

Organoclays as Soil Amendments to Increase the Efficacy and Reduce the Environmental Impact of the Herbicide Fluometuron in Agricultural Soils

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The use of pesticides in agriculture has become a source of pollution of soil and water in the last decades. Extensive pesticide transport losses due to leaching and runoff produce nonpoint source contamination of soils and water. One of the soil processes that reduce pesticide transport losses is adsorption by soil particles; therefore, enhancement of pesticide retention by soil can be used as a strategy to attenuate the environmental impact of pesticides. In this work, organoclays were prepared by treating Wyoming montmorillonite (SWy-2) and Arizona montmorillonite (SAz-1) with different organic cations and were assayed as soil amendments to enhance the retention and reduce the leaching losses of the herbicide fluometuron [*N,N*-dimethyl-*N'*-[3-(trifluoromethyl)phenyl]urea] in soils. Two agricultural soils from Southern Spain were selected for being high-risk scenarios of ground and surface water contamination. First, a batch adsorption study was conducted to identify organoclays with high affinity for fluometuron. Among the different organoclays assayed, spermine-treated Wyoming montmorillonite (SW-SPERM) displayed high and reversible adsorption of fluometuron and was selected as an amendment for subsequent persistence, leaching, and herbicidal activity experiments of fluometuron with unamended and amended soils. Amendment of the soils with SW-SPERM at rates of 1%, 2%, and 5% greatly enhanced fluometuron retention by the soils and retarded fluometuron leaching through soil columns. Incubation experiments revealed that the persistence of the herbicide in the amended soils was similar to that in unamended soils and that most of the herbicide was ultimately available for degradation. Bioassays demonstrated that the reduced leaching losses of fluometuron in soils amended with SW-SPERM may result in increased herbicide efficacy if heavy rainfall events occur shortly after herbicide application.

KEYWORDS: Adsorption; fluometuron; leaching; organoclays; soil amendments

INTRODUCTION

The environmental problems associated with the use of pesticides in agriculture are a matter of increasing concern because pesticides are increasingly being detected in ground and surface waters. One main problem associated with pesticide use results from extensive pesticide transport losses through leaching and runoff processes. Such losses can be particularly noticeable in the case of highly mobile, soluble pesticides. This has led to a considerable amount of research directed to predict the environmental fate of agricultural pesticides and to prevent their adverse environmental effects, such as ground and surface water pollution (1, 2).

The environmental fate of pesticides is greatly dependent on site-specific environmental variables, such as soil characteristics or climatic conditions (3). In Southern Spain, two high-risk scenarios of ground and surface water contamination by pesticides are

cotton and olive crops. Adequate weed control has traditionally been more difficult to achieve in cotton than in other spring crops because cotton grows slowly early in the season and thus is less competitive with weeds (4). In olive groves, soil composition and pronounced slopes favor herbicide leaching and runoff (5). The risk of herbicide transport losses is exacerbated in Southern Spain because most soils are poor in organic matter (i.e., < 2%), and short but heavy rainfall events are relatively common, particularly in spring and autumn, when herbicides are commonly applied. These entire factors make Southern Spain a high-risk scenario for ground and surface water contamination (6), and appropriate management practices are needed to minimize pesticide transport losses and movement to ground and surface water.

Fluometuron [*N,N*-dimethyl-*N'*-[3-(trifluoromethyl)phenyl]urea] is a pre- and early postemergence phenylurea herbicide widely used to control grass and broad-leaf weeds in cotton and olive crops. Several studies have been conducted to understand the behavior of this herbicide in soils, including studies on the effects of tillage and cover crops (7–10), degradation studies (11–13), as well as the development of different strategies to reduce herbicide losses and mitigate pollution, such as the use

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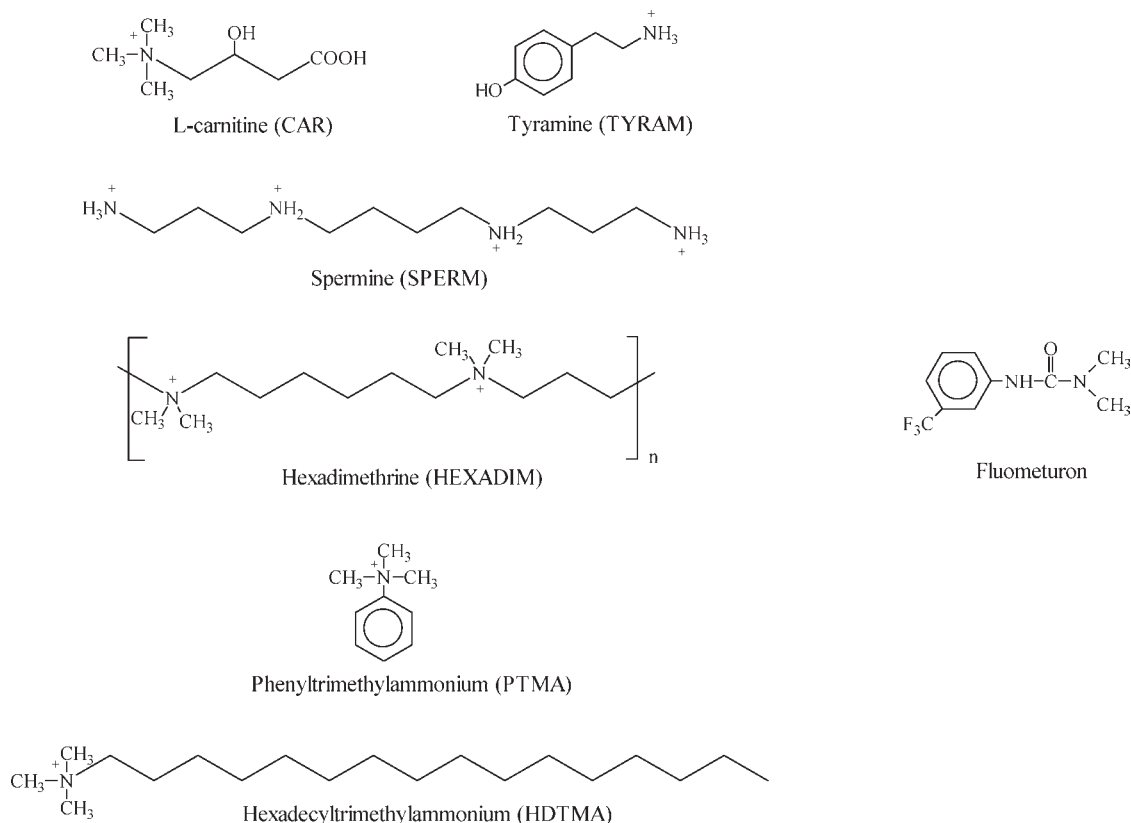


Figure 1. Chemical structures of fluometuron and the organic cations.

of organic amendments (14) and controlled release formulations (15).

Unaltered and modified clay minerals have been proposed as adsorbents to reduce the environmental impact of pesticides (16–19). Clay minerals are very good adsorbents mainly for cationic and highly polar, neutral pesticides. Nevertheless, they can be easily modified to enhance their affinity also for hydrophobic pesticides. Organoclays, that is, natural clay minerals with their original inorganic exchange cations replaced with organic cations, have been proven to be very good adsorbents for different classes of pesticides because the organic cations change the nature of the clay mineral surface from hydrophilic to hydrophobic, thus increasing its affinity for hydrophobic compounds (19–21). The modification of clay minerals with naturally occurring organic cations has recently been pointed out as particularly interesting to reduce concern about the incorporation of these materials into soil and aquatic environments for practical applications (5, 6, 22, 23).

