CLAY-BASED FORMULATIONS OF SIMAZINE TO REDUCE HERBICIDE LEACHING IN SPORT TURFGRASSES

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ABSTRACT

The risk of ground water contamination resulting from rapid leaching of highly mobile pesticides can be reduced through the application of the pesticide adsorbed on a carrier to limit the amount of pesticide immediately available for undesirable transport losses. In this work, the herbicide simazine was used as a model of highly mobile herbicide used in sport turfgrass surfaces to investigate the ability of selectively modified clays to retard the release of the herbicide into the aqueous soil solution and to reduce the herbicide leaching in soil. Fe^{3+}-Wyoming montmorillonite (Fe-SW), octadecylammonium-Arizona montmorillonite (ODA-SA) and hexadecyltrimethylammonium-Arizona montmorillonite (HDTMA-SA) were mixed with simazine following two different protocols and the resulting complexes were assayed as slow release formulations of the herbicide. In the laboratory, batch release and column leaching experiments showed that all clay-based formulations of simazine released the herbicide slowly into aqueous solution, which resulted in reduced simazine leaching through soil columns compared to the application of the free herbicide. In field experiments, a Fe-SW-based formulation of simazine (4% active ingredient) was applied to 1 m^2 field plots, previously seeded with Princess 77 bermudagrass to simulate a typical sport turfgrass surface. It was found that, under field conditions, the clay-based formulation of simazine displayed similar herbicidal efficacy and slower vertical movement of the herbicide compared to a standard commercial formulation. Therefore, the results of this work indicate that clay-based formulations of simazine could be useful to reduce the risk of ground water contamination derived from herbicide application to sport turfgrass surfaces.

Key words: leaching, simazine, slow release, sorption, sport turfgrasses

1. INTRODUCTION

The environmental problems associated with the use of highly mobile pesticides are a current issue because these compounds are increasingly being detected in ground and surface waters (Celis *et al.*, 2002). The demand of high-quality turfgrasses with a perfect uniformity, density and aesthetical value in the large developing golf industry in Spain requires very intensive level of maintenance and inputs and therefore the severe use of chemicals to control turf pests and diseases. The general properties of the soils used in golf courses in Southern Spain imply low organic matter content and high permeability. These soil properties linked with intensive use of pesticides on turf surfaces, intense irrigation programs and heavy rainfall events make golf courses in Southern Spain a high risk scenario for groundwater contamination.

An approach to minimize the risk of groundwater contamination by highly mobile herbicides in high-risk scenarios, such as golf fairways, consists of applying the herbicide adsorbed on a carrier, in order to reduce the amount of pesticide immediately available for undesirable leaching losses (Johnson and Pepperman, 1998; Fernández-Pérez *et al.*, 1998). The use of clays as a herbicide carrier is particularly interesting due to their low cost, natural occurrence in the environment and the possibility to selectively modify their surfaces to improve the affinity for a particular herbicide (Lagaly, 2001; Celis *et al.*, 2002; Hermosín *et al.*, 2006).

In this work, the herbicide simazine is used as a model of highly mobile herbicide used in sport turfgrass surfaces to investigate the ability of selectively modified clays to retard the release of the herbicide into the aqueous soil solution and reduce the herbicide leaching in soil. Fe^{3+}-Wyoming montmorillonite (Fe-SW), octadecylammonium-Wyoming montmorillonite (ODA-SW) and hexadecyltrimethylammonium-Arizona montmorillonite (HDTMA-SA) were mixed with simazine in different ways and the resulting complexes were assayed as slow release formulations of the herbicide.

2. MATERIALS AND METHODS

2.1. Materials

The clay minerals used in this study were SWy-2 Wyoming montmorillonite and SAz-1 Arizona montmorillonite, supplied by The Clay Minerals Society (Columbia, Missouri). The cation exchange capacities (CEC) of SWy-2 and SAz-1 are 74.6 and 120 $cmol_c$ kg^{-1}, respectively. Fe^{3+}-saturated Wyoming montmorillonite (Fe-SW) was obtained by treating 10 g of SWy-2 with 100 ml of a 1 M $FeCl_3$ solution (Celis et al., 2002). After treatment (24 h, three times), the solid was washed with distilled water until Cl-free, and then lyophilized. For the preparation of the montmorillonites exchanged with octadecylammonium (ODA-SA) and hexadecyltrimethylammonium (HDTMA-SA), 10 g of SAz-1 were treated with 100 ml of an ethanol:water (1:1) solution containing an amount of alkylammonium (chloride salt) equal to 50% (ODA) or 100% (HDTMA) of the CEC of the clay. The suspensions were shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized (Celis et al., 1999).

