Leaching behavior of metolachlor in soil

Yasser El-Nahhal

Abstract: This work estimated the leaching behavior of metolachlor from montmorillonite-based and commercial emulsifiable concentrate (EC) formulations in soil columns and field plots by using bioassay and chemical techniques. A montmorillonite-based formulation of metolachlor was prepared by adsorbing metolachlor to montmorillonite–benzyltrimethylammonium (BTMA) complex from aqueous solution. Bioassay and gas chromatography (GC) techniques detected high metolachlor concentrations in the top soil layers (0–9 cm) in soil columns and field plots sprayed with montmorillonite–BTMA–metolachlor complex. These results were also evident by severe growth inhibition restricted to the top soil layers (0–9 cm) and normal growth at deeper layers in soil columns and field plots. A wider range of metolachlor concentrations were detected in soil layers in columns treated with EC formulation in both soil columns and field plots. Relatively higher metolachlor concentrations were detected in the soil layers in field plots than in soil columns. A bioassay technique was a more sensitive tool than chemical technique and detected diluted concentration of metolachlor at deeper layers. The different leaching behavior of metolachlor applied as montmorillonite–BTMA complex is due to the adsorption capacity of montmorillonite–BTMA complex.

Key words: metolachlor, montmorillonite–BTMA, leaching, soil columns, field plots.

Résumé : Ce travail estime la lixiviation du métolachlore de formulations à base de montmorillonite et de concentré émulsionnable industriel dans les colonnes de sols et des parcelles expérimentales en utilisant des techniques chimiques et des essais biologiques. Une formulation de métolachlore à base de montmorillonite a été préparée en adsorbant le métolachlore sur un complexe de montmorillonite–benzyltriméthylammonium (BTMA) dans une solution aqueuse. Les essais biologiques et les techniques de chromatographie en phase gazeuse ont détecté de fortes concentrations de métolachlore dans les couches de sol supérieures (0–9 cm) dans les colonnes de sol et les parcelles expérimentales parsemées avec un complexe montmorillonite–BTMA–métolachlore. Ces résultats étaient également évidents par la grave inhibition de croissance dans les couches de sol supérieures (0–9 cm) et la croissance normale dans les couches plus profondes des colonnes de sol et des parcelles expérimentales. Une plus grande plage de concentrations de métolachlore a été détectée dans les couches de sol des colonnes traitées avec une formulation de concentré émulsionnable. Des concentrations relativement plus élevées de métolachlore ont été détectées dans les couches de sol des parcelles expérimentales que dans celles des colonnes de sol. L'essai biologique s'est avéré être une technique plus sensible que la technique chimique et a permis de détecter une concentration diluée de métolachlore dans les couches plus profondes. Le différent comportement de lixiviation du métolachlore sous forme du composé d'addition montmorillonite–BTMA relève de la capacité d'adsorption de ce composé d'addition.

Mots clés : métolachlore, montmorillonite–BTMA, lixiviation, colonnes de sols, parcelles expérimentales.

[Traduit par la Rédaction]

Introduction

Chloroacetamide herbicides (e.g., metolachlor) are widely used in agriculture to eradicate weeds such as crabgrass (*Digitaria ciliaris* (Retz) Koel), foxtails (*Setaria viridis* L.), pigweed (*Amaranthu hybridus* L.), purslane (*Portulaca oleracea* L.), and the perennial weed yellow nutsedge (*Cyperus esculentus* L.) in irrigated crops such as potato, peanuts, corn, and sunflower. Leaching of metolachlor may result in contamination of ground and surface water (Masse et al. 1994; Pasquarell and Boyer 1996; Riparbelli et al. 1996; Ng et al. 1995) or a wide distribution in the soil profile (Ritter et al. 1996; Clay et al. 1995; Cooper and Zheng 1994; Wietersen et al. 1993). It was found that increased application rate (Zheng et al. 1993), rainfall, or irrigation rate strongly enhance migration of metolachlor in soil (Bowman 1990). The magnitude of herbicide movement in soil depends on the spatial and temporal distribution of soil water, which is normally different under fallow conditions than under cropped conditions and in interrow vs. intrarow positions (Keller and Weber 1997). Dissipation of 50% of metolachlor ranged from 85 to >106 d (Burgard et al. 1993). Greater persistence was reported at colder temperatures and at lower depth (Bouchard et al. 1982). Increased sorption of metolachlor in soil has been positively correlated with clay (Bossetto et al. 1994; Zheng and Cooper 1996) and organic matter con-

Received 30 June 2003. Revision accepted 17 October 2003. Published on the NRC Research Press Web site at http://jees.nrc.ca/ on 22 March 2004.

Y. El-Nahhal.[1] Department of Environmental Chemistry, Environmental Protection and Research Institute (EPRI), Gaza, P.O. Box 1175, Palestine (e-mail: y_el_nahhal@hotmail.com).

Written discussion of this article is welcomed and will be received by the Editor until 30 September 2004.

[1] Present Address: Christian-Albrechts-Universität zu Kiel, Institut für Anorganische Chemie, D-24098 Kiel, Germany.

 doi: 10.1139/S03-075

tent (Kozak et al. 1983). It is well established that the herbicidal activity of metolachlor may be lost because of its mobility in the soil profile.

