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Slow-Release Formulations of Sulfometuron Incorporated in Micelles Adsorbed on Montmorillonite

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The design and tests of slow-release formulations of sulfometuron (SFM), an anionic sulfonylurea herbicide, are described. The formulations are based on incorporation of the herbicide in octadecyltrimethylammonium (ODTMA) micelles, which adsorb on a clay mineral, montmorillonite. An optimization of herbicide/micelle clay ratios yielded high adsorption of SFM (95%), and at a 1% (w/w) water suspension only 0.5% of the adsorbed SFM was released at times varying from hours to 9 days. An analytical test in Seville soil showed that under excessive irrigation (400 mm) 100% of the commercial formulation leached, whereas the micelle−clay formulations showed only 50−65% elution. A plant bioassay in Rehovot soil showed that the commercial dispersible granule formulation (Oust, 75% ai sulfometuron methyl) yielded only 23% root elongation inhibition at the top 5 cm of the soil, whereas complete inhibition was achieved with the micelle−clay formulation. The detected concentration of SFM for the micelle−clay formulation at a depth of 15−20 cm was half of that detected for the commercial one, indicating a reduction in leaching when applying the micelle−clay formulation. A 10-fold reduction in the applied dose of SFM in the micelle−clay formulations resulted in good herbicidal activity of 60−87% inhibition. These characteristics make the new formulation promising from the environmental and economic points of view.

KEYWORDS: Octadecyltrimethylammonium; micelles; montmorillonite; sulfometuron; slow release; soil column; bioassay

INTRODUCTION

The increasing use of agrochemicals, such as herbicides, poses health and environmental problems due to leaching and surface migration, which can cause surface water and groundwater contamination (*1*). These factors reduce the herbicidal efficacy, causing an increase in frequency and dose of herbicide application, which increases the ecological contamination and cost.

The herbicide sulfometuron (SFM), a sulfonylurea herbicide, is active at very low doses in inhibiting one of the early steps in the biosynthesis of branched amino acids in plants. This herbicide, which is a weak acid, is negatively charged at moderately basic pH, and its solubility in water increases with the pH (*2*). Basic pH is common in calcareous soils in the Mediterranean region (*3*). A severe problem encountered at a basic pH is leaching of the herbicide molecules to deep soil layers and thus reduction of the herbicidal efficacy and migration to nontarget areas (*4*−*8*).

One approach to solve the problem of herbicide leaching and migration is to design controlled-release formulations, which will decrease the dose and rate of release of the active ingredient. A few approaches were taken to prepare controlled release formulations: formulations based on alginate (*9*), cyclodextrin complexes (*10*), formulations based on lignin (*11*), polymer encapsulation (*12*), formulations based on starch (*13*), and formulations based on organo-clays (*14, 15*). These formulations were designed for hydrophobic herbicides.

This work presents formulations based on a new approach, which is particularly suitable for anionic herbicides such as the sulfonylureas, imidazolinones, triazolopyrimidines, and others. The formulations are based on SFM incorporated in positively charged quaternary amine cation micelles, which are adsorbed on a negatively charged clay mineral, montmorillonite. Anionic herbicides such as SFM do not adsorb directly on the clay mineral (*16*).

Designing optimal formulations was based on a detailed study of the herbicide−micelle−clay system (*16*). Optimal formulations should yield maximum adsorption and slow desorption of the herbicide and at the same time be active in inhibiting weed growth.

The biological efficacy of the formulations and the efficiency to reduce leaching were tested by using soil columns. To detect

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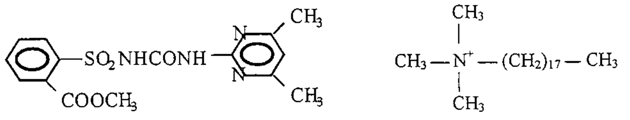

Sulfometuron (SFM) **ODTMA**

Figure 1. Structural formulas of the molecules used.

sulfonylurea residues in the soil at low concentrations (ppb) it is necessary to use a plant bioassay (*17*). Consequently, a plant bioassay was employed at low added amounts of SFM and an analytical method was employed at relatively higher added amounts.

