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Use of modified montmorillonites to reduce herbicide leaching in sports turf surfaces: Laboratory and field experiments

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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 suitable carrier, which limits the amount of pesticide readily available for undesirable leaching losses. The herbicide simazine was used as a model of highly mobile herbicide applied in sports turf surfaces. We investigated the ability of selectively modified montmorillonites to retard the release of the herbicide into the aqueous soil solution and to reduce herbicide leaching from the soil. Fe^{3+}-Wyoming montmorillonite (Fe-SW), hexadecyl trimethylammonium-Arizona montmorillonite (HDTMA-SA) and octadecylammonium-Arizona montmorillonite (ODA-SA) were mixed with simazine following two different protocols. The resulting complexes were assayed as slow release formulations of the herbicide. In the laboratory, batch release and column leaching tests showed that all montmorillonite-based formulations of simazine released the herbicide slowly in aqueous solution, which resulted in reduced simazine leaching through soil columns compared to the application of the free herbicide. Pretreatment of the soil surface layer with Fe-SW was also effective in retarding the leaching of free simazine through the soil column compared to its leaching in untreated soil columns. In a field experiment, a Fe-SW-based formulation of simazine was applied to 1 m^2 field plots, previously seeded with Princess 77 bermudagrass to simulate a typical sports turfgrass surface. The field experiment revealed that the montmorillonite-based formulation of simazine displayed similar herbicidal efficacy and slower vertical movement of the herbicide compared to a standard commercial formulation. This study shows the usefulness of montmorillonite to reduce ground water contamination by intensive herbicide application in high-risk scenarios such as sports turfgrass surfaces.

Keywords: Adsorption; Clay minerals; Herbicide; Leaching; Montmorillonite; Simazine; Slow release; Turfgrass

1. Introduction

The environmental problems associated with the use of highly mobile pesticides in agricultural and urban areas are of growing concern because these compounds are increasingly being detected in ground and surface waters (Hoffman et al., 2000; Lapworth et al., 2006; Woudneh et al., 2007). Turfgrass is one of the most intensively managed biotic systems in urban landscapes. In particular, sports turf surfaces such as golf courses receive more pesticides than most other types of turfgrass (Wu et al., 2002), and they are considered to be high pollution potential areas compared with agricultural land (Suzuki et al., 1998; Armbrust and Peeler, 2002). This is because golf courses demand high-quality turf surfaces with a perfect uniformity, density and aesthetical value, which requires very intensive level of maintenance and inputs and therefore the severe use of chemicals to control turf pests and diseases.

The environmental fate and risks associated with pesticides in the turf environment are greatly affected by site-specific environmental conditions and management practices (Perris, 1996; Wu et al., 2002). In Southern Spain, climatic conditions and the general properties of the soils used in the large developing golf industry exacerbate the risk of ground water pollution by pesticides. The soils used in golf courses in Southern Spain are characterized by low organic matter contents and high permeability. These soil properties linked with intensive use of pesticides, intense irrigation programs, and short but

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Table 1
Some characteristics of the modified montmorillonites

Clay abbreviation	Montmorillonite	Main interlayer cation	OC[a] (%)	OCtS[b] (%)	d_{001}[c] (nm)
Fe-SW	SWy-2	Fe(III)	–	–	1.3
HDTMA-SA	SAz-1	Hexadecyl trimethylammonium	22.5	83	2.4
ODA-SA	SAz-1	Octadecylammonium	17.2	67	3.7

[a] Organic carbon content.
[b] Organic cation saturation: percentage of the CEC of SAz-1 occupied by organic cations.
[c] Basal spacing.

heavy rainfall events make golf courses in Southern Spain a particularly high-risk scenario for ground water contamination.

