Organo-clay formulations of pesticides: reduced leaching and photodegradation

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Abstract

Adsorption of organic cations on several clay minerals is reviewed with an emphasis on the effect of ionic strength and modeling. The clay exchanged with suitable organic cations forms a basis for ecologically acceptable formulations of herbicides with reduced leaching, ground water contamination and enhanced weed control efficacy. Incomplete neutralization of the clay surface charge by an organic cation may be advantageous in achieving maximal adsorption of hydrophobic herbicides. One conclusion from these studies is that optimization of clay-based herbicide formulations requires a selection of structurally compatible organic cations preadsorbed on the clay at optimal coverage. New experimental results are presented for alachlor formulations, which significantly reduce herbicide leaching under conditions of heavy irrigation. We were able to demonstrate that organo-clay formulations of alachlor and metolachlor can increase crop yields in a 1-year field experiment. The photostabilization of pesticides is reviewed and improved organo-clay formulations of the herbicides trifluralin and norflurazon are described. A pillared clay, nanocomposite micro- and/or meso porous material, was effective in reducing leaching and in conferring photostabilization, without added organic cations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Herbicide run-off and leaching down the soil profile have become a serious environmental prob-

lem and a primary source for polluting surface- and groundwater (Carter, 2000). Widely used herbicides such as atrazine, isoproturon, diuron and mecoprop are the main herbicides found in groundwater in the UK, whereas atrazine, alachlor and metolachlor were detected in ground water in other European countries and the US (El-Nahhal et al., 1997, 1999a). Herbicide movement in the soil profile is highly dependent

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on the soil characteristics, such as structure, organic matter content, pH and biological activity. It is also influenced by tillage, the amount and timing of rainfall or irrigation.

Leaching may reduce the concentration of herbicides in the topsoil below the threshold needed for weed control. The leached compounds may accumulate in the crop's root zone to levels that endanger crop safety. Leaching into deeper layers of the soil profile may increase the residual activity of the herbicide, as the microbial activity responsible for the degradation of most herbicides in these depths is lower.

This article focuses on reviewing progress in the design of clay-based formulations of herbicides, which can yield slow release and consequently re-duce significantly herbicide leaching in soil. Clays constitute a natural component of soils and can serve as a cheap ingredient in such formulations. Since clay minerals are negatively charged and hydrophilic, their modification is required for the sorption of hydrophobic herbicides, such as alachlor, metolachlor, or acetochlor. Using hexadecyltrimethylammonium (HDTMA) (El-Nahhal et al., 1998) as the exchanging cation did not yield satisfactory results in terms of enhancing the ability of montmorillonite to adsorb and control the release of the above herbicides. Since the above herbicides have a phenyl ring, several organic cations with a phenyl ring, such as benyzyltrimethylammonium (BTMA) (see Fig. 1) were extensively applied. This application generates structural similarity between the exchanged organic
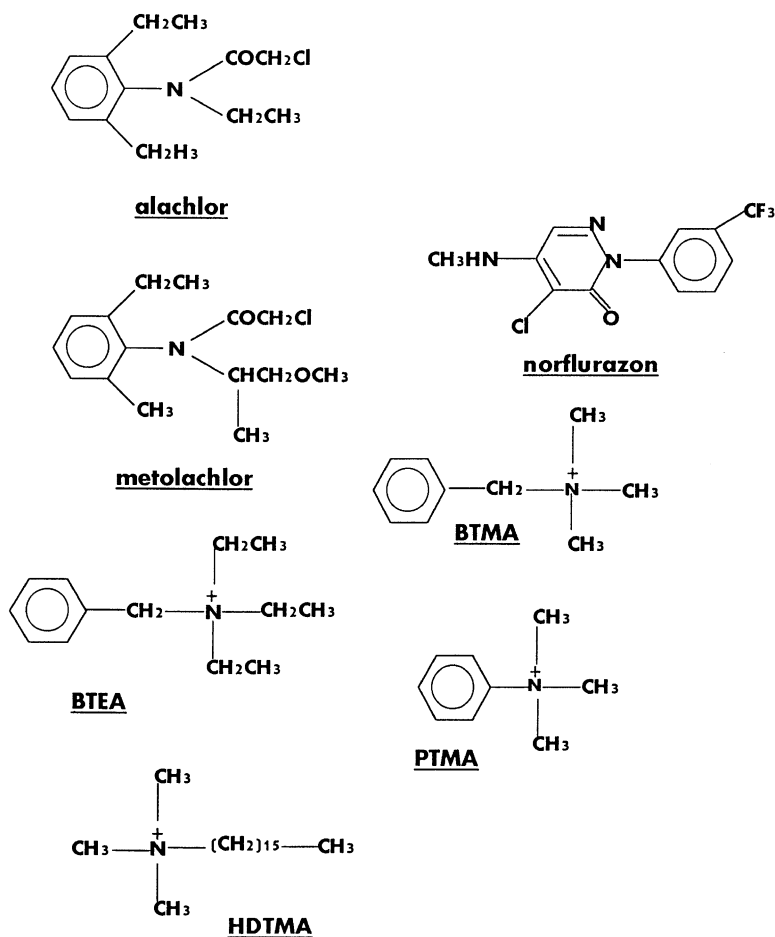

Fig. 1. Molecular structures.

cation and the herbicide molecules. This similarity may enhance the interactions between the herbicide and adsorbed organic cation, and increase herbicide adsorption on the organo-clay complex. We will review the outcome of studies that have yielded satisfactory organo-clay formulations of alachlor and metolachlor. Encouraging preliminary results have already been obtained in the case of acetochlor.

We will also present preliminary results on the design of organo-clay formulations of anionic herbicides, such as sulfometuron, by preadsorbing a monovalent organic cation on the clay at a loading above the cation exchange capacity (CEC) of the clay mineral. Clearly, an adequate design of organo-clay formulations is based on an understanding of interactions of organic molecules with clay minerals. We review the adsorption of organic cations by clay minerals, and describe a model that can predict the extent of adsorption in a system containing several cations at various ionic strengths. Photodecomposition of pesticides can also be reduced by the use of organo-clay formulations. A survey of such studies is presented, including some unpublished results.

In addition, we describe the results of tests and a 1-year field experiment which demonstrates that the application of alachlor as an organo-clay formulation under conditions of heavy irrigation, reduced its leaching and hence increased crop yield.

2. Materials and methods

2.1. Preparation of formulations

Herbicide formulations were prepared as previously described (El-Nahhal et al., 1998, 1999a). In this method, appropriate amounts of herbicide dissolved in acetone were added to the suspended powdered organo-clay in the same solvent, giving a total volume of 100 ml. The solvent was evaporated under reduced pressure as previously described (Margulies et al., 1988a, 1992). Clay complexes with varied loadings of herbicide active ingredients were prepared and examined. In another method, we used water as a solvent. In this case, the clay complex obtained by centrifugation at $20,000 \times g$ was used. Herbicide concentration in the supernatant was determined by GC (El-Nahhal et al., 1998, 1999a).

Here we only show the results of formulations prepared by the first method with a herbicide content of 13% w/w.