We will show that the designed micelle−clay formulations reduce herbicide leaching in comparison with the commercial dispersible granule formulation (DuPont, Wilmington, DE) and consequently can yield larger herbicidal activity at the top layers of the soil.

MATERIALS AND METHODS

Materials. The clay used was Wyoming Na-montmorillonite (SWy-2) obtained from the Source Clays Repository of the Clay Minerals Society (Columbia, MO). Octadecyltrimethylammonium (ODTMA) was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO). Sodiumtetraborate-10-hydrate was obtained from Riedel-de Haen (Seeize, Germany). HPLC−acetonitrile and HPLC−water were purchased from Merck (Darmstadt, Germany). Sulfometuron, 2-[3-(4,6-dimethylpyrimidin-2-yl) ureidosulfonylbenzoic acid (analytical grade) and a commercial formulation (Oust 75% ai; dispersible granule sulfometuron methyl) were obtained from E. I. Du Pont de Nemours & Company (Wilmington, DE). Dialysis bags made of regenerated cellulose 1000D were obtained from Bio Lab LTD (Jerusalem, Israel). The structural formulas of the herbicide and the organic cation are shown in **Figure 1**.

Two soils were used for an analytical test and for a plant bioassay. The upper horizon of a Typical Xeropsamment soil from Coria, Sevilla, Spain was used after being dried and passed through a 2-mm sieve. Its characteristics are as follows: pH 8.0, carbonate content 6.9%, organic matter content 0.92%, sand 87.5%, silt 4%, and clay 8.4%.

The Rehovot soil was collected from the top 30 cm of a sandy loam soil at the Faculty's Experimental Farm in Rehovot, Israel, air-dried, and sieved through a 2-mm screen. The pH of the soil is 7.5, carbonate content 0.0%, organic matter content 0.2%, sand 95.5%, silt 3.3%, and clay 1.2% (*14*). A sorghum (Sorghum bicolor) cultivar, R.S.-610 (Hazera-Quality Seeds, Israel), was used as a test plant.

SFM Adsorption and Desorption. All solutions of SFM were prepared in a buffer solution (pH 8.5) of 70% 0.05 M sodium tetraborate-10-hydrate and 30% 0.1 M HCl. SFM and ODTMA solutions were prepared by first adding SFM to the buffer solution, and then adding a desired amount of ODTMA. Solutions of SFM and ODTMA at different concentrations (10 mL) were added to different clay concentrations (5 mL) in 40-mL polycarbonate centrifuge tubes, reaching a final volume of 15 mL. The final concentrations were as follows: 0.05−0.5 mM SFM, 0.25−12 mM of ODTMA, and 0.25−10 g clay/L (**Tables 1** and **2**). The suspensions were kept under continuous agitation for 3 days, reaching equilibration. Supernatants were separated by centrifugation at 15000*g* for 30 min and SFM was measured. Desorption was detected after 20 min up to 9 days, by replacing the supernatants with water at different clay concentrations (**Table 2**). Subsequently, supernatants were separated by centrifugation and the desorbed SFM was measured.

For SFM analysis, all supernatants were filtered with Teflon filters (ISI, Petach Tikva, Israel) of 0.2-μm pore diameter. SFM was analyzed by HPLC (Merck Hitachi 6200, Tokyo, Japan) equipped with PDA detector set at a wavelength of 232 nm. The reverse-phase column was LiChrospher 100 RP-18 (5 mM) (Merck, Darmstadt, Germany). The mobile phase was 70% acetonitrile and 30% water with trifluoroacetic acid. The flow rate was 1.0 mL min^{-1}. The retention time was 2.7 min. The presence of ODTMA did not cause any interference with SFM detection.

Table 1. SFM–Micelle–Clay Formulations

formulation preparation			
clay added (g/L)	ODTMA added (mM)	SFM added (mM)[b]	notation of formulation
2.5	2.5	0.125	2.5/2.5/0.125
5	5	0.25	5/5/0.25
5	5	0.25	5/5/0.25 w[a]
5	5	0.05	5/5/0.05

[a] The formulation (5 g/L) was washed with water. [b] In the first three cases % (w/w) of SFM in the formulations was 1.6%, whereas for 0.05 mM added it was 0.32%.

