JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2008,** *56,* 9159–9165 **9159**

Herbicide Solubilization in Micelle−Clay Composites as a Basis for Controlled Release Sulfentrazone and Metolachlor Formulations

DANA ZIV AND YAEL G. MISHAEL*

Seagram Center for Soil and Water Sciences, Faculty of Agricultural, Food and Environmental Quality Sciences, Hebrew University of Jerusalem, Rehovot 76100, Israel

Sulfentrazone and metolachlor have been detected in groundwater due to extensive leaching. To reduce herbicide leaching and increase weed control, we have developed, designed, and tested controlled release formulations (CRFs) for both herbicides based on their solubilizion in cationic micelles and adsorption of the mixed micelles (surfactant and herbicide) on a clay mineral, montmorillonite. A better understanding of solubilizing anionic (sulfentrazone) and nonionic (metolachlor) organic molecules in cationic micelles was reached. The percent of active ingredient in the formulations was much higher than previously designed CRFs due to the enhanced solubilization of the herbicides in the micelles and due to their adsorption on the clay. Both CRFs demonstrated controlled release (compared to the commercial formulations) when applied to a thin soil layer. A bioassay in soil columns determined that the new sulfentrazone and metolachlor CRFs significantly improve weed control and reduce leaching (for the latter) in comparison with the commercial formulations.

KEYWORDS: Sulfentrazone; metolachlor; controlled release formulations; micelle−clay composites

INTRODUCTION

Herbicides are applied to control weeds both in agricultural fields, increasing yield (*1*), and in nonagricultural areas such as railways and road sides (*2*). Although herbicides provide substantial agronomic and economic benefits, their increasing use poses environmental problems, due to leaching and surface migration, which can cause soil, surface, and groundwater contamination (*1, 3−6*). In addition, herbicide migration results in insufficient weed control due to the decrease in herbicide concentration at the root zone. One of the approaches pursued to reduce contamination and increase weed control is designing herbicide formulations with improved properties, that is, controlled release formulations (CRFs) (*7−25*). Such formulations can reduce migration and leaching while improving weed control by slowly releasing the active ingredient (ai) at the desired doses.

Both sulfentrazone (SFZ) and metolachlor (MTC) have a relatively high water solubility and, therefore, extensively leach and have been detected in groundwater (*26−29*). SFZ (water solubility of ~280 ppm) is an anionic herbicide ($pK_a = 6.56$), its mobility is enhanced with an increase in soil pH, and its adsorption to the soil especially at alkaline pH values is negligible (*30*). MTC, although nonionic, is relatively soluble in water (490 ppm) (*31*), and its sorption to the soil organic matter and to clays is considered low (*32, 33*).

* To whom correspondence should be addressed. Tel: 972-8-948-9171. Fax: 972-8-948-9856. E-mail: mishael@agri.huji.ac.il.

Because of the extensive leaching of SFZ and MTC, developing CRFs for these herbicides has been studied (*9, 19, 23−25*). The MTC formulations were prepared by adsorbing quaternary amine cations, such as phenyltrimethyl ammonium and berberine, to the clay surface and then binding the herbicide to the organo-clay composite (*24, 25*). The SFZ formulations were based on solubilizing the herbicide in cationic micelles of octadecyltrimethyl ammonium (ODTMA) and adsorbing the mixed micelles on the clay (*19*).

Although the CRFs described above demonstrated good herbicidal activity and the MTC formulation also demonstrated reduced leaching, their performance was not efficient enough for field application, and it was not practical to apply them in the field due to their low percent of ai, 4 and 5−11% for the SFZ and MTC formulations, respectively (*19, 23, 24*). In the current study, we aimed to increase the percent of ai by utilizing a well-known phenomenon, micelle solubilizations, which has been exploited in many fields (see below) but surprisingly has not been applied for the design of herbicide CRFs.

The phenomenon of solubilization, increasing the solubility of an insoluble or poorly soluble organic substance in a surfactant solution, has been widely studied for many decades and is well-established (*34−39*). A variety of applications in different fields such as medicine, cosmetics, detergency, and environment, are based on solubilization of organic compounds. Most environmental research has focused on “enhanced pump and treat” soil remediation techniques (pumping surfactants into the soil to solubilize trapped organic pollutants and then

10.1021/jf801892w CCC: $40.75
Published on Web 09/10/2008

pumping them out) (*40*−*42*). In previous studies on micelle (ODTMA)−clay CRFs (*16, 17, 21*), it was demonstrated that herbicide (sulfumeturon and sulfosulfuron) adsorption to the clay is enhanced when the surfactant is adsorbed as micelles (vs monomers). However, these studies did not take into account the potential of enhancing herbicide solubility in the micelle solution, that is, adding the herbicide above its water solubility to the micelle solution. In the current study, we did exploit this advantage, and by increasing herbicide (SFZ and MTC) concentrations (∼3-fold) in the micelles, we succeeded to increase the percent of ai in the formulations from 4 to 16% (w/w, herbicide/composite) for the SFZ formulation and from 11 to 34% for the MTC one.

Another goal of this study was to reach a better understanding of solubilizing anionic (SFZ) and nonionic (MTC) organic molecules in cationic micelles and to study the subsequent adsorption of the mixed micelles to a negatively charged surface. We characterized and compared the solubilization of MTC and SFZ in ODTMA and the adsorption/desorption of the herbicides on montmorillonite via their solubilization in the micelles. In spite of the differences between the two designed formulations, both of them demonstrated slow release (in comparison to the commercial formulations) in batch experiments and when applied to a thin soil layer. Not only did they show slow release, but when applied to soil columns, a bioassay indicated that the newly designed SFZ and MTC CRFs significantly improve weed control and reduce leaching for the latter (in comparison to the commercial formulations).