2.2. Herbicide leaching in laboratory experiments

The soils used and the detailed experimental protocol have been described elsewhere (El-Nahhal et al., 1998, 1999a). In these experiments, herbicide persistence in soil was estimated from its biological activity. Accordingly, organo-clay formulations and the commercial one (EC) were sprayed on the soil surface at the field rate (2 kg ai/ha) followed by irrigation (50 mm).

The macro-column surface (10×10 cm) with 25 cm length and the micro-columns 5 cm^2 with 25 cm length were packed manually with a sandy soil sieved with 2 mm mesh. The macro-column was sprayed with various formulations of alachlor at 2.0 kg ai/ha using an atomizer, whereas in a micro-column the herbicide was applied to the soil surface with a pipette. The columns were carefully irrigated with 500–1000 m^3/ha applied in portions for 3–5 h with 20-min intervals. The macro-columns were left for 24–48 h for equilibration and then the macro-columns were sliced along their lengths, hence forming two pots, $10 \times 5 \times 25$ cm each. Two test plants, green foxtail (*Setaria viridis*) and wheat, were sown in each pot in two rows. The pots were sprinkler-irrigated as needed. The micro-columns were sealed at the top, placed horizontally, and the polyethylene tubes were sliced along their lengths. One row of green foxtail or wheat was sown along the length of the micro-columns. Shoot height and weight were determined 16 days after sowing and used as indicators to estimate the herbicide presence at different soil depths in the column. Growth inhibition was calculated according to the following equation:

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

where P_c and P_t are the shoot height of the control and the treated samples at a given soil.

2.3. Herbicide leaching in the field

Persistence of organo-clay formulations under extremely wet condition was tested in winter in Rehovot sandy soil which is similar to that in Gaza

(El-Nahhal et al., 1998). In this experiment, the field plots were sprayed with the herbicide formulation using a motorized sprayer with a spray volume of 300 l/ha at 245 kpa (El-Nahhal et al., 1998). The plots were sprinkler-irrigated at 500 m^3/ha followed by 130 mm rainfall precipitated in 2 days. Herbicidal efficacy was assessed from a reduction in the shoot fresh weight and by visual evaluation of the weed control efficacy after 1, 2, 4 and 8 weeks of treatment. Ratings were based on a scale of 0 (no control) to 100 (complete control). The planted test species as well as the natural weed species uniformly infesting the control plots were included in the ratings. The experimental layout was a randomized block design replicated five times.

Soil samples were taken from the top 25 cm to assess the persistence of the tested herbicides in different depth. A column was used to collect the soil samples by gently inserting it into a depth of 25 cm in each plot. A wide spatula was used to ensure complete removal of the soil in the column. The full column was carefully removed and transferred to a greenhouse. One row each of green foxtail or wheat seeds were sown in each column as described above. Activity of the herbicide formulations was estimated at various soil depths by a reduction of the shoot height or fresh weight of the test plant. The results indicated how deep the herbicide had leached after 50 mm of irrigation followed by 130 mm of rainfall. The columns were arranged in a completely randomized design with five replications per treatment.

2.4. Effect of herbicide formulation on crop yield

Experiments were conducted at one location in EPRI, Gaza Strip in 1996 and 1997. Beds (1 m wide and 5 m long) were prepared using a rotary tiller and planted with green foxtail (200 seeds/m row) in summer. Several rates of EC formulation of alachlor (2, 4 and 6 kg ai/ha) and one rate (2 kg ai/ha) of the organo-clay (alachlor-BTMA 0.5; alachlor-BTEA 0.8) formulations along with the organo-clay complex without alachlor were applied pre-emergence using a back-pack manual sprayer at spray volume of 300 l/ha. A sprinkler irrigation system was used to water the field sites at 50 mm. Nine pairs of peanut (*Arachys hypoeae*) seeds were sown in 3 rows/m^2. No fertilizers were added during the growing season.

Irrigation was continued as needed to maintain soil moisture for plant growth. Four months after sowing, the crop was collected manually. The experimental layout was a randomized block design containing two control samples, one infested with the green foxtail as a weed, and the second control sample was without weed infestation.

2.4.1. Data analysis

Growth inhibition of the test plant was subjected to analysis of variance, and main effects and interactions were tested for significance using repeated measures ANOVA (Analysis Of Variances). Univariate comparisons of mean peanut yields at different treatments were performed by Tukey's test ($\alpha = 0.05$).

3. Adsorption of organic cations on clay minerals

Organic cations are adsorbed on clay mineral surfaces by neutralizing the negative electrical charge responsible for the cation exchange capacity of the mineral. Adsorption is also influenced by other types of interactions such as van der Waals forces, ion-dipole forces, and hydrogen bonding (Mortland, 1970). Their importance depends on such factors as nature of the functional groups present in, molecular weight, and configuration of the organic molecules. Clay minerals were transformed from hydrophilic to hydrophobic by coating them with different types of alkylammonium and alkylpyridinium ions. The hydrophobicity increased with the degree of coverage and the alkyl chain length (Lagaly, 1987). Organic cations can be adsorbed beyond the cation exchange capacity (CEC) of clays (Grim et al., 1947; Margulies et al., 1988b; Jaynes and Boyd, 1991; Rytwo et al., 1991, 1995, 1996a; Zhang et al., 1993; Nir et al., 1994; Xu and Boyd, 1994, 1995). Alignment of organic cations on the clay surface is an important aspect of organo-clay interactions. Depending on the organic cation size and the mineral charge, the alkyl chains of *N*-alkylammonium cations may form either monolayers, bilayers, pseudotrimolecular layers, or paraffin complexes (Lagaly, 1982; Jaynes and Boyd, 1991). It was suggested that small organic molecules, such as trimethylammonium (TMA), BTMA, or BTEA exist as discrete entities in the siloxane sheets

of smectites (Boyd and Jaynes, 1992; Polubesova et al., 1997).

The geometry of organic molecules and charge density of the clay minerals affect the orientation of molecules in the interlayer space. Wolfe et al. (1985) found that dodecylammonium ions were oriented parallel to the bentonite basal plane surface, whereas propylammonium ions were oriented perpendicular to this surface. For crystal violet, a tilted configuration was suggested (Yariv et al., 1989; Rytwo et al., 1995), and similarly for methyl green (Margulies and Rozen, 1986).

The adsorption of organic cations can change the rheological properties of clays. For example, progressive coverage by methylene blue of sepiolite leads to a sharp decrease in the viscosity of the gels (Aznar et al., 1992). Sander and Lagaly (1983) found that the viscosity of dispersions of hydrophobic smectites in polar organic solvents (e.g., tetradecyl-ammmonium montmorillonite in dimethyl sulfoxide) could be considerably increased by addition of certain salts (e.g., CsI and LiCl). This effect was explained by the effect of the salts on the liquid structure.

Our focus here is on reviewing the experimental results of and modeling the adsorption of organic cations by clays.

3.1. Modeling of adsorption of organic cations

The modeling of experimental adsorption data can be carried out by one of two approaches: (i) empirical models, and (ii) mechanistic models. Empirical models give a simple description of the experimental data with no particular theoretical basis. An example is the frequent employment of the Freundlich isotherm. Mechanistic or surface complexation models make reference to thermodynamic concepts such as reactions described by the mass action law and material balance equations, and/or electrostatic equations.