Starch-encapsulated and emulsifiable concentrate (EC) formulations of metolachlor gave similar weed control at low weed densities (122 total plants m^{-2}), whereas less weed control was observed with starch encapsulation than with EC formulation at a high weed density (Buhler et al. 1994). Organoclay formulations of metolachlor gave excellent weed control for a long period (El-Nahhal et al. 1999*a*).

The present investigation was designed to obtain comparative information on the leaching behavior of metolachlor formulations using biological and chemical techniques for metolachlor determination in laboratory and field experiments.

Materials and methods

Herbicide formulations

Commercial EC formulation (Dual, active ingredient, 980 g/kg) was used as a standard formulation. Sodium montmorillonite SWy-1, with a cation exchange capacity (CEC) of 0.8 mol/kg clay (Rytwo et al. 1991), was used to prepare the organoclay formulation. Sandy soil was collected from 0 to 30 cm depth at Agricultural Experimental Station of EPRI in the Gaza Strip. Soil properties are pH 8, organic matter 0.7%, sand 93%, silt 1%, clay 6%, and $CaCO_3$ 4.9%.

It is important to note that only soil particle size comprise 100%, and the other components (e.g., $CaCO_3$) can be found at any part of the solid phase of soil.

Preparation of montmorillonite-based formulation of metolachlor

Preparation of montmorillonite–benzyltrimethylammonium complex

montmorillonite-benzyltrimethylammonium (BTMA) complex was prepared as described in El-Nahhal (2003*a*), by suspending 1 g of montmorillonite clay in 1 L of distilled water. An appropriate amount of BTMA chloride salt, equivalent to 0.5 mmol/g montmorillonite was added to the system under continuos stirring for 72 h at room temperature. The system was left for 6 h to precipitate. The precipitate was separated by centrifugation (30 min, 6000 *g*), washed three times with distilled water, lyophilized, ground to <50 μm, and kept at room temperature. The cationic load was determined by using a CNHSO analyzer.

Encapsulation of metolachlor

Encapsulation of metolachlor in montmorillonite–BTMA complex was conducted by dissolving 200 mg of technical grade metolachlor in 1 L of distilled water. One gram of dry montmorillonite–BTMA complex was added to the solution under continuous stirring for 24 h. The precipitate was separated by centrifugation, at 6000 *g*, air dried or lyophilyzed, and kept in a plastic bottle at room temperature. The equilibrium concentration of metolachlor in the supernatant was determined by GC as described below.

Adsorption of metolachlor

This experiment was undertaken to understand the behavior of metolachlor on montmorillonite–BTMA prepared by the above-mentioned method, which is different from the previous method of organoclay complex preparation (El-Nahhal et al. 1998, Margulies et al. 1992), and to determine the amount of metolachlor encapsulated (adsorbed) in montmorillonite–BTMA complex. In this experiment adsorption isotherms of metolachlor were determined in the range of 0–700 μmol metolachlor per gram montmorillonite–BTMA. A stock solution of metolachlor was prepared by dissolving 200 mg of analytical grade (purity 99%) metolachlor in 5 mL of methanol and diluting it to 1 L with distilled water. Appropriate aliquots of the stock solution of metolachlor were diluted in 30 mL of distilled water and added to a glass tube containing 25 mg of montmorillonite–BTMA complex. The final concentration of the montmorillonite–BTMA complex was 0.83 g/L. The samples were kept under continuous horizontal agitation at 25 ± 1 °C for 24 h. The supernatant was separated by centrifugation at 6000 *g* for 1 h. Metolachlor was extracted by adding (2.4 g) sodium chloride into a glass tube, combined with 10 mL of supernatant and 10 mL of HPLC grade ethyl acetate/isooctane (1:9 v/v). The tubes were sealed, vortexed for 2 min, and left at room temperature for 1 h. The ethyl acetate – isooctane layer was collected into 25-mL volumetric flasks. The extraction procedure was repeated twice. The extracts were brought to volume (25 mL) with the same solvent mixture, transferred to crimp vials, sealed, and analyzed by a Hewlett-Packard Model 6890 gas chromatograph, equipped with electron-capture detector and an Rtx®-5MS capillary column (30 m $\times$ 0.25 mm internal diameter, 0.25 μm film). Blank recovery was 94.3 $\pm$ 3%. The difference between the initial and equilibrium concentrations gave the amount of metolachlor adsorbed to the montmorillonite–BTMA complex. The adsorption experiment was conducted in triplicate, and adsorption data were analyzed using a linear regression equation.