Organoclays have extensively been proposed as adsorbents to remove pesticides from water and as supports in pesticide slow release formulations; however, literature on the potential usefulness of organoclays as soil amendments to enhance the pesticide retention process in soil with the purpose of optimizing the behavior of pesticides in agricultural soils is scarce (24). The objectives of this article were (i) to develop organoclays with high affinity for the herbicide fluometuron and (ii) to evaluate, under laboratory conditions, the effects of adding organoclays to two soils from Southern Spain on fluometuron sorption, persistence, leaching, and bioefficacy in the soils. Beneficial effects of the addition of organoclays to the soils with regard to efficacy and environmental impact of the herbicide fluometuron are discussed.

MATERIALS AND METHODS

Herbicide, Soils, and Organoclays. Fluometuron (Figure 1) is a phenylurea herbicide with a molecular weight of 232.2 g mol^{-1} and a water

solubility of 110 mg L^{-1} at 20°C . Pure analytical fluometuron (purity = 99.5%) purchased from Sigma-Aldrich (Spain) was used to prepare the external standards for fluometuron analysis and the initial solutions used in the batch adsorption experiments. Commercial fluometuron (Dinagam Linz, 50% suspension concentrate) from Bayer (Spain) was used in the persistence, column leaching, and bioassay experiments.

Two soils (A and B) from Seville (SW Spain) were used in this study. The two soils had similar pH and organic carbon contents, but they had markedly different textures (Table 1). Soil A was a clay soil sampled from a cotton area located in Las Cabezas de San Juan (Seville, Spain) and was found to contain a background concentration of fluometuron of 0.24 mg kg^{-1} , presumably resulting from previous applications of this herbicide to the soil as an agricultural practice. Soil B was a sandy loam soil sampled from an olive grove located in Coria del Río (Seville, Spain) and contained no background concentration of fluometuron. The soils were sampled (0–20 cm), air-dried, sieved (2 mm), and stored at 4°C until used.

The synthesis and characterization of the organoclays used in this work have previously been described in detail in Celis et al. (6). Briefly, Na-rich Wyoming montmorillonite (SWy-2) and Ca-rich Arizona montmorillonite (SAz-1) from The Clay Minerals Society (Purdue University) were modified with the following organic cations (Figure 1): L-carnitine (CAR), spermine (SPERM), hexadimethrine (HEXAD), tyramine (TYRAM), phenyltrimethylammonium (PTMA), and hexadecyltrimethylammonium (HDTMA). Modification was carried out through ion exchange reactions by treating the montmorillonites with solutions containing an amount of organic cation equal to 100% of the cation exchange capacity of the clays ($CEC_{\text{SWy-2}} = 76.4 \text{ cmol}_c \text{ kg}^{-1}$; $CEC_{\text{SAz-1}} = 120 \text{ cmol}_c \text{ kg}^{-1}$). All organic cations were supplied by Sigma-Aldrich as high-purity chloride or bromide salts (purity > 98%). The nomenclature and some characteristics of the unmodified and modified montmorillonite samples used in this work are summarized in Table 2.

Adsorption of Fluometuron by the Organoclays. Adsorption of fluometuron by the unmodified and modified montmorillonite samples was determined at a single initial herbicide concentration $C_{\text{ini}} = 1 \text{ mg L}^{-1}$ using the batch equilibration procedure. Triplicate 20 mg montmorillonite samples were equilibrated with 8 mL of an aqueous solution of fluometuron (1 mg L^{-1}) by shaking for 24 h at $20 \pm 2^\circ\text{C}$. After equilibration, the

Table 1. Physicochemical Properties of the Soils Used

soil	texture	sand (%)	silt (%)	clay (%)	organic C (%)	pH	fluometuron content ^a (mg kg ⁻¹)
soil A	clay	15	26	59	0.73	7.2	0.24
soil B	sandy loam	67	8	25	0.52	7.2	

^a Background concentration of fluometuron (mg kg⁻¹ air-dried soil) determined by extraction of 4 g of soil with 10 mL of methanol.

Table 2. Nomenclature and Some Characteristics of the Unmodified and Modified Montmorillonites Used in This Work

montmorillonite		organic cation	OCIS ^a (%)	d ₀₀₁ ^b (Å)
SWy-2 (Blank)	SWy-2		0	15.1
SW-CAR	SWy-2	L-carnitine	61	14.2
SW-SPERM	SWy-2	spermine	96	13.0
SW-HEXADIM	SWy-2	hexadimetre	88	14.0
SW-TYRAM	SWy-2	tyramine	62	14.4
SW-PTMA	SWy-2	phenyltrimethylammonium	82	14.6
SW-HDTMA	SWy-2	hexadecyltrimethylammonium	93	18.0
SAz-1 (Blank)	SAz-1		0	15.2
SA-CAR	SAz-1	L-carnitine	41	14.8
SA-SPERM	SAz-1	spermine	96	13.0
SA-HEXADIM	SAz-1	hexadimetre	88	14.2
SA-TYRAM	SAz-1	tyramine	50	15.0
SA-PTMA	SAz-1	phenyltrimethylammonium	79	15.0
SA-HDTMA	SAz-1	hexadecyltrimethylammonium	101	24.0

^a Organic cation saturation: percentage of the CEC of SWy-2 or SAz-1 compensated by organic cations (calculated from the N content of the samples).

^b Basal spacing values for air-dried oriented specimens.

suspensions were centrifuged, and 4 mL of the supernatant solution was removed, filtered using glass fiber filters (pore diameter = 0.45 μm), and analyzed by high-performance liquid chromatography (HPLC) to determine the equilibrium concentration, C_e (mg L⁻¹), of fluometuron. The amount of fluometuron adsorbed, C_s (mg kg⁻¹), was determined from the difference between the initial (C_{ini}) and equilibrium (C_e) herbicide concentrations. Triplicate fluometuron initial solutions (1 mg L⁻¹) without adsorbent were also shaken for 24 h and served as controls. The percentage of fluometuron adsorbed (% Ads) was calculated by using the following formula: % Ads = [(C_{ini} - C_e)/C_{ini}] × 100. Distribution coefficients for organoclays, K_d (L kg⁻¹), were calculated as K_d = C_s/C_e.

For the organoclays displaying the greatest affinity for fluometuron (SA-HDTMA, SW-SPERM, and SW-HDTMA), adsorption-desorption isotherms were also obtained. Triplicate 20 mg adsorbent samples were equilibrated by shaking for 24 h at 20 ± 2 °C with 8 mL of solutions with different initial fluometuron concentrations (C_{ini} = 0.1, 0.2, 1, and 2 mg L⁻¹). After equilibration, the suspensions were centrifuged, and 4 mL of the supernatant solutions were removed, filtered, and analyzed by HPLC. The amount of herbicide adsorbed was calculated from the difference between the initial and equilibrium fluometuron concentrations. Desorption was measured immediately after adsorption from the highest equilibrium point of the adsorption isotherm. The 4 mL of supernatant removed for the adsorption analysis was replaced with 4 mL of distilled water. After shaking for 24 h at 20 ± 2 °C, the suspensions were centrifuged, and the herbicide concentration was determined in the supernatant. This desorption procedure was repeated three times. Adsorption isotherms were fit to the logarithmic form of the Freundlich equation: log C_s = log K_F + N_F log C_e, where C_s (mg kg⁻¹) is the amount of fluometuron adsorbed at the equilibrium concentration C_e (mg L⁻¹), and K_F and N_F are the empirical Freundlich constants.

Adsorption of Fluometuron by Unamended and Amended Soils.

