Development and Employment of Slow-Release Pendimethalin Formulations for the Reduction of Root Penetration into Subsurface Drippers

Yifat Zait, Dekel Segev, Avraham Schweitzer, Yaakov Goldwasser, Baruch Rubin, and Yael G. Mishael

ABSTRACT: Subsurface drip irrigation supplies water directly to the root zone and is an efficient irrigation technology. One of the main challenges is preventing plant roots from clogging the drippers. With the aim of inhibiting root penetration, slow-release pendimethalin formulations based on its solubilization in micelles adsorbed and unadsorbed to clay were developed. In the past unadsorbed micelles were considered inadequate for slow release, because release was too fast. In contrast, the advantage of a two-mode release formulation, composed of adsorbed and unadsorbed micelles, is demonstrated. A bioassay to study pendimethalin leaching at a refined scale of 1–2 cm was developed and reduced leaching from the micelle–clay formulations in comparison to the commercial formulation (Stomp) was exhibited. In a greenhouse study the application of the formulations by injection into an irrigation system was extremely efficient with 0–10% root penetration in comparison to 100% penetration upon Stomp injection.

KEYWORDS: subsurface irrigation, herbicide, drippers, pendimethalin, slow-release formulations, micelle–clay formulations, leaching

INTRODUCTION

The shortage in water for irrigation along with the awareness of water conservation enhanced the interest and application of subsurface drip irrigation systems all around the world. Subsurface drip irrigation supplies water directly to the root zone through buried drippers and is one of the most efficient water-saving irrigation technologies. The advantages of the technology include improved water and nutrient management and in many cases also improved yield and enhanced crop quality.

One of the main challenges of subsurface drip irrigation for long-term operation is preventing roots from penetrating and clogging the drippers. Due to high water and nutrient content in the soil around the drippers, the concentration of crop roots in the soil increases with proximity to the dripper. High root concentration near the drippers increases the probability of roots penetrating the dripper. Drripper penetration and clogging are enhanced when irrigation is lowered or terminated between crops and the remaining roots seek water in the emitters.

To prevent root penetration self-protection drippers with impregnated trifluralin are manufactured. The incorporated trifluralin is released slowly after the system is buried and sufficient concentrations remain in the vicinity of the drippers to protect against root penetration. Although the reduction in root penetration employing the self-protected drippers was efficient for turf grass irrigation, it is not economically feasible for lower value crop production. A more economical approach is injecting root growth inhibitors through the subsurface drip irrigation system such as thiazopyr, phosphoric acid, or trifluralin, as demonstrated in a detailed field study with winter wheat showing the high efficiency of trifluralin injection. These authors point out that the main advantages of trifluralin are its long half-life time (a few months) and its extremely low migration in the soil, so it remains in close proximity to the dripper as simulated by numerical calculations.

In 2007 trifluralin was excluded from Annex I due to its toxicity to aquatic organisms including fish (Kyprianou). In contrast, pendimethalin, which is also a dinitroaniline herbicide with a bioactivity similar to that of trifluralin, was included. Pendimethalin is commonly used for pre-emergence control of grass and broad-leaved weed seedlings in several broad-leaved crops and in corn, sugar cane, and spring wheat. It is usually applied before sowing and incorporated into the soil to prevent its volatilization and photodegradation. Although pendimethalin migration is considered low, it is higher than the migration of trifluralin. Minimizing pendimethalin leaching would concentrate it in close proximity to the dripper, root penetration would be eliminated, and adequate dripper protection would be achieved.

The main approaches to reduce herbicide leaching are herbicide dose optimization, site-specific weed management, and nonchemical weed control such as mechanical and thermal methods. These strategies are more relevant for surface application. Another approach widely pursued in the past few decades is developing slow-release formulations, many of which are based on organically modified clay minerals.
and micelle–clay interactions in previous studies applying adsorption isotherms, modeling, X-ray diffraction, freeze–fracture electron microscopy, herbicide solubilization measurements, fluorescence studies, and FTIR analysis. The solubilization of several herbicides was further explored in our more recent studies.