Analytical grade simazine, purity= 99.9% (Riedel-de Haen), was used to prepare the clay-based formulations of simazine and the initial herbicide solutions used in adsorption experiments. Commercial simazine (50% concentrated suspension, Lainco S.A., Spain) was used as a reference standard formulation in the field experiment.

The soil used in the experiments was a sandy clay loam soil (0-20 cm) with 59% sand, 19% silt and 22% clay from an experimental plot located in Seville (Spain). It had 0.99% organic matter and 1.04% Fe_2O_3. The pH measured in a 1:2 (w:w) soil:deionized water suspension was 7.9.

2.2. Adsorption experiment

Simazine adsorption-desorption isotherms on the selected clays were obtained by the batch equilibration technique. Duplicate 20 mg clay samples were equilibrated with 8 ml of simazine initial solutions (1-20 μM) by shaking mechanically at 20 ± 2ºC for 24 h. After equilibration, the suspensions were centrifuged and the equilibrium concentrations were determined in the supernatants by HPLC. The amount of simazine adsorbed was calculated from the difference between the initial and equilibrium solution concentrations. Desorption was measured immediately after adsorption from the highest equilibrium point of the adsorption isotherms. The 4 ml of supernatant removed for the adsorption analysis were replaced with 4 ml distilled water. The samples were resuspended, shaken for another 24 h, centrifuged and the equilibrium concentration was determined. This desorption cycle was conducted three times.

2.3. Preparation of the clay-herbicide complexes

Two types of clay-simazine complexes were prepared for each selected clay. First, a medium strength complex (MC) was prepared by adding 2 ml of methanol to 1 g of a mechanical mixture containing 40 mg of analytical grade simazine and 960 mg of clay, and then air-drying. Second, a strong complex (SC) was prepared by adding 10 ml of methanol to a similar clay-herbicide mechanical mixture, then shaking for 24 h and air-drying. The amount of simazine in the complexes corresponded to a 4% content in active ingredient (a.i.). The complexes were allowed to dry at air and then were thoroughly ground in an agate mortar before used.

2.4. Batch release experiment

Two milligrams of simazine (a.i.) as clay complexes were added to 250 ml of distilled water in glass bottles sealed with screw caps. At selected times, the bottles were hand-shaken, allowed to settle for 10 minutes, and then 2 ml of the supernatant solution was removed, filtered, and analyzed by HPLC to determine the simazine concentration.

2.5. Column leaching experiment

Leaching was studied in 30 cm length x 3 cm internal diameter glass columns. The top 5 cm were filled with sea sand and the bottom 5 cm with sea sand plus glass wool, to prevent losses of soil during the experiment. The other 20 cm were hand-packed with air-dried soil, then saturated with 0.01 M $CaCl_2$ and allowed to drain for 24 h. The calculated pore volume of the column after saturation was 60 ± 5 ml. The amount of simazine corresponding to an application rate of 2.5 kg ha^{-1} (0.2 mg a.i.) was applied to the top of duplicate soil columns as free technical compound (dissolved in 5 ml methanol) or as clay complexes. The columns were leached with 0.01 M $CaCl_2$ at a rate of 15 ml day^{-1}. The leachates were collected daily and the concentration of simazine was determined by HPLC.

2.6. Field experiment

Simazine was applied at a rate of 3 kg ha^{-1} to triplicate 1 m^2 plots as a standard commercial formulation or as a clay-herbicide complex (Fe-SW, MC) suspended in 3 l of water. The bioefficacy and leaching of simazine was evaluated by controlling *Sinapis alba* population that had been previously seeded at a rate of 36 seeds per plot over an established Bermudagrass sward (Princess 77). A sprinkle irrigation schedule was set up to promote simazine movement through the soil profile. At selected times after herbicide application, duplicate soil samples (5 g) of each plot were taken from different soil depths (0-5, 5-10, 10-15 cm), and extracted with 10 ml methanol to determine the simazine concentration. The herbicidal efficacy of the formulations was determined 3 weeks after herbicide application by visual evaluation of *Sinapis alba* germination.