The use of slow release formulations has been proved to be an efficient strategy to reduce herbicide leaching to ground water. This is because slow release formulations supply the herbicide into the soil solution gradually over time, thus limiting the amount of herbicide available for undesirable leaching losses (Gerstl et al., 1998; Johnson and Pepperman, 1998; Fernández-Pérez et al., 1998; Celis et al., 2002; Hermosín et al., 2006). Among the different materials used as herbicide carriers, the use of clay minerals has been subjected to considerable attention due to their low cost, ubiquitous occurrence in nature and the possibility of modifying their surfaces to improve their affinity for a particular herbicide (El-Nahhal et al., 1998; Carrizosa et al., 2000; Lagaly, 2001; Celis et al., 2002; Hermosín et al., 2006). Although the aim of the earlier studies on clay minerals as pesticide carriers was to protect the pesticide from photodegradation (Margulies et al., 1987, 1992, 1993), more recently research has focused on the ability of unaltered and modified clay minerals to reduce pesticide leaching in soil, to minimize the risk of ground water contamination (Undabeytia et al., 2000; Hermosín et al., 2001; Nennemann et al., 2001; Carrizosa et al., 2003). Unaltered and modified clay minerals have also been proposed, alone or mixed with soil, as reactive barriers for the prevention of ground water pollution by pesticides (Rodríguez-Cruz et al., 2007).

The objective of this study was to investigate the usefulness of montmorillonite-based formulations to reduce the leaching of the herbicide simazine in sports turf environments typical of Southern Spain. The herbicide simazine was chosen on the basis of its widespread use in sports turf surfaces, such as golf courses, of Southern Spain and its high leaching potential when applied to such surfaces. Different simazine complexes were prepared with two montmorillonites (SWy-2 and SAz-1) modified with Fe^{3+}, hexadecyl trimethylammonium or octadecylammonium cations. Laboratory and field experiments were designed to test the ability of the complexes to slow the release of the herbicide into the aqueous soil solution and to retard its leaching under conditions encountered in sports turf scenarios typical of Southern Spain. The ability of the Fe^{3+}-modified montmorillonite (Fe-SW), mixed with soil, to act as a barrier to reduce simazine leaching through soil columns was also investigated.

2. Materials and methods

2.1. Materials

Na-rich Wyoming montmorillonite (SWy-2) and Ca-rich Arizona montmorillonite (SAz-1), supplied by The Clay Minerals Society (Columbia, Missouri), were modified with Fe^{3+}, hexadecyl trimethylammonium (HDTMA) or octadecylammonium (ODA) cations to improve their affinity for the herbicide simazine. The cation exchange capacity (CEC) of SWy-2 and SAz-1 was 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 hexadecyl trimethylammonium (HDTMA-SA) and octadecylammonium (ODA-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, Sigma, Spain) equal to 100% (HDTMA) or 50% (ODA) of the CEC of the clay mineral. The suspensions were shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized (Celis et al., 1999). The main characteristics of the three montmorillonites are summarized in Table 1.

Analytical grade simazine, purity = 99.9% (Riedel-de Haën), was used to prepare the montmorillonite-based formulations of simazine and the herbicide solutions used in the laboratory tests. 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 laboratory experiments was a Typic Rhodoxeralf from Seville (Southern Spain). The soil was sampled (0–20 cm), air-dried, sieved (2 mm), and stored at 4 °C until used. The field experiment was conducted in a field plot from the same area (Seville, Southern Spain) and with similar soil characteristics. The physicochemical characteristics of the soils are reported in Table 2. Soil texture was determined by sedimentation (Jackson, 1975), soil pH was measured in a 1:2 (w:w) soil:deionized water suspension, and the organic carbon content was determined according to the Walkley–Black method (Jackson, 1975).

2.2. Adsorption experiment

Simazine adsorption–desorption isotherms on the selected montmorillonites (Fe-SW, HDTMA-SA and ODA-SA) were obtained by the batch equilibration technique. Duplicate 20 mg montmorillonite samples were equilibrated with 8 ml of simazine initial solutions (0.2–4 mg/l) by shaking mechanically at 20 ± 2 °C for 24 h. After equilibration, the suspensions were centrifuged and the equilibrium concentration was determined in the supernatant solutions by high performance liquid chromatography (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 of distilled water. The samples were redispersed, shaken for another 24 h, centrifuged and the equilibrium concentration was determined. This desorption cycle was conducted three times.

