhal et al. (23). Green foxtail [*Setaria viridis* (L.) Beauvois] was used as a test plant. Analytical grade acetochlor, purity = 98%, was purchased from ChemService USA and was used for making the organoclay formulation. The commercial formulation (EC) of acetochlor (Harness, 980 g of ai/kg) was from Monsanto Chemicals.

Preparation of Organoclay Complexes at Extreme NaCl Concentration. The organoclay complexes were prepared by the addition of BTMA or PTMA as solid material (20) to a 0.1% (w/v) aqueous

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saline suspension of montmorillonite containing NaCl (150 g/L) as described recently (24). After 3 days of continuous rotary shaking, the produced organoclay complex was separated after 30 min of centrifugation (6000g). The precipitate was washed several times with distilled water to have it free from NaCl. This was tested by silver nitrate. The organoclay complex was freeze-dried, ground to <50 μm , and kept in plastic bottles at room temperature (RT) for preparation of formulations.

Adsorption of Acetochlor in the Presence of High NaCl Concentrations. Adsorption of acetochlor on montmorillonite alone or exchanged with PTMA/BTMA was measured at several concentrations of NaCl (0.0, 10, 40, 80, and 150 g of NaCl/L). In this procedure appropriate aliquots of an aqueous solution of acetochlor (28 mg/L) were diluted in 25 mL of distilled water and were added to 0.025 g of clay-PTMA or -BTMA at a loading of the organic cation of 0.5 mmol/g, in a 30 mL centrifuge tube containing an appropriate amount of NaCl. The final concentration of the organoclay was 1 g/L. The samples were vortexed for 3 min to ensure complete solution of NaCl and kept under continuous rotary shaking for 48 h at 25 ± 1 °C. The supernatant was separated by centrifugation at 6000g for 1 h, and acetochlor was determined by HPLC as described in ref 21. Acetochlor formulations in the presence of high NaCl concentrations (0.0, 50, 100, and 150 g/L) were prepared on the basis of the description above.

Release of Acetochlor. Release of acetochlor from different formulations was conducted using a Büchner funnel. In this procedure, 50 g of air-dried sandy soil was added to a Büchner funnel (10 cm internal diameter) that had a filter paper in the bottom. The soil layer was homogenized to a 0.5 cm height. The soil surface was sprayed with different organoclay formulations prepared as described above. The organoclay or EC formulation applied contained 1.72 mg of acetochlor. The amount of herbicide applied represents the recommended field rate (2 kg/ha). The soil layer in each funnel was carefully irrigated with 500 m³/ha applied in 10 portions during 2.5 h. Each washing (43 mL) was collected after 10 min of application in a separate flask and analyzed by HPLC. To determine the wetting and drying cycle effect on the release from the formulations, three additional washes were applied 1 week later after the funnels had been allowed to dry under room temperature and humidity. The experiment was conducted with two replications, two funnels for each formulation.

Bioassay Test. Standard Curve. Air-dried soil samples were treated with 0.0, 0.055, 0.11, 0.22, and 0.44 μg of technical acetochlor/g of soil. The soil was mixed through polyethylene plastic bags to ensure homogenized distribution of acetochlor concentration. The treated soils were transferred to five black plastic pots. The pots had four holes at the bottom covered by tissue paper. Ten seeds of the test plant were placed in each pot. Shoot height and fresh weight were determined 2 weeks after treatment, and percent growth inhibition was calculated using eq (1)

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

where P_c and P_t are the shoot height of the control and treated samples, respectively.

Persistence and Leaching of Acetochlor in Soil Columns in a Greenhouse. Persistence and leaching in soil columns was evaluated by estimating the relative concentration of acetochlor released from clay-BTMA, clay-PTMA, and/or commercial formulation at different soil layers using the bioassay and column techniques as recently described (25).

