

Clay-based formulations of metolachlor with reduced leaching

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Abstract

The current research in herbicide application aims to develop formulations that reduce leaching of the herbicide to deep layers of the soil and to concentrate its biological activity at the top layers. Adsorption of metolachlor on clay minerals, their organic derivatives or pillared forms provides the best possibility to develop slow-release formulations. Metolachlor is a selective pre-emergence herbicide widely used in irrigated crops to control annual weeds. It is adsorbed by bentonites and montmorillonites, but the amount adsorbed strongly depends on the type of bentonite and possible pretreatment reactions. Wyoming bentonites adsorbed considerable amounts of metolachlor but other bentonites did not bind this herbicide. An acid-activated pillared montmorillonite was also an effective adsorbent of metolachlor. Modification of this sample by preadsorbing different amounts of benzyl trimethylammonium ions did not influence the level of herbicide adsorption. The biological efficiency of the formulations was tested with bioassay soil columns. Slow-release formulations could be prepared with raw bentonites and the acid-activated pillared montmorillonite. A formulation, prepared by adsorbing metolachlor from aqueous solution on the acid-activated pillared montmorillonite, showed high herbicide activity at the top 10 cm, and did not diffuse significantly to greater depths. This formulation should allow a better weed control than the commercial formulations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The increased use of herbicides poses environmental and economic problems. Volatilization and photodegradation reduce the active amounts, leaching and surface migration contaminate surface and ground water. The loss of efficiency must be com-

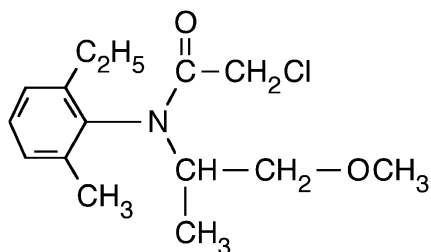
pensated by increasing frequency and dose of herbicide application and, therefore, raises contamination and costs.

Metolachlor is a selective pre-emergence herbicide widely used in irrigated crops such as potato, peanuts, corn and sunflower to control annual weeds. Due to the relatively high solubility of metolachlor in water (530 mg/l), it has a high potential to leach and migrate through the soil profile and contaminate ground water (Cohen et al., 1984, 1986; Chesters et

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al., 1989; Gallagher et al., 1996; Pasquarell and Boyer, 1996). Metolachlor was also detected in streams and rivers (Albanis et al., 1994; Fischer et al., 1995), in lakes (Schottler and Eisenreich, 1993; Spalding et al., 1994) and in surface water at the highest concentration out of 17 herbicides (Senseman et al., 1997).



Metolachlor

A positive correlation was reported between the organic matter, the clay mineral content (in weight percent), the surface area of the soil and its capacity to adsorb metolachlor. There was a negative correlation between these properties and the migration rate of metolachlor in the soil (Peter and Weber, 1985; Bosetto et al., 1994; Zheng and Cooper, 1996).

Several attempts were made to prepare formulations of metolachlor that pose less environmental risk and improve agricultural economy. These attempts involved the use of starch encapsulation (Gorski et al., 1989; Wienhold et al., 1993) and formulations based on alginate (Vollner, 1990; Gerstl et al., 1998a,b). Clays and clay minerals represent another group of additives for slow-release formulations. 2:1 clay minerals provide different adsorption sites for neutral molecules (external and internal cations, surface oxygen atoms, silanol and aluminol groups at the edges, etc.). By modifying the clay minerals with organic cations, the surface is made hydrophobic and the adsorption of pesticide molecules is enhanced. Decades ago, pyridinium montmorillonite was used to stabilize the herbicide *N*, *N*-di-*n*-propyl thiocarbamate (Mortland and Meggitt, 1966; Mortland, 1968). Later, this idea was taken up to protect herbicides against photodegradation (Margulies et al., 1992, 1993; El-Nahhal et al., 1999a) and to reduce leaching and volatility of alachlor and metolachlor. Adsorption of alachlor and metolachlor on a bentonite (SWy-1, Source Clays

Repository) was very efficient when the clay mineral was modified by cation exchange with benzyl trimethyl ammonium ions (BTMA). The raw bentonite only adsorbed 3% of the amount of metolachlor added, whereas bentonite preadsorbed with 0.5 mmol BTMA/g and 0.8 mmol BTMA/g adsorbed, respectively, 25% and 20% of the amount added (El-Nahhal et al., 1998, 1999b).