Preparation of SFM−ODTMA−Montmorillonite Formulations. A buffer solution of SFM and ODTMA (10 mL) was added to a clay suspension (5 mL). The final concentrations of formulations and the weight percent of SFM in the formulation are shown in **Table 1**. Formulation 5/5/0.25 was washed at a clay concentration of 5 g/L (formulation 5/5/0.25 w), to release the SFM molecules that were loosely bound.

Leaching Studies in Soil Columns. *Analytical Test.* Methacrylate tubes of 3.0-cm diameter were cut into 4- and 8-cm sections, and five units of 4 cm were glued together with an 8-cm unit at one end to construct a 28-cm column. The column was covered at the end opposite to the 8-cm unit with 1-mm nylon screen padded with a thin layer of glass wool (0.5 g) to hold the soil firmly in the column. The soil (0.246 kg) was packed from the top of the column (8-cm section), creating a 24-cm soil column that could be readily separated into 4-cm segments. A thin layer of glass wool was placed on top of the soil column to maintain a homogeneous surface during the irrigation.

In a preliminary experiment, two soil columns were saturated with distilled water to obtain moisture content of the soil column of 100% of the soil capacity. The difference between the weight of the saturated soil column and its dry weight gave a value of 57 mL for 1 pore volume (vol).

The columns were treated with 5 pore voles of a 0.01 M $Ca(NO_3)_2$ solution followed by 1 pore vol of distilled water before spraying with 10 mL of the commercial and clay−micelle formulations of SFM at a 420 g/ha^{-1} dose. Distilled water, in an amount equivalent to $^1/_2$ pore vol of the soil column, was added every 24 h at the top of the column, and the leachate was collected and analyzed for SFM. The same procedure was repeated for 20 days. The leaching experiments were done in triplicate for each formulation.

Plant Bioassay. Seville. After 20 days each soil column used in the analytical test was separated into six 4-cm segments and the soil was dried at 40 °C. A bioassay was used to calculate the residual activity of SFM along the length of the soil column by measuring the root inhibition of sorghum seedlings. A 5-g sample of soil from each segment was thoroughly mixed with 60 g of sand and kept, after addition of 14 mL of water, under darkness in Petri dishes, where 9 seeds of sorghum were planted per dish. The Petri dishes were kept in a dark room, tilted at an angle of 60°, and after 9 days the elongation of the roots was measured. The inhibition percent was calculated as the reduction in the elongation of the roots in comparison to the length of the roots in the nontreated soil.

Rehovot. Tin columns, with an upper exposed surface of 100 cm^2 and 20 cm long, were filled with a sandy Rehovot loam soil. The column surface was sprayed with the SFM−micelles−clay formulations, the commercial formulation, and with water (control) at a rate of 0.1−2 g ai/ha. The columns were carefully irrigated with 500 m^3 water/ha (a total of 500 mL per column), adding 50 mL every 10 min. This irrigation level was selected to ensure water movement up to the 20-cm depth. The columns were left for 24 h for equilibration and then sliced along their length to obtain two pots.

Each pot was sliced into segments representing different soil depths. Three to four Petri dishes were filled with the soil from each slice. To

Table 2. Adsorption and Desorption of SFM From Different Clay–Micelle Formulations

SFM adsorption				SFM desorption					
clay (g/L)	ODTMA (mM)	SFM (mM)	SFM adsorbed (%)	SFM desorbed (%) after 24 h^{a}					clay (g/L)
0.25	0.25	0.05	9.4			nd			10
2.5	2.5	0.125	91.9			0.8			10
2.5	2.5	0.25	85.7			1.3			10
1.6	2.5	0.25	82.4			12.7			1.6
1.6	5	0.5	52.9			15.6			1.6
5	5	0.25	95.3	20 min	1 h	24 h	48 h	9 d	10
				0.4^{b}	0.6^{b}	0.5^{b}	0.5^{b}	0.5^{b}	
						2.1			5
						13.2			0.3
5	5	0.05	94.6			1.1			5
5	8	0.25	93.5			2.3			5
10	8	0.5	92.3			7.8			10
10	10	0.5	95.7			3.0			10
10	12	0.5	95.9			1.2			10