A main difference between the mechanistic models used relates to the descriptions of the electric double layer, which are based on the Helmholtz, Gouy–Chapman and Stern–Grahame theories. These models simplify the ion distribution next to the surface, and require that the ions be located on some planes at specified distances from the surface . The

models differ in the number of specific planes, in the way that the surface reaction is conceived, and how the electrostatic potential is assumed to change between the planes (Sposito, 1984; Westall, 1986).

A model that could predict the adsorption of monovalent and divalent organic cations by clay minerals at different ionic strengths in solution has been developed (Nir, 1986; Margulies et al., 1988b; Nir et al., 1994; Rytwo et al., 1995, 1996b). The model considers the simultaneous adsorption of any number of cations and can also be used to account for the aggregation of organic cations in solution (Rytwo et al., 1995). In a recent study, on sepiolite, two types of surface binding sites were considered: charged and neutral ones (Rytwo et al., 1998).

The model is based on the following main elements:

1. Consideration of specific binding to the surface. The cations adsorbed are divided between cations bound (in the Stern layer) and those residing in the electrical double layer.
2. The electrostatic Gouy–Chapman equations are solved for a suspension containing cations and anions of various valencies. Changes in surface charge density are explicitly considered.
3. The amount of sites in the sorbent is considered, which results in a decrease in the concentration of the cations in solution due to their adsorption in a closed system.

The binding equations are given below. Let X_i^+ denote a monovalent cation that binds to a singly charged negative site P^- on the clay surface:

$$P^- + X_i^+ = PX_i \qquad (1)$$

with a binding coefficient, K_i, given by

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

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

An additional type of complexation was considered:

$$PX_i + X_i^+ = P(X_i)_2^+ \qquad (3)$$

with a binding coefficient

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

In Eqs. (2) and (4), the concentrations are given in units of mol l^{-1}, or M, and the unit of K_i or $\bar{K}_i$ is M^{-1}. The model equations include the relation:

$$X_i(0) = X_i Y_0^{Z_i} \tag{5}$$

where X_i is the molar concentration of cation i in its monomeric form in the steady-state solution, Y_0 is defined as $Y_0 = \exp(-e\varphi_{(0)}/kT)$, Z_i is the valence of the given ion, e is the absolute magnitude of an electronic charge, $\varphi_{(0)}$ is the surface potential, k is the Boltzmann constant, and T is the absolute temperature.

For a negatively charged surface, $Y_0 > 1$, and the concentration of the cation at the surface, $X_i(0)$, may be significantly larger than X_i. If charge reversal due to cation binding occurs, $\varphi_{(0)}$ is positive and $Y_0 < 1$, i.e., the concentration of cations in the double-layer region may be significantly smaller than their solution concentration.

The intrinsic binding coefficients K_i and $\bar{K}_i$ which reflect the strength of the chemical binding in Eqs. (2) and (4) can be determined from adsorption data (Margulies et al., 1988b; Rytwo et al., 1995). First, the binding coefficient $\bar{K}_i$ was fixed from adsorption results near and slightly above the CEC and then the parameter K_i was determined.

3.2. Maximal loads and adsorption affinities of organic cations

Data on the adsorption by clays of the monovalent organic cations: methylene blue (MB), crystal violet (CV), acriflavin (AF), thioflavin T (TFT), BTMA, BTEA, phenyltrimethylammonium (PTMA), mepiquat, chlordimeform, and of the divalent organic cations diquat (DQ) and paraquat (PQ) are presented in Table 1. The first four monovalent cations listed are organic dyes, which exhibit very large binding

Table 1

Binding coefficients and maximum amounts adsorbed for selected organic cations on montmorillonite, sepiolite and illite

Organic cation	Amount of added cation (mol_C kg^{-1})	Maximum amount adsorbed (% of CEC)	Binding coefficients			References
			K (M^{-1})	$\bar{K}$ (M^{-1})	K_n (M^{-1})	
Montmorillonite CEC = 0.76–0.8 mol_c kg^{-1}						
TFT(+1)	1.5	140	10^9	1.5×10^6	–	Margulies et al. (1988a,b)
MB(+1)	3.5	150	3×10^8	10^6	–	Rytwo et al. (1995)
AF(+1)	3.5	175	10^9	6×10^5	–	Rytwo et al. (1995)
CV(+1)	3.5	200	10^6	8×10^9	–	Rytwo et al. (1995)
BTMA(+1)	3.3	104–108	5×10^3	20	–	Polubesova et al. (1997)
BTEA(+1)	4.4	98–108	5×10^3	5	–	Polubesova et al. (1997)
PTMA(+1)	5.0	122	1500	300	–	El-Nahhal et al. (2000)
Chlordimeform(+1)[a]	20	91	90	–	–	Undabeytia et al. (1999)
Mepiquat(+1)	7.0	106	300	10	–	Polubesova et al. (2001)
DQ(+2)	2.8	125	2.7×10^5	1.4×10^5	–	Rytwo et al. (1996b)
PQ(+2)	2.8	100	4.4×10^6	10^3	–	Rytwo et al. (1996b)
Sepiolite CEC = 0.14–0.15 mol_c kg^{-1}						
MB(+1)	0.9	405	3×10^8	10^6	3×10^6	Rytwo et al. (1998)
CV(+1)	0.9	460	10^6	8×10^9	3×10^6	Rytwo et al. (1998)
Illite CEC = 0.25 mol_c kg^{-1}						
CV(+1)	0.8	148	10^4	8×10^9	–	Polubesova and Nir (1999)
BTMA(+1)	2.5	100	500	–	–	Polubesova and Nir (1999)
BTEA(+1)	3.0	100	480	–	–	Polubesova and Nir (1999)

The numbers in parentheses indicate the valance status of the organic cation. The negative signs indicate absence of calculated value.

[a] In this case, the clay used was Ca-montmorillonite (CEC = 1.235 mol_c kg^{-1}). In all other cases, Na-montmorillonite was used.

affinities, i.e., large binding coefficients and adsorption beyond the CEC of the clay.

3.2.1. Montmorillonite

The monovalent cations BTEA and BTMA have large binding coefficients relative to monovalent inorganic cations, such as Na^+ ($K_{Na} = 1$ M^{-1}), but their adsorption is in most cases up to the CEC. Adsorption of PTMA can exceed the CEC. Its K-value for formation of neutral complexes is smaller than for BTMA/BTEA, whereas the $\bar{K}$-value for formation of charged dimers is larger. These three organic cations have been extensively used to produce organo-clay complexes, which form a basis for formulations of non-polar herbicides, such as alachlor or metolachlor. Mepiquat, a systemic plant growth regulator, is a monovalent cation, which commonly adsorbs up to the CEC, but still forms a small fraction of charged complexes. The monovalent organic cation chlordimeform is a pesticide whose adsorption does not exceed the CEC. Its binding affinity is the smallest of the above cations, but it is still several-fold larger than that of Na^+.

The divalent organic cations DQ and PQ are widely used herbicides. Both have very large binding coefficients, but only DQ adsorbs on montmorillonite above the CEC (Rytwo et al., 1996b).

3.2.2. Sepiolite

The large excess of MB and CV adsorption above the CEC of sepiolite is due to their adsorption on a substantial number of neutral sites of the clay, whose number was estimated between 3.4–4-fold of the charged sites (Rytwo et al., 1998).