The columns were made from tin with 10 \times 10 cm² surface area and 25 cm height. The bottoms of the columns contained several microholes of 2 mm mesh. The columns were filled with an air-dried, sandy soil, sieved through a 2 mm screen. The soil surfaces were sprayed with the field rate (2.0 kg of ai/ha) of either organoclay formulation (clay-BTMA-acetochlor, 28 mg/g; clay-PTMA-acetochlor, 28 mg/g) or EC commercial formulation of acetochlor using an atomizer. The columns were carefully irrigated with 500 m³ of water/ha applied in portions during 4 h with 30 min intervals. The columns were left for 48 h for equilibration and sliced along their lengths, hence forming two pots. The test plant (*S. viridis*) was sown in each column half in two rows. The pots were sprinkle irrigated as needed. The relative concentration of acetochlor could be determined at various soil

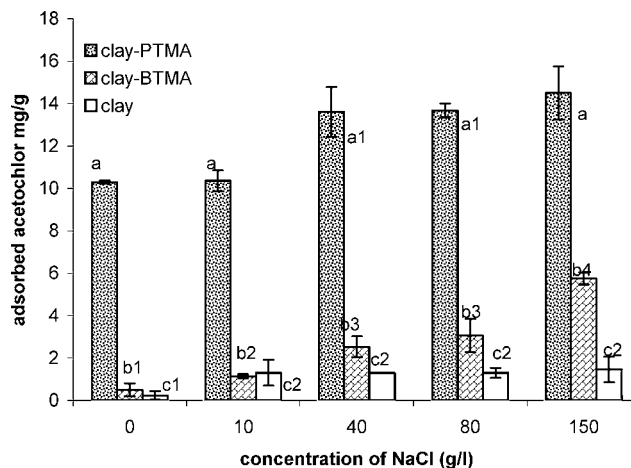


Figure 1. Adsorption of acetochlor at different NaCl concentrations. The initial acetochlor concentration was 28 mg/L; 1 g/L clay or organoclays. Bars indicate standard deviation. Columns having the same letter are not significantly different at the $p = 0.05$ level of significance.

depths by a reduction in tissue fresh weight or height of the bioassay test plant using eq 1 and application of a linear regression equation generated from the standard curve (2).

$$Y = 412.22X \quad (2)$$

Y represents growth inhibition of the test plant determined by eq 1, and X represents acetochlor concentration ($\mu\text{g/g}$ of soil). Relative concentrations and leaching depths of different formulations were compared by Tukey's test at $\alpha = 0.05$, following one-way ANOVA.

RESULTS AND DISCUSSION

The organoclay complexes prepared were clay-BTMA and clay-PTMA. These complexes are white powder with mesh size of <20 μm . They contain 12–14% (w/w) of organic carbon.

The idea underlying the preparation of the organoclay complex in the presence of high concentrations of NaCl is to produce an organoclay complex free from loosely bound BTMA or PTMA molecules, which may occur via hydrophobic interaction when the ion exchange process with montmorillonite surfaces is in the presence of distilled water.

It was reported that a fraction of 10–15% of BTMA can be desorbed from the montmorillonite complex as it was exposed to an increased salinity from 0 to 100 g/L (24, 26). This was attributed to a loosely bound fraction. Accordingly, this fraction is dissolved in water and increases the dissolved organic carbon. Consequently, the solubility of adsorbed acetochlor may be enhanced and more release or leaching may be observed. This loosely bound fraction of BTMA was responsible for the release of phenanthrene from the clay-BTMA complex when the complex was prepared from distilled water (24). Consequently, to avoid this effect in the design of ecologically acceptable organoclay formulations, the organoclay complex was prepared in a medium with high concentrations of NaCl (100–150 g/L).

Adsorption of Acetochlor. Adsorption of acetochlor on montmorillonite alone or exchanged with BTMA or PTMA under variable salinity is shown in Figure 1. As previously demonstrated for adsorption from distilled water, little acetochlor was adsorbed on montmorillonite alone, whereas a dramatic increase in the adsorbed amounts of acetochlor was observed on montmorillonite exchanged with PTMA or with BTMA (1).

In contrast, extreme salinity levels resulted in enhancing the adsorption of acetochlor.

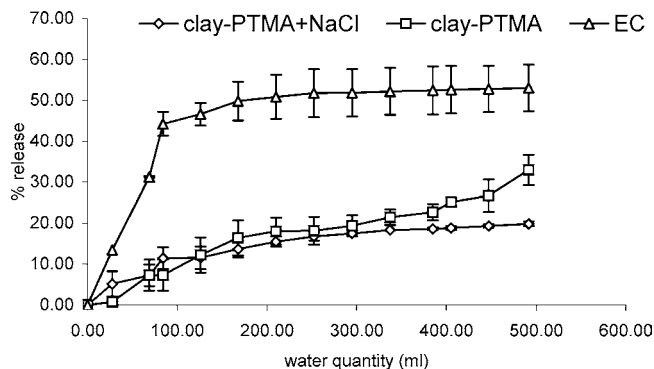


Figure 2. Release of acetochlor from different formulations. Bars indicate standard error.