A further possibility is opening the interlayer spaces by pillaring reactions to promote penetration of the pesticide molecules between the layers. In addition, modification of the gallery by organic cations or molecules can increase adsorption (Zielke and Pinnavaia, 1988; Srinivasan and Fogler, 1990; Michot and Pinnavaia, 1991; Mishael et al., 1999). Studies on the release of alachlor from Al-pillared montmorillonite and its transport in soil columns revealed the potential use of pillared montmorillonites for slow-release formulations of herbicides (Gerstl et al., 1998a).

We describe the application of unmodified bentonites, montmorillonites, and an acid-activated pillared montmorillonite in slow-release formulations. The reduced leaching by montmorillonite modified with benzyl trimethylammonium cations was reported in the two preceding papers (El-Nahhal et al., 1998, 1999a,b).

2. Materials and methods

2.1. Metolachlor

Metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide], C₁₅H₂₂ClNO₂, molecular mass 283.8, was received from Chem Service (West Chester, PA, USA, purity 99%). Agan Chemical (Israel) provided the commercial formulation of this herbicide.

2.2. Bentonites and montmorillonites

Bentonites from Otay, Wyoming, Greece and Turkey (Table 1) were used in raw and purified form. The sodium montmorillonites were obtained by two methods: as described by Stul and van Leemput (1982) and Tributh and Lagaly (1986), carbonates were removed by sodium acetate/acetic acid buffer, iron oxides by dithionite/sodium citrate, and

Table 1
Layer charge and interlayer cation exchange capacity of montmorillonites

Sample	Layer charge, eq/(Si,Al) ₄ O ₁₀	Interlayer CEC, meq/g
Otay bentonite (API #24)	0.33	0.89
Wyoming Bentonite (M40A)	0.29	0.78
Wyoming Bentonite (M40A) (dithionite/citrate method)	0.29	0.79
Wyoming Bentonite (M40B)	0.28	0.75
Milos Bentonite (M48)	0.31	0.84
Milos Bentonite (M48) (dithionite/citrate method)	0.33	0.89
Ordu Bentonite (M50)	0.33	0.90

organic materials by hydrogen peroxide. The bentonite was then fractionated by sedimentation to obtain the montmorillonite-rich fraction < 2 μm . In other experiments, only carbonates and iron oxides were decomposed by reaction with hydrochloric acid and sodium oxalate (Janek et al., 1997). To ensure complete transformation into the sodium form, all samples were washed several times with 1 M NaCl, dialyzed and freeze-dried.

2.3. Pillared montmorillonite

The acid-activated pillared montmorillonite was prepared in kg batches at the National Technical University of Athens, as described elsewhere (Jones et al., 1997). The precursor montmorillonite was Fulcat F22B (Laporte). The pillared montmorillonite (Al-Fulcat batch w1) had a specific surface area of 256 m²/g. The micropore walls contributed by about 50% to the total surface area. The low micropore volume (0.04 cm³/g) compared to the total pore volume (0.26 cm³/g) reflected the mesoporous character of this sample. The cation exchange capacity, CEC, was 0.53 meq/g (Cu²⁺ (ethylenediamine) exchange, Bergaya and Vayer, 1997).

2.4. Organo derivatives

The raw Wyoming bentonite M40B was exchanged with benzyl trimethylammonium chloride (BTMA, purum grade, Fluka). A 5% (w/w) aqueous dispersion of the bentonite was mixed with the same volume of an aqueous solution of benzyl trimethyl-

ammonium chloride. The amount of BTMA was 7.5 mmol (corresponding to twice the interlayer exchange capacity, Table 1). The dispersion was held at 60–70°C for 24 h. The exchange reaction was repeated after centrifugation. The sample was washed with water–ethanol (1:1 per volume) in a flow-through cell (Lagaly, 1994) and freeze-dried. CHN analysis revealed a BTMA content of 0.70 meq/g.

BTMA-pillared montmorillonite (0.14 and 0.2 mmol BTMA/g pillared montmorillonite) was prepared by dropwise addition of aliquots of 0.01 M BTMA bromide (Aldrich) to 200 ml of 0.5% (w/v) clay suspensions under continuous stirring (Mishael et al., 1999). After 24 h of stirring, the suspensions were centrifuged at 16 000 $\times g$ for 30 min; the supernatants were discarded and the samples were freeze-dried. The BTMA concentration in the supernatants was measured by UV–Vis absorption (spectrophotometer Uvikon 810, Hewlett-Packard, Germany). The amounts of BTMA cations adsorbed were determined from the depletion of the solutions.