[a] The standard deviations obtained for SFM adsorption and desorption range between 0.1 and 1.0%; nd indicates not determined. [b] The concentrations measured are at the HPLC limit of detection.

stay in the range of sensitivity of the plants (0.1−2 ppb) the three lower slices, 5−10 cm, 10−15 cm, and 15−20 cm, were diluted 5, 10, and 20 times, respectively. Samples from the top 5 cm were not diluted or diluted 10 times. The soil slices were diluted by mixing them with the relevant amount of soil. Five seeds of sorghum were placed on the soil in each Petri dish. The plates were sealed and held tilted (60°) in the dark as described above. After 5 days, the root length was measured. The percent of root growth inhibition was calculated by comparing the root length of each sample to the average length of the roots from the control columns. A calibration curve (root length versus SFM concentration) was estimated by using Petri dishes with known amounts of SFM (0−5 ppb). At concentrations above 2 ppb there was no elongation; hence, we aimed to work at concentrations below 2 ppb. The calibration curve ($R^2 = 0.993$) for this experiment was as follows: $C = -0.5 \ln(R - 0.4)/5.66$, where C is the concentration (ppb) of the herbicide in the soil and R is the root length (cm). The amount of SFM in each unknown sample was calculated by using this calibration curve.

Data Analysis. The leaching depths of the different formulations through the soil columns were subjected to analysis of variance, and the main effects and interactions were tested for significance using repeated measures ANOVA. The means of effects of different formulations were compared by Student's *t*-test ($\alpha = 0.05$), following one-way ANOVA. The concentration at each length was analyzed by using the standard error.

RESULTS AND DISCUSSION

SFM Adsorption and Desorption. Understanding SFM speciation in the SFM−micelle−clay system by using dialysis bag experiments, freeze-fracture microscopy, and X-ray measurements (*16*) led us to choose SFM, ODTMA, and clay concentrations that would yield a large adsorbed fraction of SFM. In the current work we first focused on testing the SFM release in aqueous suspensions and selecting formulations which yielded a slow release (**Table 2**).

For a clay concentration of 0.25 g/L, adding ODTMA at a concentration close to the critical micelle concentration (CMC) of 0.25 mM, and 0.05 mM SFM, only 9.4% of the SFM added adsorbed on the clay, because there are only monomers in the system (**Table 2**). At the same clay/ODTMA ratio, but adding 5 mM ODTMA with the same concentration of SFM, 94.6% of the SFM added adsorbed, reinforcing our conclusion from the dialysis bag experiments (*16*) that SFM adsorbs on the clay because of its incorporation in micelles.

An additional conclusion from the dialysis bag experiments was that, for enhancing SFM adsorption it is necessary to increase the clay concentration, but up to a certain limit, to avoid micelle decomposition. As can be seen in **Table 2**, increasing the clay concentration from 1.6 g/L to 2.5 g/L in one case, and to 5 g/L in another case, increased the percent of SFM adsorbed. When adding 2.5 mM ODTMA the increase was from 82.4% SFM adsorbed to 85.7%, and when adding 5 mM ODTMA the increase was more pronounced, from 52.9 to 95.3% SFM, due to the increase in clay concentration and decrease in SFM concentration (0.5 to 0.25 mM), which enables a larger fraction of SFM to be bound to the micelles. An additional increase in the clay concentration to 10 g/L with higher ODTMA concentrations did not significantly increase the SFM adsorption, as expected, since the maximal SFM adsorption was already reached.

In most cases SFM desorption from the formulations in water was measured after 1 day at different clay concentrations (**Table 2**). The desorption of SFM from the different formulations ranges between 0.5 and 15.6%. As expected, the percent of SFM desorbed (0.5−13.2%) decreased as the clay concentration in the solution increased (0.3−10 g/L). A small percent of SFM desorbed even at a very low clay concentration, which may simulate its concentration at the top of the soil following irrigation. Consequently, a few formulations listed in **Table 2** may have a potential for slow release.