The novelty of this investigation covers three different aspects; formulation design, bioassay design, and application. More specifically the originality of this study involves the development of (1) two-mode formulations (in the past, unadsorbed micelles were considered not adequate for slow release, because the release was too fast, but here we demonstrate the advantage of having both modes of micelles, adsorbed and unadsorbed), (2) a bioassay to study herbicide migration at a refined scale of 1–2 cm, and (3) the application of slow release herbicide formulations for the reduction of root penetration into subsurface irrigation drippers.

Materials and Methods

Materials. Wyoming sodium montmorillonite (SWy-2) (cation exchange capacity, 0.76 mmol/g; surface area, 700 m²/g) was obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO, USA). Octadecyltrimethylammonium bromide (ODTMA) and Triton X-100 were purchased from Sigma-Aldrich (Stuttgart, Germany). Pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine (technical grade 96%) and Stomp 330 (a commercial formulation containing 330 g/L pendimethalin) were applied as a control. A second formulation (with a lower concentration of 100 mg/L) was used as a benchmark for the greenhouse study a one-mode formulation was designed for enhanced herbicidal activity, but reduced leaching was not tested.

Hence, the main goal of this study was to develop and examine slow-release formulations of pendimethalin for the reduction of root penetration into subsurface irrigation drippers. The formulations developed were based on pendimethalin solubilization in octadecyltrimethylammonium bromide (ODTMA) micelles adsorbed and unadsorbed on montmorillonite. We have characterized in detail the ODTMA (as monomer and as micelles)–clay interactions in previous studies. Pendimethalin solubilization in ODTMA micelles was studied in batch experiments in triplets. Supernatants were separated by centrifugation at 15,000 g. To prepare the one-mode formulation the herbicide–micelle solution was added to a clay suspension (final concentrations of 3–10 g/L) at 40 °C. The tubes were agitated for 24 h (equilibrium reached) in a hot tub with the relevant temperatures, and pendimethalin concentration was measured by UV–vis spectrophotometry as described. The concentration of adsorbed pendimethalin was then calculated.

Pendimethalin (300 mg/L) adsorption on montmorillonite (3–10 g/L) via its solubilization in ODTMA micelles (10 mM) was studied at 40 °C in batch experiments in triplets. Pendimethalin solubilization was performed as described above. The herbicide–micelle solution was added to a clay suspension (final concentrations of 3–10 g/L) at 40 °C. The tubes were agitated for 24 h (equilibrium reached) in a hot tub with the relevant temperatures, and pendimethalin concentration was measured by UV–vis spectrophotometry as described. The concentration of adsorbed pendimethalin was then calculated.

The morphology of montmorillonite and the ODTMA–clay samples was studied by SEM and elemental analysis. Samples were prepared on Akulon stubs using double-sided sticky tape. The microphotographs were recorded using scanning electron microscope JEOL model JSM-5410 LV. The images were taken with an accelerating voltage of 20 kV, at low vacuum mode (28 Pa), and backscattered electron detection.

Pendimethalin Solubilization in Micelles and Adsorption to Montmorillonite. The solubilization of pendimethalin (50–900 mg/L, 0.18–3.2 mM) in ODTAM micelles (10 mM) was studied in batch experiments (final concentrations). The solutions were stirred for 24 h in covered glass tubes (to avoid photodegradation) and then filtered. If complete solubilization of pendimethalin was not reached, its precipitation was observed. This precipitate was separated by centrifugation at 15,000 g for 20 min at 40 °C. The concentration of pendimethalin in solution was determined by using a UV–vis spectrophotometer (Evolution 300, Thermo Scientific, Waltham, MA, USA). For herbicide concentrations <50 mg/L the measurement was with a 1 cm glass cuvette at 200–800 nm with λmax = 423 nm. For herbicide concentrations ≥50 mg/L the measurement was with a 0.2 cm glass cuvette (to avoid dilution and micelle decomposition).