2.5. Adsorption isotherms

The adsorption of metolachlor on the bentonites and montmorillonites was measured by batch experiments at solid contents of 2.5 g/l. Amounts of 100 mg of the adsorbent were dispersed in aqueous solutions of increasing metolachlor concentration (0–1400 $\mu\text{mol/l}$). Water was added to reach a final volume of 40 ml. The dispersions were equilibrated in an overhead shaker at room temperature (20 \pm 3°C) overnight. Amounts of 2 ml of the dispersions were centrifuged at 10 000 $\times g$ for 1 h at 20°C. The supernatants were analyzed by HPLC (Waters, reversed phase system; NovaPak RP18 column, 15 cm, particle size 4 μm ; eluent: methanol/water (3:1 per volume), flow rate 1 ml/min; UV detection at 220 nm).

The metolachlor isotherms on the pillared montmorillonite were measured in the concentration range of 0–1056 $\mu\text{mol/g}$ montmorillonite. Aliquots of an aqueous stock solution of 10^{−3} M metolachlor were diluted with distilled water to 25 ml and added to 5 ml of a 0.5% (w/v) clay suspension under continuous stirring. After shaking the samples for 24 h at 20 \pm 1°C, the suspensions were centrifuged at 10 000 $\times g$ for 30 min. Metolachlor was extracted from the

supernatant by ethyl acetate/isooctane (1:9 v/v, HPLC grade, Sigma, Aldrich). Its concentration was measured by gas chromatography, and the amount adsorbed was determined from the difference (El-Nahhal et al., 1999b). Hewlett-Packard gas chromatograph 6890, electron-capture detector; Rtx[®]-5MS Capillary Column, 30 × 0.25 mm, film thickness 0.25 μm, from Restek, Bellefonte, PA, USA; carrier gas: nitrogen at a flow-rate of 2 ml/min. The nitrogen set-up flow rate was 30 ml/min. The injector and detector temperatures were 250°C and 280°C, respectively. The column was held at 170°C for 1 min; the temperature was then increased to 250°C at a rate of 5°C/min and held at this temperature for 5 min. Blank recovery was 102 ± 3%.

2.6. Preparation of formulations

2.6.1. Bentonite

Formulations were prepared with bentonite M40B and its BTMA derivative (100% exchange). An amount of 1 g of metolachlor was dissolved in 50-ml methanol. This solution was added dropwise to 600 ml of a 1.9% dispersion of bentonite in methanol. Stirring was continued for 12 h. Methanol was evaporated in a rotational evaporator at 40°C; the solid material was then dried at 60°C and ground in a ball mill. The metolachlor content was 9.93% (w/w). A formulation with BTMA-bentonite was prepared in the same manner (metolachlor content 11.0% w/w).

In addition, formulations containing mixtures of metolachlor-loaded BTMA-bentonite and unloaded bentonite were prepared. The idea was that a diffusion of metolachlor between BTMA bentonite and bentonite may delay the release of metolachlor. Therefore, 7.5 g BTMA bentonite was dispersed in 500 ml methanol (overhead shaker, overnight), and 1.7 g metolachlor dissolved in 200 ml methanol was added under continuous stirring. The dispersion was stirred for 24 h before the methanol was evaporated. The powder was dried at 65–75°C and mixed with 7.2 g bentonite and ground in a ball mill. The metolachlor content was 9.6% (w/w).

2.6.2. Acid-activated pillared montmorillonite

Appropriate amounts of technical grade metolachlor dissolved in acetone (denoted a) were added to the dispersed pillared montmorillonite (Al-Fulcat

w1) or the BTMA derivative in acetone with a total volume of 100 ml. The solvent was evaporated under reduced pressure. Some of the formulations from acetone were washed with distilled water (3000 ml/2.5 g clay, denoted a–w), centrifuged at 16 000 × g for 30 min.; the supernatant was discarded and the solid material was freeze-dried. The metolachlor content was 6.5% (w/w). In addition, formulations (denoted w) were prepared from aqueous solutions by adding technical grade metolachlor to the montmorillonite dispersions as described for the adsorption measurements (metolachlor content: 7% w/w).

2.7. Leaching studies

Tin columns, 10 × 10 cm and 25 cm long, were filled with a sandy soil (collected from the top 30 cm of a sandy loam soil at the Faculty's Experimental Farm in Rehovot, air-dried and sieved < 2 mm) (El-Nahhal et al., 1998). The column surface was sprayed with the metolachlor formulations (Table 1) at a rate of 2.0 kg active ingredient/ha. The experiment was performed in triplicates for each formulation. The columns were carefully irrigated with 500 m³ water/ha applied in portions during 3–5 h with 20-min intervals. This irrigation level was selected to ensure water movement up to 30 cm depth. The columns were left for 72 h for equilibration and then sliced along their length to obtain two pots 10 × 5 × 25 cm. Two test plant species, green foxtail (*Setaria viridis* L. *beauvies*) and wheat (*Triticum aestivum*, cv. *ariel*), were sown in two rows in each pot. To ensure germination and growth, the pots were sprinkle-irrigated when needed. Sixteen days after sowing, the shoot height of the test plants was measured to estimate the herbicide activity in the column at different soil depths.