The desorption of SFM from the 5/5/0.25 formulation at a relatively higher clay concentration of 10 g clay/L was also measured after 20 min, 1, 24, and 48 h, and 9 days by using separate tubes for each sample, or by discharging the supernatant each time and adding water for the next release. This last method is closer to the situation in the soil, where the leached herbicide is washed out. In both methods a small percent of the herbicide was released (±0.5%) (**Table 2**). The concentration of SFM measured in the supernatant was at the HPLC detection limit.

The observation that a prolongation of the time of release in aqueous solutions had little effect on the fraction released was also noted in the case of organo-clay formulations of hydrophobic herbicides (*15*). The interpretation of this outcome might be that initially a large fraction of the desorbed herbicide is due to relatively more loosely bound molecules. For instance, in (*16*) we found that a few percent of the adsorbed SFM arises from direct SFM adsorption on the ODTMA−clay mineral, which might be positively charged by adsorption of ODTMA monomers above the cation exchange capacity.

Leaching Studies in Soil Columns. *Analytical Test*. The breakthrough curves of the commercial and clay-based formulations of SFM are shown in **Figure 2**. The total recovery of SFM from the commercial formulation amounts to 99.2 ± 0.3%, which is in agreement with previous studies indicating low adsorption of sulfonylureas in most agricultural soils, due to

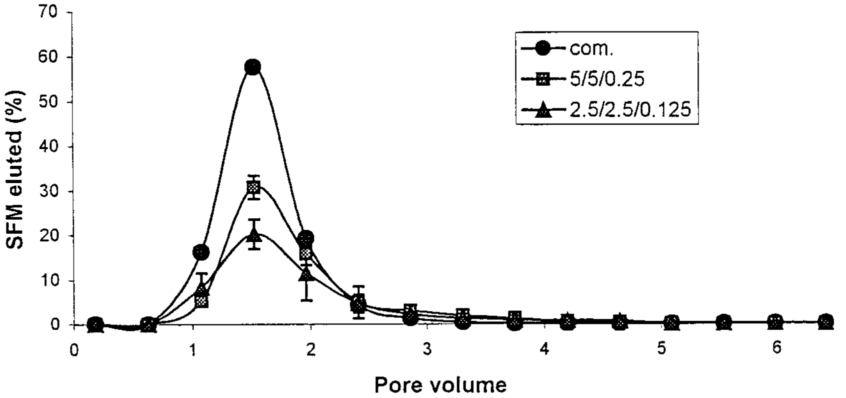

Figure 2. Elution curves of SFM in columns with Seville soil of the commercial formulation and of formulations 5/5/0.25 and 2.5/2.5/0.125.

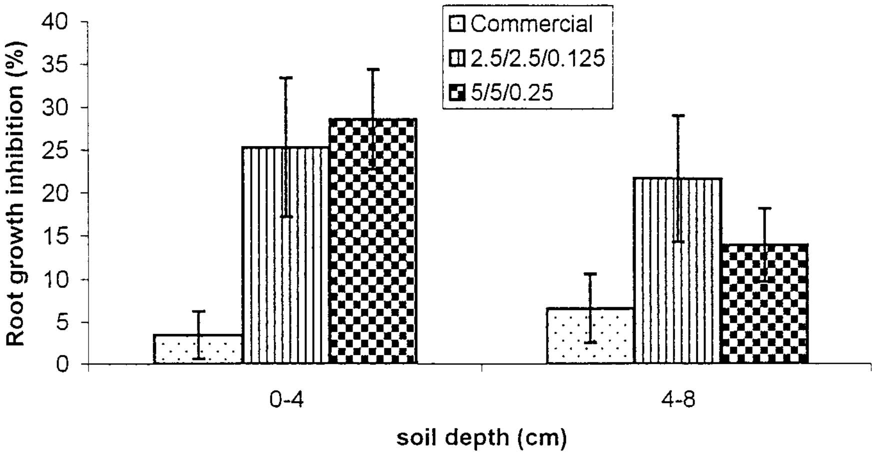

Figure 3. Root growth inhibition of a test plant (Sorghum) as a function of the depth of soil columns sprayed with the SFM commercial formulation, formulation 2.5/2.5/0.125, or formulation 5/5/0.25.