Pendimethalin solubilization was calculated by subtracting the solution concentration from the initial concentration. The contribution of pendimethalin in water, 0.275 mg/L, not solubilized in micelles, is negligible.

Pendimethalin (300 mg/L) adsorption on montmorillonite (3–10 g/L) via its solubilization in ODTMA micelles (10 mM) was studied at 40 °C in batch experiments in triplets. Pendimethalin solubilization was performed as described above. The herbicide–micelle solution was added to a clay suspension (final concentrations of 3–10 g/L) at 40 °C. The tubes were agitated for 24 h (equilibrium reached) in a hot tub with the relevant temperatures, and pendimethalin concentration was measured by UV–vis spectrophotometry as described. The concentration of adsorbed pendimethalin was then calculated.

Herbicide–Micelle–Clay Formulation Preparation. Pendimethalin (300 mg/L) was solubilized in ODTMA (10 mM) as described above. To prepare the one-mode formulation the herbicide–micelle solution was added to a high clay concentration (7 g/L) at 27 °C, and to a low clay concentration (2 g/L) at 27 °C. The tubes were agitated for 24 h (equilibrium reached) in a hot tub with the relevant temperatures, and pendimethalin concentration was measured by UV–vis spectrophotometry as described. The absorption of pendimethalin in the supernatants was determined by UV–vis spectrophotometer measurements, and the absorbed pendimethalin was calculated. The percentages of active ingredient in the one- and two-mode formulations were 1.6–2.7 and 3.2–4.8%, respectively.

Pendimethalin Desorption from the Formulations. The one- and two-mode formulations were suspended in 20 mL for 24 h at 27 °C in batch experiments in triplets. Supernatants were separated by centrifugation at 15,000 g for 20 min, and pendimethalin concentration was measured by UV–vis spectrophotometer as described.

Pendimethalin Desorption and Leaching through Thin Soil Layers. The release and leaching of pendimethalin from the one- and two-mode formulations and from the commercial formulation, Stomp 330, was measured by applying the formulations on a thin sandy soil layer (160 g and approximately 1 cm) deposited on a filter paper (Whatman 1442-125) in a Buchner funnel (area of 7.85 × 10⁻³ m²). No herbicide adsorption was detected on the filter paper. The formulations were applied in 30 mL of water at a rate of 1.4 mg of active ingredient (ai) per funnel, equivalent to 1.8 kg ai/ha. Water was applied as a control. A second filter paper was placed on top of the soil to ensure uniform water distribution and to minimize disruption of the
soil surface. The funnels were irrigated five times with 50 mm of water (40 mL per funnel) at uniform intervals between irrigations. The leachates were collected after each irrigation, and herbicide concentrations were measured by UV–vis spectrophotometer. Each treatment was performed in triplicate.

Bioactivity and Reduced Leaching of Pendimethalin in the Soil: Laboratory Essays. The release, leaching, and bioactivity of pendimethalin applied as Stomp 330 or one- and two-mode formulations were measured by applying the formulations (0.3 kg ai/ha) on sandy soil columns of 10 cm diameter and 5 cm height. Water was applied as control. Each treatment was performed in triplicates. The columns were irrigated with 60 mL of water, covered with paper to prevent photodegradation, and after 60 h, each centimeter of the top 3 cm was pushed from the bottom up and removed. The soil from each depth was transferred to Petri plates (in triplicates). Ten Sorghum seeds were sown in each plate, and plates were covered, sealed with tape, and placed in a 27 °C dark room at a 45° angle to force roots to grow downward along the Petri dish cover. After 60 h, root length was measured for each treatment.

Pendimethalin leaching and bioactivity were calculated by measuring the degree of root growth inhibition at each depth, which was calculated by comparison to untreated control.