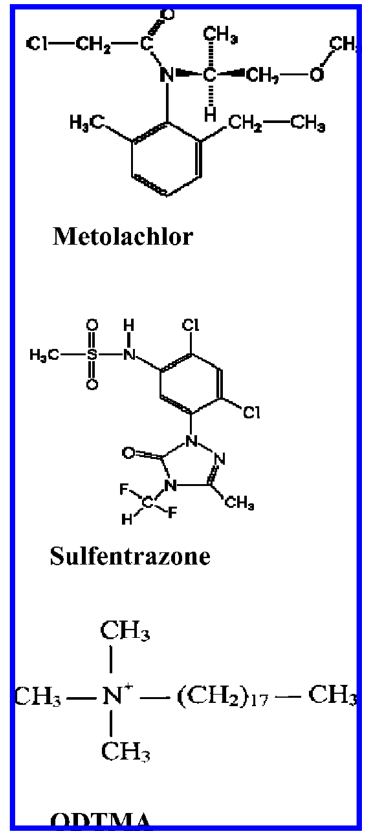

Figure 1. Structural formulas of the herbicides and of the surfactant.

MATERIALS AND METHODS

Materials. The clay used was a Wyoming Na-montmorillonite (SWy-2) (cation exchange capacity, 0.76 mmol/g; surface area, 700 m^2/g) obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO). ODTMA was purchased from Sigma-Aldrich (Stenheim, Germany). Acetonitrile and water, high-performance liquid chromatography (HPLC) grade, were purchased from Merck (Darmstadt, Germany). SFZ *N*-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]phenyl] methane-sulfonamide technical (purity 91.3%) was received from FMC (Princeton, NJ). A Boral commercial formulation of SFZ (75% ai, water dispersible granular) (480 g ai/L, liquid), MTC 2-chloro-*N*-(6-ethyl-*o*-tolyl)-*N*-[(1*RS*)-2-methoxy-1-methylethyl] acetamide (MTC) technical (purity 98.6%), and commercial MTC (Dual-Gold 915 g ai/L liquid) were obtained from Agan Chemicals (Ashdod, Israel). Dialysis bags made of regenerated cellulose 1000 D were purchased from Spectrum Laboratories (Rancho Dominguez, CA). Rehovot sandy soil (*43*) was collected (top 20 cm) from the faculty's experimental farm. The samples were air-dried and sieved through a 2 mm screen. The soil was used for analytical release tests and for the soil column plant bioassays. The test plant for the SFZ and MTC bioassay was *Setaria italica* (L.) P. Beauv. The structural formulas of the herbicides and the organic cation are shown in **Figure 1**.

Methods. *Preparation and Characterization of Herbicide−Micelle−Clay Composites Herbicide Solubilization.* Dialysis bags with ODTMA (10 mL, 2.5 mM) were placed in solutions (20 mL) of SFZ (80−560 ppm, final concentrations) or of MTC (170−730 ppm, final concentrations) in Teflon centrifuge tubes. SFZ and MTC were added (by weight) at concentrations below and above their water solubility. The concentrations indicated are the final concentrations calculated for 30 mL (in the presence of the micelles the herbicides solubilized). The tubes were kept at 25 ± 1 °C under continuous agitation for 24 h to reach complete herbicide solubilization in the micelles. The herbicide concentrations inside and outside the dialysis bags were measured. To determine the percent of herbicide solubilized in the micelles, the concentration outside was subtracted from that inside, assuming that the herbicide equilibrium concentration outside the bags is equivalent to that inside the bags and should not exceed the herbicide's solubility.

SFZ and MTC Adsorption and Desorption. SFZ (40−800 ppm, final concentrations) or MTC (400−1500 ppm, final concentrations) was added to a micelle solution of 2.5 mM ODTMA. The herbicide−micelle solutions were kept at 25 ± 1 °C under constant stirring overnight. The mixed micelles (10 mL) were added to a montmorillonite suspension (5 mL of 2 g/L, final concentration) in Teflon centrifuge tubes. The tubes were kept at 25 ± 1 °C under continuous agitation until the equilibrium was reached (for 24 h). Supernatants were separated by centrifugation at 15000*g* for 20 min, and the herbicide concentration in supernatants was measured by HPLC. Herbicide desorption was measured after 4 h by resuspending the precipitate with 15 mL of distilled water. Supernatants were separated by centrifugation, and the desorbed herbicide was measured. All samples were preformed in triplicate.

For SFZ and MTC analysis, all supernatants were filtered with acrodisc (polypropylene) filters (Pall Corp., MI) of 0.45 μm pore diameter. SFZ and MTC were analyzed by HPLC L-7100 LaChrom (Merck Hitachi, Darmstadt, Germany) equipped with diode array detector L-7455 set at a wavelength of 254 nm for SFZ and 225 nm for MTC. The reverse-phase column was LiChrospher 100 RP-18 (5 μm) (Merck). For SFZ detection, the mobile phase was 50% acetonitrile and 50% water with trifluoroacetic acid, pH ∼ 3. The flow rate was set to 1.0 mL/min. For MTC detection, the mobile phase was 70% acetonitrile and 30% water. The flow rate was set to 1.0 mL/min. The presence of ODTMA did not interfere with herbicide detection.