their presence as anionic forms (pH > 6) which results in their minimal adsorption on soil colloids (*18*). Though an increase in the organic matter content enhances the adsorption of sulfonylureas to soil particles, the organic mater content of the soil used (0.92%) is typical for most of the agricultural soils used in Mediterranean areas, indicating a high leaching potential in these soils.

When adding 1.5 pore volumes, which is equivalent to 121 mm of rain, the cumulative amounts of SFM eluted were 73.8, 35.9, and 28.6% for the commercial formulation, the 5/5/0.25 formulation, and the 2.5/2.5/0.125 formulation, respectively, amounting to a 51 and 61% reduction in leaching from the micelle–clay formulations of SFM. At 5 pore volumes (403 mm rain), where complete leaching of the commercial formulation occurred, the total leaching percents were 64.6 ± 7.4% and 50.5 ± 5.2% for the 5/5/0.25 and 2.5/2.5/0.125 formulations, respectively.

Plant Bioassay. Seville. The herbicidal activity of SFM formulations at the top of the soil columns was tested by measuring root growth inhibition of sorghum seeds (**Figure 3**). The herbicidal activity of the commercial formulation was very low at depths of 0–4 and 4–8 cm, just 3.4 and 6.5% inhibition, respectively. The root growth inhibition measured when applying the clay–micelle formulations was 7 to 8 times higher than that measured for the commercial formulation, which is in agreement with the analytical tests. It should be noted that the soil columns were excessively irrigated with 5 pore volumes, which amounts to 403 mm rain.

The combined results of the breakthrough curves and bioassays in Seville soil indicate that the micelle–clay formulations yield a very significant reduction in SFM leaching; consequently, they also yield significantly better herbicidal activity at the top of the soil.

Rehovot. Three micelle–clay formulations of SFM, 5/5/0.25, 5/5/0.25 w, and 5/5/0.05 (**Table 1**), and a commercial formulation were tested using the plant bioassay in soil columns. Four depths of the soil columns were considered for estimating SFM amounts: the top 5 cm, 5–10 cm, 10–15 cm, and the deepest segment at 15–20 cm. Root growth inhibition of the test plant (sorghum), placed in the soil in the Petri plates, was measured. By using a calibration curve of root length as a function of herbicide concentration in the soil we calculated the herbicide concentration at each depth (the four slices), and the amount of SFM in each fraction was estimated. A comparison of the sum of the amounts of SFM in the slices with the amount of SFM applied on each column gave a reasonably good mass balance (80 to 95%), indicating that essentially no SFM from the formulations leached out of the columns.

The main requirements for an efficient formulation are high biological activity at the root zone and little activity at depths where no biological activity is needed, where the herbicide can only cause harm by leaching and contaminating groundwater. The commercial formulation does not fulfill these basic requirements, as can be seen by the distribution of SFM in the soil (**Figure 4A**). Only 2.6% of the applied commercial formulation was detected in the top 5 cm of the soil, and 65% was detected at a depth of 15–20 cm (**Figure 4A**). This trend of herbicide distribution throughout the soil depth is certainly undesired. On the other hand, a high percent (41.5%) of SFM applied as a micelle–clay formulation (5/5/0.05) was detected in the top 5 cm of soil and only 26.5% leached to a depth of 15–20 cm. Formulations 5/5/0.25 and 5/5/0.25 w also showed better