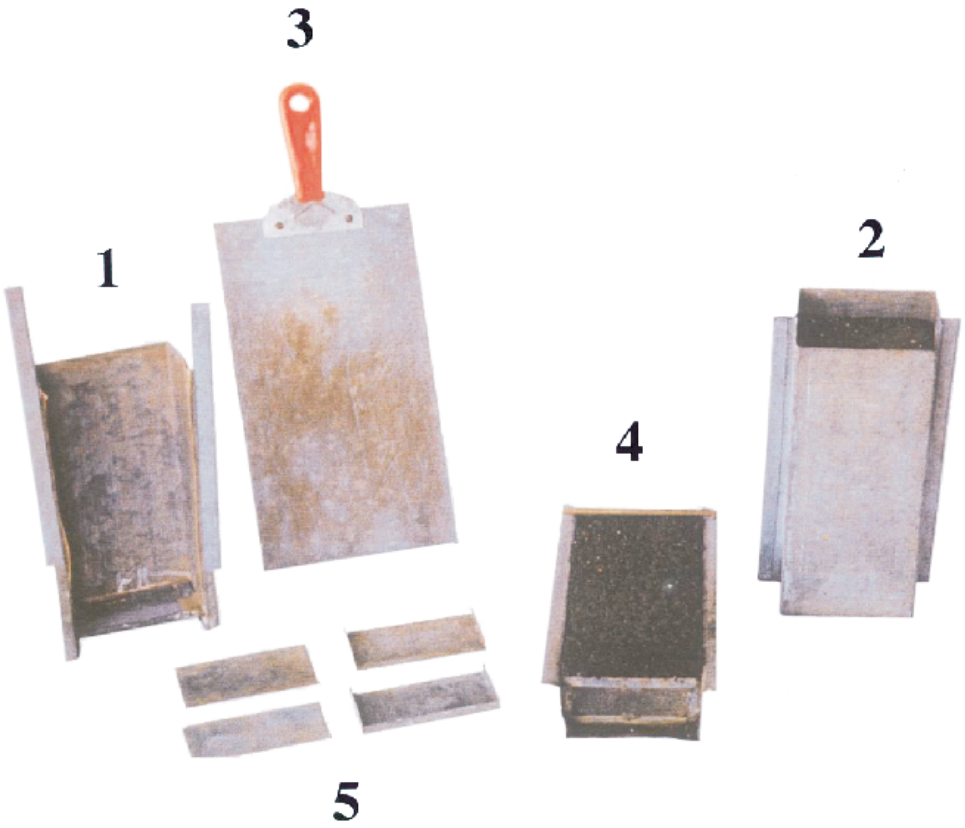
Leaching behavior of metolachlor in soil columns and field plots

Bioassay technique

Standard curve of metolachlor

A dose response curve was prepared by treating air dried soil samples with 0.0, 0.013, 0.027, 0.055, 0.11, 0.22, 0.44, and 0.88 mg technical metolachlor per kilogram of soil. The soils were mixed in polyethylene plastic bags to insure homogenized distribution of metolachlor. To avoid losses of metolachlor due to sorption to the polyethylene bags because of mixing, an appropriate metolachlor solution was incorporated of in the soil sample, followed by a manual rotary mixing using a glass rod. The treated soils were transferred to five black plastic pots.

Fig. 1. Columns techniques used for leaching experiments: 1, empty half column; 2, complete column full of soil; 3, special spatula to divide the column; 4, a half column ready for sowing test plants; 5, stoppers.



Each pots had four holes at the bottom covered by tissue paper. Ten seeds of the test plant, green foxtail (*S. viridis*), 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].

$$[1] \qquad \%\ \text{Growth Inhibition} = 100(P_c - P_t)/P_c$$

where P_c and P_t are the shoot height of the control and the treated samples, respectively. The growth inhibition data were subjected to analysis by ANOVA.

Leaching behavior in soil columns

Leaching of metolachlor in soil columns was performed as described in El-Nahhal (2003*b*). The persistence and mobility of metolachlor in soil were evaluated by estimating the relative concentration of metolachlor released from montmorillonite–BTMA0.5 and (or) commercial EC formulation at different soil layers using bioassay and column techniques (Fig. 1). The columns were made from tin with 10 cm × 10 cm surface area and 25 cm height. The bottom of the columns contained several micro-holes 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 (active ingredient 2.0 kg/ha) of either montmorillonite–BTMA0.5–metolachlor or commercial EC formulation of metolachlor using an atomizer. The columns were carefully irrigated with 500 m^3/ha applied in portions over 4 h at 30 min intervals. The columns were left for 48 h for equilibration and sliced along their lengths, hence forming two pots. One pot was used for bioassay in the greenhouse and the other pot was used for chemical assay. In the greenhouse, the test plant (*S. viridis*) was sown in one column half in two rows. The pots were sprinkle irrigated as needed. Relative concentration of metolachlor could be determined at various soil layers by a reduction in tissue dry weight or height of the test plant using eq. [1] and application of a linear regression equation generated from the standard curve eq. [2].

$$[2] \qquad Y = 1527.4X$$

Y represents growth inhibition of the test plant determined by eq. [1], and X represents metolachlor concentration (milligrams metolachlor per kilogram soil).

Leaching behavior in the field plots

In the field plots, beds (1 m wide and 3 m long) were prepared using a rotary tiller. Emulsifiable concentrate and montmorillonite–BTMA0.5 metolachlor formulations at 2.0 kg/ha active ingredient, were applied pre-emergence using a back pack motorized sprayer calibrated to discharge 300 L/ha. A sprinkler irrigation system was used to water the field plots at 500 m^3/ha. Two soil samples were taken from each plot using the two halves of the tin column (Fig. 1) gently inserted to a depth of 25 cm and supported with a wide spatula to ensure the complete removal of the soil in the column. The soil columns were carefully transferred to the greenhouse and chemical laboratory for bioassay

and GC determination. Bioassay of each column was conducted as described above and chemical assay was conducted following the procedure described below. Leaching experiments were five replicates and metolachlor concentration was an average of five replicates; the standard deviation was calculated for each sample.