Formulation Preparation. The tested micelle−clay formulations were prepared by mixing 800 or 1500 ppm SFZ or MTC, respectively, with 2.5 mM ODTMA for 24 h and then adsorbing the mixed micelles on 2 g/L montmorillonite. The suspensions were centrifuged for 20 min at 15000*g*. Supernatants were removed, and herbicide concentrations were measured by HPLC to determine the percent ai in the micelle−clay formulation. The herbicide−micelle−clay precipitates were frozen and lyophilized. The formulations were denoted according to their percent of ai, that is, 16% SFZ−micelle−clay for a SFZ formulation with 16% ai and 34% MTC−micelle−clay for a MTC formulation with 34% ai.

Release Kinetics of SFZ and MTC in Water. The herbicide−micelle−clay formulations were prepared as described above. The herbicide−micelle−clay formulations were resuspended with water (90 mL) reaching a clay concentration of 2 g/L. At times ranging between 5

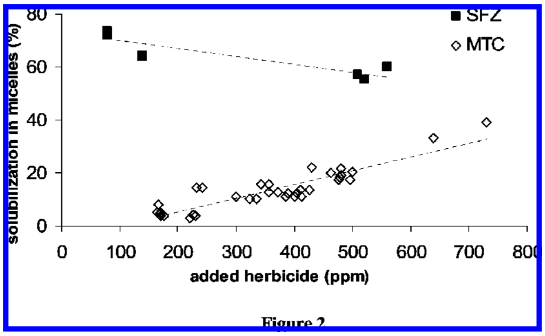

Figure 2. SFZ and MTC solubilization in ODTMA micelles. The standard deviation is ±2−4%.

and 60 min (from the time water was added), 2 mL of suspension was removed and immediately filtered with acrodisc (polypropylene) filters (Pall Corp.) of 0.45 μm pore diameter, and the desorbed herbicide concentration was measured by HPLC. All samples were performed in triplicate.

Testing the Herbicide−Micelle−Clay CRFs. *Herbicide Release from a Thin Soil Layer.* The release of SFZ and MTC from micelle−clay formulations and from the commercial formulations was measured by applying the formulations on a thin layer of Rehovot sandy soil (50 g) deposited on a filter paper in a Buchner funnel (area of $7.85 \times 10^{-3} m^2$) (as described in ref *19*). The formulations were sprayed as a suspension on the soil. The 16% SFZ−micelle−clay formulation and the commercial one, Boral, were applied to the soil at a rate of 1 mg ai per funnel, equivalent to 1200 g/ha. The 35% MTC−micelle−clay formulation and the commercial one, Dual-Gold, were applied at the same rate. Water was sprayed as a control. Application rates were determined according to the HPLC detection limit. The funnels were irrigated 10 times (every 15 min) with 5 mm of water (40 mL per funnel), reaching a total irrigation of 50 mm water. The leachates were collected after each irrigation, and herbicide concentrations were measured by HPLC. Each treatment was preformed in triplicate.

Leaching Studies in a Soil Column Bioassay. Plastic sleeves ($12.2 \times 10^{-3} m^2$ surface area and 20 cm long) were filled with the Rehovot sandy soil (1600 g soil) and used as columns. The micelle−clay formulations, the commercial formulations, and 10 mL of water (control) were applied to the top of the columns (five columns for each treatment). The dose applied for SFZ was 240 g ai/ha, equal to 600 g /ha of the commercial SFZ formulation, whereas the recommended doses are between 600 and 900 g/ha. For MTC, the applied dose was 980 g ai/ha, equal to 1300 g/ha of the commercial MTC formulation, where the recommended doses are between 1200 and 1300 g/ha. The columns were irrigated with tap water, 200 m^3/ha, by adding 50 mL (five times) every 10 min. The irrigation volume ensured water movement through the column without leaching. The columns were left to equilibrate for 24 h, laid horizontally, and then sliced open. Foxtail seeds were sowed. After 14 days, the plant height throughout the columns was measured, and plant growth inhibition as a function of soil depth was calculated by comparison to the control treatment.

Data Analysis. The leaching depths of the commercial and of the micelle−clay formulations through the soil columns were subjected to a two-way analysis of variance model in a "split-plot" design using the formulation (CRF vs commercial formulation) and the depth as main effects. Multiple comparisons were done using a *t* test.

RESULTS AND DISCUSSION

Solubilization. The percentages of SFZ and MTC solubilized in ODTMA micelles as a function of their added concentrations are shown in **Figure 2**. At the herbicide concentrations measured, the percentage of SFZ solubilized in the ODTMA micelles (72−60%) was higher than the percentage of MTC solubilized in these micelles (5−40%). The high solubilization of SFZ in the ODTMA micelles can be explained by the two mechanisms: (i) The cationic ODTMA micelles enhance SFZ dissociation resulting in SFZ^- anion formation, which binds electrostaticly to the cationic micelles (*19*). (ii) SFZ molecules can interact with the hydrophobic micelle core (solubilized into the micelle). Upon increasing SFZ concentrations in the solution, its solubilization in the micelles decreased (72−60% of the SFZ added). Because of the increase in SFZ concentration in the micelles, the positive charge on the micelles decreases, which results in lower affinity of SFZ to the micelle. Previous studies reported 86−89 and 73−76% binding of the anionic herbicides sulfosulfuron (*17*) and sulfometuron (*21*) to ODTMA micelles (2.5 mM), respectively. High solubilization percentages were obtained in those studies since the herbicide concentrations examined were low (below solubility).