3. Results and discussion

3.1. Adsorption on bentonites and montmorillonites

Adsorption of metolachlor from aqueous solutions basically represents an adsorption process from binary liquid mixtures (Dékány et al., 1986a,b; Szántó et al., 1986; Berger et al., 1997). Because of the low

solubility of metolachlor in water, the adsorption process may be similar to the adsorption of butanol or pentanol from water on modified silicates (Regdon et al., 1994, 1998; Dékány et al., 1996). In fact, metolachlor was preferentially adsorbed from aqueous solutions. Surprisingly, several bentonites adsorbed metolachlor in amounts comparable to the amounts adsorbed by the organo derivatives and the pillared forms (Fig. 1). The adsorption strongly depended on the type of montmorillonite and pretreatment reactions (Figs. 2 and 3). Wyoming bentonite M40A adsorbed the highest amounts of metolachlor, about 50% of the amount of metolachlor added. At equilibrium concentrations of 175 ppm metolachlor, $\sim 180 \mu\text{mol/g}$ were adsorbed. The reduced adsorption by Wyoming bentonite M40B, 25–35% of the amount of metolachlor added, may be a surprise but variations are not unexpected when we consider the large Wyoming bentonite deposit consisting of different types of bentonites (Odom, 1984). Calcium bentonite of Milos adsorbed less than $50 \mu\text{mol/g}$ metolachlor (about 16% of the amount added), and the Turkish and Otay calcium bentonite were inactive.

Both Wyoming bentonites are sodium-rich and the superiority to the other bentonites may be caused by the delamination in water, which increases the surface area accessible to the adsorptive. However, transformation of the Milos and Ordu bentonites to

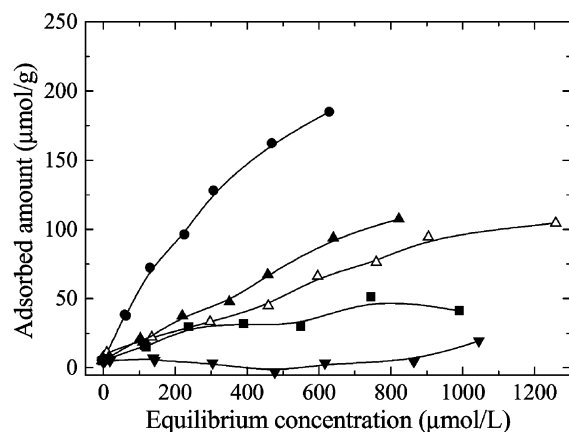


Fig. 1. Adsorption of metolachlor on raw bentonites and on the BTMA derivative of Wyoming bentonite. (●) Wyoming bentonite (M40A); (▲) Wyoming bentonite (M40B); (■) Milos bentonite (M48); (▼) Ordu bentonite (M50); (△) BTMA derivative of Wyoming bentonite (M40B).

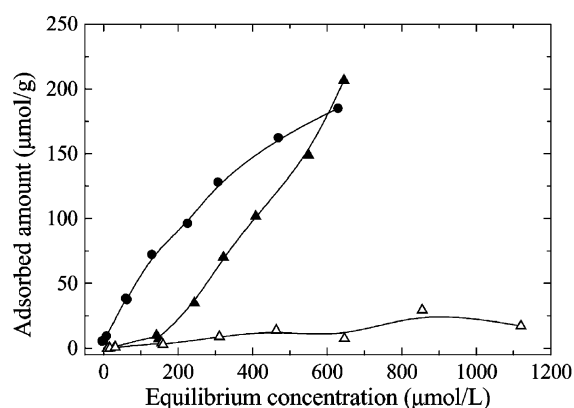


Fig. 2. Adsorption of metolachlor on the sodium montmorillonite prepared from Wyoming bentonite (M40A). (●) Raw Wyoming bentonite; (▲) sodium form (dithionite/citrate extraction and H_2O_2 treatment); (△) sodium form (oxalate method).

the sodium form further reduced metolachlor adsorption. Also, the sodium form of Otay bentonite did not adsorb metolachlor.