It can be seen that adsorbed amounts of acetochlor either on clay-PTMA or clay-BTMA or on the clay alone are increased as the concentration of NaCl is increased in the solution. These results are in agreement with previous results (21). An explanation of these results is that the addition of NaCl to the solution may have a salting-out effect on the adsorption process similar to that of partitioning nonionic compound into two phases, one of them being water. In this case, the addition of sodium salt may decrease the solubility of acetochlor in water and thus increase its partitioning in the nonpolar phase, which is the solid phase (clay-PTMA; clay-BTMA).

The salting-out effect on the adsorption process may be qualitatively pictured as follows: the ions of NaCl in the equilibrium solution tightly bind water molecules into hydration shells, which has long been recognized to reduce the volume of aqueous solution even macroscopically by a process known as electrostriction (27). These tightly bound water molecules are unavailable to dissolve into. Consequently, as more and more salt is added to the aqueous solution, less and less water remains to create a cavity in which an organic solute can be accommodated. This may reduce the aqueous solubility of acetochlor and thus increase its diffusion in the organic phase, and adsorption may be increased.

Consequently, hydrophobic adsorption sites may be generated and adsorption may be increased. El-Nahhal (20) reported increased adsorption of chlorpyrifos under high salt concentration. Recently, El-Nahhal and Safi (22) found similar results for the adsorption of phenanthrene. However, Li et al. (28) tested the effect of different KCl and CaCl₂ concentrations in the adsorption of pesticides and hypothesized that the magnitude of pesticide sorption to soil minerals is proportional to the fraction of clay interlayers saturated with K⁺ ions.

The organoclay formulations prepared were analyzed for residual NaCl using AgNO₃. The amount of NaCl found was extremely lower than the natural concentration of NaCl present in natural water used for either irrigation or pesticide application.

In addition, application of pesticides in the field is usually performed by using a motorized sprayer at a spray volume of 300 L of water/ha. This high volume extremely dilutes the residual amount of NaCl. Furthermore, the bioassay test we performed does not show any toxic effect on the test plants. Accordingly, this procedure of pesticide formulation does not present any harmful effect to plants.

Release of Acetochlor. Release results of acetochlor from different formulations are presented in **Figure 2**. It is evident that upon application of 5 mm (first washing), 50% of the initial acetochlor concentration was released from the commercial formulation, whereas 22 and 18% of acetochlor concentrations were released from clay-PTMA prepared from distilled water and saline solution, respectively.

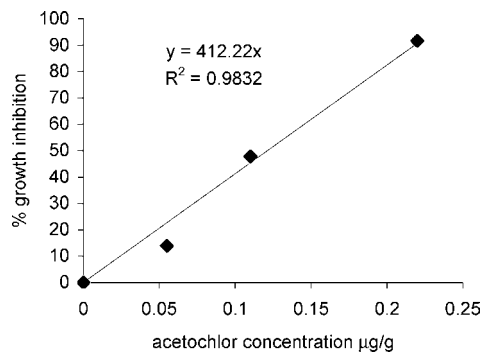


Figure 3. Dose response curve of acetochlor concentration for *S. viridis* as a test plant.

Thus, the release of acetochlor from the commercial formulation was significantly more extensive and faster than that from clay-PTMA formulations prepared either from distilled water or from saline solution. The explanation of these results is that the release from the commercial formulation is controlled by the octanol/water partitioning coefficient (K_{ow}), whereas in the case of organoclay formulation the release is controlled by the binding distribution coefficient (K_d) values of 16000 (1), which are higher than K_{ow} , 300 (29). However, K_d is a measure of interaction between the herbicide and the organoclay complex. El-Nahhal (30) found similar results for release and leaching of metolachlor from different formulations.