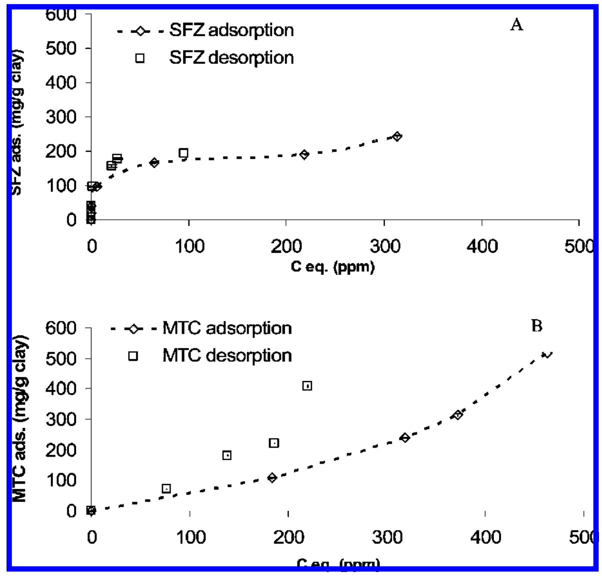

Figure 3. Adsorption and desorption of herbicides solubilized in ODTMA micelles on/from montmorillonite (2 g/L) of (**A**) SFZ and (**B**) MTC. The standard deviation is ±1−4 mg/g.

MTC solubilization in micelles is only attributable to its partitioning between the hydrophobic core and the water solution and, therefore, is lower than the solubility obtained for SFZ. However, MTC solubilization in ODTMA did not show a constant percent of solubilization as expected in a partition mechanism, but it increased (10−40% solubilization) with an increase in the added herbicide concentration. This enhancement in solubilization as the initial concentration increases is probably due to synergistic effects. The micelle affinity to solubilize MTC molecules grows as the concentration of MTC in the micelle increases, perhaps based on the phenomena that "like" dissolves in "like".

SFZ solubility in water (~280 ppm) was increased in the presence of ODTMA micelles (by its uptake into the micelles), suggesting that its adsorption to the clay (mg SFZ/g clay) will increase as well, as seen in **Figure 3**. Further increasing the SFZ concentration (beyond 800 ppm) will not result in higher adsorption on the clay since the micelles are nearly neutralized (0.8 mol/mol ratio) upon adding 800 ppm SFZ to the micelle solution. Therefore, we expect that SFZ adsorption to the clay (via its solubilization in ODTMA micelles) reaches a plateau upon adding herbicide at such concentrations (~800 ppm) (**Figure 3A**). The solubility of MTC is enhanced with its concentration, which suggests that its adsorption on the clay will also increase with its added concentration reaching a high percent of ai (**Figure 3B**).

Herbicide Adsorption−Desorption Isotherms. SFZ does not adsorb directly on montmorillonite, and MTC adsorption is limited (40 mg/g clay). The adsorption isotherms of SFZ and

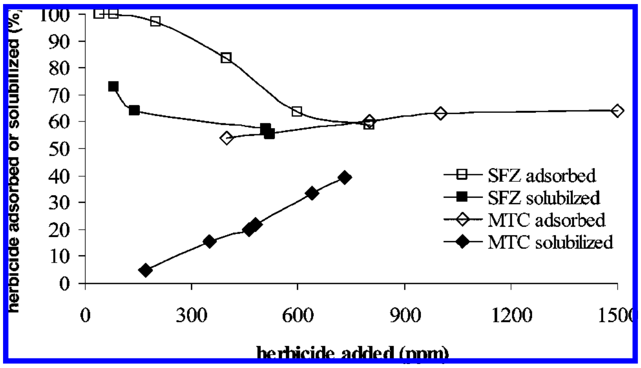

Figure 4. SFZ and MTC solubilization in ODTMA micelles and adsorption on montmorillonite.

MTC, solubilized in ODTMA, on montmorillonite are shown in **Figure 3A,B**, respectively. In both cases, SFZ and MTC loadings (at high added concentrations) were high in comparison to previous reports (*19, 23*) and the release was inhibited. However, the isotherms show a different behavior. The SFZ adsorption reaches a plateau (resembles an L-shape isotherm), whereas the MTC adsorption increases in a semiexponential matter (resembles an S-shape isotherm). This difference can be attributed to the negative charge on SFZ and nonionic properties of MTC.

The shape of both adsorption isotherms can be explained by the mechanisms of their solubilization as elaborated above. At low SFZ concentrations, micelle affinity to the clay is high (100% adsorption) since its charge is not neutralized, but as SFZ concentrations increase, micelle adsorption to the clay does not increase but reaches a plateau because its positive charge is reduced resulting in a lower affinity to the clay (reaching maximum of 60% adsorption at high SFZ added concentration). For these reasons, SFZ release from the micelle−clay composite increases with the increase in SFZ loading in the composite. In contrast, MTC release (%) decreases as its loading on the clay increases due to its synergistic solubilization behavior (seen in **Figure 2**). For the same reason, the MTC isotherm has a semiexponential shape. These characteristics, high loading with inhibited release, are desired for CRFs.