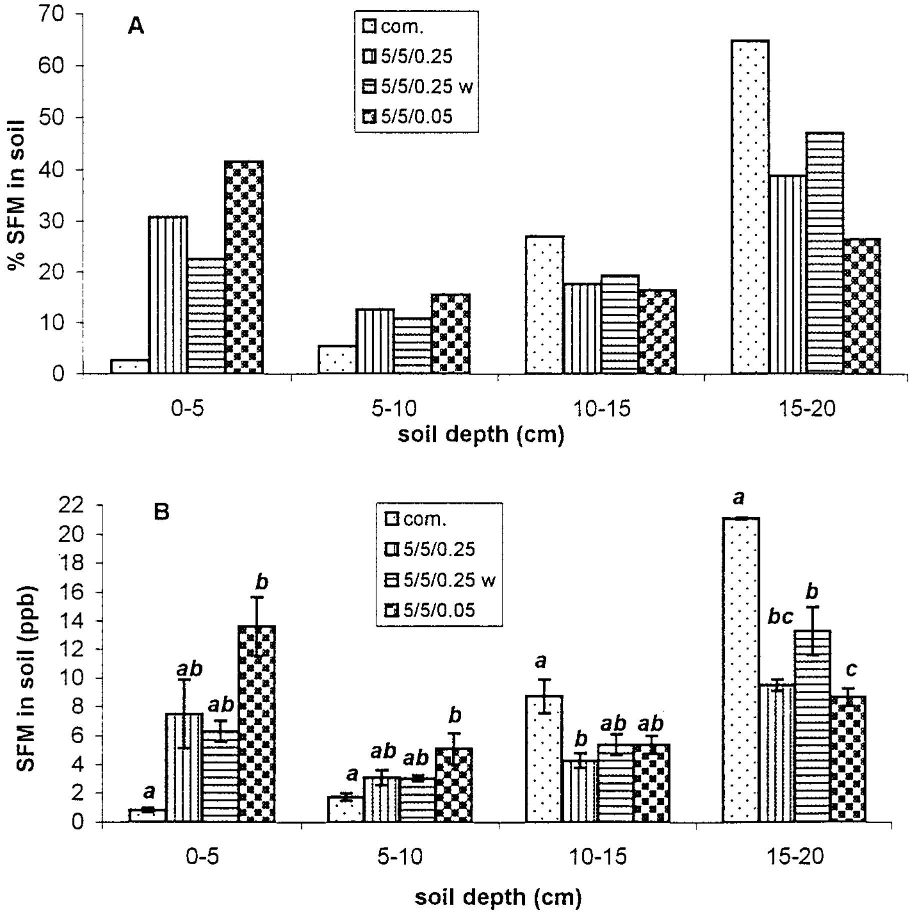

Figure 4. (A) Percent of SFM at different depths of soil from soil columns sprayed with the SFM commercial formulation, formulation 5/5/0.25, formulation 5/5/0.25 w, or formulation 5/5/0.05. (B) SFM Concentration at different depths of soil from soil columns sprayed with the SFM commercial formulation, formulation 5/5/0.25, formulation 5/5/0.25 w, or formulation 5/5/0.05.

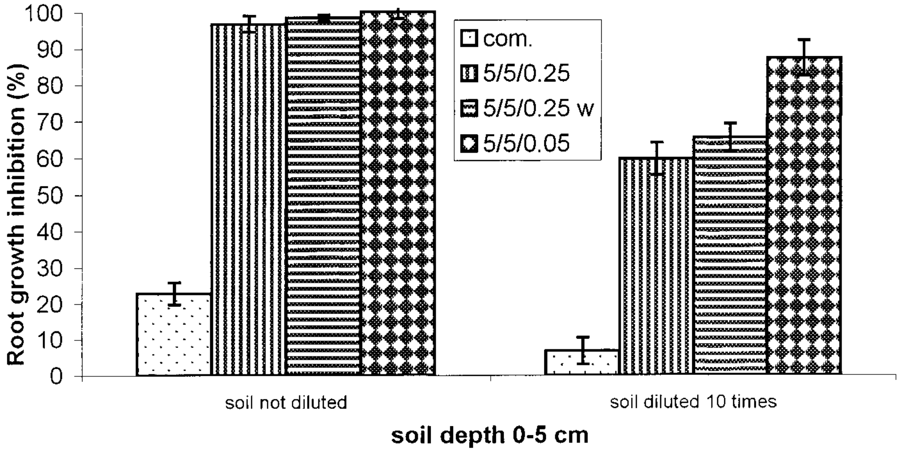

Figure 5. Root growth inhibition of a test plant (sorghum) as a function of the depth of soil columns sprayed with the SFM commercial formulation, formulation 5/5/0.25, formulation 5/5/0.25 w, or formulation 5/5/0.05.