2.3. Preparation of montmorillonite-simazine complexes

Two types of montmorillonite-simazine complexes were prepared with each montmorillonite (Hermosín et al., 2001; Celis et al., 2002). First, a weak complex (WC) was prepared by adding 2 ml of methanol to 1 g of a mechanical

Table 2
Physicochemical characteristics of the soils

Soil	pH	Organic carbon (%)	Sand (%)	Silt (%)	Clay (%)
Laboratory experiments	8.2	1.0	73	7	20
Field experiment	8.5	1.4	62	16	22

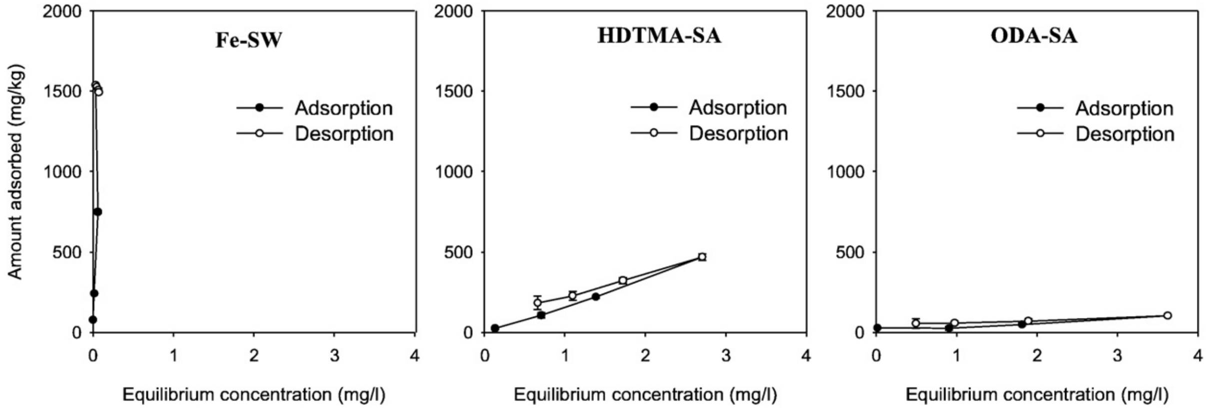

Fig. 1. Simazine adsorption–desorption isotherms on Fe-SW, HDTMA-SA and ODA-SA.

mixture containing 40 mg of analytical grade simazine and 960 mg of montmorillonite, and then air-drying. Second, a strong complex (SC) was prepared by adding 10 ml of methanol to a similar montmorillonite-herbicide mechanical mixture, then shaking for 24 h, and then air-drying. The amount of simazine in the complexes corresponded to a 4% content in active ingredient (a.i.). Once air-dried, the complexes were thoroughly ground in an agate mortar and stored at room temperature until used.

2.4. Batch release kinetic experiment

Two milligrams of simazine (a.i.) were added as 50 mg of montmorillonite complexes to 500 ml of distilled water in glass bottles sealed with screw caps. At selected times, the bottles were hand-shaken, allowed to settle for 10 min, and then 3 ml of the supernatant solution were removed, filtered, and analyzed by HPLC to determine the simazine concentration. In all cases, the release kinetics was obtained in duplicate.

2.5. Column leaching tests

Leaching was studied in 30 cm length × 3.1 cm internal diameter glass columns. The top 5 cm of the columns 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 160 g of air-dried soil, then saturated with distilled water and allowed to drain for 24 h. The calculated pore volume of the soil columns after saturation was 60 ± 5 ml.

The effect of formulation on simazine leaching was investigated by applying the herbicide at a rate of 2.5 kg ha^{-1} (0.2 mg a.i.) to the top of triplicate soil columns either as free technical compound (dissolved in 1 ml methanol) or as montmorillonite complexes. Every day, the columns were leached with 15 ml of distilled water, the leachates were collected and filtered, and the concentration of simazine in the leachates was determined by HPLC. At the end of the leaching experiment, i.e. after application of 600 ml of water, soil samples from different depths of the soil columns (0–5, 5–10, 10–15 and 15–20 cm depth) were extracted with 100 ml of methanol by shaking mechanically at 20 ± 2 °C for 24 h. The suspensions were centrifuged, filtered, and analyzed by HPLC in order to determine the residual amount of simazine at the different depths of the soil column.