Bioassay Test. A linear relationship between acetochlor concentration and growth inhibition was observed at low concentrations (**Figure 3**). This indicates a high sensitivity of the method used and a strong positive association. Thus, a linear regression equation was used to determine the relative concentration of acetochlor in soil or solution samples. The regression equation gave an R^2 value of 0.9832.

Persistence and mobility tests in the soil columns showed that the relative concentration of acetochlor applied as commercial EC formulation was depleted in the top soil layer (0–5 cm) and accumulated in the middle soil layers (10–16 cm). The concentration in the top 5 cm of the column was below the detection limit (**Table 1**). The highest concentrations (0.78 ± 0.02 mg/kg) were found at depths of 13–16 cm for soil treated with the EC formulation at the field rate. This result indicates that acetochlor disappeared from the top soil layer and accumulated at a deeper depth. In contrast, the relative concentration of acetochlor remained in the top soil layer when it was applied as the organoclay formulation prepared from saline solution. The average acetochlor concentrations found in the top soil layer (0–5 cm) were 0.79 ± 0.05 and 0.81 ± 0.03 mg/kg of soil for clay-BTMA formulations prepared from distilled and saline water, respectively. It is evident that formulating acetochlor with clay-BTMA0.5 in the presence of a high NaCl concentration resulted in a significant modification of herbicide movement. Acetochlor accumulated in the top 9 cm of the soil column, indicating long persistence and lower mobility to deeper layers.

An interesting outcome of this work is that the clay-PTMA formulation prepared at 10% NaCl solution resulted in a retention of >60% of the applied acetochlor in the top 0–5 cm of the soil layer. Concentrations of acetochlor in the same treatment at a soil layer of 10 cm and deeper were below the detection limit. These results are further supported by the data of leaching experiments (**Figures 4** and **5**). A possible explanation for these results is that adsorption of acetochlor under extreme salt concentration may result in a reduction in the swelling properties of the montmorillonite or its organoclay

Table 1. Relative Concentration of Acetochlor (Milligrams per Kilogram of Soil) at Different Soil Depths As Determined by Bioassay Techniques

soil depth, cm	type of formulation ^a tested in soil columns				
	clay-BTMA ^d	clay-BTMA ^s	clay-PTMA ^d	clay-PTMA ^s	EC
0-5	0.79 ± (0.05) ^b	0.81 ± (0.03)	0.85 ± (0.2)	1.2 ± (0.3)	BD ^c
6-7	0.68 ± (0.01)	0.72 ± (0.01)	0.79 ± (0.151)	0.5 ± (0.1)	0.09 ± (0.01)
8-9	0.33 ± (0.1)	0.29 ± (0.05)	0.12 ± (0.02)	0.1 ± (0.12)	0.25 ± (0.09)
10-12	0.15 ± (0.01)	BD	0.08 ± (0.09)	BD	0.69 ± (0.1)
13-16	BD	BD	BD	BD	0.78 ± (0.21)
17-25	BD	BD	BD	BD	0.12 ± (0.01)

^a d and s represent distilled and saline solutions. ^b The number in parentheses indicates standard deviation. ^c Below detection limit.

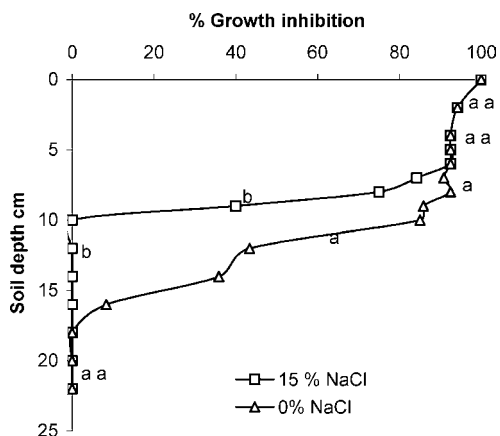


Figure 4. Leaching of acetochlor from different clay-BTMA0.5 formulations prepared at different NaCl concentrations under greenhouse conditions. Means followed by a different letter at a representative depth are significantly different at the $p = 0.05$ level. Standard deviation was $<0.9\%$.