The organoclays with higher affinity for fluometuron (SA-HDTMA, SW-SPERM, and SW-HDTMA) were selected as soil amendments to determine their effect on fluometuron adsorption by the soils. For this purpose, triplicate 4 g soil samples were amended with SA-HDTMA, SW-SPERM, or SW-HDTMA at different rates (0%, 1%, 2%, and 5%) and then equilibrated by shaking for 24 h at 20 ± 2 °C with 8 mL of an aqueous

solution of fluometuron with an initial concentration C_{ini} = 1 mg L⁻¹. After equilibration, the suspensions were centrifuged, and 4 mL of the supernatant solution was removed, filtered, and analyzed by HPLC. The amount of fluometuron adsorbed (C_s) was determined by the difference between the initial (C_{ini}) and equilibrium (C_e) herbicide concentrations. For soil A, the initial concentration of fluometuron was corrected by taking into account the additional amount of herbicide already present in the 4 g of soil, which represented about 10% of the fluometuron added in the initial solution. Percentages of fluometuron adsorbed (% Ads) and distribution coefficients, K_d (L kg⁻¹), were calculated as described above.

Persistence Experiment. The persistence of fluometuron in unamended and amended soils was determined by means of an incubation experiment in which samples of 100 g of soil, either unamended or amended with SW-SPERM at different rates (1%, 2%, and 5%), were spiked with the commercial formulation of fluometuron (2 mg a.i. kg⁻¹ soil) and then incubated in glass jars at 20 ± 2 °C for up to 75 days. The moisture content was maintained at a constant level (40% for soil A and 30% for soil B), close to the water holding capacities of the soils, throughout the experiment by adding distilled water as necessary. Periodically, duplicate 3 g soil aliquots were sampled and frozen until analyzed. Fluometuron residues in the 3 g soil aliquots were determined by extraction with 8 mL of methanol (24 h shaking), followed by centrifugation and analysis of the supernatant by HPLC. Preliminary experiments had shown that this extraction procedure recovered >95% of the fluometuron freshly applied to the soils.

Column Leaching Experiment. A column leaching experiment was designed to assess the ability of spermine-exchanged montmorillonite (SW-SPERM) as a soil amendment to reduce the leaching of fluometuron through the soil profile. Leaching was studied in glass columns of 30 cm length × 3.1 cm i.d. The top 5 cm of the columns was filled with 10 g of sea sand and the bottom 5 cm with 10 g of sea sand plus glass wool, to prevent the loss of soil during the experiment. The rest of the column (20 cm) was hand-packed with 160 g of either unamended or amended soil. Amendment consisted of mixing the upper 10 g of soil (i.e., about 1.25 cm) with SW-SPERM at a rate of 1%, 2%, or 5%. The amounts of SW-SPERM added corresponded to 1325, 2650, or 6625 kg ha⁻¹. The unamended and amended soil columns were saturated by adding 100 mL of distilled water to the top of the columns, then allowing them to drain for 24 h. The calculated pore volume of the columns after saturation was 63 ± 1 mL for soil A and 56 ± 1 mL for soil B. The amount of commercial formulation of fluometuron corresponding to an agronomic dose of 2 kg a.i. ha⁻¹ was applied to the top of the saturated soil columns. Daily, 15 mL of deionized water was added to the top of the columns, the leachates were collected, and the concentration of fluometuron in the leachates was determined by HPLC. At the end of leaching experiment, soil samples of approximately 40 g were taken from different depths of the columns (0–5, 5–10, 10–15, and 15–20 cm) and were extracted once with 100 mL of methanol by shaking mechanically at 20 ± 2 °C for 24 h. The suspensions were centrifuged, filtered, and analyzed by HPLC to determine the residual amounts of fluometuron at different depths of the soil columns. All leaching experiments were conducted in triplicate.

Bioassays. To evaluate the weed control efficacy of fluometuron in SW-SPERM-amended soil, a bioassay was conducted. *Eruca vesicaria* seeds (Vilmorin, France) were planted in duplicate 6 cm height × 50 cm² surface pots filled with 200 g of soil B. The upper 56 g (i.e., about 1.25 cm) of soil was amended with SW-SPERM at different rates (0%, 1%, 2%, and 5%). The pots were saturated with water, allowed to drain for 24 h, and 15 seeds of *Eruca vesicaria* were arranged on the soil surface. The commercial formulation of fluometuron was applied at a rate of 2 kg ha⁻¹. Control pots of unamended soil without herbicide were also prepared. The pots were watered daily with about 10 mL of distilled water. Two weeks after herbicide application, *Eruca vesicaria* plants (shoots and leaves) were cut and weighed to determine herbicide efficacy in the unamended and amended soils.

A separate experiment was designed to assess whether the reduced leaching of fluometuron in SW-SPERM-amended soil could result in improved weed control efficacy of the herbicide after a high water input event just after herbicide application. For this purpose, control, unamended, and SW-SPERM (1%-amended) soil pots were prepared as described above. Afterward, fluometuron was applied at a rate of 2 kg ha⁻¹, and immediately, 300 mL of distilled water was added to each pot,

thus simulating a water input of 60 mm. The pots were allowed to drain for 4 days, and leachates were collected and analyzed to determine the amount of fluometuron leached from each pot. Then, 15 seeds of *Eruca vesicaria* were planted, and three weeks after herbicide application, *Eruca vesicaria* plants were cut and weighed to compare the herbicidal efficacy of the residual amount of fluometuron present in the unamended and amended soil pots.

Analysis of Fluometuron. Fluometuron was determined by HPLC using a Waters 600E chromatograph coupled to a Water 996 diode-array detector. The conditions used were as follows: Novapak C18 column (150 mm length \times 3.9 mm i.d.), 60:40 water/acetonitrile eluent mixture at a flow rate of 1 mL min⁻¹, 25 μ L injection volume, and UV detection at 243 nm. External calibration curves with four standard solutions between 0.1 and 2 mg L⁻¹ were used in the calculations. Instrumental LOD was calculated as the lowest observable concentration giving a signal-to-noise (S/N) ratio of 3:1, while instrumental LOQ was calculated as the concentration resulting in an S/N ratio of 10:1. The LOD and LOQ were 0.01 mg L⁻¹ and 0.03 mg L⁻¹, respectively (25).

RESULTS AND DISCUSSION

Fluometuron Adsorption by the Organoclays. A preliminary adsorption experiment at a single initial herbicide concentration of 1 mg L⁻¹ was conducted to determine the affinity of fluometuron for different organoclays (Figure 2). The extent of fluometuron adsorption by the organoclays greatly depended on the nature of the modifying organic cation. The organoclays SA-HDTMA, SW-SPERM, and SW-HDTMA adsorbed much more herbicide than the unmodified montmorillonites. This result is very similar to that previously reported for the adsorption of the herbicide diuron by the same organoclays and under the same experimental conditions (6). Fluometuron is a phenylurea herbicide very similar to diuron and accordingly follows a very similar