The method of bentonite purification is also important (Figs. 2 and 3). The classical procedure (dithionite/citrate method) reduced the amounts adsorbed and changed the shape of the adsorption isotherm. The S-shape indicated a cooperative character of the adsorption on the pure sodium montmorillonite, i.e. adsorbed molecules favor the adsorption

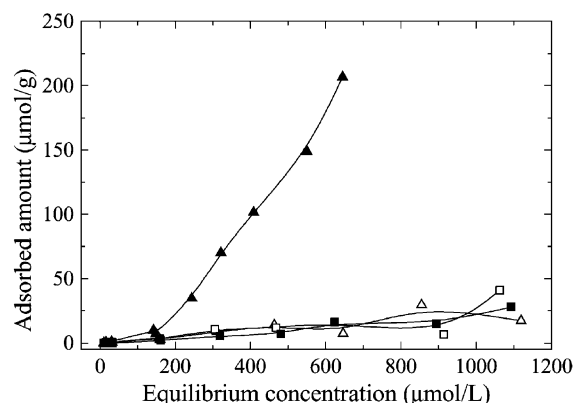


Fig. 3. Adsorption of metolachlor on sodium montmorillonites prepared from Wyoming (M40A) (▲, △) and Milos (M48) bentonite (■, □). (▲, ■) dithionite/citrate extraction and H_2O_2 treatment (△, □) oxalate method.

of further adsorptive (Giles et al., 1960; Gregg and Sing, 1967). In contrast, the raw bentonite showed an L-type isotherm which indicated the absence of adsorbate–adsorbate interactions at the surface. Pre-treatment with oxalate/HCl reduced adsorption to extremely small amounts.

It follows from this behavior that neither adhering organic material nor the iron oxides must be considered as important adsorption sites of metolachlor. Most likely, the herbicide adsorbs at the silicate surface itself between the charged sites (the uncharged siloxane groups are hydrophobic), and may be held there by accepting hydrogen bonds from water molecules around the interlayer cations. The presence of calcium ions in the raw Wyoming bentonites promotes the adsorption, in comparison with the pure sodium form (Fig. 2). The cause is that the metolachlor is trapped between the silicate layers of tactoids or coagulated particles (Nennemann et al., 2001). It is difficult to understand why oxalate treatment impedes metolachlor adsorption. The colloidal dispersion of this sodium montmorillonite is less stable, the montmorillonite particles settle within hours. It may be that the rapid aggregation impedes the herbicide adsorption. In addition, one cannot exclude that chemical changes of the edge regions by the acid and the oxalate ions influence the hydrophobic/hydrophilic character of the layers (see below).

The different behavior of the Wyoming, Milos and Ordu bentonites is related to the different ability of these bentonites to stabilize oil–water emulsions. For instance, stable paraffin oil–water emulsions could be prepared with the Wyoming bentonites. Ordu bentonite stabilized these emulsions only in the presence of a layered double hydroxide (Abend et al., 1998; Abend, 1999). Evidently, the Wyoming montmorillonites are more hydrophobic than the other samples. These differences may be caused by the chemical nature of the silicate layers. Yariv et al. (Schrader and Yariv, 1991; Yariv, 1992; Yariv and Michaelian, 1997; Garfinkel-Shweky and Yariv, 1997) discussed the influence of tetrahedral substitutions on the hydrophobic/hydrophilic balance of the oxygen plane of the silicate layers. Without tetrahedral substitution the surface is hydrophobic in nature, but becomes hydrophilic to some extent when Si–O–Si siloxane groups are replaced by Si–O–Al groups.

3.2. Adsorption by pillared montmorillonites

The adsorption isotherms of metolachlor on pillared montmorillonite, preadsorbed with different amounts of BTMA (0, 0.14, 0.20 mmol/g), are presented in Fig. 4. The amounts adsorbed are similar in all three cases, between 19% and 25% of the amount added. In contrast to the behavior of bentonite Swy-1 (Source Clays Repository), preadsorption of BTMA cations did not enhance metolachlor adsorption. Nir et al. (1999) suggested that the adsorption of metolachlor on BTMA–montmorillonite is promoted by the interaction between the phenyl ring of BTMA and the phenyl ring of metolachlor. Hydrogen bonds do not play an important role because metolachlor can only function as an acceptor, and the interlayer space of the BTMA montmorillonite has no donor sites for hydrogen bonds. Only hydration water around the remaining inorganic interlayer cations (at incomplete exchange) can provide protons for hydrogen bonds. In contrast, the acid-activated pillared montmorillonite provides many donor sites for hydrogen bonds. The oxygen atoms of metolachlor act as acceptors. The quaternary nitrogen atom is shielded by the alkyl chains and does not contribute to hydrogen bonds. This may explain the similar high level of metolachlor adsorption on the pillared montmorillonite and its BTMA derivatives.