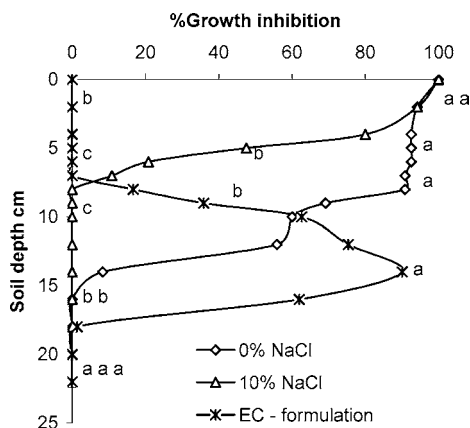


Figure 5. Leaching of acetochlor from clay-PTMA0.5 formulation prepared in the presence of different NaCl concentrations. Means followed by a different letter at a representative depth are significantly different at the $p = 0.05$ level. Standard deviation was $<0.9\%$.

complexes. Accordingly, the possible contact between water molecules and the adsorbed acetochlor molecules on the clay-BTMA0.5 or -PTMA0.5 complex is reduced. Consequently, the release or leaching of acetochlor to water or soil solution is more inhibited. As a result, a longer period of weed control may be expected. The presented results support the idea that using a concentrated NaCl solution in the process of formulation preparation may further improve organoclay-based herbicide formulations.

Leaching Studies in the Greenhouse. Leaching results of acetochlor formulations prepared in the presence of different NaCl concentrations are presented in **Figures 4** and **5**. It is obvious that leaching of acetochlor from clay-BTMA prepared in the presence of NaCl was significantly inhibited and that the

herbicidal activity was retained in the top 10 cm of the soil layer (**Figure 4**). The commercial formulation disappeared from the top 7 cm and was detected at a deeper depth.

Leaching of acetochlor was further inhibited when it was formulated with clay-PTMA at 10% salinity (**Figure 5**). The explanation of this observation is that higher adsorption of acetochlor was observed on clay-PTMA at higher salinity than on clay-BTMA at the same salinity level. This is probably due to better geometrical fit of the phenyl ring of acetochlor interaction with PTMA than with BTMA as previously reported (*1*).

However, it was observed that formulating acetochlor with clay-PTMA at 10% salinity inhibited the leaching more than at a higher salinity level of 15%, whereas clay-BTMA formulations prepared at higher salinity (15%) inhibited the leaching more than did those prepared at a lower salinity (10%) (results not shown). The explanation of these results may be due to the stability of the organoclay complex at various salinities. El-Nahhal and Safi (*24*) found relatively 10% of BTMA molecules were desorbed from clay-BTMA due to extreme salinity levels. This desorbed fraction tends to enhance the solubility of acetochlor, and more leaching may be expected when the interactions between the molecules are higher as for the case of PTMA. Consequently, better formulation was observed at 10% salinity. For the case of clay-BTMA, El-Nahhal and Safi (*24*) found that the adsorption capacity of clay-BTMA was not significantly changed by further elevating the salinity.

However, the small difference between the results in **Figures 2** and **5** may be explained by the fact that **Figure 2** is a chemical determination of acetochlor concentration on water released from various formulations. This chemical technique determined the total acetochlor concentration in the water used for the experiment. **Figure 5** is a bioassay technique that successfully evaluated acetochlor concentrations in different soil layers. This evaluation is based on a variety of factors such as the response (sensitivity) of the test plant to various concentrations of herbicide, soil texture, and the adsorption behavior of the herbicide in soil. Differences between chemical and bioassay techniques in the determination of herbicide concentrations in soil samples were recently reported for other cases (*30*).

Concluding Remarks. This study presents a new methodology for designing ecologically acceptable acetochlor formulations to reduce the leaching and migration in soil. This method combined two principles:

1. The montmorillonite surface was modified from hydrophilic to hydrophobic by preadsorbing it with an organic cation under a high concentration of NaCl to reduce possible formation of loosely bound BTMA or PTMA to the organoclay complex.
2. The herbicide was adsorbed onto the organoclay complex under a high concentration of NaCl to reduce the swelling

properties of the clay and to promote salting-out of the organic molecules into the organoclay.

The formulations prepared at the highest NaCl concentration (150 g/L) were optimal in reducing herbicide leaching and in maximizing herbicidal activity in the top soil layer. Thus, the application of the new methodology in designing organoclay formulations of acetochlor may enable a reduction in the applied amounts, relative to those prepared previously from distilled water (I). These characteristics make the new methodology promising from the environmental and economical points of view.

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