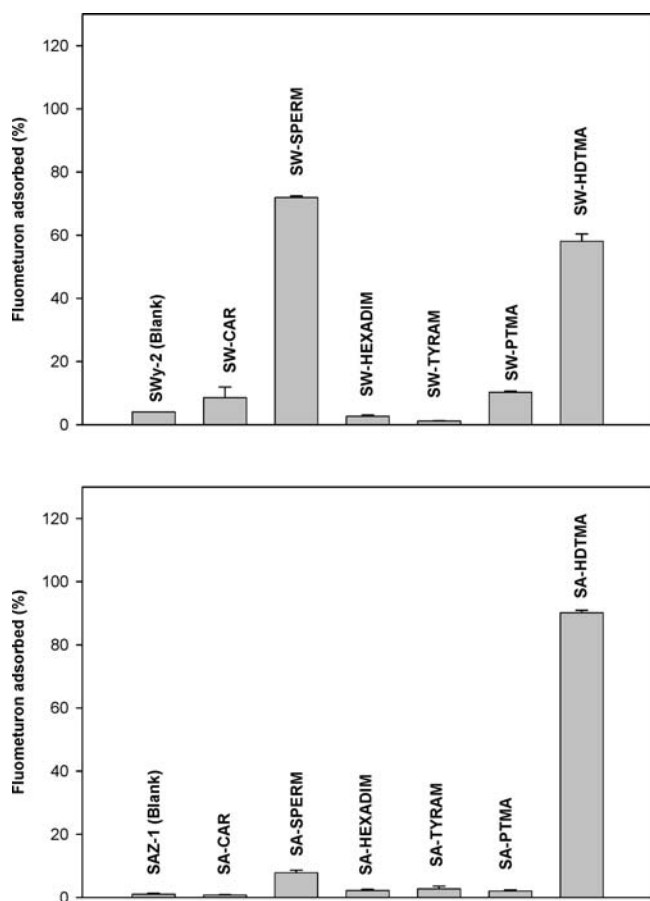


Figure 2. Percentages of fluometuron adsorbed on unmodified and modified montmorillonites at an initial herbicide concentration of 1 mg L⁻¹.

adsorption pattern on organoclays. Nevertheless, the adsorption values shown in Figure 2 are slightly less than those reported by Celis et al. (6) for diuron, most likely because the higher water solubility of fluometuron compared to that of diuron slightly reduces its adsorption by the organoclays. The high affinity of fluometuron for SW-HDTMA and SA-HDTMA can be attributed to hydrophobic interactions between the herbicide and the alkyl chains of HDTMA cations, whereas its high affinity for SW-SPERM could be due to a combination of (i) hydrophobic

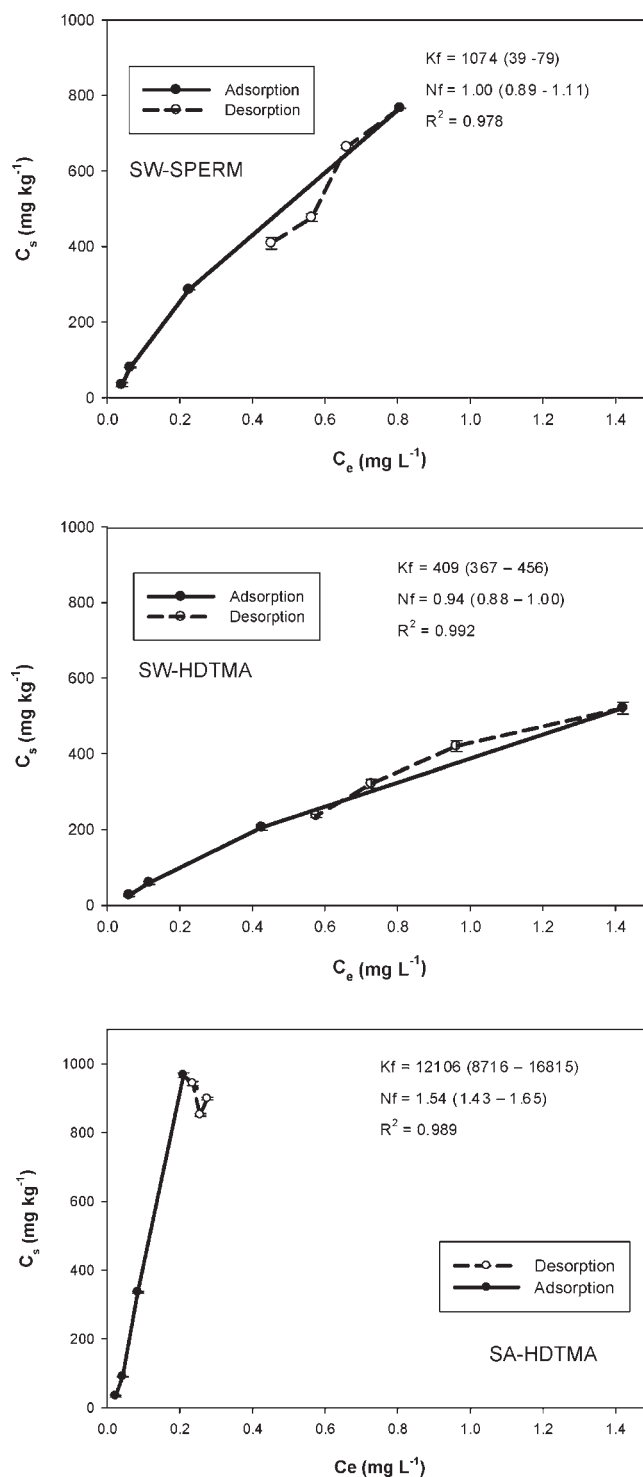


Figure 3. Fluometuron adsorption–desorption isotherms on SW-HDTMA, SW-SPERM, and SA-HDTMA and corresponding Freundlich coefficients for each adsorption isotherm. Values in parentheses correspond to the ranges of the Freundlich coefficients (K_f and N_f).

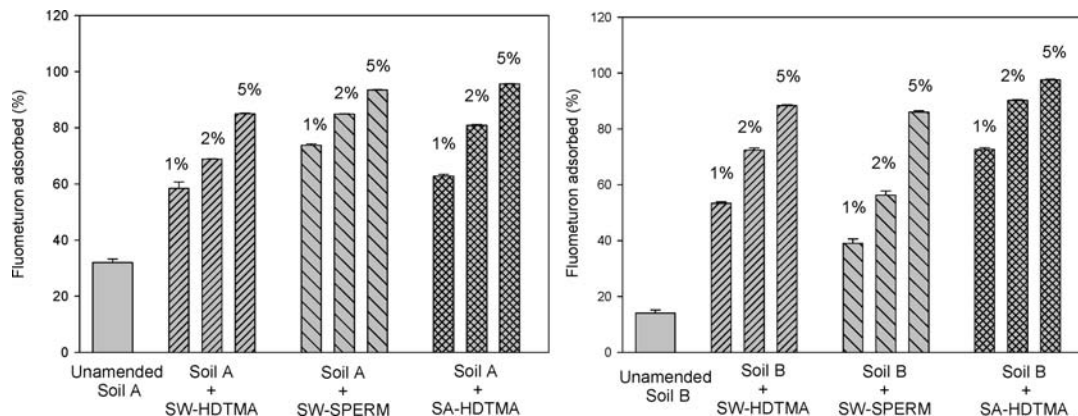


Figure 4. Percentage of fluometuron adsorbed on unamended and organoclay-amended soils at an initial herbicide concentration of 1 mg L⁻¹.

interactions between the herbicide and the alkyl chains of spermine and (ii) the formation of hydrogen bonding between the C=O group of the herbicide and the -NH₃⁺/-NH₂⁺ groups of spermine, as proposed for diuron (6).

On the basis of the adsorption results obtained at a single initial concentration 1 mg L⁻¹, the organoclays with higher affinity for fluometuron (SA-HDTMA, SW-SPERM, and SW-HDTMA) were selected to obtain adsorption-desorption isotherms (Figure 3). Freundlich parameters derived from the adsorption isotherms are included in Figure 3. *K_f* values increased in the following order: SW-HDTMA < SW-SPERM < SA-HDTMA, which is consistent with the results obtained at a single initial herbicide concentration of 1 mg L⁻¹. Desorption curves showed high reversibility for SW-HDTMA and SW-SPERM. The SA-HDTMA desorption curve was not well defined because the high adsorption fluometuron on this sample resulted in very low equilibrium concentrations, which made the desorption analysis complicated (6, 26).