Chemical technique

Soil extraction and analysis

Pots from soil columns and field plots were used for chemical analysis. In this procedure, the soil column was divided into 10 layers of 2.5 cm long. The soil layers were air dried in a 250 mL glass beaker and mixed thoroughly. El-Nahhal et al. (1999*b*) found that loss of metolachlor due to photochemical degradation or volatilization was not significant below 8 h of exposure to direct UV rays. Metolachlor was extracted from 100 g air-dried soil by mixing the soil with 100 mL of HPLC-grade ethyl acetate, isooctane (9:1 (v:v)) with distilled water 1:1 (v:v). The organic layer was collected in a 250 mL glass beaker. The extraction procedure was repeated twice with the same solvent. The extracts were evaporated under reduced pressure to 1 mL and analyzed by GC as described above.

Results and discussion

Preparation of montmorillonite–BTMA complex

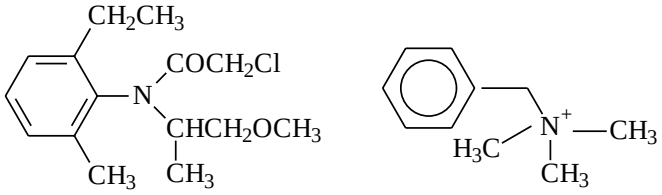
Detailed information about the adsorption isotherm of the cationic surfactant (BTMA) on montmorillonite was previously reported (El-Nahhal et al. 1998). The montmorillonite–BTMA complex prepared and used in this study was montmorillonite pre-adsorbed with BTMA at loads of 0.5 mmol/g. This surfactant was selected because it has an aromatic ring similar to that of metolachlor (Fig. 2). Thus BTMA is expected to enhance $\pi-\pi$ interaction and thereby facilitate increased sorption of metolachlor.

Adsorption isotherms of metolachlor

The adsorption isotherms of metolachlor on montmorillonite alone and montmorillonite–BTMA at 25 °C are shown in Fig. 3. As expected, metolachlor was poorly adsorbed on montmorillonite alone, whereas its adsorption on the montmorillonite–BTMA0.5 complex increased appreciably.

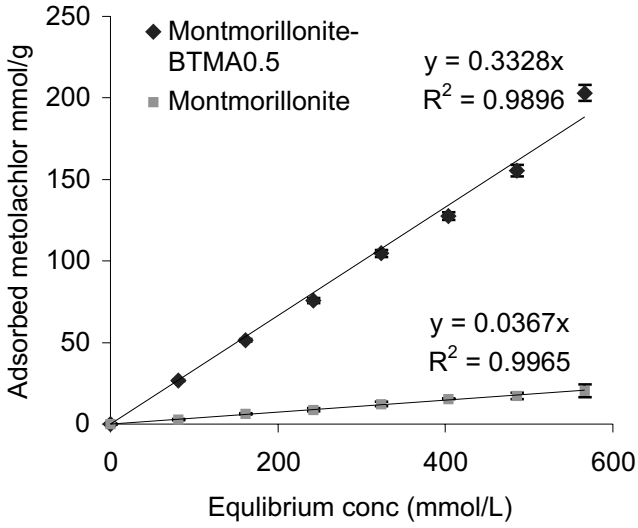
The low adsorption of metolachlor to montmorillonite alone is due to its hydrated surfaces and the hydrophobicity of metolachlor molecules. The adsorption of metolachlor to montmorillonite–BTMA0.5 increases linearly as its concentration in the equilibrium solution is increased. The dramatic increase in the adsorbed amounts of metolachlor to montmorillonite–BTMA0.5 is likely due to the interaction of metolachlor molecules and the adsorbed BTMA molecules on montmorillonite surfaces. Similar results were obtained previously (El-Nahhal et al. 1999*a*). These results suggest that interaction of metolachlor with montmorillonite–BTMA prepared as described by El-Nahhal (2003*a*) is similar to the interaction with the same organoclay prepared by previous methods (El-Nahhal et al. 1998; Margulies et al. 1992). These results validate the new method of organoclay preparation. The presented results also agree with Nennemann et al. (2001), who reported that metolachlor was adsorbed by raw and purified bentonite but the amount adsorbed depends on the type of bentonite and its pretreatment with benzyltrimethyl ammonium cation.

Fig. 2. Chemical structures of metolachlor and BTMA.



Metolachlor BTMA

Fig. 3. Adsorption isotherms of metolachlor on montmorillonite alone and montmorillonite–BTMA0.5. Bars indicate standard errors.