3.2.3. Illite

The maximal adsorption of CV on illite was 148% of the CEC. The K-value of BTMA and BTEA was 10 times less for illite than for montmorillonite (Polubesova and Nir, 1999).

3.3. Effect of pH and ionic strength on adsorption of organic cations

The effect of pH on the adsorption of several monovalent dyes and the divalent cations diquat and paraquat on montmorillonite was studied by Narine and Guy (1981). In all cases, the amount adsorbed did not change over the pH range 4.5–8.5 but steadily decreased at pH < 4, suggesting that hydrogen ions competed effectively for adsorption sites on the clay mineral.

Ionic strength affects the adsorption of organic cations. Narine and Guy (1981) showed that an increase in ionic strength from 0 to 0.5 M led to a decrease in adsorption of up to 15% for monovalent dyes (methylene blue and malachite green) and up to 36% for divalent cations (paraquat and diquat) in bentonite. Ben-Hur et al. (1992) found that the presence of electrolytes in suspensions of montmorillonite and illite induced clay flocculation. This reduced the surface accessible to cationic polymers, thus leading to decreased adsorption. Another reason for the decrease in adsorption is competition with inorganic cations for the negatively charged sites on the clay surface. Xu and Boyd (1994) who studied the adsorption of HDTMA on a vermiculitic subsoil found decreased adsorption with increasing ionic strength (1–5 mM NaCl). Adsorption also decreased in $CaCl_2$ solutions. Their explanation was that the clay flocculated in the electrolyte solution before HDTMA was added, restricting access of HDTMA to exchangeable sites on external surfaces and those near the edges. Clay flocculation also reduced the adsorption of chlordimeform (Undabeytia et al., 1999).

According to Eq. (5), the concentration of cations near negatively charged surfaces is larger than that in the bulk solution. For monovalent organic dyes adsorbing on montmorillonite, the binding coefficients, K_i, range from 6×10^5 to 10^9 M^{-1}, and $\bar{K}_i > 10^5$ M^{-1}, in comparison with K_i-values of up to 200 M^{-1} for inorganic cations. Thus, in the case of dyes, an increase in ionic strength up to the 1 M range had practically no effect on adsorption by montmorillonite below its CEC. However, Eq. (5) indicates reduced concentrations of cations near the surface, when adsorption occurs beyond the CEC, i.e., when $\varphi(0) > 0$. The model predicts enhanced adsorption of monovalent dyes beyond the CEC as ionic strength increases, causing a reduction in $\varphi(0)$. Indeed, the saturation adsorption values of the dyes could be raised significantly in media of high ionic strength. An illustration is given in Table 2 for montmorillonite and illite.

Table 2
Effect of ionic strength on adsorption of organic cations

Organic cation	Clay concentration (%)	Amount of added cation ($mol_C \ kg^{-1}$)	Electrolyte added		Amount of adsorbed cation ($mol_C \ kg^{-1}$)	References
			Type	Concentration (mM)		
Montmorillonite						
TFT(+1)	0.167	0.5	−	0	0.5	Margulies et al. (1988a,b)
TFT(+1)	0.167	0.5	CsCl	3500	0.5	Margulies et al. (1988a,b)
AF(+1)	0.167	1.2	−	0	1.025	Nir et al. (2001)
AF(+1)	0.167	1.2	LiCl	3500	1.190	Nir et al. (2001)
MB(+1)	0.167	1.2	−	0	0.892	Nir et al. (2001)
MB(+1)	0.167	1.2	LiCl	3500	1.178	Nir et al. (2001)
BTMA(+1)	0.167	0.55	−	0	0.55	Polubesova et al. (1997)
BTMA(+1)	0.167	0.55	CsCl	333	0.14	Polubesova et al. (1997)
DQ(+2)	0.167	1.2	−	0	0.87	Rytwo et al. (1996b)
DQ(+2)	0.167	1.2	CsCl	500	0.68	Rytwo et al. (1996b)
PQ(+2)	0.167	1.2	−	0	0.79	Rytwo et al. (1996b)
PQ(+2)	0.167	1.2	CsCl	500	0.69	Rytwo et al. (1996b)
Mepiquat(+1)	0.5	7.0	NaCl	0	0.87	Polubesova et al. (2001)
Mepiquat(+1)	0.5	7.0	NaCl	500	0.71	Polubesova et al. (2001)
Chlordimeform(+1)	0.5	0.2	NaCl	10	0.166	Undabeytia et al. (1999)
Chlordimeform(+1)	0.5	0.2	NaCl	100	0.127	Undabeytia et al. (1999)
Illite						
CV(+1)	0.167	0.15	−	0	0.135	Polubesova and Nir (1999)
CV(+1)	0.167	0.15	NaCl	333	0.12	Polubesova and Nir (1999)
CV(+1)	0.167	0.80	NaCl	0	0.37	Polubesova and Nir (1999)
CV(+1)	0.167	0.80	NaCl	333	0.72	Polubesova and Nir (1999)
BTMA(+1)	0.167	0.5	−	0	0.094	Polubesova and Nir (1999)
BTMA(+1)	0.167	0.5	KCl	333	0.010	Polubesova and Nir (1999)

The numbers in parentheses indicate the valance status of the organic cation. Negative signs means no electrolyte was added.

The adsorption of other monovalent organic cations such as BTMA, mepiquat, and chlordimeform whose binding coefficients are small, was reduced with an increase in ionic strength. In the case of the divalent organic cations DQ and PQ whose binding coefficients are intermediate between those of the dyes and the other monovalent organic cations, the reduction in adsorption with increased ionic strength was relatively small.

The degree of reduction is also influenced by the binding coefficients of the added inorganic cations according to the sequence $Cs^+ > K^+ > Na^+ > Li^+$.

In studying the interactions of methyl green with montmorillonite and sepiolite, Rytwo et al. (2000) found that this divalent organic cation underwent a slow transformation (6 h) to a monovalent cation upon dilution of its solution (10 mM), or in a buffer at neutral pH. Different patterns of its adsorption,

UV-visible spectra and basal spacing were elucidated for the mono- and divalent forms of the cation.

4. Herbicide formulations

4.1. Reduction of herbicide leaching by organo-clay formulations

Chloroacetanilide herbicides (alachlor, metolachlor, butachlor and acetochlor) are pre-emergence herbicides for selective weed control in various field crops, such as corn, cotton, peanuts, peas, sunflower, and soybeans. The available commercial formulations (emulsifiable concentrate, EC) of alachlor, metolachlor and butachlor may lose a great deal of their biological activity due to leaching down the soil profile, which may result in contamination of

groundwater (Cohen et al., 1986; Chesters et al., 1989; Yen et al., 1994; El-Nahhal et al., 1998).

For alachlor the parent compound and/or its metabolite (oxoethane sulfonate) were detected in shallow water in North America (Chesters et al., 1989; Koterba et al., 1993; Ritter et al., 1996; Thurman et al., 1996) and Europe (Riparbelli et al., 1996). Leaching and surface mobility of alachlor and metolachlor were correlated with their water solubility and the organic matter content of the soil (Spillner et al., 1983; El-Nahhal et al., 1999b). A high organic matter content may enhance persistence in the topsoil. Significant reduction in alachlor movement was observed in soils modified by carbon-rich waste (Guo et al., 1993) and organic cations (El-Nahhal, unpublished data). Leaching increases with the rates of water application (Peter and Weber, 1985). Although some leaching is necessary to achieve proper weed control, there are three problems associated with alachlor leaching: (1) leaching to the root zone of sensitive non-target crops resulting in crop injury; (2) leaching below the root zone of the target weeds may reduce herbicidal activity; and (3) leaching may result in ground water contamination.