The formulations chosen for further testing (release, leaching, and biological activity) and compared to the commercial formulations have a high percent of ai (**Figure 3**). The SFZ formulation reached 16% ai, 16% SFZ−micelle−clay, and the MTC formulation reached 34% ai, 34% MTC−micelle−clay. In previous studies related to CRFs based on modified clays of SFZ and MTC, the highest ai percentage was of 4% ai for SFZ CRFs (*19*) and of 11% ai for MTC CRFs (*24*). By enhancing the herbicides solubility in ODTMA micelles, the percent of ai in the formulations was significantly increased.

Percentage of Solubilized Herbicide vs Percentage of Adsorbed Herbicide. Our hypothesis, which was supported by the results presented in **Figures 2** and **3**, was that SFZ and MTC adsorbed on the clay via their solubilization in the ODTMA micelles. SFZ does not adsorb directly on the clay, and MTC adsorption is limited (40 mg/g clay). The percentages of herbicide solubilized in the micelles (from **Figure 2**) and adsorbed on the clay (from **Figure 3**), for given herbicide concentrations, are compared in **Figure 4**. For both herbicides, the percent of herbicide adsorbed on clay is higher than that solubilized in the micelles. The enhanced herbicide adsorption suggests a positive synergistic effect brought on by the micelle−clay composites.

Kinetics of SFZ and MTC Release from Micelle−Clay Composites. Herbicides release from the 16% SFZ−micelle−clay

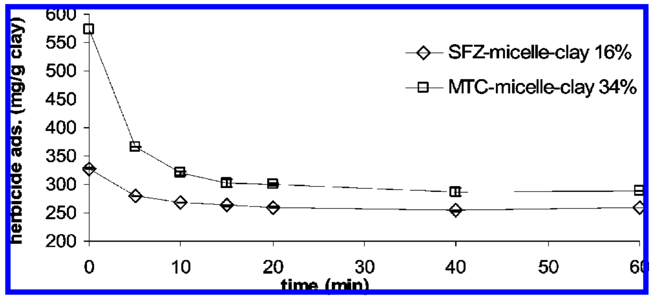

Figure 5. Kinetics of herbicide release from 16% SFZ−micelle−clay and from 34% MTC−micelle−clay formulations. The standard deviation is ±0.5−6 mg/g.

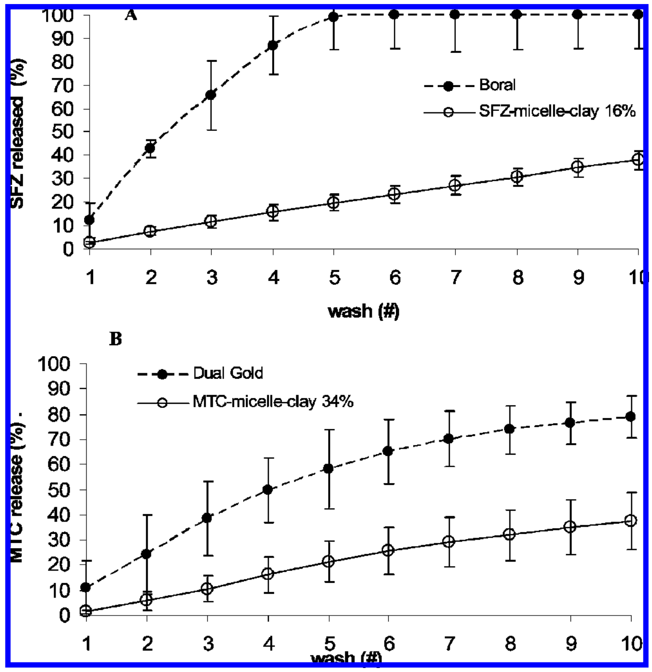

Figure 6. Herbicide release from commercial and micelle−clay formulations applied on a thin soil layer (**A**) SFZ and (**B**) MTC.

and from the 34% MTC−micelle−clay formulations was studied in batch experiments at a low clay concentration of 2 g/L and at times ranging from 0 to 240 min (**Figure 5**). In both cases (SFZ and MTC), the vast amount of herbicide released within the first 15 min. Nearly no herbicide released after the first 20 min. SFZ release was somewhat slower than the release of MTC.

These batch experiment results do not directly indicate controlled release behavior of the herbicides; however, they do suggest that 60 or 80% of the adsorbed MTC or SFZ, respectively, is tightly bound to the composite. The more tightly bound herbicide is expected to slowly release under irrigation. This was further tested in release experiments of the herbicides from the formulations applied on a thin soil layer (see **Figure 6**).

SFZ and MTC Release from CRFs and from Commercial Formulations Applied on a Thin Soil Layer. SFZ and MTC release from the commercial and from the micelle−clay formulations was tested by applying the formulations to a thin soil layer at a rate equivalent to 1200 g ai/ha, irrigating 10 times and measuring herbicide concentration in the leachates (**Figure 6**). SFZ and MTC release from the micelle−clay formulations was significantly slower than their release from the commercial formulations. After five irrigations (equivalent to 25 mm of rain), 100% of the SFZ from the commercial formulation (Boral) leached through the thin soil layer, whereas only 20% leached