distribution in the soil in comparison with that of the commercial formulation (**Figure 4A**). There are no significant differences in the detected concentrations of SFM, at the different soil depths, between formulations 5/5/0.25 and 5/5/0.25 w (**Figure 4B**). Due to the low desorption of SFM when applying prewashing to the 5/5/0.25 formulation there is no significant difference between the two formulations (**Table 1**), and their activity in the soil should be similar.

The concentration of SFM that leached from the commercial formulation and was detected at a depth of 15−20 cm is more than twice as high as the concentration detected at this depth in the soil treated with the micelle−clay formulation. Thus, applying the micelle−clay formulation can reduce herbicide leaching to harmful depths.

The concentration of SFM released from the formulation 5/5/0.05 and detected in the top 5 cm of the soil is 15 times higher than that found for the commercial formulation (**Figure 4B**). At a depth of 5−10 cm, where weed seeds may germinate, there is also a significantly higher concentration of SFM in the case of the micelle−clay formulations.

Formulation 5/5/0.05 shows better biological activity at the top 5 cm of the soil and leaches less than the 5/5/0.25

formulations (**Figure 4**). This advantage is not statistically significant in most of the cases. The weight percent of SFM in formulation 5/5/0.05 is lower than that in the 5/5/0.25 formulations. A higher clay herbicide ratio reduces SFM desorption from the formulation (**Table 2**) and enables slower release.

The micelle−clay formulations yielded close to 100% root growth inhibition in the top 5 cm, whereas the commercial formulation gave only 23% inhibition (**Figure 5**). Even when diluting the soil 10 times, i.e., also diluting the active ingredient, the clay−micelle formulations still yielded 60−87% root growth inhibition, whereas the commercial formulation had hardly any effect (only 7% inhibition). This indicates that applying 10-fold lower doses of the micelle−clay formulation could still result in good herbicidal activity, better than that obtained with the commercial formulation at the recommended doses.

If we consider leaching at a depth of 15−20 cm as potentially harmful, then the leaching observed in the case of the formulation 5/5/0.05 is less than half of that of the commercial formulation. Hence, the combined results of **Figures 4** and **5** indicate that an application of the micelle−clay formulation of SFM (5/5/0.05) at 10-fold smaller amounts than the recommended rate may reduce SFM leached amounts 20-fold below those resulting from applying the commercial formulation, while achieving 3-fold more biological activity of the herbicide at desirable depths.

The benefit from reducing the applied doses of the formulation is both economic and environmental. The ability to apply lower doses of the micelle−clay formulation than the recommended doses for the commercial formulation, while maintaining good herbicidal activity, is a significant advantage.

CONCLUDING REMARKS

This study presents an attempt to reduce the leaching and migration of the anionic herbicide sulfometuron in soil by applying micelle−clay formulations. The stages of the work have involved elucidation of the characteristics of ODTMA−clay, ODTMA−(micelles)−SFM, and SFM−micelles−clay interactions, which enabled achievement of a large adsorbed fraction of the herbicide. In the next stage, a selection of a suitable formulation was made on the basis of slow release in water. The released amount hardly changed with incubation times from 20 min to several days, but most of the herbicide was retained; hence, the designation of optimal SFM−micelle−clay formulations as slow-release formulations does apply. The analytical and bioassay column tests indicate that, in comparison with the available commercial formulation of SFM, the micelle−clay formulations yield a significant reduction in leaching and a significant enhancement in biological activity. Consequently, the micelle−clay formulations of SFM, and perhaps other anionic herbicides, have promising characteristics from the environmental and economic points of view.

ABBREVIATIONS USED

SFM, sulfometuron; ODTMA, octadecyltrimethylammonium; CMC, critical micelle concentration; CEC, cation exchange capacity.

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