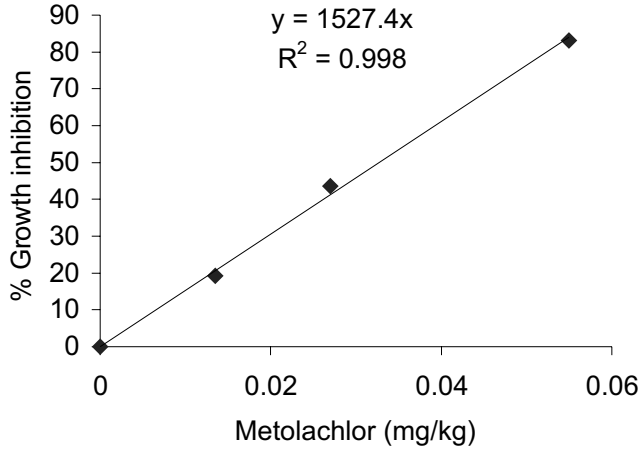


Fitting the results in Fig. 3 to a linear regression shows R^2 values close to unity (see Fig. 3) and binding distribution coefficient (K_d) values 0.0367 and 0.3328 on montmorillonite and montmorillonite–BTMA0.5, respectively. However, K_d is a measure of interaction between the herbicide and the organoclay complex. A standard distribution coefficient is a ratio of the concentration of a herbicide in a single defined form to its concentration in the same form in the other phase at equilibrium. These results indicate good fits and positive association. The results of metolachlor adsorption to the montmorillonite–BTMA0.5 could be explained by a linear distribution model (eq. [3]).

$$[3] \qquad Q_s = K_d C_e$$

where Q_s and C_e are the adsorbed and solution concentrations of metolachlor, respectively, and K_d is the binding distribution coefficient.

Fig. 4. Responses of green foxtail to different concentrations of metolachlor.



Bioassay techniques

Standard curve

A linear relationship between metolachlor concentration and growth inhibition was observed (Fig. 4). This indicates a high sensitivity of the method used and a strong positive association. Thus a linear regression equation, eq. [2] ($R^2 = 0.998$), was used to determine the relative concentration of metolachlor in soil samples.

Leaching behavior in soil columns and field plots

The relative concentrations of metolachlor in soil columns and field plots estimated by bioassay are presented in Table 1. High relative concentrations of metolachlor were detected in the top soil layers, whereas low concentrations were detected in deeper layers in soil columns sprayed with montmorillonite–BTMA–metolachlor complex.

Approximately 83% and 88% of metolachlor applied as montmorillonite–BTMA complex was retained in the top soil layers (0–9 cm) in soil columns and field plots, respectively. Only 17% and 12% of applied metolachlor were found in deeper layers (10–15 cm) in soil columns and filed plots, respectively. On the other hand, 60.7% and 73.8% of metolachlor applied as EC formulation were retained in the top soil layer (0–9 cm). Nearly 27.8% and 22.4% of metolachlor were detected in deeper layers (10–15 cm). About 11.4% and 3.8% of metolachlor concentrations were detected in the deepest layers (16–20 cm) in soil columns and field plots, respectively. These results indicate that leaching of metolachlor was restricted when it was adsorbed to montmorillonite–BTMA complex. These findings are also supported by the data of growth inhibition (Figs. 5 and 6), as discussed below.

Growth inhibition results of soil columns showed that EC–metolachlor formulation totally inhibited the growth of the test plant in the top soil layers (0–15 cm). A moderate growth inhibition was observed in the 3 cm below the above-mentioned layers. Normal growth of the test plant was observed at the bottom of the column, indicating that metolachlor is below detectable concentration (Fig. 5). The percent of growth inhibition at the top soil layer was about 95%. On the other hand, in columns sprayed with montmorillonite–BTMA–metolachlor complex, severe growth inhibition was restricted to the top soil layers (0–9 cm), followed by a relatively weaker growth inhibition at a deeper layer (10–12 cm). Normal growth of the test plant was observed in the deepest layers (13–24 cm). These result are consistent with Nennemann et al. (2001), who found that leaching of metolachlor was restricted when it was formulated with raw bentonite or activated pillared montmorillonite, and with Singh et al. (2002), who found that metolachlor leached to 8.5 cm in packed columns filled with loamy silt soils.

Severe growth inhibition of the test plant was observed on the top soil layers (0–9 cm) and (0–15 cm) in field plots sprayed with montmorillonite–BTMA0.5–metolachlor and EC metolachlor formulations, respectively (Fig. 6). A comparison of metolachlor concentrations in soil columns and field plots (Table 1) clearly shows that metolachlor concentrations were higher in the top soil layer (0–9 cm) in field plots sprayed with either montmorillonite–BTMA–metolachlor or EC formulations than in soil columns. These results are in agreement with the data of chemical analysis (Table 2).

Chemical technique

Table 2 represents metolachlor concentration in different soil layers determined by gas chromatography (GC). About 83% and 88% of metolachlor concentrations were retained in the top soil layer (0–9 cm) sprayed with the montmorillonite–BTMA0.5–metolachlor complex. Only 17% and 12% of metolachlor concentrations were detected in deeper soil layers (10–15 cm) in soil columns and field plots, respectively. On the other hand, in soil sprayed with EC formulations, 64% and 81% of metolachlor concentrations were retained in the top soil layer (0–9 cm). About 30% and 19% of metolachlor concentrations were detected in deeper soil layers (10–15 cm). Only 5.9% and 0.0% of metolachlor concentrations were detected at the deepest layers (16–20 cm) in soil columns and field plots, respectively.