Fluometuron Adsorption by Unamended and Amended Soils. Figure 4 shows the percentages of fluometuron adsorbed on the unamended soils and on the soils amended with different amounts of SA-HDTMA, SW-SPERM, and SW-HDTMA. The adsorption of fluometuron on unamended soil A was greater than that on unamended soil B, probably because soil A had greater clay content and also slightly greater organic matter content than soil B. For both soils, amendment with all three organoclays led to an increase in fluometuron adsorption. The increase in adsorption depended on the soil and on the nature and amount of organoclay added, being more noticeable in soil B because this soil had lower affinity for fluometuron than soil A.

The experimentally measured distribution coefficients, *K_{d-meas}*, for fluometuron adsorption on the amended soils are compared in Table 3 with the expected values, *K_{d-calc}*, calculated assuming an independent adsorption behavior of the soil and the organoclay in the mixtures. Assuming linear adsorption, such expected values can be calculated according to the following equation:

$$K_{d-calc} = K_{d-soil}f_{soil} + K_{d-OCI}f_{OCI} \quad (1)$$

where *K_{d-soil}* and *K_{d-OCI}* are the individual distribution coefficients for fluometuron adsorption on soil and organoclay, respectively, and *f_{soil}* and *f_{OCI}* are the fraction of soil and organoclay, in the mixture, respectively (27). It is worth noting that although the organoclays increased the adsorption of fluometuron by the soils, the increase was always less than what could be expected from the individual adsorption constants and the fraction of soil and organoclay in the mixtures (*K_{d-meas}* < *K_{d-calc}*). This result reveals that organoclays are less effective in adsorbing fluometuron in the presence of soil than in the absence of soil.

Table 3. Measured and Calculated Distribution Coefficients, *K_d* (L kg⁻¹), for Fluometuron Adsorption on Unamended and Organoclay-Amended Soils^a

treatment	soil A		soil B	
	<i>K_{d-meas}</i>	<i>K_{d-calc}</i>	<i>K_{d-meas}</i>	<i>K_{d-calc}</i>
unamended	0.9 ± 0.1 ^b		0.3 ± 0.1	
SW-HDTMA- 1%	2.8 ± 0.3	6.5	2.3 ± 0.1	5.9
SW-HDTMA- 2%	4.3 ± 0.1	11.9	5.2 ± 0.2	11.3
SW-HDTMA- 5%	10.8 ± 0.1	27.5	14.2 ± 0.4	27.0
SW-SPERM- 1%	4.7 ± 0.1	11.1	1.3 ± 0.1	10.5
SW-SPERM- 2%	11.0 ± 0.1	21.1	2.6 ± 0.2	20.5
SW-SPERM- 5%	27.4 ± 0.4	49.8	11.8 ± 0.5	49.2
SA-HDTMA- 1%	3.4 ± 0.1	37.8	5.3 ± 0.2	37.2
SA-HDTMA- 2%	8.3 ± 0.1	73.9	18.2 ± 0.6	73.3
SA-HDTMA- 5%	41.4 ± 0.8	178.1	78.2 ± 8.4	177.5

^a The initial herbicide concentration was 1 mg L⁻¹. ^b Mean ± standard error.

Probably, the interaction of certain soil components with the organoclays resulted in competition for sorption sites or surface blockage effects which reduced the performance of the organoclays in adsorbing fluometuron (28). However, differences between *K_{d-meas}* and *K_{d-calc}* depended not only on the organoclay but also on the soil to which the organoclay was added. Thus, for SW-SPERM such differences were more noticeable in soil B, whereas for SW-HDTMA and SA-HDTMA, they were more pronounced in soil A.

Persistence, Leaching, and Bioefficacy of Fluometuron in Unamended and SW-SPERM-Amended Soils. For subsequent persistence, leaching, and herbicidal activity experiments, we selected the sample SW-SPERM as a soil amendment, on the basis of its high affinity for the herbicide and the natural origin of spermine, which is a desirable characteristic to reduce concern about incorporation of the adsorbent into natural ecosystems for practical applications (5, 6, 22, 23).

Persistence. Dissipation curves for fluometuron in the unamended and SW-SPERM-amended soils after application of the herbicide at a rate of 2 mg kg⁻¹ are shown in Figure 5. The sigmoidal shapes of the fluometuron dissipation curves in both soils are typical of the degradation of compounds used as the microbial growth substrate (29). Previous work has shown that fluometuron in soil is dissipated mainly by microbial degradation, with formation of the metabolites desmethylfluometuron (DMF), trifluoromethyl phenylurea (TFMPU), and trifluoromethylaniline (TFMA) (10, 30, 31). Accumulation of DMF and, to a lesser extent, TFMA was detected by HPLC in the course of the persistence experiment with our soils (data not shown).

Dissipation of fluometuron occurred faster in soil A than in soil B. This can be attributed to the fact that soil A received previous

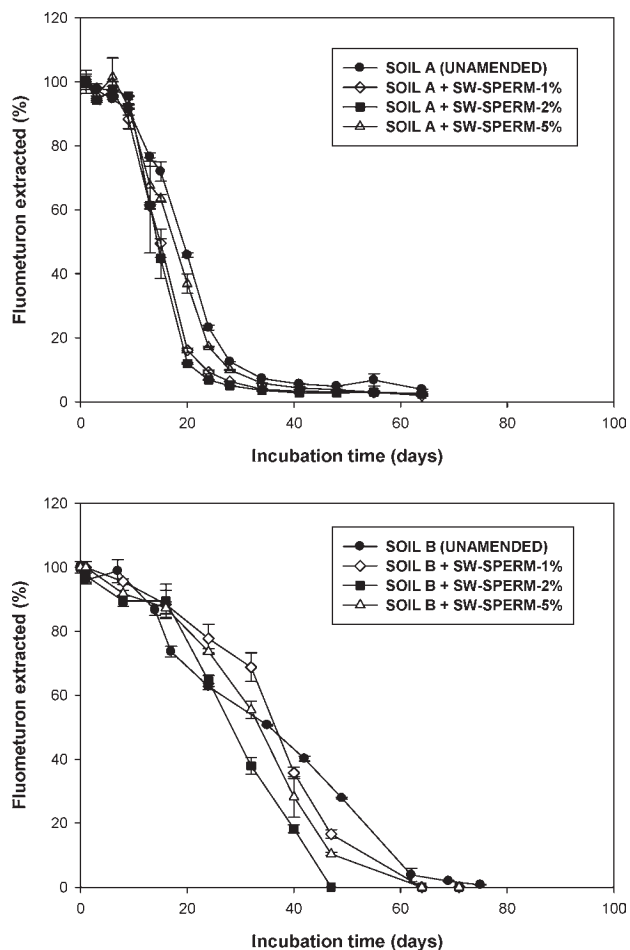


Figure 5. Dissipation curves for fluometuron in unamended and SW-SPERM-amended soils.

applications of fluometuron as an agricultural practice for cotton growing and hence probably contained a greater amount of fluometuron-degrading microorganisms (32). Interestingly, the addition of SW-SPERM did not hinder the dissipation of fluometuron in the soils, indicating that fluometuron degradation was not related to fluometuron adsorption. In no case the higher adsorption of fluometuron by the amended soils resulted in reduced degradation compared to that in the unamended soils. This may be indicative that in accordance with the high reversibility of fluometuron adsorption by SW-SPERM desorption occurred rapidly and was not a limiting step for herbicide degradation in the amended soils.