Bioactivity and Reduced Leaching of Pendimethalin in Soil: Greenhouse Assays. The efficiency of the micelle–clay formulation and of Stomp 330 to reduce root penetration into the drippers was studied in a greenhouse setup. The study was conducted in large pots (1 m × 0.5 m and a depth of 0.35 m total volume of 175 L) filled with a soilless mix of sand with compost 70/30% (Givat Adda, Israel). The subsurface irrigation drippers were buried at a depth of 15 cm, two rows per pot including 10 drippers per pot. Lettuce (Lactuca sativa L.) seedlings at the 12–13 BBCH growth stage were transplanted, 10 per pot, and grown by regular protocol. Each treatment was repeated five times. Three weeks from planting irrigation was reduced gradually to induce root penetration into the drippers. Five weeks after planting the two-mode formulation, Stomp 330, or water (as control) was applied at 0.06 g ai per dripper (10 g from the two-mode formulation in 100 mL of water or 2 mL of Stomp 330 in 100 mL of water). Three weeks after pendimethalin application, the drippers were removed and root penetration was evaluated. The penetration was ranked from 0 to 3 (low to high) and compared to the control.

A second greenhouse scale test (same setup) was performed to test an earlier application of the formulations. In this study tomato (Lycopersicum sculentum Mill.) seedlings at the 12–13 BBCH growth stage were planted and the growth period was extended to 4 months to increase the probability of root penetration into drippers. Three weeks from planting the one- and two-mode formulations were injected through the irrigation system (early application). Eight weeks after planting, irrigation was reduced gradually to induce root penetration. Ten weeks after planting, the one-mode and Stomp formulations were injected through the irrigation system (regular application).

Data Analysis. The statistical analysis was carried out using JMP 7.0.1 (SAS 2007) and p = 0.05. The bioactivity study at the laboratory scale was subjected to a two-way ANOVA model in a "split-plot" design, where the treatment (formulation), the depth, and root length were used as the main effects. Multiple comparisons were done using a new t test. The bioactivity study at the greenhouse scale was subjected to the same analysis with treatment (formulation and application timing) and root penetration as main effects.

RESULTS AND DISCUSSION

Effect of Temperature on ODTMA Adsorption to Montmorillonite. The effect of temperature on ODTMA adsorption from a micelle solution (concentrations above the critical micelle concentration (CMC)) and at temperatures above the Tg to montmorillonite was explored (Figure 1). As previously reported for ODTMA adsorption from a micelle solution, adsorption was extremely high, reaching loadings of >2-fold the cation exchange capacity (CEC) of the clay, which was explained in terms of micelle adsorption. The adsorption was complete up to the CEC of the clay at both temperatures but decreased with temperature at adsorbed concentrations exceeding the CEC. These trends indicate that the adsorption reaction, exceeding the CEC, is most likely exothermic. The adsorption reaction below the CEC, under the current experimental conditions, is complete and therefore cannot be determined; that is, it may be endothermic or exothermic.

Enthalpies of adsorption of organic molecules to clay minerals are generally exothermic, because the molecules leaving the solution and attaching to the surface lead to a decrease in the dispersion of the energy, a decrease in the entropy, and 32,35 Processes with decreasing entropy might be spontaneous only if they are exothermic (definition of Gibbs' free energy). However, sorption of organic cations to montmorillonite are usually exchange processes, and the release of inorganic cations with their hydration shells may bring on an overall increase in entropy, and endothermic adsorption processes have been reported in a few cases. The adsorption of ODTMA monomers to the clay surface below the CEC is indeed due to cation exchange, that is, possibly an endothermic reaction. The adsorption of ODTMA from a micelle solution is driven by two forces; cation exchange (up to the CEC) and a bilayer that is formed on the surface due to hydrophobic interactions between the surfactants, which involve only confinement. The release of exchangeable cations (with their hydration shell) increases entropy, but this increase may be smaller than the loss of entropy due to both electrostatic and hydrophobic confinement, explaining the overall decrease in enthalpy, that is, an exothermic reaction at adsorbed concentrations exceeding the CEC.

Little has been reported in the literature on the effect of temperature on monomer and micelle adsorption. Nevertheless, trends similar to those found in this study were reported for micelle adsorption of sodium dodecyl sulfate and micelle to hydrofalcate.