A comparison between the data obtained from soil columns and field plots (Table 2) clearly shows that the amounts of metolachlor retained at the top soil layer (0–9 cm) in the field plots were higher than those retained in the same layer in the soil columns. These results agree with the data in Table 1 and are corroborated by growth inhibition as shown in Fig. 6. However, the presented results also agree with the results obtained by Singh et al. (2002) who used HPLC for determination of metolachlor in soil leachate.

Low concentrations of metolachlor were found in deeper layers (10–15 cm) in both soil columns and field plots sprayed with montmorillonite–BTMA–metolachlor complex.

Relatively higher metolachlor concentrations were found at deeper soil layers (10–15 cm) in soil sprayed with EC formulation in soil columns than in field plots. These data agree with Vasilakoglou et al. (2001), who found greater amount of metolachlor leached through soil layers because of lower adsorption in soil.

Table 1. Metolachlor concentration (mg/kg) in soil layers estimated by bioassay technique.

	Soil columns				Field plots			
	Mont-BTMA0.5		EC-formulation		Mont-BTMA0.5		EC-formulation	
Soil layer (cm)	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
0–5	0.84 ± (0.09)	83	0.71 ± (0.12)	60.7	0.91 ± (0.23)	88	0.82 ± (0.15)	73.8
6–9	0.73 ± (0.1)		0.51 ± (0.08)		0.80 ± (0.17)		0.73 ± (0.11)	
10–12	0.23 ± (0.05)	17	0.35 ± (0.09)	27.8	0.15 ± (0.08)	12	0.32 ± (0.09)	22.4
13–15	0.09 ± (0.03)		0.21 ± (0.05)		0.09 ± (0.05)		0.15 ± (0.1)	
16–18	Bd		0.15 ± (0.03)	11.4	Bd		0.08 ± (0.05)	3.8
19–20	Bd		0.08 ± (0.05)		Bd		Bd	
21–24	Bd		Bd		Bd		Bd	

Note: Bd = below detection limit, average ± standard deviation.

Table 2. Gas chromatography analysis of metolachlor concentration (mg/kg) in soil layers.

	Soil columns				Field plots			
	Mont-BTMA0.5		EC-formulation		Mont-BTMA0.5		EC-formulation	
Soil layer (cm)	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
0–5	0.9 ± (0.1)	83	0.75 ± (0.07)	64	0.93 ± (0.12)	88	0.87 ± (0.13)	81
6–9	0.81 ± (0.09)		0.65 ± (0.05)		0.81 ± (0.09)		0.76 ± (0.07)	
10–12	0.25 ± (0.05)	17	0.41 ± (0.07)	30	0.14 ± (0.1)	12	0.26 ± (0.03)	19
13–15	0.11 ± (0.07)		0.25 ± (0.06)		0.09 ± (0.07)		0.13 ± (0.05)	
16–18	Bd		0.13 ± (0.03)	5.9	Bd		Bd	Bd
19–20	Bd		Bd		Bd		Bd	
21–24	Bd		Bd		Bd		Bd	

Note: Bd = below detection limit, average ± standard deviation.

It is evident from the data (Tables 1–2, Figs. 5–6) that the montmorillonite–BTMA-based formulation leaches less in comparison with the commercial EC formulation. Furthermore, in the upper layer (0–9 cm) more metolachlor has been retained in the field plots than in soil columns. The explanation of these results is that metolachlor intacts strongly with the montmorillonite–BTMA complex because of physical forces and metolachlor molecules may penetrate through the interlayer spacing on montmorillonite sheets as recently demonstrated (El-Nahhal 2003*c*). In addition, dryness conditions in the field may reduce the contact with water molecules; accordingly reduced release and leaching are expected. On the other hand, metolachlor in EC formulation is readily exposed to water molecules. Accordingly its release and leaching processes are controlled by its octanol water partitioning coefficient (K_{ow}) value; metolachlor has a low value because of its high solubility in water. In addition, lower leaching under field conditions may also be due to two factors. First, metolachlor may move in two directions, horizontal and perpendicular. Second, there is an upward movement of metolachlor in response to water evaporation in addition to the downward movement in water rainfall or irrigation.

The presented results clearly demonstrate the reduced leaching of metolachlor adsorbed to montmorillonite–BTMA0.5, which also gave severe growth inhibition in the top soil layers (Figs. 5–6). A comparison between bioassay technique (Table 1) and chemical technique (Table 2) clearly shows that metolachlor determined by GC was relatively higher than estimated by the bioassay technique, in most cases. This is probably due to total extraction of metolachlor from soil samples.

Conclusions

More than 80% of the metolachlor applied as montmorillonite–BTMA0.5 complex was retained in the top 0–9 cm of soil. Low concentrations were detected at deeper layers in soil columns or field plots sprayed with metolachlor adsorbed to the montmorillonite–BTMA0.5 complex. Encapsulation of metolachlor in montmorillonite–BTMA significantly retained the herbicide in top soil layers because of slow release mechanisms. The bioassay technique successfully determined metolachlor concentrations in different soil layers. It is a more sensitive tool than the chemical technique to detect relatively low concentration of metolachlor at deeper soil layers. It was also able to demonstrate the effectiveness of montmorillonite–BTMA0.5 to maintain metolachlor concentrations in surface soil layer. The disadvantage of the bioassay technique is that the test plant may not give a true response at high metolachlor concentrations. In addition, the adsorbed fraction of herbicide may not be available to the test plant. However, at a low adsorbed fraction of herbicide, the herbicide may not be bio-available to the test plant because of a slow release process; accordingly the response of the test plant may not be sensitive enough to generate a dose

Fig. 5. Leaching of metolachlor from montmorillonite–BTMA 0.5 complex and EC formulation in the soil columns, using green foxtail as a test plant. Columns having the same letter at a representative soil layer are not significantly different at $p = 0.05$ level.