Leaching. Figure 6 shows the breakthrough curves (BTCs) of fluometuron in unamended and SW-SPERM-amended soils. The BTCs of fluometuron in soil A revealed greater retention of the herbicide and lower herbicide concentrations in leachates than the BTCs in soil B. This reflects the different textures of the soils and their different affinity for fluometuron. It should be noted that two different regions can be identified in the BTCs of soil A. At up to 100–150 mL of water added, the herbicide detected in the leachates should correspond to the endogenous fluometuron present in the soil (Table 1), whereas the fluometuron added to the soil columns appeared in the leachates at water volumes greater than 100 mL (Figure 6).

For both soils, amendment with SW-SPERM resulted in enhanced retention of the added herbicide within the soil column, leading to lower concentration of fluometuron in leachates, flattening of the relative BTCs, and shifting of the maximum concentration peaks to larger volumes of water added. These

Table 4. Observed (RF_{obs}) and Calculated (RF_{calc}) Retardation Factors for Leaching of Fluometuron in Unamended and SW-SPERM-Amended Soil Columns

treatment	soil A		soil B	
	RF_{obs}	RF_{calc}	RF_{obs}	RF_{calc}
unamended	3.3	3.4	1.8	1.9
SW-SPERM- 1%	5.0	5.0	2.6	3.7
SW-SPERM- 2%	5.7	6.6	4.0	5.5
SW-SPERM- 5%	7.4	11.1	6.6	10.5

effects increased with the amount of SW-SPERM added to the soils. For soil A, leaching of the endogenous fluometuron was not affected by the amendment since the organoclay was added only to the top 1.25 cm of soil, the rest of the column being free of amendment.

Retardation coefficients (RF) were derived as the position of the maximum concentration peaks of each BTC. The RF values reflect the number of pore volumes at which the maximum concentration of the herbicide appears in leachates (33). Observed RF values (RF_{obs}) were compared with calculated RF values (RF_{calc}), the latter calculated assuming linear, instantaneous, and reversible adsorption conditions (34):

$$RF_{calc} = 1 + (\rho/\theta)K_d \quad (2)$$

In eq 2, ρ is the bulk density of the soil (g cm^{-3}); θ is the soil volumetric water content ($\text{cm}^3 \text{cm}^{-3}$); and K_d (L kg^{-1}) is the adsorption distribution coefficient for the herbicide in the soil column. For the amended soil columns, K_d was calculated according to eq 1, f_{soil} and f_{OC1} being the fractions of soil and organoclay in the soil column, respectively, and K_{d-soil} and K_{d-OC1} the individual distribution coefficients for fluometuron adsorption on the soil and organoclay, respectively (27, 35).

Table 4 summarizes the observed and calculated RF values for fluometuron leaching in the unamended and amended soil columns. For the unamended soils, RF_{obs} values were very close to RF_{calc} values, and both RF_{obs} and RF_{calc} values increased upon soil amendment. However, it is important to highlight that RF_{calc} values overpredicted the retention of fluometuron in the amended soil columns, although this overprediction was less than that observed in Table 3 for the distribution coefficients, K_d . This result reflects that also under column leaching conditions, the performance of SW-SPERM in adsorbing fluometuron is reduced by the presence of the soil but to a lesser extent compared to the reduction observed under batch adsorption conditions. In this regard, it should be kept in mind that in the soil column experiment the soil/water ratio was greater than that in the batch adsorption experiments and that the amended soil represented only about 6% of the total weight and length of the soil column.

Fluometuron cumulative BTCs (Figure 6) showed that the total amount of herbicide leached from the sandy loam soil (soil B) amended with SW-SPERM (39–62%) was less than that from the unamended soil (79%) and that the amount leached decreased with the amount of SW-SPERM added (Table 5). The amounts of fluometuron extracted from the soil columns at the end of the leaching experiment were less than 1% so that the amount not recovered probably corresponded to the degradation of the herbicide within the soil column and/or the formation of strongly bound herbicide residues. For the unamended clay soil (soil A), the total amount of fluometuron leached was less than that from soil (B), most likely due to the rapid degradation of the herbicide in soil A or the greater formation of bound residues. Amendment of soil A with SW-SPERM resulted in less amount of herbicide leached only at the highest dose of organoclay added (i.e., 5%). Therefore, the herbicide leaching pattern depended on both the

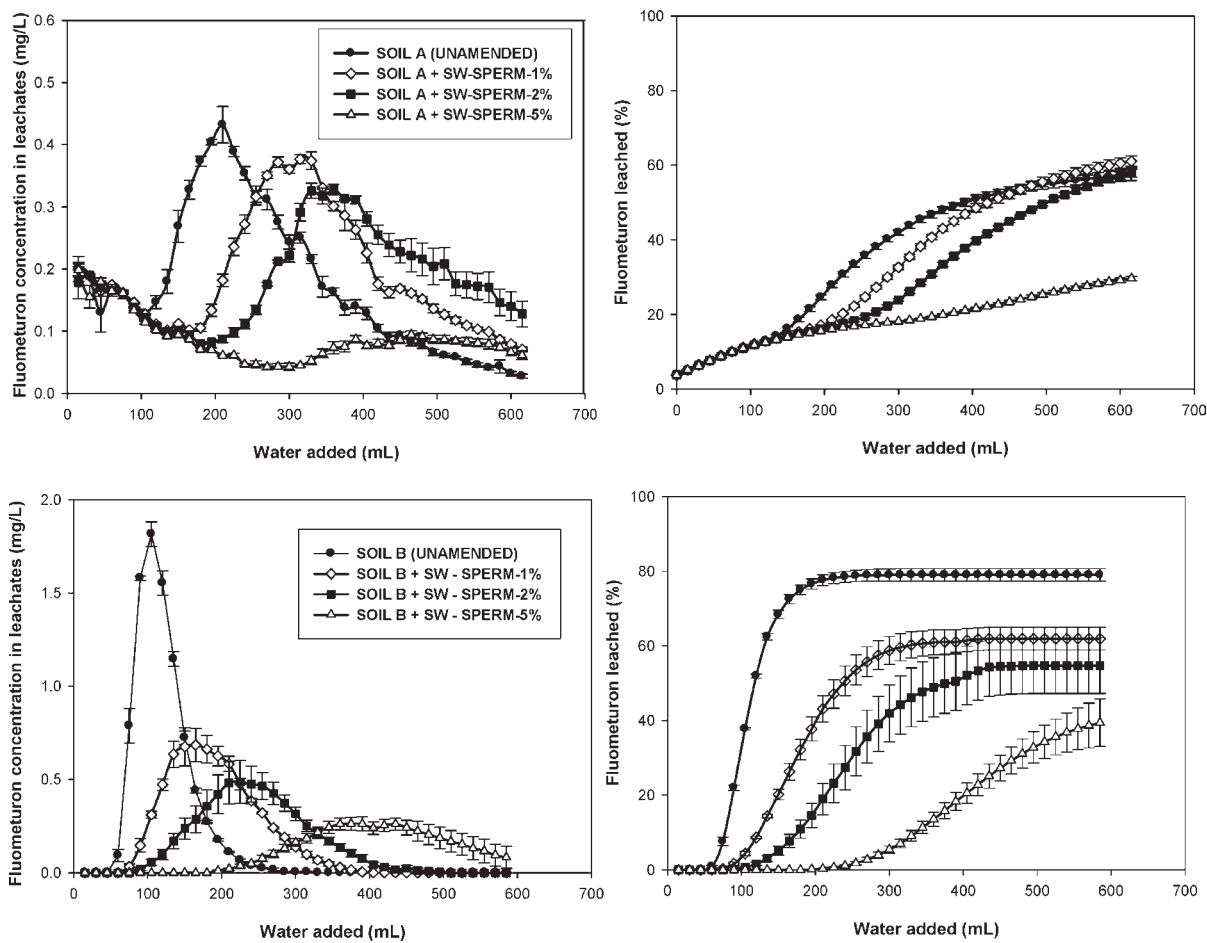


Figure 6. Relative (left) and cumulative (right) breakthrough curves (BTCs) of fluometuron in unamended and SW-SPERM-amended soils.