The release of alachlor and atrazine into aqueous solution and into soil from controlled release formulations prepared from alginate and pectin, with and without the addition of clay minerals, was studied by Gerstl et al. (1998a,b). The rate of release from pectin-based controlled release formulations was generally greater than that from the alginate-based counterparts. In column studies, the leaching of alachlor, atrazine and trifluralin from controlled release formulations, was considerably reduced in comparison with of the same compounds from commercial formulations.

Abend et al. (1998) found that heterocoagulates of hydrotalcite and montmorillonite can stabilize emulsions without a coemulsifier. Stabilization of metolachlor in the form of Pickering emulsions with hydrotalcite/montmorillonite hetetocoagulate particles is another promising approach, since the emulsions were very stable, easy to handle, and remain stable after dilution.

Formulations that can significantly reduce leaching, and hence enable reduction in the applied amounts of the herbicides alachlor (El-Nahhal et al., 1997, 1998) and metolachlor (El-Nahhal et al., 1999b) and other cases (Strek, 1998) were designed and tested.

The herbicides were adsorbed on montmorillonite whose surface had been made hydrophobic by exchanging the inorganic ions with organic cations containing a phenyl ring, such as BTMA (see Fig. 1). Alachlor and metolachlor formulations based on montmorillonite-BTMA 0.5 (that is montmorillonite with 0.5 mmol BTMA/g clay) yielded significantly reduced leaching. At the same time, herbicidal activity in the topsoil was retained as assessed by bioassays using green foxtail as a test plant. Laboratory and field experiments showed improved weed control. The results demonstrated that the new formulations can significantly reduce the applied amounts of herbicides. However, further improvement was recently achieved by exchanging montmorillonite with the smaller organic cation, PTMA, which also has a phenyl ring (El-Nahhal et al., 2000). Thus, at this stage the use of mont-PTMA 0.5 will be the starting point in designing formulations for other herbicides, such as acetochlor.

An optimal formulation of norflurazon which yielded its reduced leaching, as tested by a bioassay, was obtained by adding the compound to montmorillonite-TFT 0.5 (Undabeytia et al., 2000a).

Weed control efficacy was evaluated in the field using wheat and green foxtail as test plants (El-Nahhal et al., 1997). The organo-clay formulated alachlor (BTMA 0.5) provided excellent and long lasting weed control. Evaluation at 15, 33 and 46 days after treatment (DAT) showed reduced activity of the commercial formulation, whereas the organo-clay formulated herbicide maintained an almost constant level of herbicidal activity.

Comparing formulations based on four organic cations, containing a phenyl ring: PTMA, BTMA, BTEA and benzyltributylammonium (BTBA) showed that the smaller the cation the more effective was the reduction in leaching, that is PTMA > BTMA > BTEA > BTBA. With these herbicides (alachlor, metolachlor, acetochlor) strong adsorption affinity paralleled slow release and reduced leaching.

Table 3 gives a summary of the results in terms of the binding coefficient, k (M^{-1}), by using the Scatchard (or Langmuir) equation, in which we fixed the number of sites by the CEC. This equation

Table 3
Binding coefficients (k) for the adsorption on montmorillonite and organo-clay complexes of hydrophobic herbicides with a phenyl ring, with varied loadings of herbicides

System	Organic cation	Load (mol/kg)	k (M^{-1})
Norflurazon	None	0.0	40
	BTMA	0.5	215
	BTMA	0.8	150
Alachlor	None	0.0	50
	BTMA	0.5	1000
	BTMA	0.8	750
	BTEA	0.5	420
	BTEA	0.8	520
	HDTMA	0.8	200
Metolachlor	None	0.0	45
	BTMA	0.5	680
	BTMA	0.8	480
	BTEA	0.5	340
	BTEA	0.8	400
	PTMA	0.5	2880
	PTMA	0.8	1900

Selected cases from Nir et al. (2000).

ignores interactions between the adsorbed molecules, yielding good fits of the experimental values of the adsorbed amounts. The root mean square errors are within the experimental errors, and R^2 values are close to unity (not shown).

The adsorption affinity of the herbicides increased with BTEA loading up to the CEC of montmorillonite, but reached a maximum at a BTMA (or PTMA) loading of 5/8 of the CEC. Nir et al. (2000) suggested that the enhanced adsorbed amounts of these herbicides are mainly due to interactions between the phenyl rings of herbicide molecules and organic cations. These interactions are favored with the smaller cations, BTMA and PTMA.

BTMA preadsorbed on the clay mineral up to the CEC forms a fraction (14–18%) of charged dimers so that less phenyl rings are available for interacting with herbicide molecules. This effect is small for BTEA, so that the amounts of herbicides adsorbed increase with the degree of preloading.

The adsorption (Table 3), FTIR and UV-visible spectroscopy results (Nir et al., 2000) support the hypothesis that the phenyl ring of alachlor interacts with that of the preadsorbed organic cation.

One conclusion from these studies is that optimization of clay-based herbicide formulations re-

quires a selection of structurally compatible organic cations preadsorbed on the clay at optimal coverage.

4.1.1. Slow release formulations based on pillared clay

It has been reported that pillared clay (nanocomposite micro- and/or meso porous material) can be used to prepare slow release formulations of alachlor (Gerstl et al., 1998b). Our formulations were based on acid activated pillared and organo-pillared clay. The pillared clay was preadsorbed with different loads of an organic cation in order to modify the clay surface from hydrophilic to hydrophobic. The adsorption of metolachlor on the organo-pillared clays was expected to be higher than the adsorption on pillared clay as was found with its adsorption on montmorillonite (El-Nahhal et al., 1999b). In contrast, pillared clay minerals with different loads of BTMA yielded similar levels of adsorption of metolachlor, 19–25% of the amounts added. The adsorption of metolachlor on BTMA–montmorillonite is promoted by the interaction between the phenyl ring of BTMA and that of metolachlor. The acid-activated pillared clay provides many donor sites for hydrogen bonds with the oxygen atoms of metolachlor that act as acceptors. This may explain the similar high level of metolachlor adsorbed on the pillared clay and its BTMA derivatives.

The biological efficacy of the formulation was tested by bioassay using soil columns. The most efficient formulation was obtained by adsorbing metolachlor added from an aqueous solution to the pillared clay. It showed high activity at the top 10 cm and did not leach significantly to greater depths (Nennemann et al., 2001). A formulation of norflurazon based on a pillared clay also yielded significantly reduced leaching of the herbicide (Undabeytia et al., 2000a).

4.1.2. Slow release formulations of anionic herbicides based on positively charged organo-clay complexes

Sulfometuron (SFM) is a sulfonylurea herbicide that is active at very low doses in inhibiting acetolactate synthase (ALS), the enzyme responsible for one of the early steps in the biosynthesis of branched

amino acids in plants. Being a weak acid, this herbicide is negatively charged at moderately basic pH, and becomes more water-soluble at high pH. Since the calcareous soils of the Middle East commonly have a basic pH, the herbicide molecules can leach to deep soil layers, and move to non-target areas (Sarmah et al., 1998).