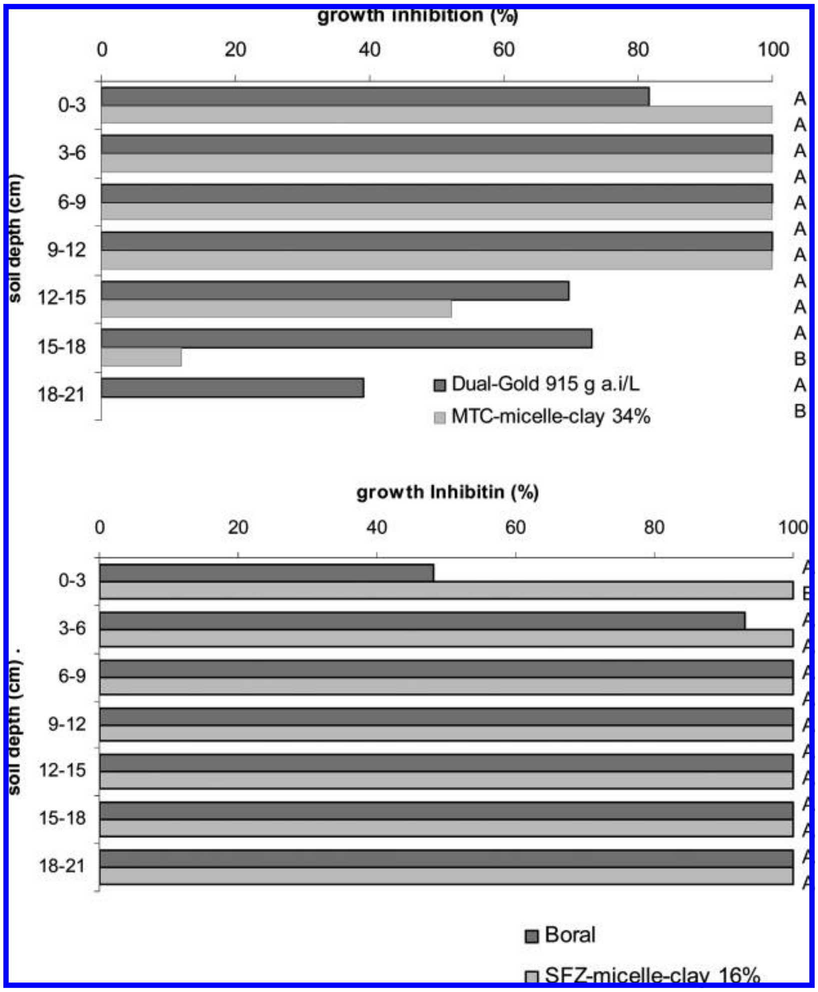

Figure 7. Shoot growth inhibition of foxtail as a function of depth in soil columns sprayed with formulations of (**A**) Boral (commercial) and 16% SFZ−micelle−clay and (**B**) Dual-Gold (commercial) and 34% MTC−micelle−clay.

from the micelle−clay formulation. MTC release from the commercial formulation (Dual-Gold) was not complete, but after 10 irrigations, 80% of the applied herbicide was washed, which was twice the amount released from the micelle−clay formulation.

The cumulative percentage of herbicide released from the CRFs (for each wash) through a thin soil layer for both herbicides was about 4% (calculated from the slope, linear regression gives an r^2 value of 0.99 and of 0.98 for SFZ and MTC, respectively). This experiment clearly shows that the micelle−clay formulations of both SFZ and MTC have displayed more controlled and slow release properties than the commercial formulations. The release test from a thin soil layer demonstrates the potential of the micelle−clay formulation to yield controlled release and reduced leaching when applied in the field.

Testing SFZ and MTC CRFs Applying a Soil Column Bioassay. The efficiency of SFZ and MTC micelle−clay CRFs to control weeds and to reduce herbicide leaching was examined by spraying the CRFs, 16% SFZ−micelle−clay and 34% MTC−micelle−clay, the commercial formulations (Boal and Dual-Gold) and water (control) on soil columns, and performing a bioassay test (**Figure 7**).

The columns treated with Boral showed germination at the top of the soil (0−3 cm), and the growth inhibition was only 48%, implying inefficient and poor weed control. In contrast, the soil columns treated with the SFZ CRF showed 100% growth inhibition at the top of the soil column, indicating good weed control. However, at depths of 6−20 cm, both treatments resulted in 100% growth inhibition, which indicates herbicide leaching. On the basis of SFZ release measurements from a thin soil layer, which showed significantly slower release of SFZ from the CRF as compared to its release from Boral, we suggest that reducing application rates of the CRF will result in reduced herbicide leaching while maintaining good herbicidal activity. This, however, would not improve the performance of the commercial formulation.

The columns treated with the MTC commercial formulation Dual-Gold showed foxtail growth at the top of the columns (0−3 cm), that is, insufficient weed control. In addition, MTC leached down to the bottom of the column (20 cm). At depths of 3−12 cm, 100% growth inhibition was obtained, and at the bottom of the columns (12−20 cm deep), 40−70% growth inhibition was observed. In contrast, 100% inhibition was observed at the top (0−12 cm) of the columns sprayed with the MTC−micelle−clay formulation, and no inhibition was detected at the bottom of the columns (15−21 cm). Because of the controlled release properties of the new formulation, good weed control was achieved at the top of the soil and MTC leaching was decreased as indicated by growth at the bottom of the soil columns. The improved performance of the CRF strengthens our hypothesis that MTC slowly diffuses from the micelle−clay composite formulation at small doses (as shown in funnel experiment) but sufficient enough to obtain good weed control.