2.7. Herbicide analysis

Simazine analysis was performed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The following conditions were used: Novapack C18 column (150 cm length x 3.9 internal diameter), 30:70 acetonitrile:water eluent mixture at a flow rate of 1 ml min^{-1}, 25 µl injection volume, and UV detector at 230 nm.

3. RESULTS AND DISCUSSION

3.1. Adsorption study

The clays (Fe-SW, ODA-SA and HDTMA-SA) were selected on the basis of a preliminary adsorption-desorption experiment revealing that they had different affinities for the herbicide simazine (Fig. 1). Desorption isotherms reflected a moderate to high reversibility of the adsorption process, which is an interesting feature for the use of the clays as supports for the slow release of the herbicide.

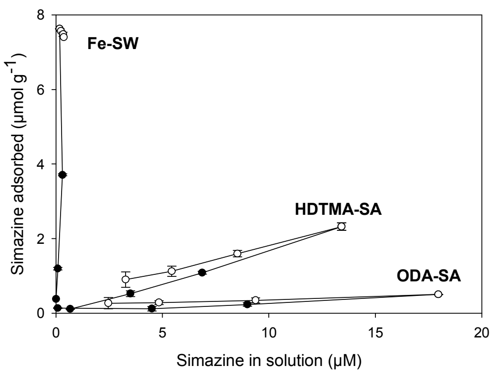

Figure 1. Simazine adsorption-desorption isotherms on the three selected clays.

3.2. Batch release study

The release patterns of simazine from the formulations based on the three selected clays (Fe-SW, ODA-SA and HDTMA-SA) are shown in figure 2. All clay-based formulations of simazine displayed slow release properties in water with an initial release from 1 to 24% and a final release from 1 to 89%. For all three clays, the release rate from the SC complex was slower than that from the MC complex (Fig. 2). In addition, the total amount of herbicide released at the end of the batch release experiment (Fig. 2) was inversely related to the affinity of the clays for the herbicide, i.e. Fe-SW >> HDTMA-SA > ODA-SA (Fig. 1). Therefore, a range of rates and extents of simazine release occurred depending on the type of clay (Fe-SW, HDTMA-SA or ODA-SA) and the preparation protocol (MC or SC). This suggests the possibility to select the most suitable clay-based formulation of simazine to achieve a desired release behavior.

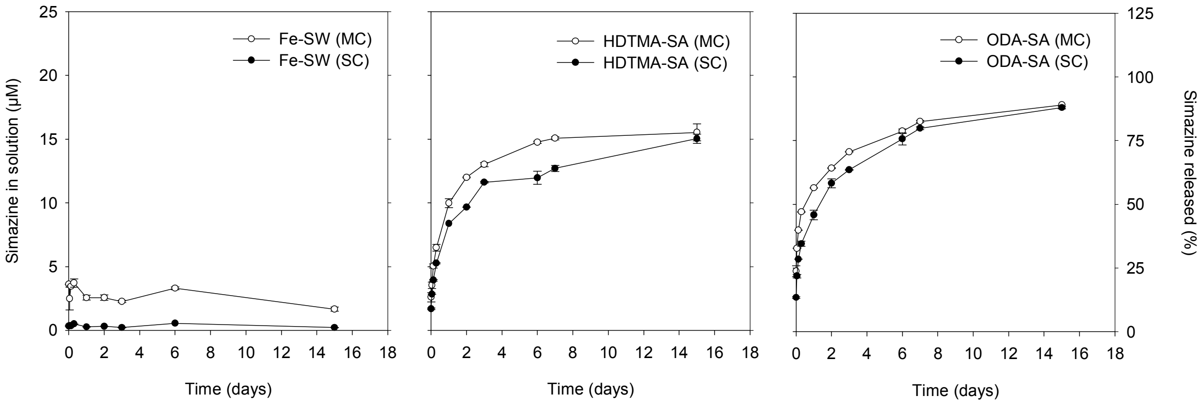

Figure 2. Simazine release kinetics into water from clay-based formulations.