The efficiency of a montmorillonite (Fe-SW) barrier in reducing the leaching of simazine through the soil column was also determined. The barrier was prepared by incorporating to the upper part of the column a mixture containing 5 g of soil and 1 g of Fe-SW. Simazine was applied at a rate of 2.5 kg ha^{-1} to the top of the columns containing the montmorillonite barrier and to control columns (without montmorillonite barrier) as free technical compound dissolved in 1 ml methanol. The columns were leached daily with 15 ml distilled water, and the leachates were collected, filtered, and analyzed as described above. At the end of the leaching experiment, i.e. after application of 500 ml of water, the residual amount of simazine at the different depths of the soil columns was also determined.

2.6. Field experiment

Simazine was applied at a rate of 3 kg ha^{-1} to triplicate 1 × 1 m field plots on which a Bermudagrass (Princess 77) cover had been previously established. Simazine was applied to the plots either as a standard commercial formulation (50% concentrated suspension, Lainco S.A., Spain) or as a montmorillonite-herbicide complex (Fe-SW, WC) suspended in 3 l of water. 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) using a

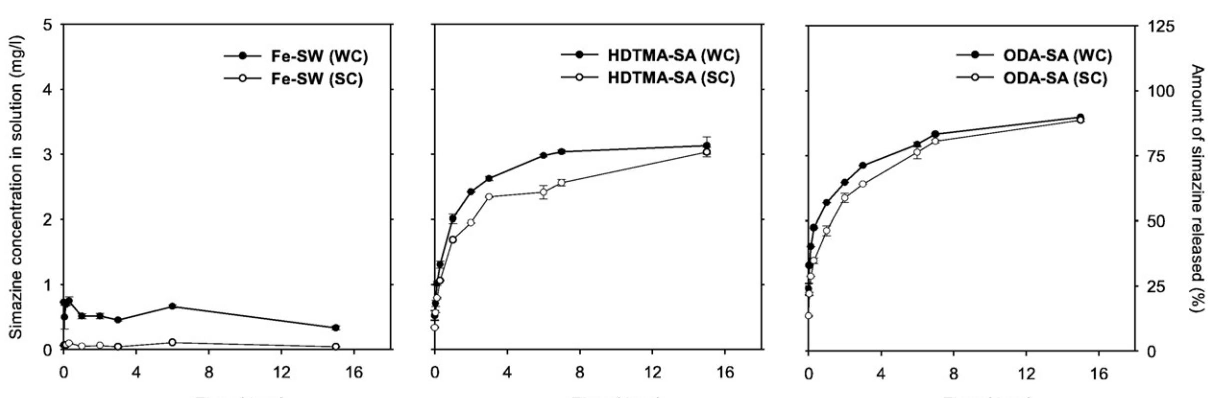

Fig. 2. Simazine release kinetics into water from montmorillonite-based formulations.

cylindrical spade, extracted with 10 ml methanol, and the extracts were analyzed by HPLC in order to determine the distribution of simazine through the soil profile. The bioefficacy of simazine was also evaluated by visual control of white mustard (*Sinapis alba*) population that had been previously seeded at a rate of 36 seeds per plot over the established Bermudagrass sward.

2.7. Herbicide analysis

Simazine analysis was performed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The analytical conditions used were: Novapack C18 column (150 mm length × 3.9 mm internal diameter), 30:70 acetonitrile:water eluent mixture at a flow rate of 1 ml/min, 25 µl injection volume, and UV detector at 230 nm. External calibration curves with standard simazine solutions between 0.02 and 4 mg/l were used in the calculations.

3. Results and discussion

3.1. Adsorption study

Preliminary adsorption–desorption experiments were conducted to determine the affinity of simazine for SWy-2 and