To conclude, to reduce herbicide leaching and increase weed control, we developed, designed, and tested CRFs for both SFZ and MTC based on their solubilizion in cationic micelles and adsorption of the mixed micelles on montmorillonite. Because of enhanced solubilization of the herbicides, the percent of ai in the formulations was much higher than in previously designed CRFs. Both CRFs demonstrated controlled release properties (as compared to the commercial formulations) when applied to a thin soil layer. A bioassay in soil columns indicated that the new SFZ and MTC CRFs (as compared to the commercial formulations) significantly improve weed control and reduced leaching for the latter. The results of this study suggest that applying the newly designed herbicide−micelle−clay formulations in the field will enable reduction of MTC and SFZ leaching while improving weed control.

ABBREVIATIONS USED

CRF, controlled release formulation; ai, active ingredient; SFZ, sulfentrazone; MTC, metolachlor; ODTMA, octadecyltrimethyl ammonium.

LITERATURE CITED

(1) Konstantinou, I. K.; Hela, D. G.; Albanis, T. A. The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. *Environ. Pollut.* **2006**, *141* (3), 555–570.
(2) Kudsk, P.; Streibig, J. C. Herbicides−A two-edged sword. *Weed Res.* **2003**, *43* (2), 90–102.
(3) Carter, A. D. Herbicide movement in soils: Principles, pathways and processes. *Weed Res.* **2000**, *40* (1), 113–122.
(4) Cerejeira, M. J.; Viana, P.; Batista, S.; Pereira, T.; Silva, E.; Valerio, M. J.; Silva, A.; Ferreira, M.; Silva-Fernandes, A. M. Pesticides in Portuguese surface and ground waters. *Water Res.* **2003**, *37* (5), 1055–1063.
(5) Planas, C.; Caixach, J.; Santos, F. J.; Rivera, J. Occurrence of pesticides in Spanish surface waters. Analysis by high resolution gas chromatography coupled to mass spectrometry. *Chemosphere* **1997**, *34* (11), 2393–2406.
(6) Richardson, M. L., Ed. *Chemistry, Agriculture and the Environment*; Royal Society of Chemistry: Great Britain, Cambridge, 1991; p 546.
(7) Carrizosa, M. J.; Hermosin, M. C.; Koskinen, W. C.; Cornejo, J. Use of organosmectites to reduce leaching losses of acidic herbicides. *Soil Sci. Soc. Am. J.* **2003**, *67* (2), 511–517.
(8) Celis, R.; Hermosin, M. C.; Carrizosa, M. J.; Cornejo, J. Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone. *J. Agric. Food Chem.* **2002**, *50* (8), 2324–2330.
(9) El-Nahhal, Y.; Nir, S.; Serban, C.; Rabinovitch, O.; Rubin, B. Montmorillonite-phenyltrimethyl ammonium yields environmentally improved formulations of hydrophobic herbicides. *J. Agric. Food Chem.* **2000**, *48* (10), 4791–4801.
(10) Fernandez-Perez, M.; Villafranca-Sanchez, M.; Flores-Cespedes, F.; Garrido-Herrera, F. J.; Perez-Garcia, S. Use of bentonite and activated carbon in controlled release formulations of carbofuran. *J. Agric. Food Chem.* **2005**, *53* (17), 6697–6703.
(11) Ferraz, A.; Souza, J. A.; Silva, F. T.; Goncalves, A. R.; Bruns, R. E.; Cotrim, A. R.; Wilkins, R. M. Controlled release of 2,4-D from granule matrix formulations based on six lignins. *J. Agric. Food Chem.* **1997**, *45* (3), 1001–1005.
(12) Garrido-Herrera, F. J.; Gonzalez-Pradas, E.; Fernandez-Perez, M. Controlled release of isoproturon, imidacloprid, and cyromazine from alginate-bentonite-activated carbon formulations. *J. Agric. Food Chem.* **2006**, *54* (26), 10053–10060.
(13) Gerstl, Z.; Nasser, A.; Mingelgrin, U. Controlled release of pesticides into soils from clay-polymer formulations. *J. Agric. Food Chem.* **1998**, *46* (9), 3797–3802.
(14) Hermosin, M. C.; Celis, R.; Facenda, G.; Carrizosa, M. J.; Ortega-Calvo, J. J.; Cornejo, J. Bioavailability of the herbicide 2,4-D formulated with organoclays. *Soil Biol. Biochem.* **2006**, *38* (8), 2117–2124.
(15) Johnson, R. M.; Pepperman, A. B.; Selim, H. M. Field mobility and persistence of alginate controlled release formulations of atrazine. *Soil Sci.* **1998**, *163* (1), 46–52.
(16) Mishael, Y. G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S. Slow-release formulations of sulfometuron incorporated in micelles adsorbed on montmorillonite. *J. Agric. Food Chem.* **2002**, *50* (10), 2864–2869.
(17) Mishael, Y. G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S. Sulfosulfuron incorporated in micelles adsorbed on montmorillonite for slow release formulations. *J. Agric. Food Chem.* **2003**, *51* (8), 2253–2259.
(18) Nir, S.; Undabeytia, T.; Yaron-Marcovich, D.; El-Nahhal, Y.; Polubesova, T.; Serban, C.; Rytwo, G.; Lagaly, G.; Rubin, B. Optimization of adsorption of hydrophobic herbicides on montmorillonite preadsorbed by monovalent organic cations: Interaction between phenyl rings. *Environ. Sci. Technol.* **2000**, *34* (7), 1269–1274.
(19) Polubesova, T.; Nir, S.; Rabinovitz, O.; Borisover, M.; Rubin, B. Sulfentrazone adsorbed on micelle-montmorillonite complexes for slow release in soil. *J. Agric. Food Chem.* **2003**, *51* (11), 3410–3414.
(20) Undabeytia, T.; Mishael, Y. G.; Nir, S.; Papahadjopoulos-sternberg, B.; Rubin, B.; Morillo, E.; Maqueda, C. A novel system for reducing leaching from formulations of anionic herbicides: Clay-liposomes. *Environ. Sci. Technol.* **2003**, *37* (19), 4475–4480.
(21) Mishael, Y. G.; Undabeytia, T.; Rytwo, G.; Papahadjopoulos-Sternberg, B.; Rubin, B.; Nir, S. Sulfometuron incorporation in cationic micelles adsorbed on montmorillonite. *J. Agric. Food Chem.* **2002**, *50* (10), 2856–2863.
(22) Radian, A.; Mishael, Y. G. Characterizing and designing polycation-clay nanocomposites as a basis for imazapyr controlled release formulations. *Environ. Sci. Technol.* **2007**, *42* (5), 1511–1516.
(23) El-Nahhal, Y.; Undabeytia, T.; Polubesova, T.; Mishael, Y. G.; Nir, S.; Rubin, B. Organo-clay formulations of pesticides:reduced leaching and photodegradation. *Appl. Clay Sci.* **2001**, *18*, 309–326.
(24) Nennemann, A.; Mishael, Y.; Nir, S.; Rubin, B.; Polubesova, T.; Bergaya, F.; van Damme, H.; Lagaly, G. Clay-based formulations of metolachlor with reduced leaching. *Appl. Clay Sci.* **2001**, *18* (5−6), 265–275.
(25) Rytwo, G.; Yotam, G.; Afuta, S., Preparation of berberine-montmorillonite-metolachlor formulations from hydrophobic/hydrophilic mixtures. *Appl. Clay Sci.* **2007**, in press.
(26) Clerk, H. *Sulfentrazone; Establishment of Tolerances*; U.S. Environmental Protection Agency: Washington, DC, 1997; pp 10703−10708.
(27) Miller, J. I. *Pesticide Fact Sheet, Registration of a New Chemical*; U.S. Environmental Protection Agency: Washington, DC, 1997; p 9.
(28) Hela, D. G.; Lambropoulou, D. A.; Konstantinou, A. K.; Albanis, T. A. Environmental monitoring and ecological risk assessment for pesticide contamination and effects in Lake Pamvotis, northwestern Greece. *Environ. Toxicol. Chem.* **2005**, *24* (6), 1548–1556.
(29) Rivard, L. *Environmental Fate of Metolachlor*; Environmental Monitoring Branch, Department of Pesticide Regulation: Sacramento, CA, 2003.
(30) Ahrens, H. W. *Herbicide Handbook*, 8th ed.; Weed Science Society of America: Champaign, IL, 2002.
(31) Ahrens, H. W. *Herbicide Handbook*, 7th ed.; Weed Science Society of America: Champaign, IL, 1994.
(32) Obrigawitch, T.; Hons, F. M.; Abernathy, J. R.; Gipson, J. R. Adsorption, desorption, and mobility of metolachlor in soils. *Weed Sci.* **1981**, *29* (3), 332–336.
(33) Patakioutas, G.; Albanis, T. A. Adsorption-desorption studies of alachlor, metolachlor, EPTC, chlorothalonil and pirimiphos-methyl in contrasting soils. *Pest Manage. Sci.* **2002**, *58* (4), 352–362.
(34) Elworthy, P. H.; Lipscomb, F. J. Solubilization of griseofulvin by nonionic surfactants. *J. Pharm. Pharmacol.* **1968**, *20* (11), 817.