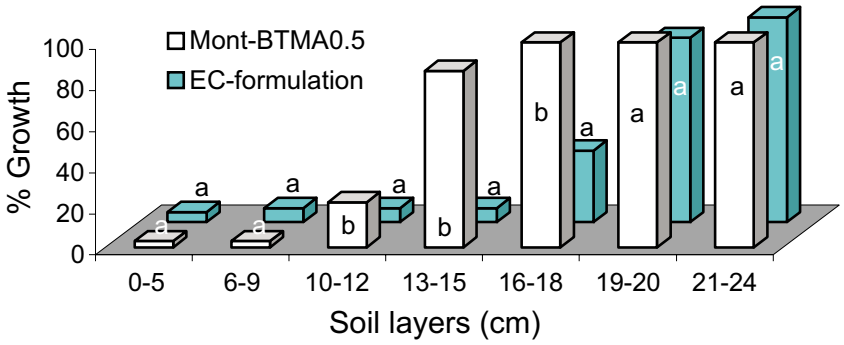
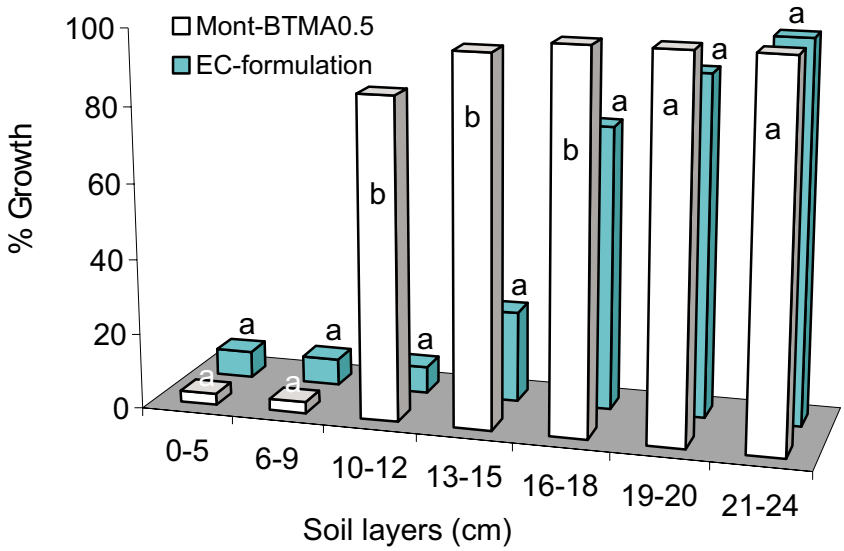


Fig. 6. Leaching of metolachlor from montmorillonite–BTMA 0.5 complex and EC formulation in the field plots, using green foxtail as a test plant. Columns having the same letter at a representative soil layer are not significantly different at $p = 0.05$ level.



response curve. Furthermore, all cases of bioassay technique need to be in the range of a linear mode of dose response curve. Thus, the dilution process may result in a loss of the active ingredient.

The chemical analysis technique was able to quantify relatively the total metolachlor concentration in the top soil layer; however, it was not sensitive enough to detect low metolachlor concentrations in deeper soil layers containing metolachlor residues that were toxic to the test plant. This technique is not able to provide evidence of the bioactivity of the determined concentration. Thus, the chemical technique may be integrated with the bioassay technique to evaluate the leaching behavior of other bio-active material in the environment. The application of montmorillonite–BTMA formulation of metolachlor may reduce the contact with water molecules owing to the hydrophobic properties of montmorillonite–BTMA. In addition, metolachlor might be able to penetrate in the interlayer spacing of the montmorillonite–BTMA complex. Accordingly, the leaching behavior of metolachlor at different environmental conditions might be changed.

Acknowledgments

I acknowledge Alexander von Humboldt Stiftung/Foundation Fellowship Grant no IV-PAL/1104842 STP, Germany.

References

Bossetto M., Arfaioli, P., and Fusi, P. 1994. Adsorption of metolachlor on homoionic montmorillonite. Agrochimica, XXXVIII-N. **1–2**: 14–24.

Bouchard D.C., Lavy, T.L., and Marx, D.B. 1982. Fate of metribuzin, metolachlor and fluometuron in soil. Weed Sci. **30**: 629–632.

Bowman, B.T. 1990: Mobility and persistence of alachlor, atrazine, and metolachlor, in Plainfield sand, and atrazine and isazofos in Honeywood silt loam using field lysimeters. Environ. Toxic. Chem. **9**: 453–461.

Buhler, D.D., Schreiber, M.M., and Koskinen, W.C. 1994. Weed control with starch encapsulated alachlor, metolachlor and atrazine. Weed Technol. **8**: 277–284.