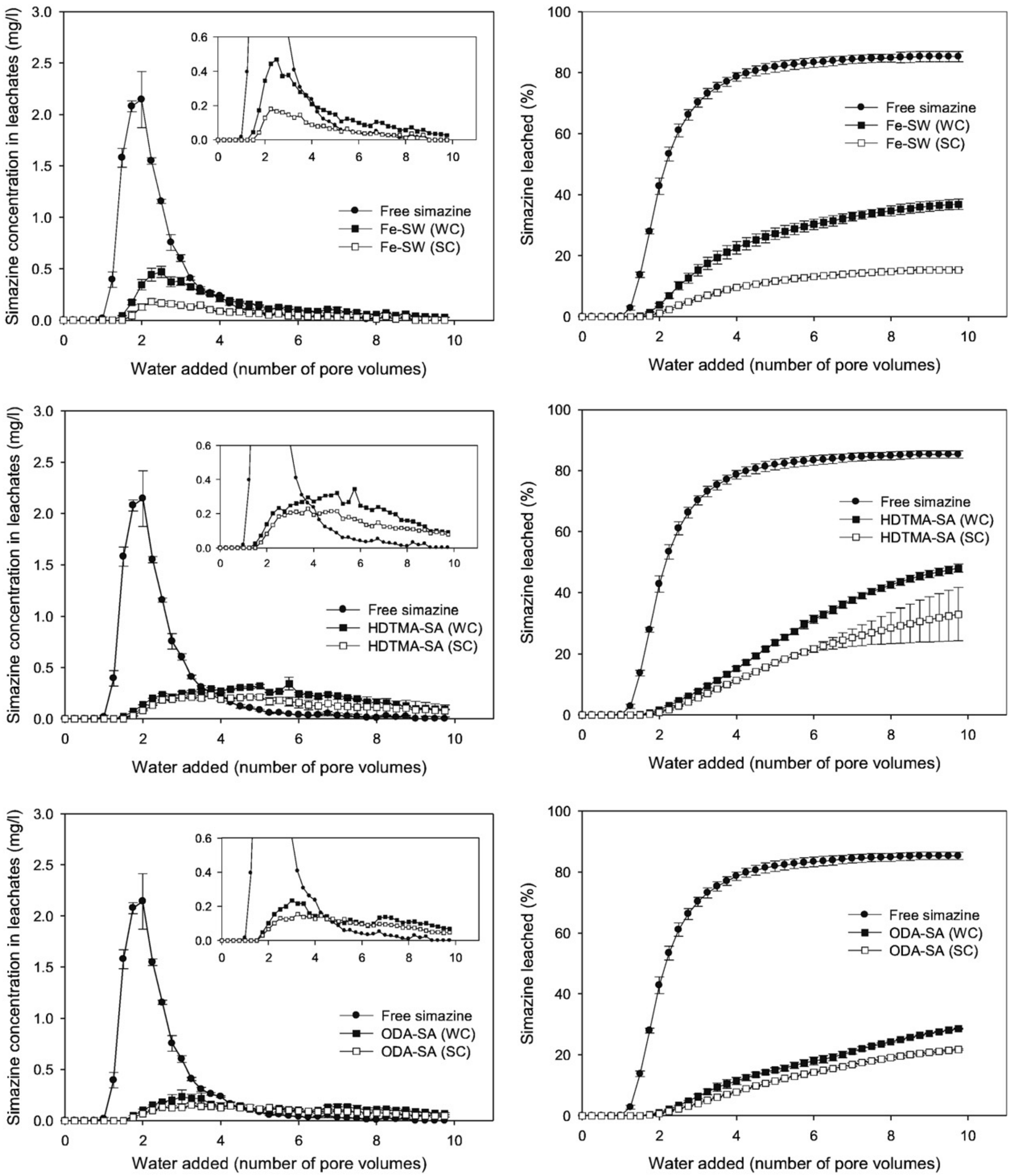

Fig. 3. Relative (left) and cumulative (right) breakthrough curves of simazine applied to soil columns as free (dissolved) herbicide and as montmorillonite-based formulations.

Table 3
Simazine leached, extracted from the soil column and not recovered after application to soil columns as free herbicide and montmorillonite-based formulations

	Free simazine	Fe-SW		HDTMA-SA		ODA-SA	
		WC	SC	WC	SC	WC	SC
Leached (%)	85±2[a]	37±2	15±1	48±1	33±9	29±1	22±1
Extracted (%)	0	9±2	14±1	12±3	9±6	15±3	14±4
Not recovered (%)	15	54	71	40	58	56	64

[a] Value±standard error.