The effect of temperature on monomer versus micelle adsorption is expressed not only by their different reaction enthalpies but also by the adsorption mode, monomer conformation, and orientation. It is well-known that a surfactant solution will spontaneously form micelles when prepared at concentrations above the CMC and above the Tg. The adsorption to montmorillonite of ODTMA at a concentration above the CMC (5 mM) and above (40 °C)
or below (27 °C) the $T_k$ was studied, and images of the precipitates were collected by SEM measurements (Figure 2). ODTMA adsorption at 27 °C to a low clay concentration (0.56 g/L) resulted in high concentrations of ODTMA, which do not adsorb, and because the solution temperature is below $T_k$ the excess surfactant precipitates as an ODTMA salt with a platter morphology (Figure 2B). In contrast, ODTMA adsorption at 40 °C from a micelle solution resulted in homogeneous surfactant adsorption, and clay exfoliation was observed (Figure 2E). Because the temperature was above the $T_k$ the excess surfactant remained in the supernatant (was removed) and did not precipitate.

To increase ODTMA (5 mM) adsorption at temperatures below the $T_k$ the clay concentration was increased (0.56–5 g/L). As expected, fewer ODTMA platters were observed as the clay concentration increased, and uniform organoclay composites were observed upon the addition of ODTMA (5 mM) to high clay concentrations 5 g/L (Figure 2C,D).

Elemental analysis (eds) supports the identification of the platters as ODTMA salt precipitation with significant amounts of carbon, nitrogen, and bromine (55, 7, and 30%, respectively). The “fluffier” material was identified as organic–clay composite samples, containing carbon and nitrogen (of the surfactant) and aluminum and silica (characteristic of the clay) (55, 7, and 12%, respectively).

The identification of two modes of ODTMA in the samples, precipitate and adsorbed to clay, was further utilized to design two-mode pendimethalin formulations.

**Pendimethalin Solubilization in Micelles and Adsorption to Montmorillonite.** The first step to design pendimethalin–micelle–clay formulations was solubilizing pendimethalin, which has extremely low water solubility (0.275 mg/L), in a micelle solution of ODTMA (10 mM) to enhance its solubility (Figure 3). Pendimethalin solubilization in a 10 mM ODTMA solution was complete up to a concentration of 300 mg/L, and above this concentration the degree of solubilization decreased but the concentration increased, reaching 550 mg/L. Pendimethalin solubility increased by 3 orders of magnitude at a herbicide/surfactant ratio of only 0.2 mol/mol. High pendimethalin solubilization in ODTMA micelles enabled high active ingredient adsorption on the clay (via micelle adsorption).

Pendimethalin (300 mg/L) adsorption on montmorillonite (3–10 g/L) via its solubilization in ODTMA micelles (10 mM) was studied at 40 °C (Table 1). Surfactant/clay molar ratio (taking the cation exchange capacity into account) has a

---

**Figure 2.** SEM images of (A) montmorillonite and ODTMA (5 mM) adsorption, (B) at 27 °C on 0.56 g/L montmorillonite, (C) at 27 °C on 4 g/L montmorillonite, (D) at 27 °C on 5 g/L montmorillonite, and (E) at 40 °C on 0.56 g/L montmorillonite.
pronounced effect on surfactant loading and adsorption/precipitation mode. A high ratio will result in unadsorbed micelles (as obtained for a clay concentration of 3 g/L), whereas a slightly low ratio, with complete surfactant adsorption, will decrease the loading (mg/g) of pendimethalin (as obtained for clay concentration of 8–10 g/L). At a very low surfactant/clay ratio, below 1, micelle decomposition and active ingredient release may occur. Complete pendimethalin adsorption on the clay (via micelle adsorption) and high herbicide loading were reached upon the addition of 10 mM ODTMA to 7 g/L montmorillonite. This surfactant/clay molar ratio of ~1.9 is within the suggested optimal range. On the basis of the results of ODTMA adsorption on low and high clay concentrations and at temperatures above and below $T_c$ (Figure 2) two types of micelle–clay formulations were designed. A one-mode formulation was prepared at 40 °C (above the $T_c$) by fully solubilizing the herbicide (300 mg/L) in micelles (10 mM) and at a surfactant/clay ratio in which surfactant adsorption is complete (7 g clay/L). A two-mode formulation was prepared by fully solubilizing the herbicide in micelles (like the one-mode) but at a surfactant/clay ratio at which surfactant adsorption is not complete (2 g clay/L) and the adsorption was at 27 °C. Due to the low temperature the unabsorbed pendimethalin, solubilized in micelles, precipitates. We hypothesized that the release from the one-mode formulation will be slower than from the two-mode and at a lower rate. The release from the two-mode formulation will be in two phases: a relatively fast phase, when the herbicide will release from nonadsorbed micelles, and a slower phase, when the herbicide solubilized in micelles adsorbed on clay will be released.