We aimed to prepare formulations of SFM that would reduce herbicide leaching and migration. The formulations were based on SFM adsorbed from a high pH solution on a positively charged organo-clay mineral, such as montmorillonite preadsorbed by high loads of CV. SFM does not adsorb on negatively charged clays. Large amounts (about 80% of the added amounts) of the herbicide were adsorbed by the complex with a high positive charge (40% above the CEC).

4.2. Leaching of alachlor under heavy irrigation

Fig. 2 shows the effect of different irrigation regimes on the leaching of the organo-clay formulation under laboratory conditions. Under heavy irrigation of 1000 m^3/ha the herbicidal activity of the organo-clay formulation was detected at the top (0–22 cm) soil layer, indicating persistence and stability of the herbicides. These data showed the effective-
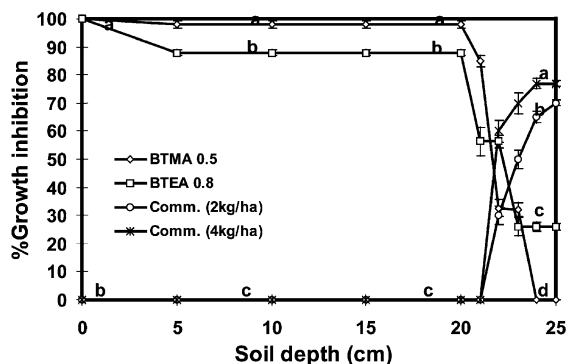

Fig. 3. Leaching of commercial formulation of alachlor (comm.) applied at 2.0 and 4.0 kg/ha and mont-BTMA 0.5 mmol/g clay and mont-BTEA 0.8 mmol/g clay containing 13% alachlor applied at 2.0 kg/ha followed by irrigation of 500 m^3/ha and 130 mm rainfall under field conditions using green foxtail as a test plant. Means followed by the same letter at a representative depth are not significantly different at $\alpha = 0.05$ level. Bars indicate standard errors.

ness of the organo-clay complexes in slowing the release process and maintaining the threshold concentration of the herbicide in the top soil, thus reducing the possible contamination of groundwater.

Fig. 3 shows the results of alachlor leaching in field experiments under heavy irrigation of 500 m^3/ha followed by 130 mm rainfall. Alachlor was applied as commercial (EC) formulation, or formulated with Mont-BTMA 0.5 and Mont-BTEA 0.8.

It is evident from the data in Fig. 3, that at such heavy water flux the organo-clay formulations were active in the top 0–20 cm of the soil profile for both formulations with lower herbicidal activity being detected at depths below 20 cm. For the commercial formulation applied at 2.0 and 4.0 kg/ha the herbicide disappeared from the top 21 cm, being detected at lower depths. A possible explanation for these results is the slow release mechanism of alachlor from the organo-clay complex as discussed previously (El-Nahhal et al., 1998, 1999a).

It can be seen that the use of a smaller aromatic organic cation (BTMA) in the formulation maintained the threshold concentration for weed control in the topsoil layer. As a result, a longer period of weed control is possible due to the slow release of the active ingredient to the soil environment (El-Nahhal et al., 1997).

Fig. 2. Effects of different irrigation quantities on the leaching of alachlor formulated with clay pre-adsorbed with BTMA at a load of 0.5 mmol/g clay, using sandy soil columns and green foxtail as a test plant. Alachlor was applied at 2.0 kg/ha followed by irrigation of 500 and 1000 m^3/ha. Means followed by the same letter at a representative depth are not significantly different at $\alpha = 0.05$ level. Bars indicate standard errors.

Figs. 2 and 3 show that there was less overall leaching of herbicide under field than under laboratory conditions. First, under field conditions, alachlor may move in two directions, horizontal and vertical, depending on the water movement (Carter, 2000). Second, in addition to the downward movement due to rainfall or irrigation, herbicides may be lost by runoff, mainly in winter time. Third, significant herbicide (e.g. alachlor) loss by volatility may occur (Wienhold et al., 1993; El-Nahhal et al., 1999b). The adsorption of alachlor to the organo-clay complex reduces volatilization (El-Nahhal et al., 1999b). In most situations, retention of the active ingredient of the herbicide in the top soil layer improves weed control efficacy, and reduces the risk of ground water contamination.

4.3. Peanut yield

Fig. 4 shows the yield from plots which were kept free of weeds manually during the growing season, and other plots which were either weeded or treated with herbicide formulations. Weed control for a long period through application of organo-clay formulations resulted in increased peanut yields compared

with plots treated with a commercial formulation, or with the weeded control. Weed growth in the weeded plots or in plots treated with commercial formulations resulted in lower peanut yield, due to competition for nutrients, water and light.

No phytotoxic effects were observed in treatments employing organo-clay complexes without the herbicide (data not shown). It is evident that the organo-clay formulations, unlike the EC formulation gave excellent weed control for an extended period. This outcome is due to the slow release of the active ingredient from the organo-clay complex into the top soil layer, thus maintaining the threshold concentration needed for weed control in the top soil layer. These results indicate the benefit of applying the herbicides as organo-clay formulations.

5. Photostabilization of pesticides by organo-clays

The amount of the active ingredient of pesticides for controlling weeds and pests can be affected by the susceptibility of pesticide molecules to undergo photo-degradation. Thus a photo-sensitive herbicide such as trifluralin, can be incorporated into the soil to avoid photo-degradation and to assure efficacy.

Direct photolysis is assumed to be operable only on or within 0.1–0.5 mm of the soil surface. Upward movement of herbicides with capillary rise of the water front to the surface can occur in the field under conditions of high evaporation (Carter, 2000).

On the other hand, indirect photolysis involving attack of the pesticide molecule by active oxygen species, formed by irradiation of soil and suspended materials, can be an important degradation mechanism (Mervosh et al., 1995; Misra et al., 1997). The presence of water may assist the diffusion of pesticide molecules across the soil, increasing the photo-degradation processes (Hebert and Miller, 1990). In addition to photo-induced oxidation, the active oxygen species can also accelerate the photo-degradation rate by energy transfer reactions, i.e., acting as photo-sensitizers (Katagi, 1991).