SAz-1 montmorillonites modified with different amounts of several inorganic and organic cations. Fe-SW, HDTMA-SA, and ODA-SA were selected on the basis of such preliminary adsorption–desorption experiments, which revealed that these montmorillonites had different affinities for simazine (Fig. 1). The very high affinity of simazine for Fe-SW is due to the strong polarizing power of Fe^{3+} cations, which promote ionization of hydration water molecules at the clay mineral interlayers, increasing the surface acidity (Celis et al., 1997). Surface acidity favors the adsorption of weakly basic pesticide molecules, such as simazine, as protonated species on exchange sites of montmorillonite (Laird, 1996; Celis et al., 1997). HDTMA and ODA are large alkylammonium cations that arrange vertically in the interlayers of SAz-1, producing an interlayer organic phase with affinity for herbicide molecules (Celis et al., 2000). HDTMA-SA has greater affinity for simazine than ODA-SA (Fig. 1), probably because the nature and amount of interlayer organic cation (Table 1) make HDTMA-SA more hydrophobic than ODA-SA. Desorption isotherms reflect a moderate to high reversibility of the adsorption process for all three montmorillonites (Fig. 1), which is an interesting feature for the use of the clay minerals as supports for the slow release of the herbicide.

3.2. Batch release study

The release kinetics of simazine from the different montmorillonite-herbicide complexes prepared in this work is shown in Fig. 2. All montmorillonite-based formulations of simazine displayed slow release properties in water with an initial herbicide release from 1 to 24% and a final release from 1 to 89%. For all three montmorillonites, the release rate from the SC complex was slower than that from the WC complex (Fig. 2). This is because the greater amount of organic solvent used to prepare the SC complexes made the interaction between the herbicide and the clay mineral more intimate, reducing the release rate (Celis et al., 2002; Hermosín et al., 2006). On the other hand, the total amount of herbicide released at the end of the batch release experiment (Fig. 2) was inversely related to the affinity of the montmorillonites 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 montmorillonite (Fe-SW, HDTMA-SA or ODA-SA) and the preparation protocol (WC or SC). This suggests the possibility to select the most suitable formulation of simazine to achieve a desired release behavior.

3.3. Column leaching experiments

Relative and cumulative breakthrough curves (BTCs) of simazine applied to soil columns as free dissolved product and as montmorillonite complexes are shown in Fig. 3. All montmorillonite-based formulations of simazine resulted in lower herbicide concentration in leachates and flattening of the relative BTCs compared to the free herbicide. In addition, for the montmorillonite-herbicide complexes, the concentration of simazine in leachates remained moderate after large volumes of water added, proving the slow release behavior of the complexes. For all three montmorillonites, the SC complexes resulted in lower simazine concentration in leachates than the WC complexes.

Cumulative BTCs show that simazine applied as montmorillonite complexes leached less than the free simazine (Fig. 3). While no simazine applied as free compound remained in the soil column at the end of the leaching experiment, some of the simazine applied as montmorillonite complexes remained in the columns (Table 3, Fig. 4), further revealing a slower movement of the herbicide. On the basis that the residual amount of simazine in the soil columns increased with depth (Fig. 4), we believe that this fraction of herbicide would eventually have leached, after irrigation of the columns with sufficient amount of water. The amount of simazine not recovered in leachates or from the soil columns (Table 3) should correspond to the sum of herbicide degraded, irreversibly bound to soil, and irreversibly

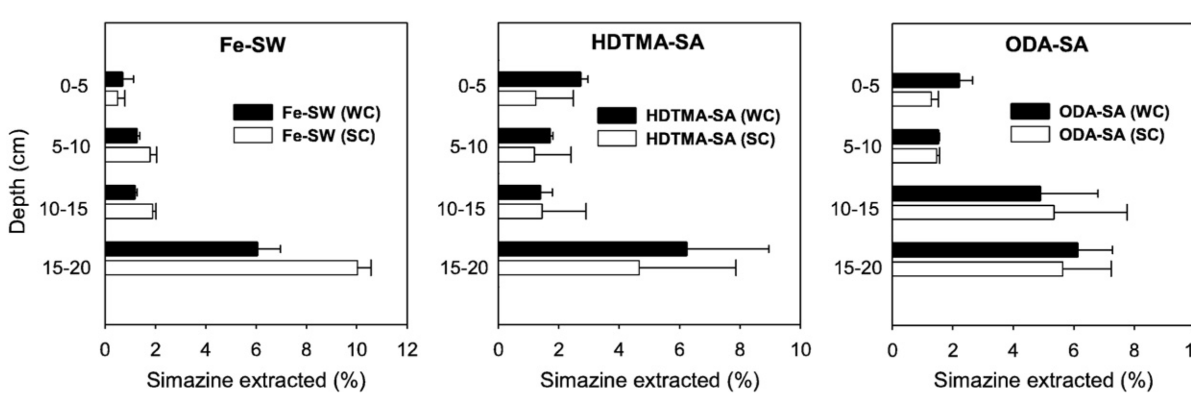

Fig. 4. Simazine extracted from different depths of the soil columns at the end of the leaching experiment.