The adsorption of neutral molecules on clay minerals can be described by the Scatchard equation,

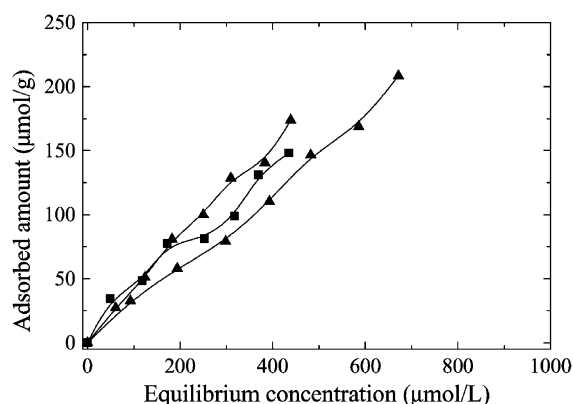


Fig. 4. Adsorption of metolachlor on acid-activated montmorillonite preadsorbed with 0 (■), 0.14 (▲), and 0.20 (◆) mmol BTMA/g.

which is equivalent to the Langmuir equation (Nir et al., 1994; Rytwo et al., 1998). The binding coefficient k (in M^{-1}) is a measure of affinity between the herbicide and the adsorbent. The applicability of the Scatchard equation was tested by the correct simulation of the adsorption isotherm. The results in Table 2 demonstrate that the Scatchard equation yields good fit to the experimental amounts adsorbed. The values of the binding coefficients provide a convenient scale for comparison, rather than absolute values of the changes of the free adsorption energy.

3.3. Leaching studies

The herbicide activity and the efficiency to reduce metolachlor leaching, in comparison with the commercial formulation, was tested with different formulations of metolachlor adsorbed on bentonites, pillared montmorillonite and on the BTMA derivatives (Table 3). Wheat displayed insufficient sensitivity to metolachlor to detect the differences between the various formulations.

3.3.1. Bentonites and montmorillonites

The simplest and most economical way in preparing slow-release formulations would be the direct use of raw bentonites. Methanol was chosen as the solvent for impregnation of the bentonite with metolachlor from a practical reason. The solubility in methanol is much higher than in water (and also higher than in acetone), which allows the preparation of the metolachlor/bentonite material without apply-

Table 3
Formulations of metolachlor

Adsorbent	Solvent
Bentonite Wyoming (M40B)	methanol
BTMA bentonite Wyoming (M40B)	methanol
BTMA bentonite loaded with metolachlor + unloaded	methanol
raw bentonite (1:1)	
BTMA bentonite loaded with metolachlor + unloaded	methanol
BTMA bentonite (1:1)	
Acid-activated pillared montmorillonite	w: water
	a: acetone
	a-w: from acetone, then water-rinsed
	B w: from water
BTMA derivative of the acid-activated pillared montmorillonite (0.14 mmol BTMA/g)	B a-w: from acetone, then water-rinsed

ing large volumes of solvent. The idea was that the clay mineral particles are covered with a film of metolachlor when the solvent is evaporated. By dispersing this material in water during application, the particles would disaggregate and delaminate to some extent. The freshly created surfaces adsorb dissolved metolachlor. In addition, the films of metolachlor surrounding the particles may not be totally dissolved so that the particles carry higher amounts of the herbicide into the dispersion than amounts corresponding to the solubility in water. Takahashi and Yamaguchi (1991) described a similar process to enhance the solubility of poorly water-soluble drugs.

Fixation of metolachlor in adsorption layers or thin coatings should reduce the release of the herbicide during irrigation. In fact, leaching tests (Fig. 5a) showed a considerable improvement in comparison with the commercial formulation. Bentonite M40B totally inhibited the growth of *Setaria* up to 10 cm; inhibition was partial between 10 and 17 cm and absent at larger depths. The growth inhibition was even slightly better than for the BTMA derivative (100% exchange). Similar results were observed when mixtures of metolachlor-loaded BTMA-bentonite and unloaded bentonite or BTMA-bentonite were used. In these cases, metolachlor released from the loaded particles could be trapped by the unloaded bentonite. If equilibrium was established, the ratio

Table 2

Binding coefficients for the adsorption of metolachlor on raw Wyoming bentonite and acid-activated pillared montmorillonite (Al-Fulcat w1)

Sample	BTMA preadsorbed, mmol/g	k , M^{-1}	R^{2a}
Wyoming M40A	0	560	0.99
Wyoming M40B	0	220	0.99
Wyoming M40B	0.70	150	0.97
Pillared clay	0	750	0.96
Pillared clay	0.14	700	0.96
Pillared clay	0.20	950	0.99

^aThe root mean square errors were within the experimental errors.