Burgard, J.D., Koskinen, W.C., Dowdy, H.R., and Cheng, H.H. 1993. Metolachlor distribution in a sandy soil under irrigated potato production. Weed Sci. **41**: 648–655.

Clay, S.A., Koskinen, W.C., and Baker, J.M. 1995. Alachlor and metolachlor movement during winter and early spring at three midwestern sites. J. Environ. Sci. Health, **30**: 637–650

Cooper, J.F., and Zheng, S.Q. 1994. Behaviour of metolachlor in tropical and Mediterranean plain field conditions. Sci. Total Environ. **153**: 133–139.

El-Nahhal , Y. 2003*a*. Adsorptive behavior of acetochlor on organoclay complexes. Bull. Environ. Contam. Toxicol. **70**: 1104–1111.

El-Nahhal , Y. 2003*b*. Persistence, mobility, efficacy and activity of chloroacetanilide herbicide formulation under greenhouse and field experiments. Environ. Poll. **124**: 33–38.

El-Nahhal , Y. 2003*c*. Adsorption mechanism of chloroacetaniled herbicides to modified montmorillonite. J. Environ. Sci. Health B, **38**: 591–604.

El-Nahhal ,Y., Nir, S., Polubesova, T., Margulies, L., and Rubin, B. 1998. Leaching, phytotoxicity and weed control of new formulations of alachlor. J. Agric. Food Chem. **46**: 3305–3313.

El-Nahhal, Y., Nir, S., Polubesova, T., Margulies, L., and Rubin, B. 1999 *a*. Movement of metolachlor in soil: Effect of organo-clay formulation. Pestic. Sci. **55**: 857–864.

El-Nahhal, Y., Nir, S., Margulies, L., and Rubin, B. 1999*b*. Reduction of photodegradation and volatilization of herbicides in organo-clay formulations. Appl. Clay Sci. **14**: 105–119.

Keller, E.K., and Weber, B.J. 1997. Soybean (*Glycine max*) influences metolachlor mobility in soil. Weed Sci. **45**: 833–841.

Kozak, J., Weber, B.J., and Sheets, J.T. 1983. Adsorption of prometryn and metolachlor by selected soil organic matter fractions. Soil Sci. **136:** 94–101.

Margulies, L., Stern, T., Rubin, B., and Ruzo, L.O. 1992. Photostabilization of trifluralin on a clay matrix. J. Agric. Food Chem., **40**: 152–155.

Masse, L., Prasher, O.S., Khan, S.V., Arjoon, D.S., and Barrington, S. 1994. Leaching of metolachlor, atrazine, and atrazine metabolites into groundwater. Trans. Am. Soc. Agric. Eng. **37**: 801–806.

Nennemann, A., Mishael, Y., Nir, S., Rubin, B., Polubesova, T., Bergaya, F., van Damme, H., and Lagaly, G. 2001. Clay-based formulations of metolachlor with reduced leaching. Appl. Clay Sci. **18**: 265–275.

Ng. H.Y.F., Gaynor, J.D., Tan, C.S., Drury, C.F., and Heatwole, C. 1995. The residues of atrazine and metolachlor in surface and subsurface drain water: a case study. Proceedings. of the international symposium, Orlando, Fla., USA, pp. 99–108.

Pasquarell, G.C., and Boyer, D.G. 1996. Herbicides in karst groundwater in southeast West Virginia. J. Environ. Qual. **25**: 755–765.

Riparbelli, C., Scalvini, C., Bersani, M., Auteri, D., Azimonti, G., Maroni, M., and Salamana, M. 1996. Groundwater contamination from herbicides in the region of Lombardy Italy. Period 1986–1993. The Environmental Fate of Xenobiotics. Proc. of the 10th Symposium Pesticide Chemistry, Castelnuovo Fogliani, Piacenza, Italy. pp. 559–566.

Ritter, W.F., Chirnside, A.E.M., and Scarborough, R.W. 1996. Movement and degradation of triazines, alachlor, and metolachlor in sandy soils. J. Environ. Sci. Health **31**: 2699–2721.

Rytwo, G., Serban, C., Nir, S., and Margulies, L. 1991. Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite. Clays Clay Miner. **39**: 551–555.

Singh, N., Kloeppel, H., and Klein, W. 2002. Movement of metolachlor and terbuthylazine in core and packed soil columns. Chemosphere, **47**: 409–415.

Vasilakoglou, B.I., Eleftherohorinos, G.I., and Dhima, B.K. 2001. Activity, adsorption and mobility of three acetanilide and two amide herbicides. Weed Res. **41**: 535–546.

Wietersen, R.C., Daniel, T.C., Fermanich, K.J., Girard, B.D., McSweeney, K., and Lowery, B. 1993. Atrazine, alachlor, and metolachlor mobility through two sandy Wisconsin soil. J. Environ. Qual. **22**: 811–818

Zheng, S.Q., and Cooper, F.J. 1996. Adsorption, desorption, and degradation of three pesticides in different soils. Arch. Environ. Contam. Toxicol. **30**: 15–20.

Zheng, S.Q., Cooper, F.J., Fontanel, P.V., Cost, C.M., and Meat, M. 1993. Distribution and dissipation of metolachlor in soil column. J. Environ. Sci. Health **6**: 641–653.