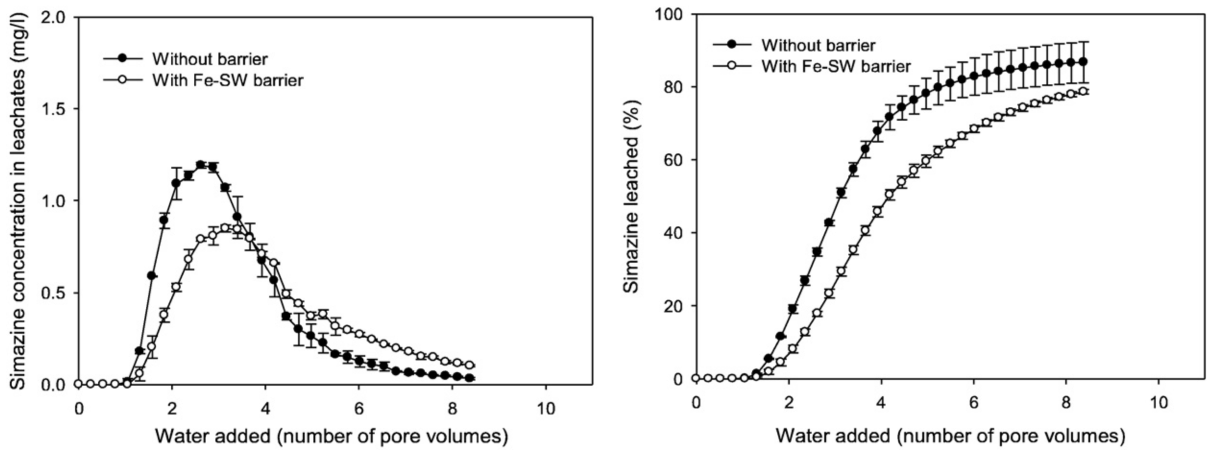

Fig. 5. Relative (left) and cumulative (right) breakthrough curves of free simazine in soil columns with and without montmorillonite (Fe-SW) barrier intercalated.

bound (or entrapped) in the montmorillonite complexes (Celis et al., 2002). This amount not recovered increased in the following order: free simazine < WC complexes < SC complexes (Table 3). The slower leaching of simazine applied as montmorillonite complexes as compared to its application as free (dissolved) herbicide prolonged the presence of herbicide within the soil column and probably enhanced its degradation.

Fig. 5 shows the effect of incorporating a montmorillonite (Fe-SW) barrier into the soil surface layer on the leaching pattern of free simazine. Pretreatment of the soil surface layer with Fe-SW resulted in lower herbicide concentration in leachates and flattening of the relative BTCs compared to the untreated soil. Nevertheless, this effect was less pronounced than that observed in the experiments with montmorillonite-based formulations of the herbicide (Fig. 3). The total amount of simazine leached from the columns in which the montmorillonite (Fe-SW) barrier had been incorporated was only slightly less than that leached from the columns with untreated soil (Fig. 5), and no herbicide remained within the soil columns a the end of the experiment (data not shown). The montmorillonite barrier was therefore less effective than the montmorillonite-herbicide complexes in reducing the leaching of simazine through the soil columns.