Table 5. Fluometuron Leached, Extracted from Soil Column, and Not Recovered after the Leaching Experiment with Unamended and SW-SPERM-Amended Soils

	Soil A			
	unamended	SW-SPERM-1%	SW-SPERM-2%	SW-SPERM-5%
leached (%)	58 ± 1 ^a	61 ± 1	58 ± 1	30 ± 1
extracted (%)	5 ± 1	9 ± 1	15 ± 2	10 ± 1
not recovered (%)	37	30	27	61
	Soil B			
	unamended	SW-SPERM-1%	SW-SPERM-2%	SW-SPERM-5%
leached (%)	79 ± 2	62 ± 3	55 ± 7	39 ± 6
extracted (%)	<1%	<1%	<1%	<1%
not recovered (%)	21	38	45	61

^a Mean ± standard error.

amount of SW-SPERM and the nature of the soil to which SW-SPERM was added.

Bioefficacy. The herbicidal efficacy of fluometuron applied to pots of soil B in which *Eruca vesicaria* had been seeded was found to decrease with the amount of SW-SPERM added (Figure 7a). The low solution concentrations of fluometuron in the soil pots amended with high rates of SW-SPERM probably reduced the herbicide efficacy in the control of *Eruca vesicaria*. The herbicide efficacy in the soil amended with SW-SPERM at a rate of 1% was, however, very similar to that in unamended soil. This indicates that low rates of SW-SPERM may combine reduced leaching of the herbicide and adequate weed control.

A separate experiment was designed to assess whether the reduced leaching of fluometuron in SW-SPERM (1%)-amended soil could result in improved weed control efficacy of the herbicide after high water input just after herbicide application. For this purpose, control, unamended, and SW-SPERM (1%)-amended soil pots were irrigated with 60 mm of water just after fluometuron application, and then *Eruca vesicaria* was seeded and the biomass determined after three weeks. Analysis of the leachates collected from the pots revealed that 88 ± 2% of the applied herbicide had been leached from the unamended soil pots, whereas only 40 ± 3% had been leached from the SW-SPERM (1%)-amended pots. Figure 7b shows that the greater amount of herbicide remaining in the amended soil pots resulted in greater

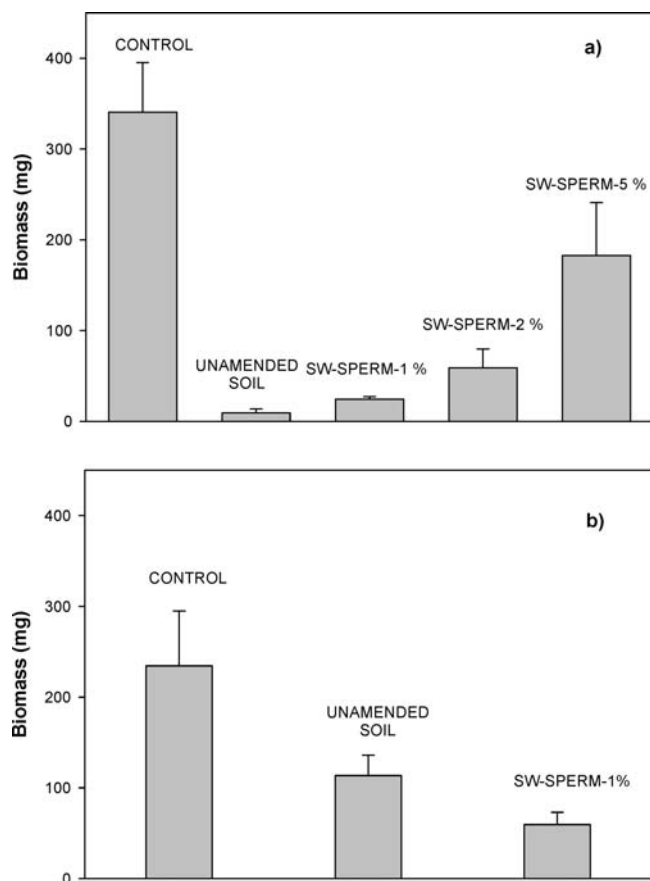


Figure 7. Effect of fluometuron on the growth of *Eruca vesicaria* in unamended and SW-SPERM-amended soil B: (a) effect of the amendment rate on herbicide efficacy; (b) effect of a high water input (60 mm) just after fluometuron application on herbicide efficacy in unamended and SW-SPERM-1% amended soils.

herbicide efficacy compared to that in the unamended soil pots, thus illustrating how the reduced mobility of the herbicide in the amended soil not only mitigated the risk of groundwater contamination but also improved the efficacy of the herbicide in the worst-case scenario of heavy rainfall event shortly after herbicide application.

In summary, the results of this work show that amendment of soils with organoclays can be a useful strategy to enhance soil retention capacity and retard the leaching of herbicides in agricultural soils. The reduced herbicide leaching in organoclay-amended soil not only mitigates the risk of groundwater contamination but also results in improved herbicide efficacy by reducing herbicide losses through transport processes. Modified clays can thus be suggested as soil amendments to optimize the behavior of pesticides in agricultural soils by increasing their efficacy and reducing the pesticide environmental impact.

ABBREVIATIONS USED

HPLC, high performance liquid chromatography; OCl, organoclay; CAR, L-carnitine; SPERM, spermine; HEXADIM, hexadimethrine; TYRAM, tyramine; PTMA, phenyltrimethylammonium; HDTMA, hexadecyltrimethylammonium; CEC, cation exchange capacity; SW-SPERM, spermine-exchanged Wyoming montmorillonite; SW-HDTMA, hexadecyltrimethylammonium-exchanged Wyoming montmorillonite; SA-HDTMA, hexadecyltrimethylammonium-exchanged Arizona montmorillonite; RF, retardation factor.