In order to reduce the environmental and economic costs due to the use of higher rates of photo-degradable pesticide, the following techniques have been employed: (1) chemical modification of pesti-
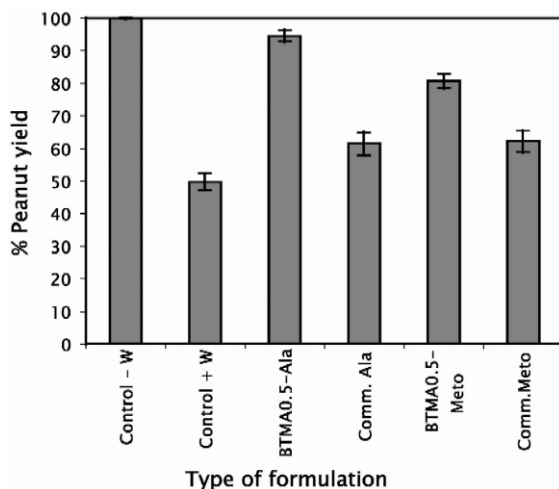

Fig. 4. Effects of different organo-clay formulations of herbicides on peanut yields. Organo-clay formulations are BTMA 0.5-Ala and BTMA 0.5-Meto. Comm.Ala and Comm.Meto represent the commercial EC formulations. Control − W, Control + W represent blank treatment without weed and with weed infestation, respectively. Bars indicate standard errors.

cide molecules to obtain photo-stable formulations; (2) the use of UV screeners in the commercial formulation; and (3) the encapsulation of the herbicide in photo-stable microspheres (Elliot et al., 1974; Sundaram and Curry, 1996; Demchak and Dybas, 1997). Margulies et al. (1985, 1993) showed the feasibility of using clay and organo-clays to obtain photo-stable formulations of pesticides. On the other hand, other studies have shown that the presence of clay minerals enhances the photolysis rate of pesticides (Nag and Dureja, 1996; Misra et al., 1997).

In Section 5.1, we review the current state of designing photo-stable formulations of pesticides, using clay and organo-clays, and we outline the mechanisms involved in photo-stabilization.

5.1. Photo-stabilization mechanisms of pesticides

The approach used consists of: (1) Adsorption of the pesticide on clay mineral surfaces; (2) energy or charge transfer from the photoexcited molecule of the pesticide to the clay; and (3) release of excess energy before undergoing a photochemical reaction. A modification of this approach is the sorption of the photolabile bioactive compound on the surface of a clay mineral preadsorbed by a selected organic chromophore. This chromophore can accept the excess energy from the excited pesticide molecules by energy-transfer or charge-transfer mechanisms, or absorb light and prevent photoexcitation of the pesticide molecule, which lengthens the lifetime of the herbicide. The surface coverage of the clay mineral with the organic chromophore can also reduce the rate of pesticide photo-degradation on the clay mineral surface (Banerjee and Dureja, 1995).

Another mechanism which may retard the photo-degradation of pesticides adsorbed on the clay surface, is steric hindrance imposed on some of the steps of the photochemical reaction by the clay mineral surface.

Light scattering by clay mineral surfaces will not be addressed in this study since it does not appear to be important for photo-stabilization of pesticides in clay formulations (Margulies et al., 1993).

5.1.1. Energy or charge transfer to the clay

Rozen and Margulies (1991) studied the photo-degradation of the insecticide NMH in its free state and when adsorbed on three different clay minerals exchanged with the dye acriflavine (AF). They concluded that the operative mechanism appeared to involve the clay mineral surface itself since the loading by AF was the same for all three minerals. It has been reported that efficient charge-transfer can take place between adsorbed species and structural ferric ions (Bergaya and Van Damme, 1983; Schoonheydt et al., 1984). The low degree of photo-stabilization obtained with hectorite, as compared with non-tronite and montmorillonite, can be related to the percentage of ferric in the structure, since iron acts as efficient energy (or charge) acceptor. The iron oxide content of hectorite, montmorillonite, and nontronite, is 0.26%, 3.72% and 29.46%, respectively.

Banerjee and Dureja (1995) found a slightly lower rate of photo-degradation for quinalphos adsorbed on palygorskite than on kaolinite, in accord with the relatively low content of structural iron in kaolinite.

5.1.2. Energy (or charge) transfer to organo-clays

As reported above, a cationic organic chromophore adsorbed on the clay can act as an energy (or charge) acceptor to the photo-excited molecule of the pesticide, which returns to its ground state and becomes photo-stabilized. The feasibility of this hypothesis was confirmed experimentally (Margulies et al., 1985, 1987, 1988a; Rozen and Margulies, 1991; El-Nahhal et al., 1999b; Undabeytia et al., 2000b).
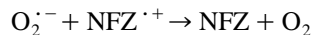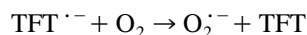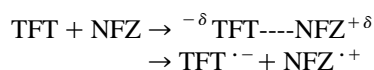
The insecticide bioresmethrin was photo-stabilized when adsorbed on montmorillonite exchanged with the dye methyl green (MG) (Margulies et al., 1985, 1987). Bioassay showed that the insecticide lost its activity during the first day of exposure to sunlight, whereas the organo-clay formulation at a load of 0.2 mmol/g was still considerably active after three days of irradiation. However, when the amount of methyl green was changed from 0.2 to 0.4 mmol/g clay, no photo-stabilization was observed (Margulies et al., 1985). This indicates the role of specific molecular interactions at the clay surface. Further experimental evidence was obtained using FTIR spectroscopy (Margulies et al., 1987). The efficiency of energy transfer depends on the matching of energy levels of donor and acceptor chromophores, the distance between them, and their relative orientations (Margulies et al., 1993). Excessive

loading of the clay surface by the organic cation can modify the spatial arrangement of the cation and impair the efficiency of energy transfer between the pesticide and the dye. Excessive loading of the surface by the organic cation may also reduce the amount of pesticide adsorbed.

Considerable improvement in the photostabilization of NMH was obtained when the cationic dye acriflavine (AF) was coadsorbed on montmorillonite at two different concentrations (20 and 50 mmol/100 g clay) while the concentration of the pesticide was kept constant at 20 mmol/100 g clay (Rozen and Margulies, 1991). The possibility of a UV screening effect by acriflavine on NMH was dismissed since the absorption intensity of acriflavine at the irradiation wavelength used (350 nm) was much lower than that of NMH. Similarly, a high degree of photo-stabilization was obtained when acriflavine was replaced by the dye thioflavin-T (TFT), whereas minimal photo-stabilization was observed with the dye methyl green (Margulies et al., 1988a). Strong interaction between acceptor and donor molecules is not required for energy transfer; only the emission spectrum of the donor molecule and the absorption spectrum of the acceptor molecule need to be overlapping. In the case of the herbicide norflurazon (NFZ), a bioassay based on the response of the aquatic plant *Lemna* showed a photo-stabilization of the herbicide up to 50% for formulations prepared from TFT-

montmorillonite, under irradiation conditions which completely inactivated the commercial formulation (Undabeytia et al., 2000b). The photo-stabilization observed was mainly due to energy transfer from the herbicide to the organic cation involving $\pi-\pi^*$ transitions between triplet states. The feasibility of energy transfer from norflurazon to TFT is shown in Fig. 5, indicating a good overlap between the emission spectrum of norflurazon and the absorption spectrum of the organic cation adsorbed on the clay. In addition, FTIR spectra indicated short-distance intermolecular interactions between the organic cation and the herbicide that should be related to the observed photo-stabilization.