3.4. Field experiment

The WC 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(III) in soil. We analyzed the 0–15 cm soil surface layer and found that the field plots treated with the commercial formulation of simazine always contained a greater amount of methanol-extractable herbicide than the field plots treated with the montmorillonite-based formulation (Fig. 6). Considering the amount extractable with methanol as an estimate of the amount of herbicide present in a potentially available form (Cox and Walker, 1999; Albarrán et al., 2003), this result indicates that the availability of simazine in the soil is reduced by its application as the montmorillonite (Fe-SW, WC) complex. In addition, soil analysis revealed that the methanol-extractable fraction of simazine moved slower when the herbicide was applied as the montmorillonite (Fe-SW, WC) complex, compared to its application as free commercial formulation (Fig. 6). This was particularly evident 33 days after herbicide application, where the maximum concentration of methanol-extractable simazine was found at 5–10 cm depth for the commercial formulation, but remained at 0–5 cm depth for the montmorillonite formulation. It should be noted that only the 0–15 cm soil surface

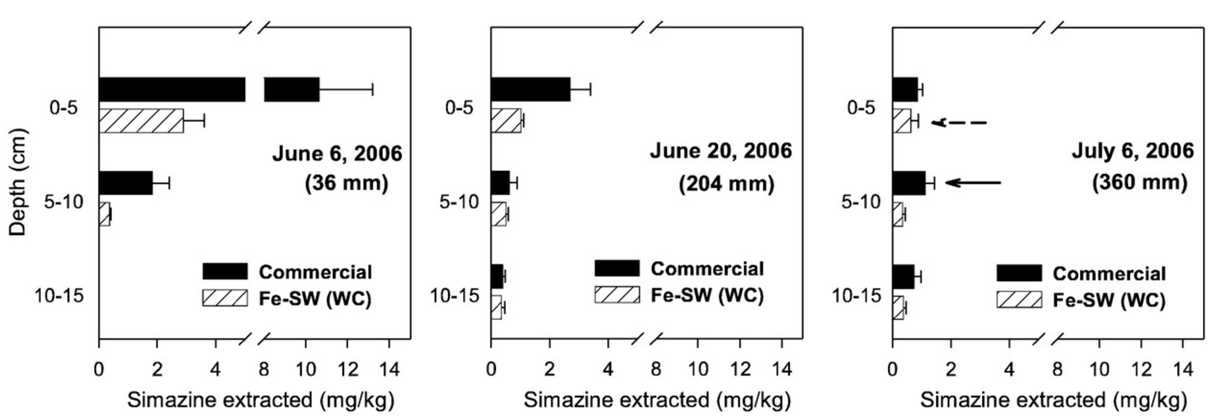

Fig. 6. Simazine extracted from different depths of field plots after herbicide application as commercial and Fe-SW (WC) formulation. Cumulative watering is indicated in the graphs.

layer was analyzed and, therefore, further leaching to a larger depth than 15 cm could have occurred, particularly for the larger amounts of water applied. On the other hand, simazine applied as the Fe-SW (WC) formulation had an herbicidal efficacy against *S. alba* similar to that of the standard commercial formulation used. Three weeks after herbicide treatment, an average of seven white mustard (*S. alba*) plants were identified in the control plots, whereas no plants were present in the plots treated with either the commercial or montmorillonite-based formulation of simazine. Therefore, the results of the field experiment confirmed that clay mineral-based formulations can be used under field conditions to reduce the amount of simazine readily available for leaching in high-risk scenarios, such as sports turf surfaces, while maintaining a weed control efficacy similar to that of standard commercial formulations.

4. Conclusions

Modification of montmorillonites (SWy-2 and SAz-1) with Fe(III), HDTMA, and ODA cations provided the clay minerals with different affinities for the herbicide simazine. Complexes between the herbicide and the modified montmorillonites were prepared and assayed as slow release formulations of the herbicide. In the laboratory, the montmorillonite-based formulations of simazine released the herbicide slowly into aqueous solution and reduced the herbicide leaching through soil columns as compared to the application of free (dissolved) herbicide. The release and leaching patterns depended on the type of montmorillonite and on the preparation protocol. Pretreatment of the surface layer of soil columns with Fe-SW was also effective in retarding the leaching of simazine, but this effect was less pronounced than that observed in the experiments with the montmorillonite-simazine complexes. A field experiment was also conducted in field plots previously seeded with Princess 77 bermudagrass to simulate a typical sports turfgrass scenario of Southern Spain. The results confirmed that montmorillonite-based formulations can be used under field conditions to reduce the amount of simazine readily available for leaching in high-risk scenarios, such as golf courses of Southern Spain, while maintaining a weed control efficacy similar to that of standard commercial formulations.

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