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LITERATURE CITED

- (1) Hapeman, C. J.; McConnell, L. L.; Rice, C. P.; Sadeghi, A. M.; Schmidt, W. F.; McCarty, G. W.; Starr, J. L.; Rice, P. J.; Angier, J. T.; Harman-Fetcho, J. A. Current United States Department of Agriculture-Agricultural Research Service research on understanding agrochemical fate and transport to prevent and mitigate adverse environmental impacts. *Pest Manag. Sci.* **2003**, *59*, 681–690.
- (2) Rice, P. J.; Rice, P. J.; Arthur, E. L.; Barefoot, A. C. Advances in pesticide environmental fate and exposure assessments. *J. Agric. Food Chem.* **2007**, *55*, 5367–5376.
- (3) Hornsby, A. G. Site-specific pesticide recommendations: the final step in environmental impact prevention. *Weed Technol.* **1992**, *6*, 736–742.
- (4) Chachalis, D.; Galanis, M. Weed control and cotton response to combinations of acetochlor with fluometuron. *J. Food. Agric. Environ.* **2007**, *5*, 198–201.
- (5) Trigo, C.; Celis, R.; Hermosín, M. C.; Cornejo, J. Organoclay-based formulations to reduce the environmental impact of the herbicide diuron in olive groves. *Soil Sci. Soc. Am. J.* **2009**, *73*, 1652–1657.
- (6) Celis, R.; Trigo, C.; Facenda, G.; Hermosín, M. C.; Cornejo, J. Selective modification of clay minerals for the adsorption of herbicides widely used in olive groves. *J. Agric. Food Chem.* **2007**, *55*, 6650–6658.
- (7) Baskaran, S.; Kennedy, I. R. Sorption and desorption kinetics of diuron, fluometuron, prometryn and pyriithiobac sodium in soils. *J. Environ. Sci. Health* **1999**, *B34*, 943–963.
- (8) Zablotowicz, R. M.; Locke, M. A.; Gaston, L. A.; Bryson, C. T. Interactions of tillage and soil depth on fluometuron degradation in a Dundee silt loam soil. *Soil Tillage Res.* **2000**, *57*, 61–68.
- (9) Gaston, L. A.; Boquet, D. J.; Bosch, M. A. Fluometuron sorption and degradation in cores of silt loam soil from different tillage and cover crop systems. *Soil Sci. Soc. Am. J.* **2003**, *67*, 747–755.
- (10) Locke, M. A.; Zablotowicz, R. M.; Steinriede, R. W.; Kingery, W. L. Degradation and sorption of fluometuron and metabolites in conservation tillage soils. *J. Agric. Food Chem.* **2007**, *55*, 844–851.
- (11) Mueller, T. C.; Moorman, T. B.; Snipes, C. E. Effect of concentration, sorption, and microbial biomass on degradation of the herbicide fluometuron in surface and subsurface soils. *J. Agric. Food Chem.* **1992**, *40*, 2517–2522.
- (12) Weaver, M. A.; Zablotowicz, R. M.; Locke, M. A. Laboratory assessment of atrazine and fluometuron degradation in soils from a constructed wetland. *Chemosphere* **2004**, *57*, 853–862.
- (13) Halladja, S.; Amine-Khodja, A.; ter Halle, A.; Boulkamh, A.; Richard, C. Photolysis of fluometuron in the presence of natural water constituents. *Chemosphere* **2007**, *69*, 1647–1654.
- (14) Wagner, S. C.; Zablotowicz, R. M. Effect of organic amendments on the bioremediation of cyanazine and fluometuron in soil. *J. Environ. Sci. Health* **1997**, *B32*, 37–54.
- (15) Zhao, J.; Wilkins, M. Controlled release of the herbicide, fluometuron, from matrix granules based on fractionated organosolv lignins. *J. Agric. Food Chem.* **2003**, *51*, 4023–4028.
- (16) Jaynes, W. F.; Boyd, S. A. Clay mineral type and organic compound sorption by hexadecyltrimethylammonium exchanged clays. *Soil Sci. Soc. Am. J.* **1991**, *55*, 43–48.
- (17) Laird, D. A. Interactions between Atrazine and Smectite Surfaces. In *Herbicide Metabolites in Surface Water and Ground Water*; Meyer, M. T., Thurman, E. M., Eds.; ACS Symposium Series 630; American Chemical Society: Washington, DC, 1996; pp 86–100.
- (18) Lagaly, G. Pesticide-clay interactions and formulations. *Appl. Clay Sci.* **2001**, *18*, 205–209.
- (19) Cornejo, J.; Celis, R.; Pavlovic, I.; Ulibarri, M. A. Interactions of pesticides with clays and layered double hydroxides: a review. *Clay Miner.* **2008**, *43*, 155–176.
- (20) Boyd, S. A.; Shaobai, S.; Lee, J. F.; Mortland, M. M. Pentachlorophenol sorption by organo-clays. *Clays Clay Miner.* **1988**, *36*, 125–130.

- (21) Groisman, L.; Rav-Acha, C.; Gerstl, Z.; Mingelgrin, U. Sorption of organic compounds of varying hydrophobicities from water and industrial wastewater by long- and short-chain organoclays. *Appl. Clay Sci.* **2004**, *24*, 159–166.
- (22) Cruz-Guzmán, M.; Celis, R.; Hermosín, M. C.; Cornejo, J. Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations. *Environ. Sci. Technol.* **2004**, *38*, 180–186.
- (23) Cruz-Guzmán, M.; Celis, R.; Hermosín, M. C.; Koskinen, W. C.; Cornejo, J. Adsorption of pesticides from water by functionalized organobentonites. *J. Agric. Food Chem.* **2005**, *53*, 7502–7511.
- (24) Cornejo, L.; Celis, R.; Domínguez, C.; Hermosín, M. C.; Cornejo, J. Use of modified montmorillonites to reduce herbicide leaching in sports turf surfaces: laboratory and field experiments. *Appl. Clay Sci.* **2008**, *42*, 284–291.
- (25) Camacho-Muñoz, D.; Martín, J.; Santos, J. L.; Aparicio, I.; Alonso, E. An affordable method for the simultaneous determination of the most studied pharmaceutical compounds as wastewater and surface water pollutants. *J. Sep. Sci.* **2009**, *32*, 3064–3073.
- (26) Barriuso, E.; Laird, D. A.; Koskinen, W. C.; Dowdy, R. H. Atrazine desorption from smectites. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1632–1638.
- (27) Rodríguez-Cruz, M. S.; Sánchez-Martín, M. J.; Andrades, M. S.; Sánchez-Camazano, M. Modification of clay barriers with a cationic surfactant to improve the retention of pesticides in soils. *J. Hazard. Mater.* **2007**, *B139*, 363–372.
- (28) Celis, R.; Barriuso, E.; Houot, S. Effect of liquid sewage sludge addition on atrazine sorption and desorption by soil. *Chemosphere* **1998**, *37*, 1091–1107.
- (29) Kearney, P. C.; Shelton, D. R.; Koskinen, W. C. Soil Chemistry of Pesticides. In *Encyclopedia of Chemical Technology*, 4th ed.; Howe-Grant, M., Ed.; John Wiley & Sons: New York, 1997; pp 419–451.
- (30) Bozarth, G. A.; Funderburk, H. H., Jr. Degradation of fluometuron in sandy loam soil. *Weed Sci.* **1971**, *19*, 691–695.
- (31) Lancaster, S. H.; Haney, R. L.; Senseman, S. A.; Kenerley, C. M.; Hons, F. M. Microbial degradation of fluometuron is influenced by Roundup WeatherMAX. *J. Agric. Food Chem.* **2008**, *56*, 8588–8593.
- (32) Cox, L.; Walker, A.; Welch, S. J. Evidence for accelerated degradation of isoproturon in soils. *Pestic. Sci.* **1996**, *48*, 253–260.
- (33) Flores-Céspedes, F.; González-Pradas, E.; Fernández-Pérez, M.; Villafranca-Sánchez, M. Effects of dissolved organic carbon on sorption and mobility of imidacloprid in soil. *J. Environ. Qual.* **2002**, *31*, 880–888.
- (34) Rao, P. S. C.; Hornsby, A. G.; Jessup, R. E. Indices for ranking the potential for pesticide contamination of groundwater. *Proc. Soil Crop Sci. Soc. Fla.* **1985**, *44*, 1–8.
- (35) Voudrias, E. A. The concept of a sorption chemical barrier for improving effectiveness of landfill liners. *Waste Manag. Res.* **2002**, *20*, 251–258.

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