**Pendimethalin Desorption from the Formulations.**

Pendimethalin desorption, in suspension, at 27 °C, after 24 h from the one-mode formulation was 0.13 ± 0.01%, whereas the release from the two-mode formulation was 10-fold higher, reaching 1.5 ± 0.3%. Higher desorption from the two-mode formulation was also observed when the desorption and leaching of pendimethalin through a thin layer of sand were studied (Figure 4). After irrigation of 5 pore volumes, 0.56 and 4% of the pendimethalin applied as one- and two-mode formulations leached through the soil, respectively. The leaching from the commercial formulation (Stomp) was significantly higher, reaching 57%.

**Bioactivity and Reduced Leaching of Pendimethalin in the Soil: Laboratory Essays.** Herbicide leaching in soil columns of several centimeters (10–100 cm) has been widely explored in bioassays. The challenge in the current study was to reach a leaching resolution of 1–2 cm. To test pendimethalin release from the formulations and leaching through 0–3 cm of soil, the formulations (and water as control) were applied to soil columns, irrigated, allowed to settle, and then sliced to depths of 0–1, 1–2, and 2–3 cm. Each soil layer was placed in a Petri dish, the test plants were sown, and root growth inhibition was measured (compared to the control) (Figure 5). Pendimethalin did not leach beyond 2 cm. Its release and leaching from the commercial formulation to 1–2 cm depth was significant, resulting in nearly 60% root growth (percent of control), whereas no release and leaching from the micelle–clay formulations were observed (Figure 5). Efficient root growth inhibition was obtained for all three formulations at the top of the soil. Root growth inhibition by the one-mode formulation was significantly higher than by Stomp. This

| Table 1. Pendimethalin (300 mg/L) Adsorption on Montmorillonite (3–10 g/L) via Its Solubilization in ODTMA Micelles (10 mM) |
|-----------------|-----------------|-----------------|
| clay (g/L) | pendimethalin adsorbed | % |
| 3 | 35.5 ± 2.0 | 35 |
| 5 | 48.2 ± 1.6 | 80 |
| 6 | 47.3 ± 0.5 | 95 |
| 7 | 42.7 ± 0.0 | 99 |
| 8 | 37.3 ± 0.0 | 99 |
| 10 | 29.9 ± 0.0 | 99 |

![Figure 3. Pendimethalin (50–900 mg/L) solubilization in ODTMA micelles (10 mM) at 40 °C.](image)

![Figure 4. Pendimethalin desorption and leaching through a thin layer of sand applied as a commercial formulation or as the one- and two-mode micelle–clay formulations.](image)