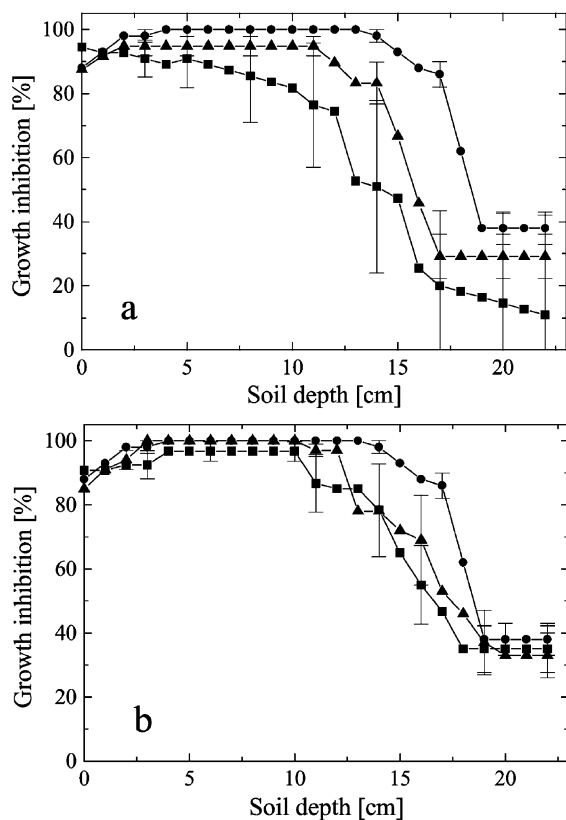


Fig. 5. Growth inhibition of green foxtail (*Setaria viridis*) as a function of the depth of soil columns sprayed with formulations of metolachlor on Wyoming bentonite (M40B). (a) ■, Raw bentonite; ▲, BTMA bentonite; ●, commercial formulation. (b) ■, Metolachlor loaded BTMA bentonite + unloaded bentonite (1:1); ▲, metolachlor loaded BTMA bentonite + unloaded BTMA bentonite (1:1); ●, commercial formulation.

metolachlor/adsorbent was half of that in the other formulations. Probably, this ratio should be further reduced to optimize the profile of herbicide activity.

There are several ways to optimize these slow-release formulations. As just mentioned, the ratio metolachlor/adsorbent is important but the solvent may also have strong influence. As revealed by the adsorption experiments, the molar ratio $\text{Ca}^{2+}/\text{Na}^{+}$ is decisive. Sodium ions increase the degree of delamination and, therefore, the possible sites of adsorption. On the other hand, formation of tactoids or aggregates by calcium ions increases the level of herbicide adsorption (Nennemann et al., 2001).

3.3.2. Acid-activated pillared montmorillonite

Figs. 6 and 7 show the growth inhibition of green foxtail by formulations with pillared montmorillonite. The activity of the commercial formulation was 100% up to a depth of ~14 cm, and the growth was partially inhibited at a depth of 16–20 cm (the depth of the soil column was 20 cm). Thus, leaching took place up to these depths. It is possible that a portion of the formulation was leached out of the columns.

Formulation a, prepared from acetone (Table 3), showed an activity similar to that of the commercial one (Fig. 6); growth inhibition was weaker at 16–20 cm, i.e. leaching was slightly reduced. The behavior of this formulation indicated that not all metolachlor was bound strongly enough and a part was leached by irrigation. Therefore, the formulation prepared from acetone and rinsed with water was more efficient than the one prepared from acetone. Growth inhibition decreased at a depth of 16–18 cm.

Most efficient was the formulation from water, which showed activity only at the top layers of the soil. Inhibition was complete at the top 10 cm, partial between 10 and 16 cm and absent at deeper layers. These results indicate that the herbicide was not leached to the deeper layers of the soil, and the activity was concentrated at the top 10 cm.

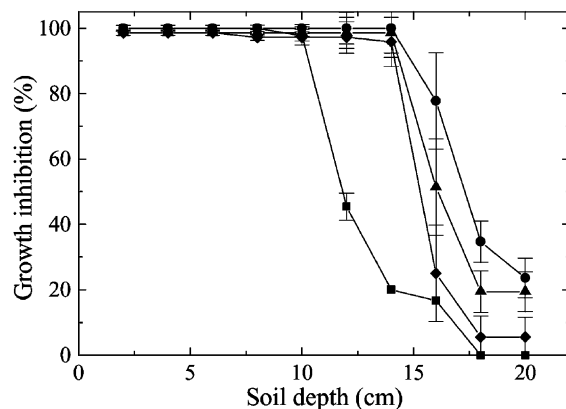


Fig. 6. Growth inhibition of green foxtail as a function of the depth of soil columns sprayed with formulations of metolachlor on acid-activated pillared montmorillonite prepared from water (■), acetone (▲), acetone and rinsed with water (◆) (see Table 1), and with the commercial formulation (●). The error bars denote the standard error.