(35) Dunaway, C. S.; Christian, S. D.; Scamehorn, J. F. Overview and history of the study of solubilization. *Surfactant Science Series* **1995**, *55* (Solubilization in Surfactant Aggregates), 3–31.

(36) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; John Wiley & Sons Inc.: Hoboken, NJ, 2004; p 444.

(37) Scamehorn, J. F.; Harwell, J. H. Surfactants in emerging technologies. In *Surfactant Science Series*; Rosen, M. J., Ed.; Marcel Dekker: New York, 1987; Vol. 26, p 169.

(38) Zana, R. Aqueous surfactant-alcohol systems: a review. *Adv. Colloid Interface Sci.* **1995**, *57*, 1–64.

(39) Nagarajan, R.; Ruckenstein, E. Theory of surfactant self-assembly−A predictive molecular thermodynamic approach. *Langmuir* **1991**, *7* (12), 2934–2969.

(40) West, C. C. Surfactant-enhanced solubilization of tetrachloroethylene and degradation products in pump and treat remediation. *ACS Symp. Ser.* **1992**, *491*, 149–158.

(41) Jafvert, C. T. *Surfactants and Cosolvents*; TE-96-02; Purdue University: Pittsburgh, 1996.

(42) Harwell, J. H.; Sabatini, D. A.; Knox, R. C. Surfactants for ground water remediation. *Colloids Surf., A* **1999**, *151* (1−2), 255–268.

(43) El-Nahhal, Y.; Nir, S.; Polubesova, T.; Margulies, L.; Rubin, B. Leaching, phytotoxicity, and weed control of new formulations of alachlor. *J. Agric. Food Chem.* **1998**, *46* (8), 3305–3313.

Received for review June 20, 2008. Revised manuscript received August 12, 2008. Accepted August 12, 2008. This research was supported by Research Grant IS-3656-05 R from BARD, The United States−Israel Binational Agricultural Research and Development Fund.

JF801892W