Charge transfer was dismissed in this case, albeit being reported for flavin and analogues, which can undergo photochemical reduction to a semiquinoid form in the presence of an electron donor and spontaneous oxidation of the reduced dye with ground-state oxygen (Draper and Crosby, 1983). If charge transfer occurs, then the following reactions can be schemed.

$$TFT + NFZ \rightarrow {}^{-\delta}TFT\text{----}NFZ^{+\delta}$$
$$\rightarrow TFT^{\cdot-} + NFZ^{\cdot+}$$
$$TFT^{\cdot-} + O_2 \rightarrow O_2^{\cdot-} + TFT$$
$$O_2^{\cdot-} + NFZ^{\cdot+} \rightarrow NFZ + O_2$$

This possibility was tested by using the electron donor EDTA as a quencher for electron transfer
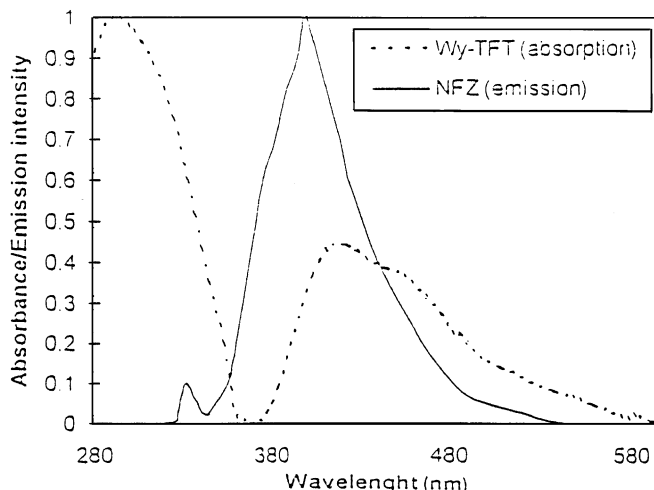

Fig. 5. Normalized emission of norflurazon and absorption spectrum of TFT adsorbed on the clay at a loading of 0.2 mmol/g clay.
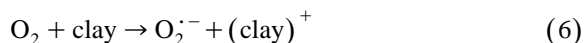
reactions. Since the extent of norflurazon degradation was not affected by the presence of EDTA, this mechanism can be ruled out.

The role of the clay in photo-stabilization of NFZ was to keep in close proximity the pesticide molecule acting as an energy donor and TFT being the energy acceptor.

5.1.3. Catalytic properties of the surface

Clay minerals have been reported to enhance the rate of photolysis of some herbicides. This was explained in terms of the interaction of the pesticides with active oxygen species formed by irradiation of oxygen or water molecules associated with the clay (Takahashi et al., 1985; Katagi, 1991, 1993; Mathew and Khan, 1996).

Che and Tench (1983) reported photo-induced electron transfer from aluminosilicates to adsorbed molecular oxygen. On this basis, Katagi (1990) proposed that hydroxy and hydroperoxyradicals are generated by reaction of water with $O_2^{\cdot-}$ formed on clays by irradiation, as shown in the following scheme:

$$O_2 + clay \rightarrow O_2^{\cdot-} + (clay)^+ \qquad (6)$$

$$O_2^{\cdot-} + H_2O \rightarrow HO_2^{\cdot} + OH^- \qquad (7)$$

$$HO_2^{\cdot} + H_2O \rightarrow H_2O_2 + HO^{\cdot} \qquad (8)$$

In addition, singlet oxygen (the exited state of molecular Oxygen) can be involved, as this species was reported to be formed on irradiated soil surfaces (Gohre and Miller, 1983) and be responsible for the degradation of the insecticide disulfoton in soils (Hebert and Miller, 1990).

Undabeytia et al. (2000b) observed enhanced photodegradation of norflurazon when the herbicide was irradiated in an aqueous suspension containing montmorillonite. The singlet oxygen species was not responsible for the enhanced photo-degradation, since the amount of herbicide degraded was not affected by the presence 2,5-dimethylfuran capable of trapping singlet oxygen. However, the production of singlet oxygen was indicated by the consumption of this trapping agent and formation of its photo-product.

The involvement of hydroxy radicals was assessed by the addition of Fenton's reagent. In addition, oxidation of ferrous ion in the presence of oxygen would generate a superoxide radical anion (Larson et al., 1991). Norflurazon was completely degraded after addition of Fenton's reagent. The loading of the clay mineral surface with organic cations may lower the production of radicals by inhibiting efficient electron transfer from the clay mineral to molecular oxygen as in Eq. (6). Photo-stabilization of the insecticide quinalphos was also achieved by covering the surface of clay minerals with the organic cation crystal violet (Banerjee and Dureja, 1995). In conclusion, the photo-stabilization of norflurazon using organo-clays such as TFT-montmorillonite is mainly due to energy transfer processes and decreased production of hydroxy radicals.

5.1.4. Steric hindrance

5.1.4.1. Trifluralin.
Margulies et al. (1992) noted that trifluralin adsorbed on montmorillonite, retained about 75% of its herbicidal activity after 96 h of irradiation, whereas the activity of the free (unadsorbed) compound dropped to 30% under the same condition. Photo-stabilization of Trifluralin was not improved when adsorbing a potential stabilizer, such as TFT to the clay. As a result the herbicidal activity dropped to 55%. This indicates that interactions between the herbicide molecules and the clay mineral surface were responsible for the obtained photo-stabilization. The photodegradation of Trifluralin adsorbed on montmorillonite, occurs by oxidation and subsequent dealkylation/cyclization (Margulies et al., 1992). They found that the ratio between photoproducts I and II decreased from 10:1 for free trifluralin to 2:1 for adsorbed trifluralin. Since the overall effect of complexation was to reduce the reaction rate, it was concluded that the photo-stabilization operated on the cyclization step leading to photoproduct I, rather than on the subsequent following reaction to photo-product II. Complexation with the clay surface inhibits the conformational change required for cyclization resulting in reduction of the overall reaction rate. In recent attempts to stabilize trifluralin we found several organo-clays to be more effective than montmorillonite alone.

One example was pillared montmorillonite. Another was montmorillonite that had been exchanged

with BTMA. Our view was that lowering the loading of BTMA can enhance the amounts of trifluralin adsorbed. Hence, one of the optimal formulations was obtained by adsorbing trifluralin on sodium montmorillonite (SWy-1) containing 0.2 mmol BTMA and 0.4 mmol/g of trifluralin. This yielded $50 \pm 10\%$ inhibition of root elongation of sorghum seedlings under irradiation conditions as compared with $25 \pm 5\%$ inhibition for the commercial formulation of trifluralin. Doubling the irradiation time inactivated the commercial formulation completely, whereas the organo-clay formulation of trifluralin still yielded $28 \pm 6\%$ of inhibition in root elongation.

5.1.4.2. Alachlor and metolachlor. El-Nahhal et al. (1999b) obtained photo-stabilization of alachlor and metolachlor adsorbed on montmorillonite. Unlike the commercial counterparts these formulations retained most of their activity after long irradiation periods. The presence of an organic cation had the effect of increasing the hydrophobicity of the clay mineral surface. As a result, herbicide adsorption increased as did the photo-stability of the clay complexes. Schmidt et al. (1995) showed the existence of several stable conformers of alachlor, suggesting that the photo-degradation products previously reported have one of these conformers as a common intermediate. Consequently, chemical environments that stabilize a different conformation may significantly prolong the half-lives of herbicides, such as alachlor and metolachlor.

Interestingly, photo-stabilization of the herbicides trifluralin, alachlor and metolachlor was achieved when they were adsorbed on the montmorillonite without an organic cation. In Section 5.1.3, however, we pointed out that enhanced photo-degradation of norflurazon occurred in aqueous suspensions of montmorillonite. One point is that the production of radicals is significantly reduced after drying the formulations. The other point is that different photo-degradation routes may operate for norflurazon and the other herbicides.

Acknowledgements

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