![Figure 5. Effect of pendimethalin, applied as formulations one-mode, two-mode, and Stomp, on root growth of sorghum as a function of soil depth.](image)
In the second greenhouse study (Figure 7) tomatoes were indeed increased root penetration for the drippers treated with the commercial formulation and the one-mode formulations (between them, the difference was not significant). To conclude, with the aim of inhibiting root penetration, slow-release pendimethalin formulations based on its solubilization in micelles adsorbed and unadsorbed to clay were developed (one- and two-mode formulations, respectively). The novelty of this investigation covers three different aspects: formulation design, bioassay design, and application. The two formulations were designed by controlling the temperature and ratio between the surfactant and clay. Although unadsorbed micelles were considered inadequate for slow release (release was too fast), we demonstrated the advantage of a two-mode release formulation. A bioassay to study pendimethalin leaching at a refined scale of 1−2 cm was developed, and reduced leaching from the micelle−clay formulations in comparison to the commercial formulation (Stomp) was exhibited. In a greenhouse study the application of the formulations by injection into the irrigation system was extremely efficient with 0−10% root penetration in comparison to 100% penetration upon Stomp injection. Reductions in root penetration and herbicide leaching upon application of the designed formulation were demonstrated.

**Figure 6.** Root penetration (percent of control) in drippers treated with Stomp, one-mode, and two-mode formulations applied 3 weeks after tomato planting (early application) or 10 weeks after tomato planting (regular application).

In the second greenhouse study (Figure 7) tomatoes were planted and the growth period was extended to 4 months, increasing the probability of root penetration. In addition, an early application of the micelle−clay formulations (one- and two-mode formulations) was explored to test whether the activity and efficiency of the formulations indeed are for a longer period. The commercial and the one-mode formulations were applied as usually practiced. Prolonging the growth period indeed increased root penetration for the drippers treated with Stomp, reaching 100% (compared to control) penetration. In contrast, only 30% penetration was observed for the drippers treated with the one-mode formulation. An early application was extremely efficient with 10 and 0% penetration for drippers treated with the one- and two-mode formulations (between them, the difference was not significant). The novelty of this investigation covers three different aspects: formulation design, bioassay design, and application. The two formulations were designed by controlling the temperature and ratio between the surfactant and clay. Although unadsorbed micelles were considered inadequate for slow release (release was too fast), we demonstrated the advantage of a two-mode release formulation. A bioassay to study pendimethalin leaching at a refined scale of 1−2 cm was developed, and reduced leaching from the micelle−clay formulations in comparison to the commercial formulation (Stomp) was exhibited. In a greenhouse study the application of the formulations by injection into the irrigation system was extremely efficient with 0−10% root penetration in comparison to 100% penetration upon Stomp injection. Reductions in root penetration and herbicide leaching upon application of the designed formulation were demonstrated.

**Figure 7.** Image of greenhouse study.
Contam. Toxicol. 2007, 79, 84–86.
(13) Franklin, R. E.; Quisenberry, V. L.; Gossett, B. J.; Murdock, E.
C. Weed Technol. 1994, 8, 6–16.
(14) Undabeytia, T.; Mishael, Y. G.; Nir, S.; Papahadjopoulos-
2003, 37, 4475–4480.
4767–4773.
1516.
(19) Mishael, Y. G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S.
(20) El-Nahhal, Y.; Nir, S.; Serban, C.; Rabinovitz, O.; Rubin, B. J.
(22) Bakhtiary, S.; Shirvani, M.; Shariatmadari, H. Chemosphere
2013, 90, 699–705.
(24) Li, J.; Jiang, M.; Wu, H.; Li, Y. J. Agric. Food Chem. 2009, 57,
2868–2874.
9165.
6605–6610.
1342.
Controlled Release 2008, 126, 122–129.
(29) Mishael, Y. G.; Undabeytia, T.; Rytwo, G.; Papahadjopoulos-
2863.
(30) Polubesova, T.; Nir, S.; Rabinovitz, O.; Borisover, M.; Rubin, B.
(31) Mishael, Y. G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S.
(35) Kumar, J.; Nisar, K.; Shakil, N. a; Wala, S.; Parsad, R. J. Environ.
(36) Pavan, P. C.; Crepaldi, E. L.; de A. Gomes, G.; Valim, J. B.
(37) Galán-Jiménez, M. D. C.; Mishael, Y.-G.; Nir, S.; Morillo, E.;