3.3. Column leaching experiment

Breakthrough curves (BTCs) of simazine applied to soil columns as free dissolved product and as clay complexes are shown in figure 3. All clay-based formulations of simazine showed a reduction in the maximum concentration of the BTC compared to the free herbicide. The presence of simazine in the leachates remained moderate after large volumes of water added, proving the slow release behavior of the complexes. In agreement with the results of the batch release experiment, for all three clays the SC complexes resulted in lower leachate concentrations compared to the MC complexes. Again, different leaching patterns can therefore be achieved depending on the type of clay and the protocol followed to prepare the clay-based formulation of simazine.

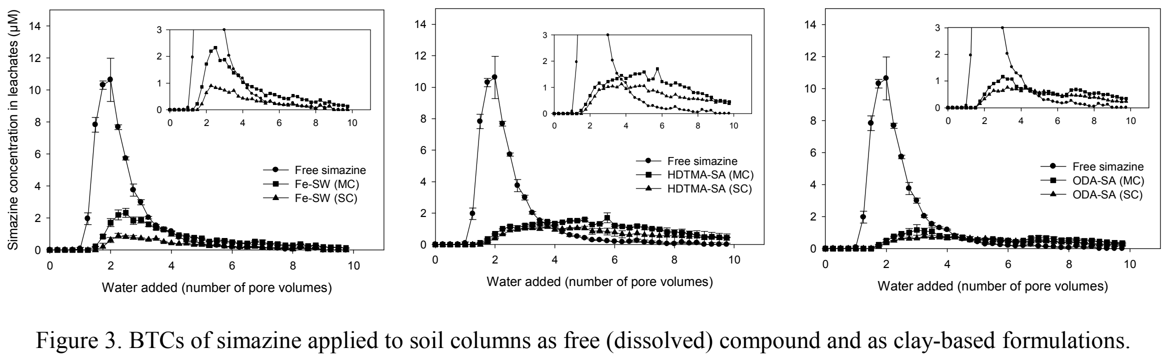

Figure 3. BTCs of simazine applied to soil columns as free (dissolved) compound and as clay-based formulations.

3.4. Field experiment

The MC preparation of Fe-SW was selected for the field experiment on the basis of its release characteristics, the simplicity of its preparation procedure and the natural occurrence of Fe in soil. Simazine applied as the Fe-SW formulation had an herbicidal efficacy against *Sinapis alba* similar to that of the standard commercial formulation used. In addition, soil analysis revealed that simazine applied as a clay formulation leached less than the commercial formulation (Fig. 4). This was particularly evident 33 days after herbicide application, where the maximum concentration of simazine was found at 5-10 cm depth for the commercial formulation, but remained at 0-5 cm depth for the clay formulation. These results confirm that clay-based formulations can be used under field conditions to reduce simazine leaching through soil in high risk scenarios, such as sport turfgrass surfaces, while maintaining a weed control efficacy similar to that of standard commercial formulations.

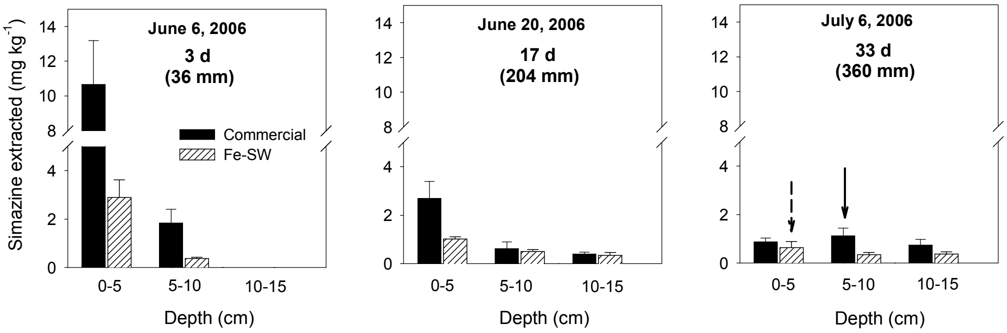

Figure 4. Simazine extracted from different depths of field plots after herbicide application as commercial and Fe-SW formulation. Days after herbicide application and cumulative watering are indicated in the graphs.

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