The use of the BTMA derivative (formulations B w, B a–w, Table 3) showed no advantage over the adsorption on the pillared montmorillonite (Fig. 7).

The formulations with pillared montmorillonite showed a similar activity as BTMA–montmorillonite formulations with 0.5 mmol BTMA/g (El-Nahhal et al., 1999b). Formulation w might have an advantage since addition of organic cations is not required. BTMA complexes with montmorillonite are not toxic (El-Nahhal, 1999a,b), whereas hexadecyltrimethylammonium cations are toxic to a few bacteria (Xu et al., 1997).

The leaching characteristic of formulation w, which was the most efficient among the five formulations studied with pillared montmorillonite, was tested under two irrigation cycles. The soil columns were sprayed with 2 kg active ingredient/ha of formulation w and a commercial formulation, irrigated with 500 m³ water/ha, left to settle for a week and were then irrigated again with 500 m³ water/ha. Fig. 8 shows the growth inhibition of the green foxtail as a function of the depth of the soil columns, after one and two irrigation cycles. The growth inhibition after one irrigation cycle was similar to the results in Fig. 6. After the second cycle, the commercial formulation led to 100% inhibition throughout the entire column; likely, a portion of the formula-

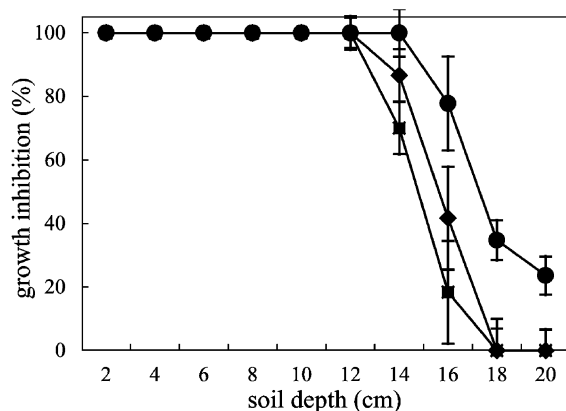


Fig. 7. Growth inhibition of green foxtail as a function of the depth of soil columns sprayed with formulations of metolachlor on acid-activated pillared montmorillonite preadsorbed with 0.14 mmol BTMA/g, prepared from water (■), acetone and rinsed with water (◆), and with the commercial formulation (●). The error bars denote the standard error.

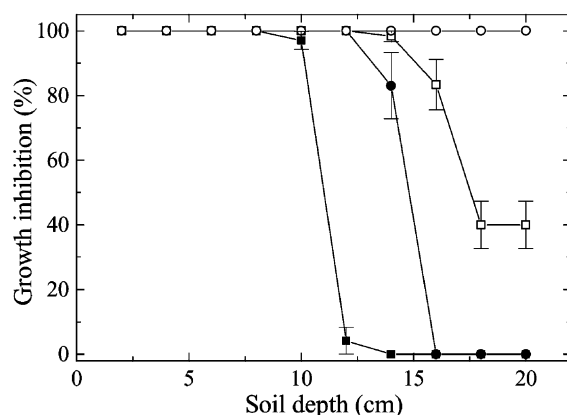


Fig. 8. Growth inhibition of green foxtail as a function of the depth of soil columns sprayed with formulations of metolachlor on acid-activated pillared montmorillonite prepared from water (■, □), and with the commercial formulation (●, ○). The error bars denote the standard error. (■, ●) after one irrigation cycle; (□, ○) after two irrigation cycles.

tion was rinsed out of the column. Formulation w totally inhibited growth up to ~16 cm and partially (80–40%) at depths of 16–20 cm.

4. Conclusion

Metolachlor is adsorbed by raw and purified bentonites but the amount adsorbed depends on the type of bentonite and pretreatment reactions. The adsorption can be enhanced by modifying the bentonite or montmorillonite with benzyl trimethylammonium cations. However, some raw bentonites can reach comparable levels of metolachlor adsorption without the organic cation, or, as in the case of Wyoming bentonite (M40A), even higher levels. Impregnation of suitable raw bentonites provides the simplest and most economical way to prepare slow-release formulations.

An efficient slow-release formulation was prepared by adsorbing metolachlor from water on an acid-activated pillared montmorillonite. This formulation showed herbicide activity only at the top layers. Different loads of BTMA did not effect the high level of metolachlor adsorption by the pillared montmorillonite. This behavior is related to the formation of hydrogen bonds between metolachlor and pillared montmorillonite.

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